STRUCTURAL STUDIES OF PHASE BEHAVIOR IN 1,6-DICYANOHEXANE/UREA AND 1,6-DIISOCYANOHEXANE/UREA INCLUSION COMPOUNDS

by

KEITH ELDRED ALQUIST III

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Mark Hollingsworth

Abstract

The crystal structures of the inclusion compounds 1,6-diisocyanohexane/urea and 1,6-dicyanohexane/urea were refined at several temperatures from X-ray data. These urea inclusion compounds are commensurate structures with host:guest ratios of 6:1. In contrast with the ordinary helical topology of the urea host, these structures have stacked loop topologies of the host hydrogen bonds and crystallize in space group $P2_1/n$. At room temperature, both structures are distorted along [001] from hexagonal metric symmetry. As in earlier studies of 1-chloro-6-cyanohexane/urea, cooling 1,6-diisocyanohexane/urea gives rise to an exothermic phase transition (ΔH^o = -856 cal mol^{-1}, ΔS^o = -5 cal mol^{-1} K^{-1}) at 175 K that results in the cooperative translation of guest molecules by 5.5 Å along the channel axis. In the low temperature form, 1,6-diisocyanohexane/urea is distorted along [100], much like $X(CH_2)_6Y$, where X, Y = Br, Cl. Although the crystal structure of 1,6-dicyanohexane/urea is essentially isomorphous with that of the high temperature form of 1,6-diisocyanohexane/urea, it does not undergo an equivalent phase transition at low temperatures. Both of these systems exhibit dynamic disorder between two gauche conformers of the guest, which have mean planes of the alkyl chains lying within 1º of [100] (major conformer) and approximately 14º from [001] (minor conformer). The temperature dependence of site occupancy factors for the disordered sites yielded enthalpy differences between major and minor sites in 1,6-diisocyanohexane/urea and 1,6-dicyanohexane/urea of 216 and 127 cal mol^{-1}, respectively. Since the low temperature form of 1,6-diisocyanohexane/urea is distorted along [100], this is favored at low temperatures by an increased concentration of the major conformer, which predominates in 1,6-dibromohexane/urea and congeners. In 1,6-diisocyanohexane/urea, the phase transition to the low temperature form occurs at a threshold concentration for the major conformer of 67%. With its shallower temperature dependence, 1,6-dicyanohexane/urea should not reach this threshold population until approximately 92 K, at which temperature the system cannot overcome the barrier for cooperative translation of guests along the channel axis.

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List of Symbols, Abbreviations and Nomenclature

Å	Angstroms
K	Kelvin
K_α	The transition used in an X-ray source

Chemical name/urea is a shorthand method of describing a urea inclusion compound. The chemical name is the included guest.

Dedication

This thesis is dedicated to my wife, Rachel. It was written in celebration of our recent marriage, and through her uninterrupted encouragement, made this thesis possible.

I express my thanks and deepest respect for Mark Hollingsworth. The direction and counsel he gave me will last throughout my career.

I wish to thank my committee members, Stefan Bossmann and Dan Higgins, and the rest of the Kansas State University Faculty for their patience.

Finally, I couldn't not have even attempted this pursuit were it not for my family, who gave me unwavering support and the directive that failure wasn't an option.

Introduction

Although it forms a tetragonal structure when crystallized by itself in polar solvents, crystallization of urea in the presence of linear chain molecules often generates a urea inclusion compound (UIC). In these structures,[1] the urea molecules form honeycomb-like channels that surround the guest molecules. The walls of the channels are formed by a hydrogen-bonded network of urea molecules that can wrap around the guest molecule in a double helical fashion.[2-4] Although the double helix motif is normally observed for UICs,[4] "stacked loop" structures are also possible.[5-7] Because the channel diameters of urea inclusion compounds are fairly narrow (5.5-5.8 Å),[8] the guests that form inclusion compounds with urea are normally unbranched or have minimal branching.[9, 4]

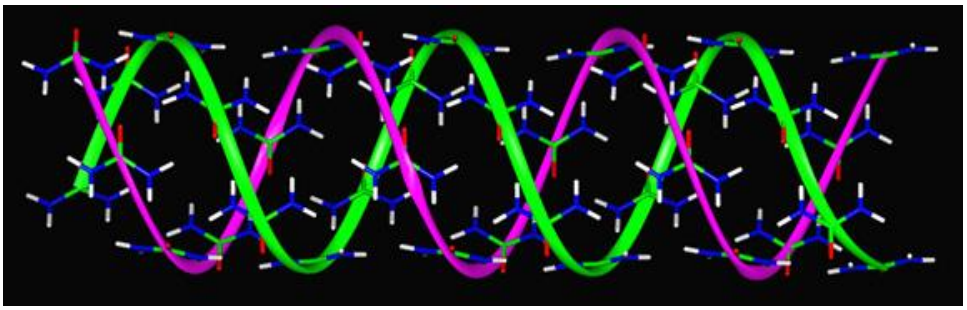

Figure 1. Helical host structure of a conventional urea inclusion compound. The two antiparallel helices are defined by the anti N-H---O=C hydrogen bonds. Reproduced with permission from Hollingsworth, *et al.*, *Trans. Am. Cryst. Assn.*, **43**,113 (2012).

Urea inclusion compounds may be classified as either commensurate[10] or incommensurate structures.[4, 11, 12] These two classes of materials are distinguished by the ratio of repeat lengths of the host (c_h) and guest (c_g) along the channel axis. When the ratio of c_h to c_g is a rational fraction containing small whole numbers (*e.g.,* 2/3), the inclusion compound is considered to be commensurate. When the ratio of host and guest repeats is an irrational fraction, then the system is considered to be incommensurate. Because the value of c_h is relatively constant (11.0 Å) from system to system, one can see that whether one observes commensurate or incommensurate

behavior is controlled by the identity of the guest. The vast majority of UICs are incommensurate structures, but certain classes of guests (*e.g.*, bis(methylketone)s have a propensity to form commensurate structures.[4, 2, 10, 12, 3]

This thesis focuses on urea inclusion compounds that are commensurate, stacked looped systems. A small number of guests, primarily ones with guest formula $X(CH_2)_6Y$ (X, Y = Cl, Br, CN, NC) are known to form these stacked loop structures, but a recent study has shown that 1,4-diiodo-1,3-butadiene also forms an inclusion compound with a stacked loop structure.[13] Unlike the helical structures, which are chiral, all of the stacked loop inclusion compounds are centrosymmetric, monoclinic structures with space group $P2_1/n$.[7] There are spectroscopic studies of some stacked loop systems.[14-16]

In the stacked loop UICs that contain $X(CH_2)_6Y$ guests, the guests are often conformationally disordered between two parts. Although the crystal structure of the host can be refined with only one site for each host molecule, the guest molecules occupy two sites, with site occupancy factors that may vary as a function of temperature. ^2H solid-state NMR studies of 1,6-dibromohexane/urea show that two gauche conformers are rapidly equilibrating in the fast motion limit at temperatures as low as 220 K, so the site occupancy factors observed for the two conformers are understood to represent equilibrium populations.

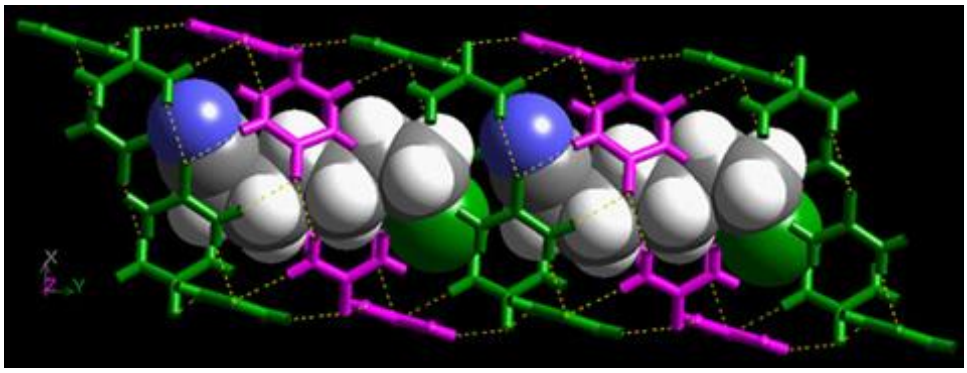

Figure 2. Stacked loop packing in 1-chloro-6-cyanohexane/urea. These centrosymetric structures have space group $P2_1/n$. Reproduced with permission from Hollingsworth, *et al.*, *J. Am. Chem. Soc.*, **124**, 2094 (2002). Copyright 2002 American Chemical Society.

Of the stacked loop structures containing guests with the formula $X(CH_2)_6Y$, the UIC containing 1-chloro-6-cyanohexane displayed the most unusual behavior (Figure 2). At -65.6 ºC (DSC warming curve), 1-chloro-6-cyanohexane/urea undergoes a phase transition in which the guest molecules jump down the channel axis by 5.5 Å.[5] In this system, the guest exhibits little disorder at -90 ºC and -64 ºC, but the conformations that predominate at these two temperatures resemble the major and minor gauche conformers that exist in 1,6-dibromohexane/urea. The undulating nature of the channel walls (Figure 3) suggests strongly that the different conformers fit best into the channel at different positions along the channel axis. In 1-chloro-6-cyanohexane/urea, this phase transition, which involves large-scale cooperative motion of the guests along the channel axis, was found to be topotactic.[5] That is, it occurred in a single crystal to single crystal fashion in which the orientation matrices of the high and low temperature forms did not change substantially.

Such large-scale motions in a single-crystal to single-crystal phase transitions have little, if any, direct precedent. Much smaller guest translations (0.8 Å) have been observed in heptanoic anhydride/urea, which is incommensurate,[17] and capillary transport has been observed in certain incommensurate urea inclusion compounds.[18, 19] Atwood and co-workers observed a large-scale reorganization of the host structure of t-butylcalix[4]arene when the apohost was immersed in vinyl bromide.[20] This too

occurred in a single-crystal to single-crystal fashion, but this system differs from 1-chloro-6-cyanohexane/urea in that this process involves the addition of a solvent molecule to the structure. The closest analog might be *all-trans*-2,5-bis(4-ethenylpyridyl)thiophene, in which conformational polymorphism leads to a cooperative "rack-and-pinion" type motion that occurs in a single-crystal to single-crystal fashion.[21]

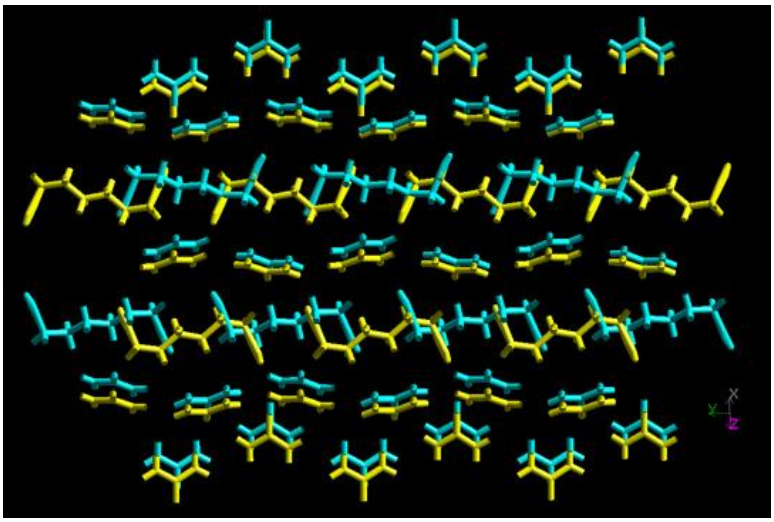

Figure 3. Overlay of packing of high temperature (yellow) and low temperature (blue) forms of 1-chloro-6-cyanohexane/urea. The structures at -64 ºC and -90 ºC show that the guest molecules translate down the channel by 5.5 Å in the phase transition at -65.6 ºC. Reproduced with permission from Hollingsworth, et al., *J. Am. Chem. Soc.*, **124**, 2094 (2002). Copyright 2002 American Chemical Society.

This thesis explores the hypothesis that in closely related materials in which both guest conformers are in equilibrium, the cooperative phase transition involving the 5.5 Å guest translation is triggered when the occupancy of the major conformer reaches a threshold value. Once this threshold is reached, the guest jumps down the channel by 5.5 Å to the position favored by the major conformer. Luckily, the guests in both 1,6-diisocyanohexane/urea and 1,6-dicyanohexane/urea have temperature-dependent populations of two gauche conformers. The enthalpy differences between these two conformers differ by less than 100 cal/mol in these two materials, but that difference is enough to trigger the cooperative phase transition in 1,6-diisocyanohexane/urea but not

in 1,6-dicyanohexane/urea. Presumably, the critical population threshold is reached in 1,6-dicyanohexane/urea at a temperature that is too low for the activation energy for this transformation to be reached.

As stated above, the disordered model in 1,6-dibromohexane/urea shows a gauche to gauche jump between the two parts.[22, 6] This gauche to gauche jump mechanism between the disordered parts found in 1,6-dibromohexane/urea was determined using solid-state deuterium NMR with separate experiments on inclusion compounds containing alpha, beta, and gamma deuterated guests.[22, 6] When the conformer populations derived from ^{2}H solid-state NMR studies were used as a constraint in the crystal structure models, the geometric parameters derived from X-ray diffraction matched the gauche to gauche conformational change predicted by solid-state NMR.

Looking down the *b* axis of 1,6-dibromohexane gives a view of the urea channel. This view shows the network of hexagons that have the guest molecule inside. With no distortions from the guest, this structure would have hexagonal metric symmetry. This hexagonal metric symmetry is idealized as hexagonal symmetry in the *ac* plane, orthogonal to the channel axis. However, 1,6-dibromohexane/urea contains a guest inside this channel, giving a deviation from the idealized hexagonal metric symmetry that is induced by the guest conformers.[6] The population of the guest molecules affects this deviation of the metric symmetry from hexagonal. As the system is cooled, the increased population of major conformer over minor conformer increases this deviation from hexagonal metric symmetry.

In X-ray crystallography, the molecular structure found from the data collected must be refined further; even after it has been solved. The refinement process reduces the error in the atomic positions while enabling the structure to be determined with thermal parameters for each atom. It provides a model and uses restraints and constraints in order to have a model that best fits the data presented. The 1,6-dibromohexane structure was determined to have its bromine placement fixed between

the two parts for the guest. In essence, the bromine moiety acts as an anchor point from which the rest of the guest molecule rotates to form the two gauche conformers.[6] In part because these models had been successful for 1,6-dibromohexane/urea, the cyano end groups in the 1,6-dicyanohexane/urea and the diisocyano end groups in 1,6-diisocyanohexane/urea structures were originally not treated as disordered by earlier researchers in the group. The refinements used in the present study allowed the nitrile and isonitrile groups to be disordered, and led to better fits to the X-ray data.

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Results and Discussion

1,6-Diisocyanohexane/urea and 1,6-dicyanohexane/urea are commensurate urea inclusion compounds with 1,6-diisocyanohexane and 1,6-dicyanohexane as the guest molecules, respectively. The guest molecules in both of these structures are disordered into two parts. The crystal systems are monoclinic with a crystal class of $P2_1/n$. The guest molecule of the 1,6-diisocyanohexane/urea crystal system exhibits a 5.5 Å jump down the channel axis when cooled through its phase transition near 175 K, whereas 1,6-dicyanohexane/urea does not display a phase change to 90 K, and quite possibly to 10 K, as evidenced by low-temperature microscopy.[1]

The disorder of the guest molecules inside the channels in the high temperature phase causes a distortion from the hexagonal metric symmetry that would be favored by the host channel network.[2] In 1,6-dibromohexane/urea, the major conformer predominates: at 213 K, for example, the ratio of major to minor conformers is 94:6.[3] Since the mean plane of the major guest lies mainly parallel to the [100] axis (*a*), 1,6-dibromohexane/urea is significantly distorted away from hexagonal metric symmetry by elongation of the *a* axis relative to the *c* axis.[3]

In both 1,6-dicyanohexane and the high temperature form of 1,6-diisocyanohexane/urea, this distortion lies primarily upon the [001] axis and is driven by the increased occupancy of the minor disordered component. In general, the mean plane of the methylenes of the major disordered guest conformer in 1,6-diisocyanohexane/urea lies around within approximately 1º of the [100] axis and is thus pointed toward the wall of the channel. The analogous plane of the minor conformer's methylene chain lies within approximately 15º of [001].

The distortion from the hexagonal metric symmetry for 1,6-diisocyanohexane/urea is caused by guest conformers that widen the channel along either [001] or [100].[3, 4] The occupancy ratio of the two disordered pairs changes as a function of temperature. As the temperature is decreased, the occupancy of the major

site increases. Since the major site's plane, as the plane intersecting the methylenes, is nearly perpendicular to the (100) plane, this would ordinarily tend to distort the [100] axis away from hexagonal metric symmetry just as in 1,6-bromohexane/urea.[2] However, the large population of the minor conformer distorts this inclusion compound along the [001] axis; as the temperature is lowered, the distortion exhibits complex behavior, although within the datasets collected with the APEX II detector, the trends are more or less as expected, with the distortion along c decreasing, especially at lower temperatures.

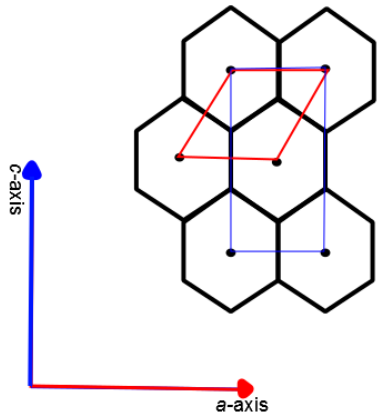

Figure 4. Schematic cross-sectional view of a urea inclusion compound. The red parallelogram denotes the unit cell if it had hexagonal symmetry. The blue rectangle shows the unit cell in monoclinic symmetry.

T	Deviation
150	2.23%
165	2.42%
183	2.37%
200	2.55%
203	2.42%
223	2.39%
243	2.33%

Table 1. Distortion from hexagonal metric symmetry for 1,6-diisocyanohexane/urea, which is elongated along the *c* axis relative to *a*.

T	Deviation
90.5	1.85%
107	1.96%
124	2.07%
141	2.11%
158	2.13%
158	2.13%
173	2.14%
188	2.16%
203	2.17%
218	2.15%
233	2.14%
293	1.90%

Table 2. Distortion from hexagonal metric symmetry for 1,6-dicyanohexane/urea, which is elongated along the *c* axis relative to *a*.

1,6-Diisocyanohexane/urea exhibits an exothermic phase transition at 175 K. In this phase transition , the guest translates by approximately 5.5 Å along the channel axis, which is half the unit cell. This translation requires cooperative motions of all of the guests in a given channel. From the DSC cooling curve, the enthalpy of this phase transition is -856 cal mol^{-1}, and the entropy is -5 cal mol^{-1} K^{-1}.

Below the phase transition, the guest no longer exhibits any measurable disorder. This is in a fashion analogous to $Cl(CH_2)_6CN$/urea. Unlike the guest in the high temperature phase, the mean plane of the alkyl chain of the guest in the low temperature phase lies within 1º of the *a* axis of the unit cell, much like the major guest in the 1,6-dihalohexane/urea series. The angle of the plane between the two disordered pair, as defined through the guest methylene carbons, is 71.29° at 140 K. The distortion

away from hexagonal metric symmetry is 9.57% at 140 K, which is very similar to that of 1,6-dichlorohexane/urea at 99 K.[3]

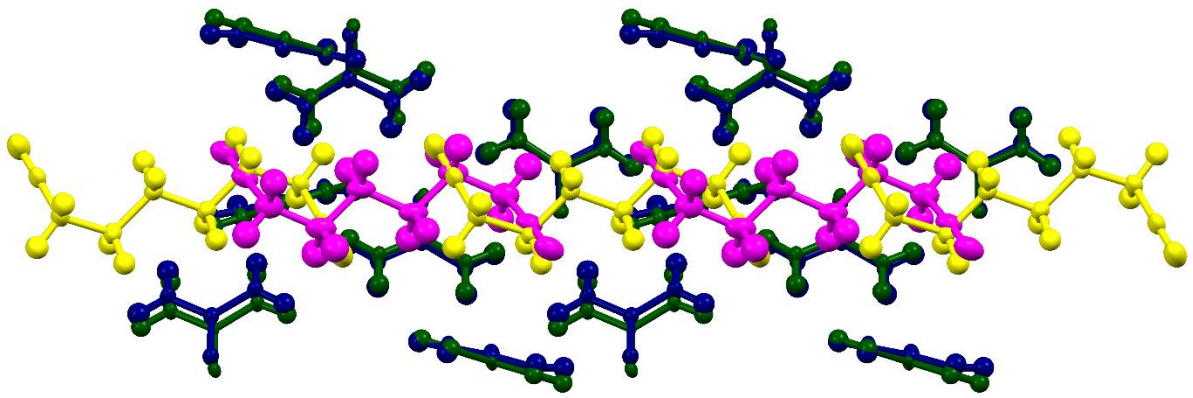

Figure 5. 1,6-Diisocyanohexane/urea at 150 K (guest shown in magenta, host shown in blue) superimposed on 1,6-diisocyanohexane/urea at 140 K (guest shown in yellow, host shown in green) as viewed down the *c*-axis (major site only) with the *b* axis horizontal. In the low-temperature phase, the guest has translated by half the unit cell, approximately 5.5 Å. Graphic made using Mercury. [5]

The structure of the high-temperature form of 1,6-diisocyanohexane/urea is nearly isomorphous with that of 1,6-dicyanohexane/urea. The striking difference between these two is that 1,6-dicyanohexane/urea does not show a phase transition when measured to 90 K.

1,6-Dicyanohexane/urea and 1,6-diisocyanohexane/urea exhibit essentially the same kind of disorder between two gauche conformers of the guests. In the major disordered conformer found in 1,6-diisocyanohexane/urea, the mean plane of the

methylene chain lies within approximately 1º of the [100] axis. This causes distortion along that axis. On the other hand, the mean plane of the alkyl chain of the minor conformer lies approximately 14º from the [001] axis. As described above, since the population of the major part increases as the crystal is cooled, the distortion along the *c* axis generally decreases as the temperature is decreased.

The disordered guests in 1,6-diisocyanohexane/urea and 1,6-dicyanohexane/urea both exhibit a gauche to gauche conformational jump, in a fashion similar to $Br(CH_2)_6Br$/urea, $Br(CH_2)_6Cl$/urea, and $Cl(CH_2)_6Cl$/urea. The disordered guests are related by a jump angle, as determined by the angle of the planes made from the carbons on the two disordered chains (Tables 3 and 4). For 1,6-dicyanohexane and 1,6-diisocyanohexane, the end groups, either cyano or isocyano, do not move very much between the disordered sites. However, the chains jump between +gauche and –gauche conformers. Ideally, such a gauche to gauche jump would require a 120º change in torsion angles. These are tabulated in Tables 5 and 6 and show that the deviation from 120º is small, especially with the data collected with the APEX-II detector.

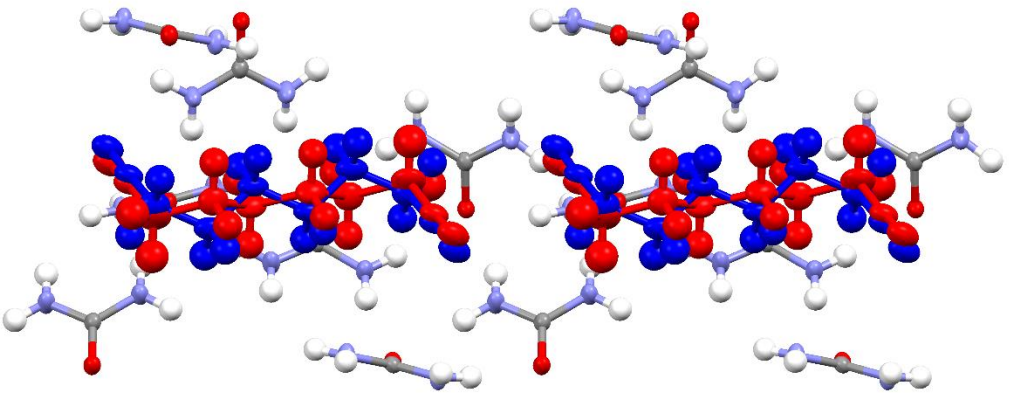

Figure 6. This view of 1,6-diisocyanohexane at 150 K is down the *c* axis with the *b* axis horizontal. The blue guest is the major conformer and red one is the minor conformer. Graphic made using Mercury.[5]

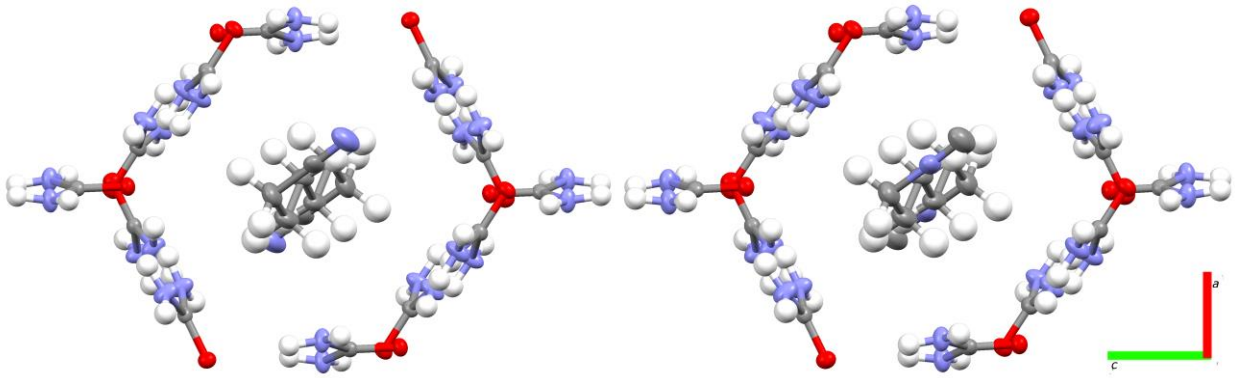

Figure 7. This image shows two structures with their major guest conformers viewed down the channel axis (*b*). The structure on the left is 1,6-dicyanohexane/urea at 158 K, and the one on the right is 1,6-diisocyanohexane/urea at 165 K. These structures are clearly very similar to one another and are isomorphous. Graphic made with Mercury.[5]

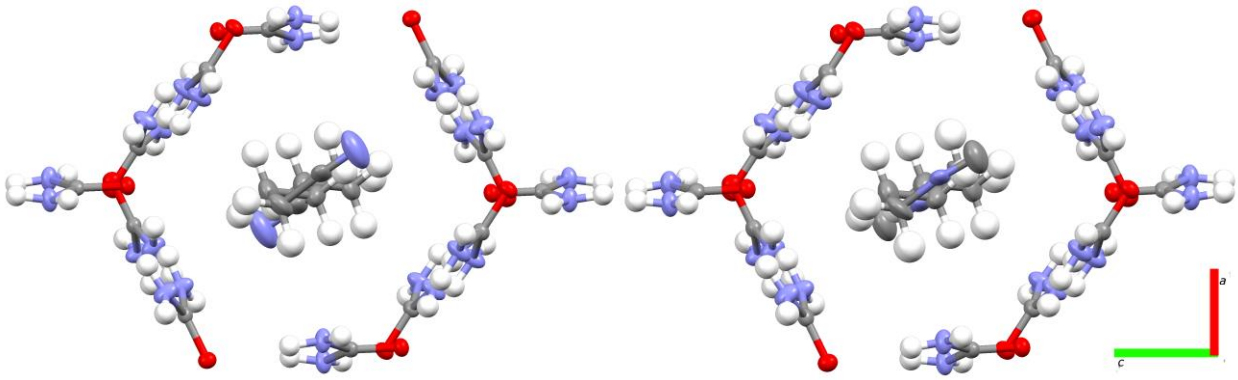

Figure 8. This image shows the two structures with their minor guest conformers viewed down the channel axis (*b*). The structure on the left is 1,6-dicyanohexane/urea at 158 K, and the one on the right is 1,6-diisocyanohexane/urea at 165 K. These structures are clearly very similar to one another and are isomorphous. Graphic made with Mercury. [5]

T/K	Jump Angle (°)
150	78.8
165	78.52
183	76.8
200	78.2
203	77.93
223	78.82
243	78.7

Table 3. The jump angle between the planes of the carbon chains of the two guest sites for 1,6-diisocyanohexane/urea.

T (K)	Jump Angle (°)
90.55	77.10
107	77.79
124	78.00
141	78.25
158	78.80
158	79.80
173	78.76
188	79.20
203	79.26
218	79.80
233	79.85
293	81.78

Table 4. The jump angle between the planes of the carbon chains of the two guest sites for 1,6-dicyanohexane/urea.

Temperature /K	Conformer Major	Minor	Delta	Detector
90.5	60.5	-61.9	122.4	APEX II
107	59.2	-59.4	118.6	APEX II
124	59.1	-59.7	118.8	APEX II
141	58.8	-59.9	118.7	APEX II
158	58.8	-58.9	117.7	APEX II
158	63.4	-63.6	127	SMART 1000
173	58.6	-58	116.6	SMART 1000
188	58.9	-57.2	116.1	SMART 1000
203	58.1	-57.7	115.8	SMART 1000
218	59.3	-55.5	114.8	SMART 1000
233	58.8	-56.6	115.4	SMART 1000
293	65.9	-66.2	132.1	APEX II

Table 5. Torsion angles calculated by SHELXL-97[6] for the cyano group in 1,6-dicyanohexane/urea at different temperatures. The value of delta is the difference between the torsion angles for major and minor conformers and is close to 120° in each case.

Temperature /K	Conformer Major	Minor	Delta	Data source
150	59.7	-59.4	119.1	APEX II
165	59.2	-58.2	117.4	APEX II
183	62.5	-70.3	132.8	SMART 1000
200	60	-57.7	117.7	APEX II
203	63.1	-69	132.1	SMART 1000
223	58.7	-57.9	116.6	SMART 1000
243	58.2	-57	115.2	SMART 1000

Table 6. Torsion angles calculated by SHELXL-97[6] for the isocyano group in 1,6-diisocyanohexane/urea at different temperatures. The value of delta is the difference between the torsion angles for major and minor conformers and is close to 120° in each case.

The occupancies of the disordered guests in 1,6-diisocyanohexane/urea change as a function of temperature. As the temperature decreases, the population of the major disordered site increases relative to that of the minor site until phase transition is reached. The first order phase transition is at 175 K as measured by the DSC cooling curve. The phase transition was found using X-ray diffraction to be between 150 K and 140 K. The discrepancy could be due to the cold stream of the X-ray instrument to be out of alignment or possibly to the use of a single crystal in the X-ray experiment (as opposed to a lightly ground powder in the DSC experiment). The phase change results in translation of the guest by 5.5 Å. It is suspected that the change in the population of the major to minor disorder site facilitates this large translation.[7]

The population change as a function of temperature can be fit as a van 't Hoff plot. This can be used to estimate the population of the major conformer at the phase transition temperature. This population may be used to determine the phase change temperature of similar systems that are difficult to determine.

T(K)	**Major**	**Minor**
150	68.9%	31.1%
165	66.6%	33.5%
200	63.6%	36.4%
183	66.3%	33.7%
203	64.7%	35.4%
223	63.0%	37.0%
243	62.8%	37.3%

Table 7. The major and minor site occupancies for 1,6-diisocyanohexane/urea as a function of temperature, as determined from isotropic refinements of the X-ray data.

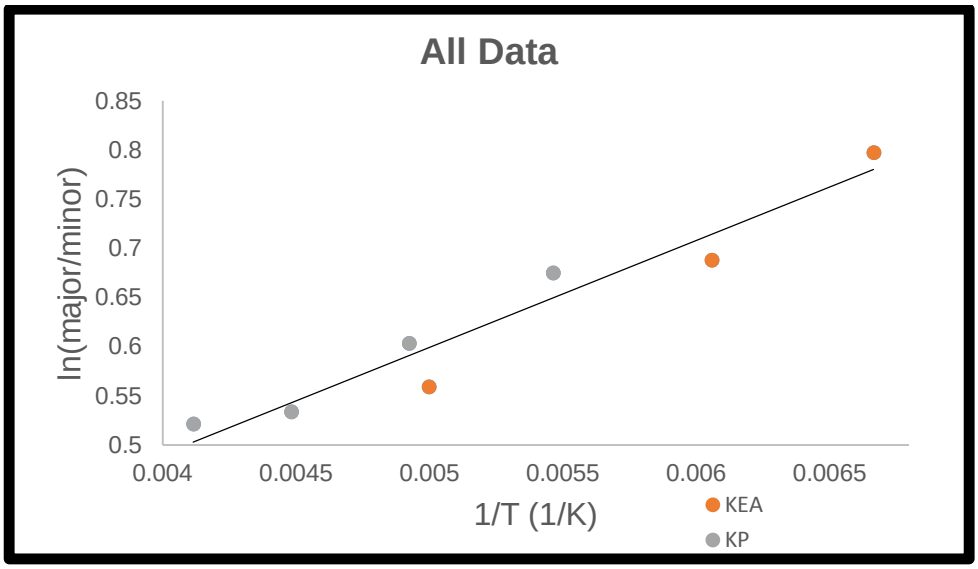

Figure 9. van 't Hoff plot for the major disorder occupancy as a function of temperature for 1,6-diisocyanohexane/urea. The orange data represents data collected by Keith Alquist, and the grey data represents data collected by Kevin Pate. The overall slope is 109.

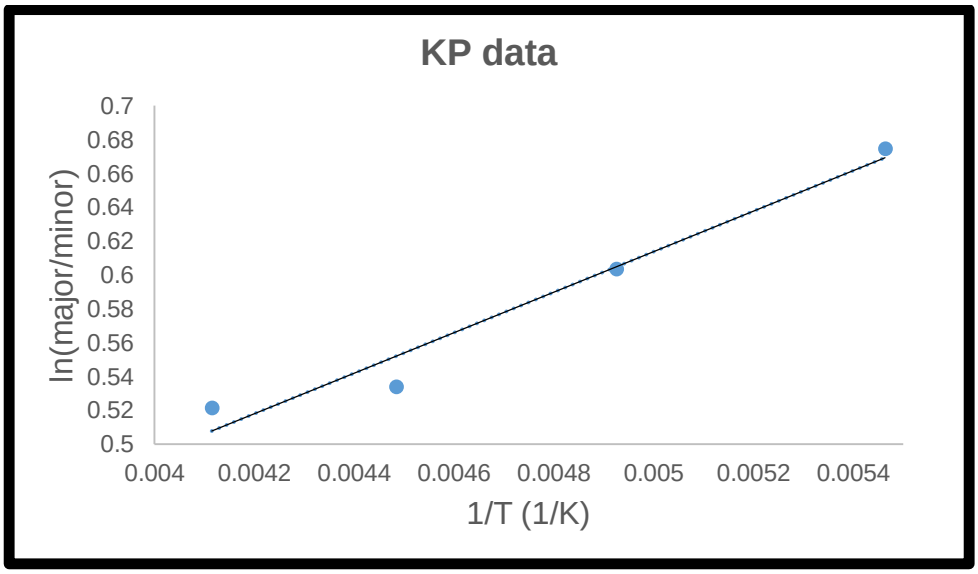

Figure 10. van 't Hoff plot for the major disorder occupancy as a function of temperature for 1,6-diisocyanohexane/urea. This is for just the data originally collected by Kevin Pate, and the slope is 120.

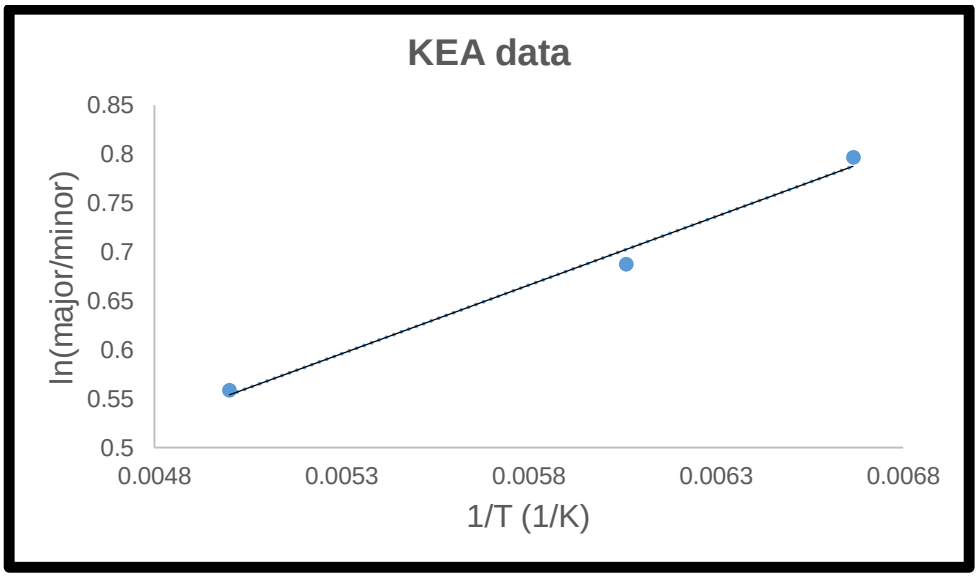

Figure 11. van 't Hoff plot for the conformer occupancies as a function of temperature for 1,6-diisocyanohexane/urea. This is for just the data originally collected by Keith Alquist, and the slope is 140.

The data was from two different experimental situations. These differed by the types of cryostreams used regulate temperature as well as the detectors. For the series,

$y = 108.67x - 0.05551$.

Here y is the natural logarithm of the ratio of major to minor sites, and x is the inverse of the temperature (in Kelvin). This equation results in a threshold populations 62.8% at 150 K, 66.7% at 145 K, and 68.9% at 140 K. The R^2 for this equation was 0.93. Using the van 't Hoff plot to find the enthalpy as the slope multiplied by the gas constant, 1.9872 cal mol^{-1} K^{-1}, gives an enthalpy difference between the major and minor sites of 216 cal mol^{-1} (here, with the minor site taken as the product of the reaction).

At 150 K, the guest molecules of this monoclinic system, 1,6-diisocyanohexane/urea, cause the distortion from hexagonal metric symmetry along the *c* axis by 2-3%. The phase change appears to be triggered by a threshold population of the major conformer of approximately 67%. The low temperature form of this system has a large distortion from hexagonal metric symmetry of around 9.5% along *a*.

The 1,6-dicyanohexane/urea system is different from the 1,6-diisocyanohexane/urea by not having an analogous phase transition. From the slope of its van 't Hoff plot, the enthalpy difference between major and minor conformers is 127 cal mol^{-1} (again, with the minor site taken as the product of the reaction). This isn't quite half of the value for 1,6-diisocyanohexane/urea, but the hypothesis is that the system doesn't have enough energy when it reaches the temperature of its potential transition, which, based on the threshold population, should be close to 92 K when using the following equation from the van 't Hoff plot.

$$y = 63.9x + 0.0027$$

T(K)	major	minor
90.5	67.5%	32.5%
107	64.8%	35.3%
124	62.7%	37.3%
141	61.3%	38.7%
158	60.0%	40.0%
293	56.9%	43.1%
158	58.8%	41.2%
173	58.9%	41.1%
188	58.0%	42.0%
203	57.9%	42.1%
218	56.8%	43.2%
233	57.2%	42.8%

Table 8. The major and minor site occupancies for 1,6-dicyanohexane/urea as a function of temperature.

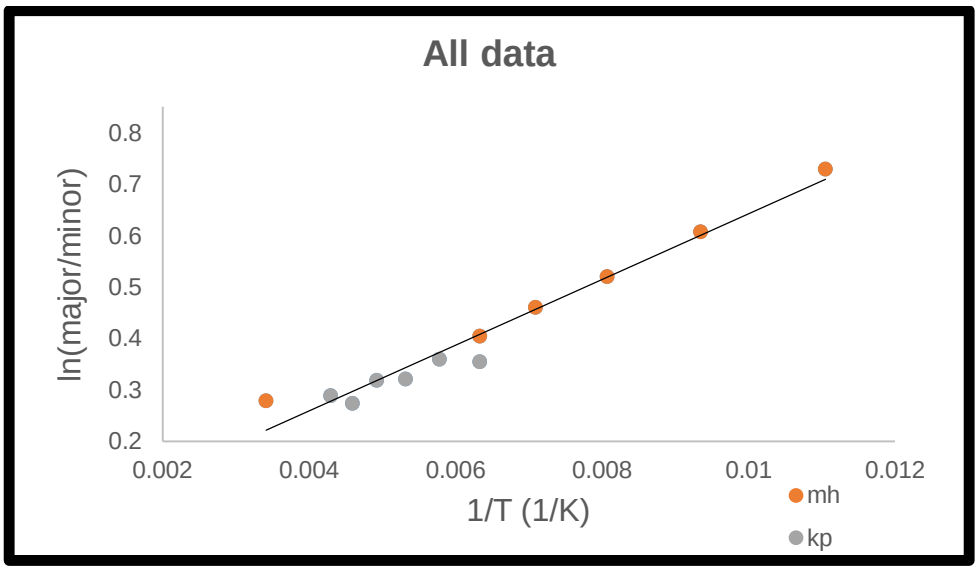

Figure 12. van 't Hoff plot for the conformer occupancies in 1,6-dicyanohexane/urea. The orange data was collected by Roman Gajda, and the grey data was collected by Kevin Pate. The overall slope is 63.9. The R^2 value for the fit is 0.96.

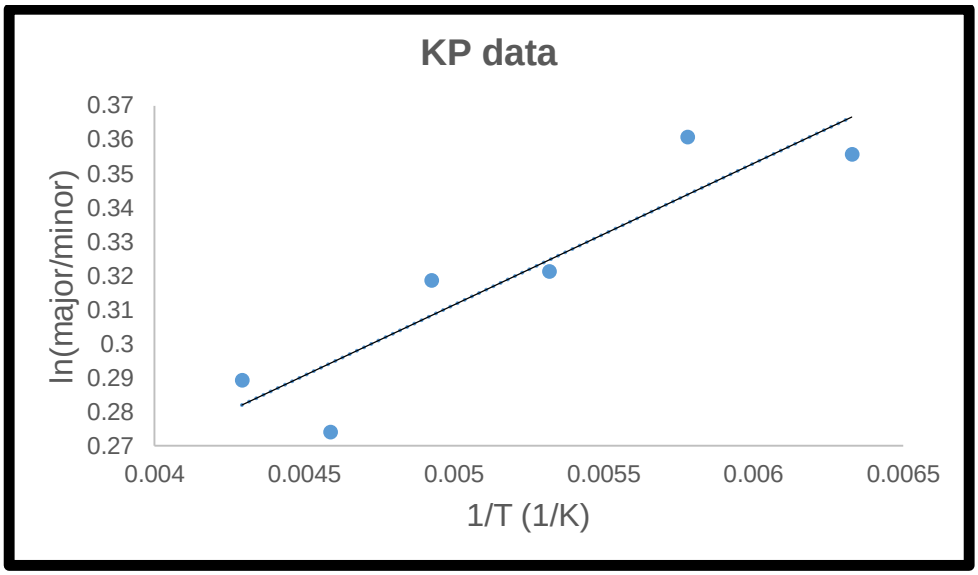

Figure 13. van 't Hoff plot for the conformer occupancies in 1,6-dicyanohexane/urea. This is for just the data originally collected by Kevin Pate, and the slope is 41.5.

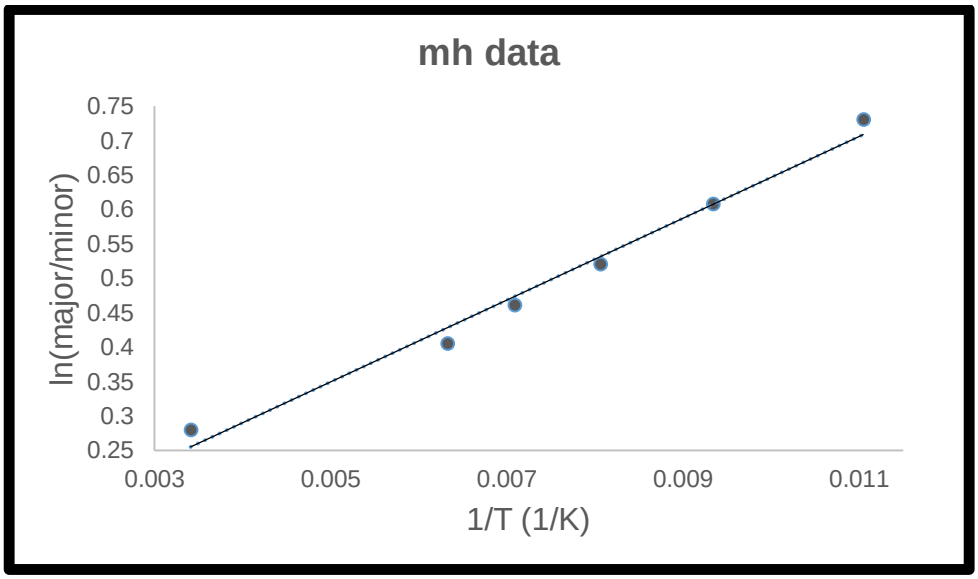

Figure 14. van 't Hoff plot for the conformer occupancies in 1,6-dicyanohexane/urea. This is for just the data originally collected by Roman Gajda, and the slope is 59.5.

Both the 1,6-dicyanohexane/urea and the 1,6-diisocyanohexane/urea crystal structures show significant thermal motion of the guest atoms along the channel axis. This was surprising since the disordered pair would “swing” to the other and the major axis of the thermal ellipsoid should therefore have reflected that by being along an arc more or less perpendicular to the channel axis. A space-filling model for this system shows that there is significant space between the guests along the channel; this would allow molecular motion back and forth along the channel.

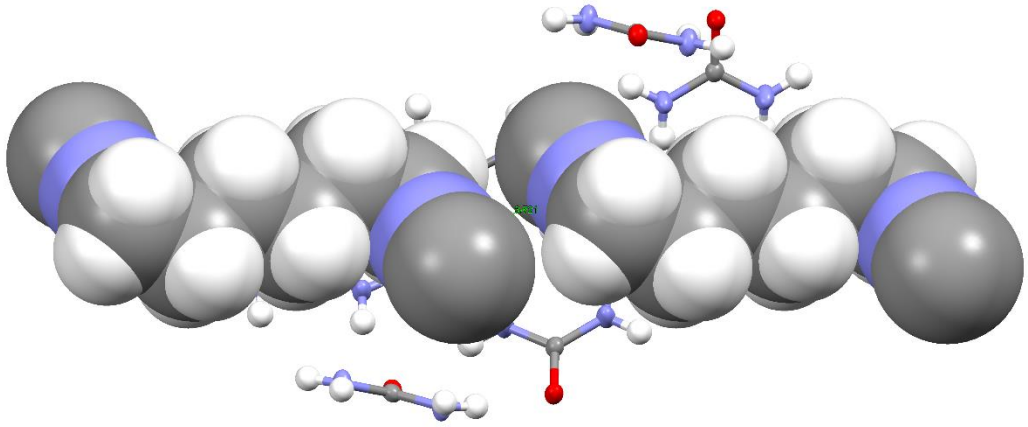

Figure 15. 1,6-Diisocyanohexane/urea at 165 K is shown here using Mercury. The guest is shown as a space filling model and the urea molecules are shown as thermal ellipsoids. The distance between the nitrogen atoms in the isonitriles is 3.721 Å. Graphic made with Mercury. [5]

References

1. Unpublished work done by Ben Champion.

2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level. Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).

3. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).

4. Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Still, E. J., Hollingsworth, M. D., Deuterium NMR studies of guest motions in urea inclusion compounds of 1,6-dibromohexane with analytical evaluation of spectra in the fast motion limit. *Appl. Magn. Reson.* **17**, 265-281 (1999).

5. Mercury CSD 3.3.1. Cambridge Structural Database

6. Sheldrick, G. M., A short history of SHELX. *Acta Crystallographica Section A* **64**, 112-122 (2008).

7. Hollingsworth, M. D., Peterson, M. L., Pate, K. L., Dinkelmeyer, B. D., Brown, M. E., Unanticipated guest motion during a phase transition in a ferroelastic inclusion compound. *J. Am. Chem. Soc.* **124**, 2094-2095 (2002).

Experimental

X-ray data collections on 1,6-dicyanohexane/urea:

The X-ray data collection on 1,6-dicyanohexane/urea were done in two parts by Kevin Pate and Roman Gadja. The two parts are in two temperature series. One series has the temperatures 158, 173, 188, 203, 218 and 233 K as collected by Kevin Pate. The other series was collected by Roman Gadja at the temperatures 158, 141, 124, 107, 90.5 K.

The temperature set collected by Roman Gadja was done on the Bruker Kappa diffractometer with a molybdenum generator with a voltage of 50.00 kV, a current of 32.00 mA, and a λ of 0.71073 Å. The monochromator was made of highly oriented pyrolytic graphite. The detector was the APEX2 CCD 512 x 512 pixels with a pixel size of 0.120 mm. The collection was done at a CCD distance of 55.00 mm with frames requested at 15 seconds and widths of 0.25º.

The temperature set collected by Kevin Pate was done on the Siemens P4 diffractometer with a SMART1000 CCD detector. The collection was done with a graphite monochromated, sealed tube Mo-K_α (λ = 0.71073 Å) radiation source using 20 second, 0.3° frames.

Detailed treatment of all data can be found in the associated structure reports in Appendix A.

X-ray collections on 1,6-diisocyanohexane/urea:

The X-ray data on 1,6-diisocyanohexane/urea was collected at the temperatures 140, 150, 165, 183, 200, 203, 223, 243 K. The datasets at 183, 203, 223, and 243 K were collected by Kevin Pate.

The temperature set collected by Kevin Pate was done on the Siemens P4 diffractometer with a SMART1000 CCD detector. The collection was done with a graphite monochromated, sealed tube Mo-K_α (λ = 0.71073 Å) radiation source using 20 second, 0.3° frames.

The datasets at 140, 150, 165, and 200 K were collected on the Bruker P4 with a molybdenum generator with a voltage of 50.00 kV and a current of 32.00 mA with a λ of 0.71073 Å. The monochromator was made of highly oriented pyrolytic graphite. The detector was the APEX2 CCD 512 x 512 pixels with a pixel size of 0.120 mm. The detector was set at a distance of 80.00 mm.

1,6-Diisocyanohexane/urea KEA-C-271 Data Set at 150 K

The 150 K data set was brought to temperature from 185 K by decreasing the temperature by 20 K per hour. The crystal used was a fragment of a crystal from MDH-K-150-19 and was 200 µm x 240 µm x 60 µm in size. It was checked for crystal uniformity under a polarized light microscope. It was placed on a MiTeGen pin with a 100 µm loop and set in place with paratone oil.

1,6-Diisocyanohexane/urea KEA-C-277 Data Set at 200 K

The 200 K data set was brought to temperature from room temperature rather quickly, as this was not a concern with temperatures that are considerably above the phase transition. This crystal was selected from a larger fragment taken from MDH-K-150-19. The fragment was 80 µm x 200 µm x 340 µm in size. The crystal was checked under a polarized light microscope for visual defects. It was then placed on a MiTeGen pin with a 100 µm loop and set in place with clean paratone oil.

1,6-Diisocyanohexane/urea KEA-C-283 Data Set at 165 K

The 165 K data set was brought to temperature from 188 K by decreasing 20 K per hour. The crystal was taken from a larger fragment taken from MDH-K-150-19. This fragment was 80 µm x 260 µm x 300 µm in size. It was found to be clear and devoid of other fragments by using a polarized light microscope. This was placed on a MiTeGen pin with a 100 µm loop and set with clean paratone oil.

1,6-Diisocyanohexane/urea KEA-C-289 Data Set at 140 K

The 140 K data set was brought to temperature from 165 K by decreasing 20 K per hour. This crystal was 60 µm x 200 µm x 300 µm in size and was taken off of a larger crystal from MDH-K-150-19. The crystal was checked for clarity and other fragments using a polarized light microscope. It was placed on a MiTeGen pin with a 100 µm loop and set with clean paratone oil.

Differential Scanning Calorimetry of 1,6-Diisocyanohexane/urea

Using the Perkin Elmer Pyris differential scanning calorimeter, 1,6-diisocyanohexane/urea was tested for its phase transition onset temperature. To a 30 µl, 96.61 mg pan, 31.29 mg of 1,6-diisocyanohexane/urea crystals were added. The crystals were previously tapped in an agate mortar with a pestle. They were not ground in the mortar. In the method used, the temperature was lowered from 283 K to 113 K at 5K per minute before the system was heated back to 283K at the same rate. The onset temperature was found from two runs to be 175.65 K and 174.77 K.

Refinement Strategy and Model Choice

The refinements for these structures was done using Shelxl 97. [1] The refinement strategy for the high temperature forms of 1,6-dicyanohexane/urea and 1,6-diisocyanohexane/urea was split into two main parts, the first being the isotropic refinement in order to determine the occupancy of the two disordered parts of the guest molecule, the second was the anisotropic refinement and weight analysis. The model used was based largely upon the work done by Kevin Pate but with this exception: the end groups of the 1,6-dicyanohexane and the 1,6-diisocyanohexane are included in the disorder. See Figures 16 and 17.

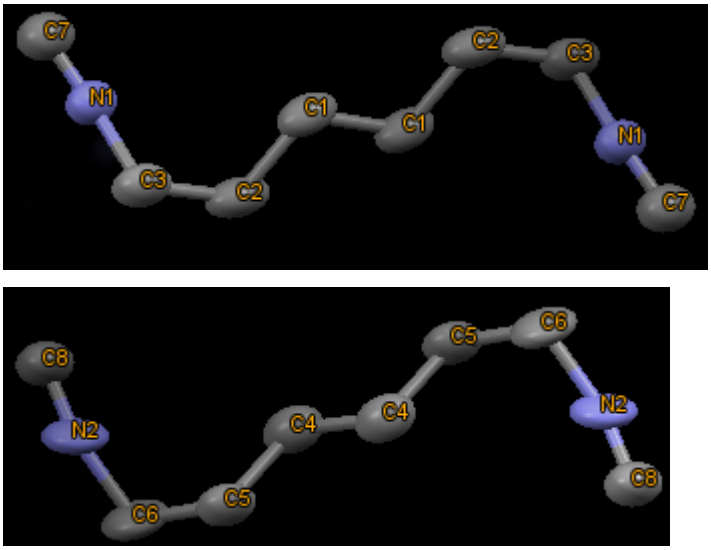

Figure 16. 1,6-diisocyanohexane/urea guest molecule in each part. The top figure is part 1 and the bottom, part 2. This is to show assignment of atoms in the guest. Graphics made using Mercury. [2]

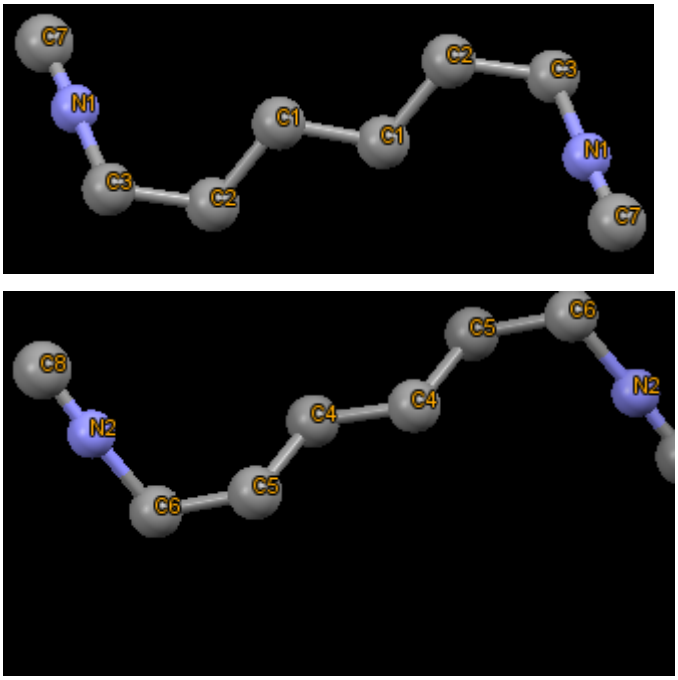

Figure 17. 1,6-dicyanohexane/urea guest molecule in two parts. The top picture is part 1 and the bottom, part 2. This is to show assignment of atoms in the guest. Graphic made with Mercury. [2]

The previous model had a two part disorder that only included the carbons of the backbone and their riding hydrogens but not the cyano or diisocyano groups. Those two groups were assumed to be static. The disordered model used here does not assume that the end groups are static.

There was a comparison refinement for the differing end-group disorder models in order to decide from the figures of merit which model would be used. The data used was from KP2300 1,6-diisocyanohexane/urea at 203 K. The first model was the original, where the isocyano groups did not have any disorder, the second model was where the isocyano groups were entirely disordered, and the third model had only the nitrogen disordered, while the fourth had only the carbon disordered. The goodness of fit was taken into consideration as to the merit of the four models but also of the angle of the carbon-nitrogen-carbon in the isocyano group. This angle should be 180º, of course, but because of the lack of a restraint to force this, one useful figure of merit would be which of these models has a C-N-C angle closest to 180º. The model with complete disorder in the end group was chosen as it had the best goodness of fit and it had the carbon-nitrogen-carbon angle in the isocyano group for part 2 closest to 180º. This is because part 2 is the minor and weakest for the reflections. The best fit for part 2 would equate to the better model.

Model #	#1	#2	#3	#4	units
R1	0.1194	0.115	0.1169	0.1164	none
GooF	1.73	1.661	1.7	1.679	none
Occupancy	0.63695	0.63741	0.62814	0.62565	none
H3A-H3B Dist	0.447	0.327	0.534	0.383	Å
CNC Angle Part1	172.24	173.07	174.04	175.32	degrees
CNC Angle Part2	171.68	172.48	166.79	170.42	degrees
Angle Difference	0.56	0.59	7.25	4.9	degrees

Table 9. A comparison of the conditions of disorder for cyano groups in 1,6-diisocyanohexane/urea at 203 K.

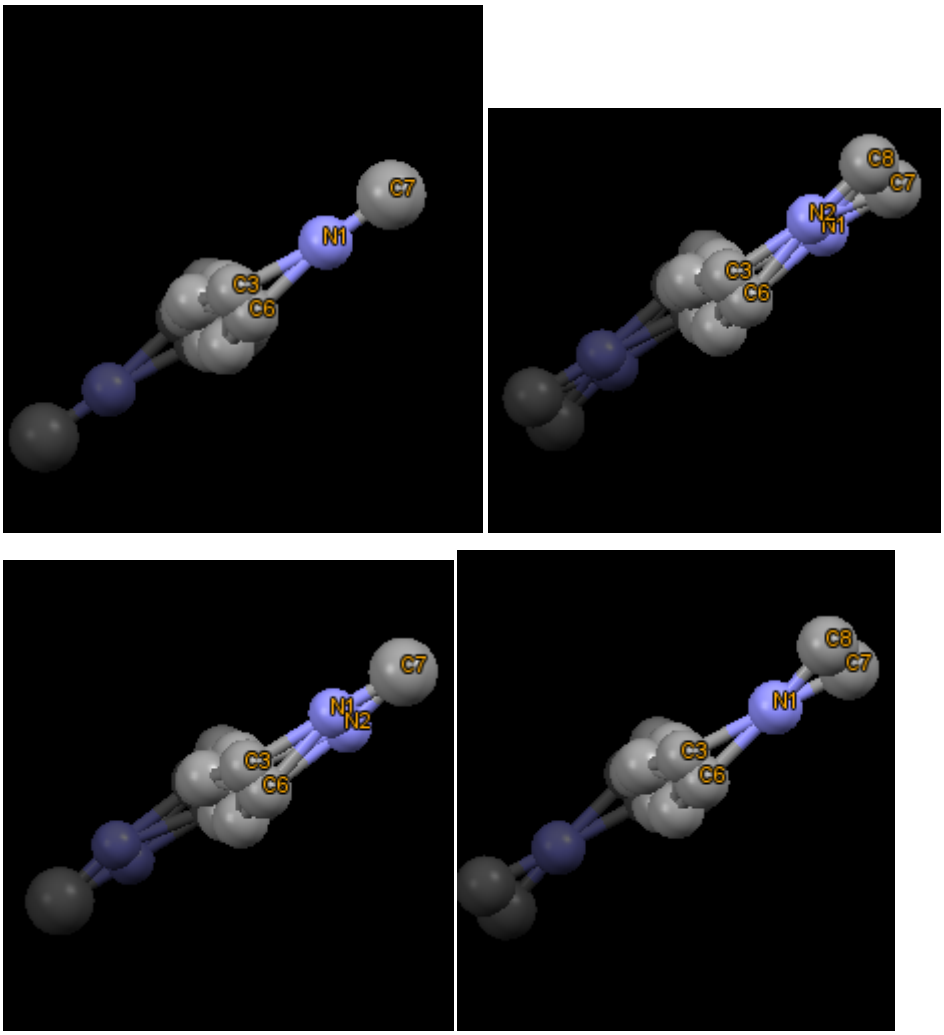

Figure 18. This is a visual representation of the models refined. From left to right, starting at top: Model #1, #2, #3, #4. Graphic made with Mercury. [2]

The model also includes commands that are used to restrain or constrain the guest molecule to reasonable relative angles and distances between its atoms. The main restraints used in ShellX-97 refinements were the SADI and FLAT restraints. The

SADI restraint attempts to retain relative distances between atoms to within the defined parameter DEFS. The constraint used was the EADP constraint. The EADP constraint, as used in this model, enforces the displacement parameters of the analogous atoms of the disorder be the same. The FLAT restraint enforces the 4 heavy atoms at the end of the guest be in a plane. The FLAT restraint was the only restraint that could help the end groups to be linear.

The use of the SADI restraint was used to keep the methylene groups on the guest chain equivalent with respect to angle and distance from each other. It was first used to keep the methyl groups the same distance from their nearest neighbor as the rest of them. It was next used to restrain the distance of alpha and gamma carbon the same, thereby making the angle of methyl groups to one another similar. The distance of the cyano and isocyano from the chain carbons was made the same between parts as well as the distance between the carbon and nitrogen atoms within the cyano and isocyano group to be the same between the two parts. In essence, the carbon-nitrogen distance in the end group should be the same in part 1 as in part 2. These restraints persisted throughout the refinement.

For the 1,6-diisocyanohexane model,

```
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 N1 C6 N2
SADI C3 C7 C6 C8
SADI N1 C2 N2 C5
```

For the 1,6-dicyanohexane model,

```
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
```

SADI C3 N1 C6 N2
SADI C7 C2 C8 C5

The EADP constraints were used for isotropic refinement but generally dropped after the model was refined to be anisotropic. The EADP was used for the atoms in the guest to have the same thermal parameters as their counterpart in its disordered pair. The FLAT constraint was used in an attempt to keep the alpha carbon and the cyano/isocyano as linear as possible. The isotropic refinements were used to find the occupancies of the disordered pair. It contained a second variable in the FVAR instruction for this use. These refinements also contained the SADI restraint as well as the EADP and FLAT constraints as explained above. It also used the disordered end group model. The refinement was given sufficient least squares cycles to have its shift converge to zero. After this refinement, the second FVAR variable was removed and the occupancy of the two parts were set based on this. The rest of the anisotropic refinements keep these occupancies set.

For the 1,6-diisocyanohexane isotropic model, the following commands were used.

EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2

FLAT C2 C3 N1 C7
FLAT C5 C6 N2 C8

For the 1,6-dicyanohexane isotropic model, the following commands were used:

EADP C3 C6

EADP C2 C5

EADP C1 C4

EADP C7 C8

EADP N1 N2

FLAT C2 C3 C7 N1

FLAT C5 C6 C8 N2

The anisotropic refinements have the occupancies set by the isotropic refinement. After the ANIS instruction was run, the remaining refinements were run generally without use of the EADP constraint. EADP constraints were occasionally used when thermal parameters of an atom were prolate. An extinction coefficient would be used in the cases that its value didn't converge upon zero while refining.

The weight analysis, as changed by using the first two variables in the WGHT instruction, was done on multiple values in order to reduce estimated standard deviations (esd) of the atom positions. This was found through averaging all the esd for the atoms in the refinement as well as finding reasonable figures of merit.

After a weight was chosen, reflections that gave a Fobs/Fcalc greater than 10 sigma would be omitted. This was not always the case where there weren't any reflections that required it. Then, a refinement using the HTAB instructions to list all of the details of all hydrogen bonds would be given as well as with the appropriate EQIV statements. Afterward, the ACTA instruction would be given to generate a *.cif file and the *.fcf files for checking with CheckCIF.

HTAB, EQIV and CONF instructions for 1,6-diisocyanohexane

EQIV $1 1-x, -y, 1-z

EQIV $2 x+1, y, z

EQIV $3 -x+0.5, y+0.5, -z+1.5

EQIV $4 -x+0.5, y-0.5, -z+1.5

EQIV $5 x-1, y, z

EQIV $6 x, y-1, z

```
EQIV $7 -x+1.5, y-0.5, -z+1.5
EQIV $8 x, y+1, z
EQIV $9 -x, -y+1, -z+1
EQIV $10 -x+1, -y+1, -z+1

HTAB N21 O10_$2
HTAB N21 O30_$3
HTAB N20 O30_$2
HTAB N20 O10_$4
HTAB N31 O20_$5
HTAB N31 O10_$4
HTAB N30 O10_$6
HTAB N30 O20_$7
HTAB N11 O30_$8
HTAB N11 O30_$9
HTAB N10 O20_$5
HTAB N10 O20_$10

CONF N2 C6 C5 C4
CONF C6 C5 C4 C4_$1
CONF N1 C3 C2 C1
CONF C3 C2 C1 C1_$1
```

HTAB, EQIV and CONF statements for 1,6-dicyanohexane/urea

```
EQIV $1 1-x, -y, 1-z
EQIV $2 x+1, y, z
EQIV $3 -x+0.5, y+0.5, -z+1.5
EQIV $4 -x+0.5, y-0.5, -z+1.5
EQIV $5 x-1, y, z
EQIV $6 x, y-1, z
```

```
EQIV $7 -x+1.5, y-0.5, -z+1.5
EQIV $8 x, y+1, z
EQIV $9 -x, -y+1, -z+1
EQIV $10 -x+1, -y+1, -z+1

HTAB N21 O10_$2
HTAB N21 O30_$3
HTAB N20 O30_$2
HTAB N20 O10_$4
HTAB N31 O20_$5
HTAB N31 O10_$4
HTAB N30 O10_$6
HTAB N30 O20_$7

HTAB N11 O30_$8
HTAB N11 O30_$9
HTAB N10 O20_$5
HTAB N10 O20_$10

CONF C7 C3 C2 C1
CONF C3 C2 C1 C1_$1
CONF C8 C6 C5 C4
CONF C6 C5 C4 C4_$1
```

References

1. Sheldrick, G. M., A short history of SHELX. *Acta Crystallographica Section A* **64**, 112-122 (2008).

2. Mercury CSD 3.3.1. Cambridge Structural Database

Conclusions

The crystal structure of the low temperature crystal form of 1,6-diisocyanohexane/urea has been determined at 140 K and shows that the guest has translated by half a unit cell (5.5 Å) along the channel axis from its position in the higher temperature form. X-ray data sets were also collected at 150, 165, and 200 K for 1,6-diisocyanohexane/urea. These data sets, as well as the data sets collected by Kevin Pate at 183, 203, 223, and 243 K were refined in a similar fashion to give both isotropic and anisotropic data. The isocyano end groups were refined with disorder. The population of the disorder for these was recorded and a van 't Hoff plot was constructed, giving a slope that correlates to an enthalpy difference of 216 cal/mol.

The disordered pair of guest molecules in 1,6-diisocyanohexane/urea has a jump angle very close to that observed in 1,6-dibromohexane/urea, which was demonstrated to be a gauche to gauche guest jump with deuterium solid state NMR. It is expected that 1,6-diisocyanohexane/urea would show similar results when such an experiment is conducted.

1,6-Dicyanohexane/urea was refined using a similar model to that used for 1,6-diisocyanohexane/urea. Its cyano end groups were also refined as disordered. The crystal structure of this system was refined at 90.5, 107, 124, 141, 158, 158, 173, 188, 203, 218, 233, and 293 K. The X-ray data sets were taken by either Kevin Pate or Roman Gajda. The refinements were done in a similar fashion to one another for consistency. A van 't Hoff plot was made for this data, and the enthalpy was found to be -127 kcal/mol. This is close to half of the value found for 1,6-diisocyanohexane and supports the hypothesis that this system does not have enough energy at its predicted phase transition temperature (92 K) to overcome the thermal barrier for a translation of its guest molecule.

Appendix A – X-ray Crystal Structure Reports

Please note that the structure reports in this appendix were generated starting with a template used in the Hollingsworth group for over 20 years to create a standardized set of structure reports. Substitutions and additions of text were made to the template to match the crystal structure determination in each of the reports. Representative examples of standard structure reports for similar systems are given in the Supporting On-line information associated with the following publications:

1. Hollingsworth, M. D.; Werner-Zwanziger, U.; Brown, M. E.; Chaney, J. D.; Huffman, J. C.; Harris, K. D. M.; Smart, S. P., "Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds," *J. Am. Chem. Soc.* **121**, 9732 (1999).
2. Hollingsworth, M., D.; Peterson, M., L.; Pate, K., L.; Dinkelmeyer, B., D.; Brown, M., E., "Unanticipated guest motion during a phase transition in a ferroelastic inclusion compound," *J. Am. Chem. Soc.* **124**, 2094 (2002).

Appendix A

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Structure report for 1,6-dicyanohexane/urea at 90 K[1]

Introduction

The data for this crystal was collected in 2010 by Roman Gajda on the Bruker Kappa diffractometer equipped with an APEX II detector and was originally labeled "mh1001e". (See laboratory notebook RBG A-60-1.) The original crystal was from Christopher J. Nichols. (CJN A-78-05). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 67.5% and 32.5%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 77.1°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 600 µm x 430 µm x 300 µm. The crystal was cooled to 90 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 15 seconds, and the frame width was 0.25º.[3] The crystal to detector distance was 55.00 mm.

The unit cell parameters were determined[3,4] from 9923 input reflections whose minimum and the maximum 2-theta values were 4.717 and 74.351, respectively. The errors are reported after corrections for the goodness of fit (9.63). The cell volume is 1251.42 (26) Å^3.

a = 8.0940 (9) Å	α = 90°
b = 10.8601 (11) Å	β = 94.613 (5)°
c = 14.2828 (15) Å	γ = 90°

For Z = 2 and F.W. = 496.57, the calculated density is 1.318 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 26000 reflections of which 649 were rejected. After merging Friedel opposites, there were 6213 unique reflections, of which 5317 had I > 2sigma(I). The R(int) was 0.0591, and the R(sigma) was 0.0415. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.104 mm^{-1}. The absorption correction was made using SADABS.[3, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in mh1001e_06.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.088 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

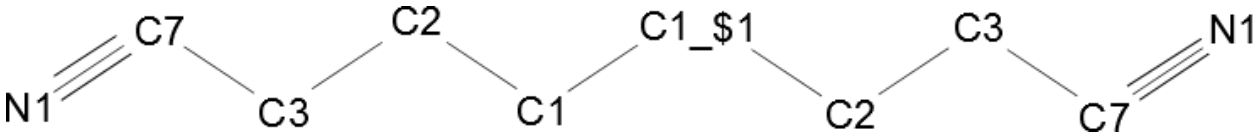


Figure 1: Atomic labeling scheme for part 1 (major part)

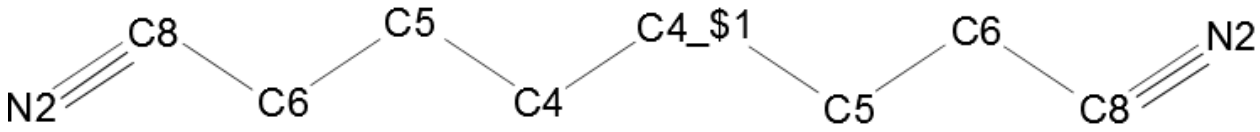


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2, and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.194 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.191 for all of the data. R1 was 0.0495 for all 6213 data and 0.0417 for data with $I>2\sigma(I)$; the wR2 value was 0.1011 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5

EADP N1 N2
EADP C8 C7
```

(The other EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms. In order to give values of the thermal parameters to the minor guest at the cyano carbons and nitrogen that are consistent with the major guest, the EADP constraints were kept for these atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	993.14
Crystal color, habit	Clear, prism
Crystal dimensions	600 x 430 x 300 μm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	9923
Lattice parameters	a = 8.0940 (9) Å b = 10.8601 (11) Å c = 14.2828 (15) Å α = 90° β = 94.613 (5)° γ = 90° V = 1251.42 (26) Å^3
Space group	P2(1)/n (#14)
Z value	1
D_{calc}	1.318
F_{000}	532
μ (MoK_α)	0.104 mm^{-1}
Temperature	90 K

B. Intensity measurements

Diffractometer	Bruker Kappa, APEX II CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K_α (λ = 0.71073 Å)
Crystal to detector distance	55 mm
Time per frame	15 s
Temperature	90 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.36°
θ_{max}	37.18°
h k l range	h = -13 to 13 k = -18 to 17 l = -21 to 24
No. of reflections measured	Total: 26000 Unique 6213 (R_{int} = 0.0591) I > 2σ(I) = 5317

Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	5317
No. variables	223
No. Restraints	27
Reflection:parameter ratio	27.86
For I > 2.00σ(I)	23.84
No. Reflections used in refinement	6213
Final R indices [I > 2σ(I)] R1	0.0417
Final R indices [all data]; R1, wR2	0.0495; 0.1011
Goodness of Fit (s)	1.191
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.530 e/Å^3
Minimum peak in final diff. map	-0.268 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	1.00070 (6)	0.42016 (4)	0.65343 (3)	0.01221 (9)	
O30	−0.02998 (6)	0.08808 (4)	0.65397 (3)	0.01192 (9)	
O10	−0.01099 (6)	0.75151 (4)	0.68258 (3)	0.01177 (9)	
N21	0.81047 (8)	0.52276 (5)	0.73133 (5)	0.01746 (12)	
H21A	0.8641 (14)	0.5910 (10)	0.7226 (8)	0.021*	
H21B	0.7237 (14)	0.5237 (10)	0.7607 (8)	0.021*	
N20	0.78577 (8)	0.31330 (5)	0.70484 (5)	0.01691 (11)	
H20A	0.8294 (14)	0.2471 (10)	0.6851 (8)	0.020*	
H20B	0.6997 (14)	0.3095 (10)	0.7361 (8)	0.020*	
N31	0.19714 (8)	0.19543 (5)	0.70954 (5)	0.01673 (11)	
H31A	0.1534 (14)	0.2619 (10)	0.6835 (8)	0.020*	
H31B	0.2942 (14)	0.1992 (10)	0.7387 (8)	0.020*	
N30	0.17891 (8)	−0.01303 (5)	0.73623 (5)	0.01746 (11)	
H30A	0.1189 (14)	−0.0791 (10)	0.7333 (8)	0.021*	

H30B	0.2647 (14)	−0.0126 (10)	0.7725 (8)	0.021*	
C20	0.86957 (8)	0.41877 (5)	0.69523 (4)	0.01125 (10)	
C30	0.11127 (8)	0.09039 (5)	0.69911 (4)	0.01059 (10)	
N11	−0.03359 (8)	0.85523 (5)	0.54436 (4)	0.01594 (11)	
H11A	−0.0464 (14)	0.9231 (10)	0.5761 (8)	0.019*	
H11B	−0.0166 (13)	0.8589 (10)	0.4865 (8)	0.019*	
C10	−0.00430 (7)	0.75170 (5)	0.59424 (4)	0.01043 (10)	
N10	0.03511 (8)	0.64918 (5)	0.54856 (4)	0.01514 (11)	
H10A	0.0334 (14)	0.5801 (10)	0.5801 (8)	0.018*	
H10B	0.0203 (13)	0.6454 (10)	0.4889 (8)	0.018*	
C3	0.5168 (4)	0.2844 (2)	0.4356 (3)	0.0262 (6)	0.6748
H3A	0.608	0.3404	0.4213	0.031*	0.6748
H3B	0.4442	0.2731	0.377	0.031*	0.6748
C2	0.59084 (16)	0.15899 (13)	0.46622 (10)	0.0273 (2)	0.6748
H2A	0.6568	0.1273	0.4159	0.033*	0.6748
H2B	0.6673	0.1709	0.5231	0.033*	0.6748
C1	0.46192 (17)	0.06261 (12)	0.48720 (11)	0.0245 (3)	0.6748
H1A	0.3821	0.0532	0.4314	0.029*	0.6748
H1B	0.3997	0.092	0.5398	0.029*	0.6748
C7	0.4212 (5)	0.3423 (5)	0.5057 (4)	0.0228 (5)	0.6748
N1	0.3383 (3)	0.3886 (4)	0.5565 (2)	0.0313 (5)	0.6748
C5	0.5044 (4)	0.1521 (2)	0.42821 (18)	0.0265 (5)	0.3252
H5A	0.389	0.1486	0.3995	0.032*	0.3252
H5B	0.5776	0.1213	0.3811	0.032*	0.3252
C4	0.5193 (4)	0.0669 (2)	0.51233 (19)	0.0237 (5)	0.3252
H4A	0.4427	0.0954	0.5585	0.028*	0.3252
H4B	0.6335	0.0722	0.5426	0.028*	0.3252
C6	0.5485 (9)	0.2862 (5)	0.4500 (5)	0.0277 (13)	0.3252
H6A	0.6647	0.2902	0.4773	0.033*	0.3252
H6B	0.5416	0.3332	0.3904	0.033*	0.3252
C8	0.4423 (13)	0.3451 (10)	0.5144 (8)	0.0228 (5)	0.3252
N2	0.3711 (7)	0.3873 (9)	0.5719 (5)	0.0313 (5)	0.3252

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0126 (2)	0.00991 (18)	0.0148 (2)	0.00023 (14)	0.00508 (15)	0.00023 (15)
O30	0.0120 (2)	0.00967 (18)	0.0139 (2)	0.00014 (14)	−0.00006 (15)	−0.00010 (15)
O10	0.0146 (2)	0.01050 (18)	0.01040 (19)	−0.00015 (14)	0.00216 (15)	−0.00003 (14)
N21	0.0194 (3)	0.0092 (2)	0.0255 (3)	0.00033 (18)	0.0123 (2)	−0.0016 (2)
N20	0.0160 (3)	0.0089 (2)	0.0272 (3)	−0.00129 (17)	0.0100 (2)	−0.0001 (2)
N31	0.0158 (3)	0.0094 (2)	0.0239 (3)	−0.00223 (17)	−0.0049 (2)	0.00164 (19)
N30	0.0187 (3)	0.0094 (2)	0.0229 (3)	0.00038 (18)	−0.0068 (2)	0.0029 (2)
C20	0.0126 (2)	0.0085 (2)	0.0130 (2)	0.00073 (17)	0.00291 (19)	0.00100 (18)
C30	0.0131 (2)	0.0086 (2)	0.0102 (2)	0.00039 (17)	0.00173 (18)	−0.00043 (17)
N11	0.0267 (3)	0.0092 (2)	0.0120 (2)	0.00141 (19)	0.0016 (2)	0.00144 (17)
C10	0.0106 (2)	0.0088 (2)	0.0119 (2)	−0.00119 (17)	0.00105 (18)	−0.00023 (18)
N10	0.0245 (3)	0.0094 (2)	0.0118 (2)	0.00130 (18)	0.0032 (2)	−0.00074 (17)
C3	0.0221 (13)	0.0368 (9)	0.0206 (9)	0.0001 (6)	0.0079 (8)	−0.0055 (6)
C2	0.0165 (5)	0.0386 (7)	0.0275 (6)	−0.0004 (4)	0.0062 (4)	−0.0089 (5)
C1	0.0140 (6)	0.0361 (7)	0.0234 (6)	0.0003 (5)	0.0020 (4)	−0.0097 (5)
C7	0.0169 (12)	0.0303 (4)	0.0215 (11)	−0.0065 (7)	0.0035 (9)	−0.0061 (5)
N1	0.0249 (11)	0.0384 (4)	0.0317 (12)	−0.0069 (10)	0.0096 (8)	−0.0125 (9)
C5	0.0292 (13)	0.0313 (12)	0.0201 (11)	0.0027 (10)	0.0088 (10)	−0.0038 (9)
C4	0.0219 (14)	0.0322 (13)	0.0165 (11)	0.0022 (10)	−0.0017 (9)	−0.0052 (9)
C6	0.018 (2)	0.0357 (19)	0.031 (3)	−0.0022 (13)	0.012 (2)	−0.0037 (15)
C8	0.0169 (12)	0.0303 (4)	0.0215 (11)	−0.0065 (7)	0.0035 (9)	−0.0061 (5)
N2	0.0249 (11)	0.0384 (4)	0.0317 (12)	−0.0069 (10)	0.0096 (8)	−0.0125 (9)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2590 (8)	C3—C2	1.537 (3)
O30—C30	1.2668 (8)	C2—C1	1.5246 (19)
O10—C10	1.2673 (8)	C1—C1i	1.525 (3)
N21—C20	1.3453 (8)	C7—N1	1.143 (3)
N20—C20	1.3438 (8)	C5—C4	1.514 (3)
N31—C30	1.3378 (8)	C5—C6	1.525 (5)
N30—C30	1.3400 (8)	C4—C4i	1.523 (5)
N11—C10	1.3420 (8)	C6—C8	1.456 (6)
C10—N10	1.3418 (8)	C8—N2	1.137 (6)
C3—C7	1.457 (3)		
O20—C20—N20	120.69 (5)	C7—C3—C2	113.8 (3)
O20—C20—N21	120.73 (6)	C1—C2—C3	113.99 (16)
N20—C20—N21	118.58 (6)	C2—C1—C1i	112.91 (14)
O30—C30—N31	120.87 (6)	N1—C7—C3	175.7 (5)
O30—C30—N30	120.53 (6)	C4—C5—C6	114.8 (3)
N31—C30—N30	118.59 (6)	C5—C4—C4i	113.5 (3)
O10—C10—N11	120.66 (5)	C8—C6—C5	114.1 (6)
O10—C10—N10	120.91 (6)	N2—C8—C6	172.9 (12)
N11—C10—N10	118.42 (6)		
C7—C3—C2—C1	60.5 (3)	C8—C6—C5—C4	−61.9 (8)
C3—C2—C1—C1i	177.2 (2)	C6—C5—C4—C4i	−177.9 (4)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. **Torsion Angles**

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	60.5 (3)
C3	C2	C1	C1	177.2 (2)
C8	C6	C5	C4	-61.9 (8)
C6	C5	C4	C4	-177.9 (4)

Table 5. **Hydrogen-bond Geometries (in Å)**

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.872 (11)	2.117 (11)	2.9844 (8)	172.5 (10)
N21—H21B···O30iii	0.846 (11)	2.177 (11)	2.9899 (8)	160.9 (10)
N20—H20A···O30ii	0.858 (11)	2.135 (11)	2.9848 (8)	170.5 (10)
N20—H20B···O10iv	0.858 (11)	2.089 (11)	2.9253 (8)	164.6 (10)
N31—H31A···O20v	0.873 (11)	2.141 (11)	2.9869 (8)	163.1 (10)
N31—H31B···O10iv	0.860 (11)	2.085 (12)	2.9273 (8)	166.0 (10)
N30—H30A···O10vi	0.866 (11)	2.211 (11)	3.0494 (8)	162.8 (10)
N30—H30B···O20vii	0.832 (11)	2.222 (12)	3.0129 (9)	158.9 (10)
N11—H11A···O30viii	0.876 (11)	2.107 (11)	2.9730 (8)	169.6 (10)
N11—H11B···O30ix	0.849 (11)	2.150 (11)	2.9837 (8)	167.1 (10)
N10—H10A···O20v	0.876 (11)	2.056 (11)	2.9282 (8)	173.5 (10)
N10—H10B···O20x	0.852 (11)	2.148 (11)	2.9731 (8)	163.1 (10)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x,
y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2 showing part 1 with 40% probability surfaces.

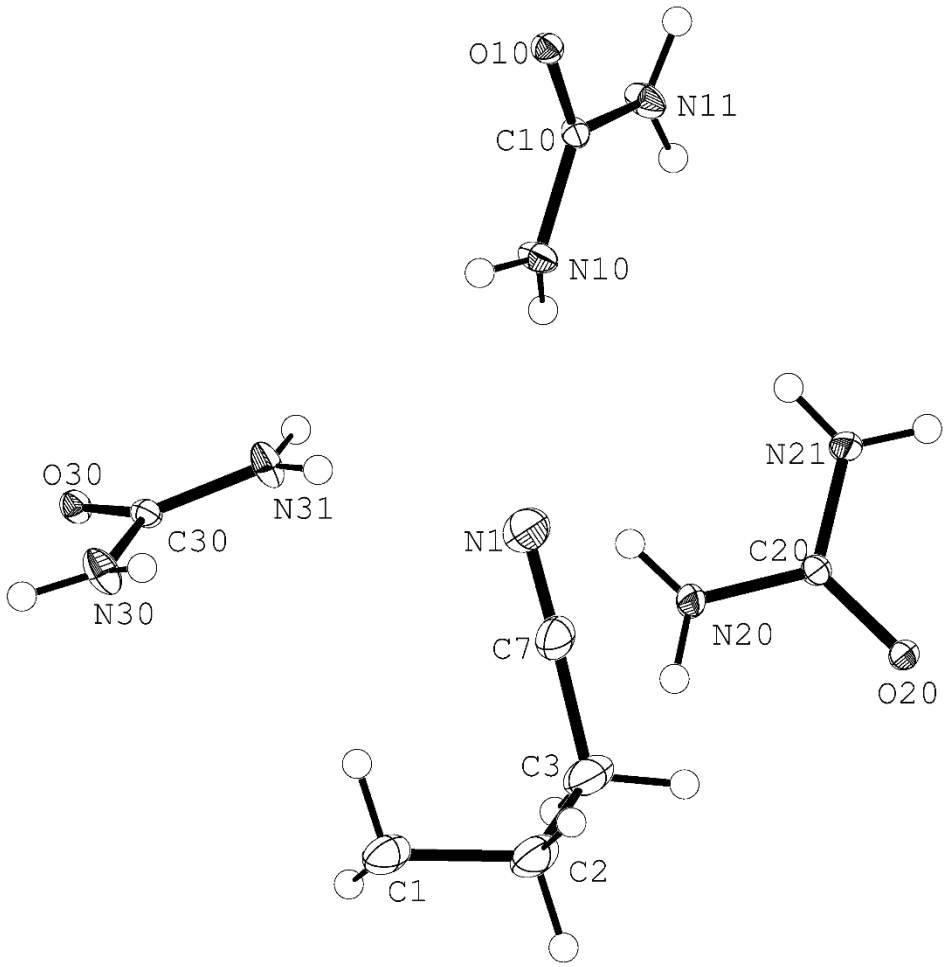
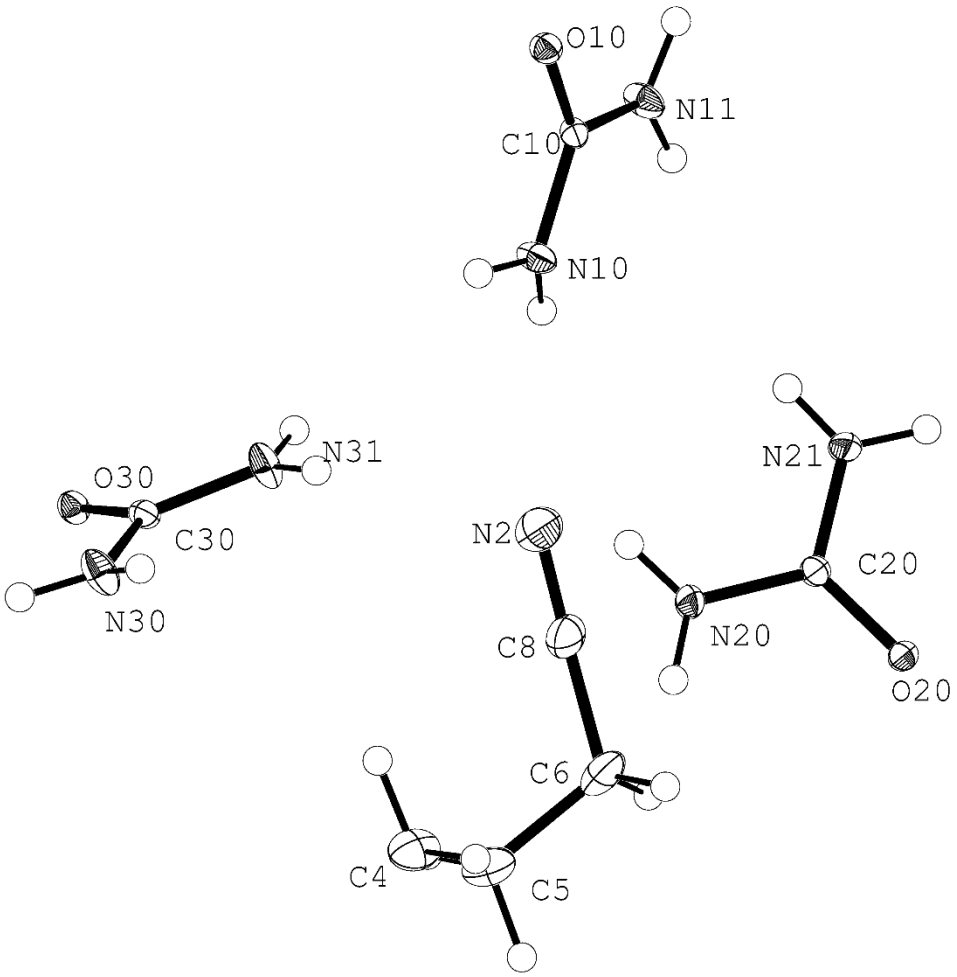


Figure 4: ORTEP rendering by OLEX2 showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 90 K (mh1001e).

2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Data collected using the Bruker APEX2 software package.
4. Bruker SAINT V8.18C
5. The SADABS program is based on the method of Blessing; see Blessing, R. H. *Acta Crystallogr.*, A**51**, 33, (1995).
6. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
7. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

Structure report for 1,6-dicyanohexane/urea at 107 K[1]

Introduction

The data for this crystal was collected in 2010 by Roman Gajda on the Bruker Kappa diffractometer equipped with an APEX II detector and was originally labeled "mh1001d". (See laboratory notebook RBG A-60-1.) The original crystal was from Christopher J. Nichols (CJN A-78-05). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 64.8% and 35.2%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 77.79°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 600 µm x 430 µm x 300 µm. The crystal was cooled to 107 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 15 seconds and the frame width was 0.25º.[3] The crystal to detector distance was 55.00 mm.

The unit cell parameters were determined[3,4] from 9941 input reflections whose minimum and the maximum 2-theta values were 5.04 and 71.48, respectively. The errors are reported after corrections for the goodness of fit (10.04). The cell volume is 1253.62 (27) Å^3.

a = 8.0936 (9) Å	α = 90°
b = 10.8667 (12) Å	β = 94.591 (5)°
c = 14.2994 (16) Å	γ = 90°

For Z = 2 and F.W. = 496.57, the calculated density is 1.307 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be:

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 25161 reflections of which 634 were rejected. After merging Friedel opposites, there were 5706 unique reflections, of which 4873 had I > 2sigma(I). The R(int) was 0.0564, and the R(sigma) was 0.0399. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.104 mm^{-1}. The absorption correction was made using SADABS.[3, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in mh1001d_06.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.088 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

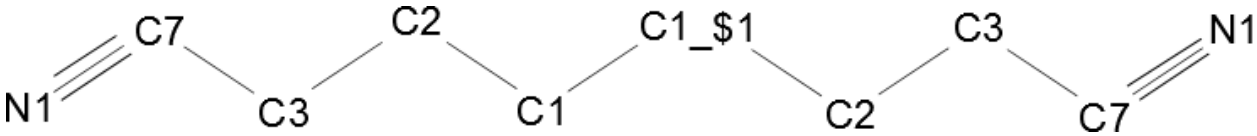


Figure 1: Atomic labeling scheme for part 1 (major part)

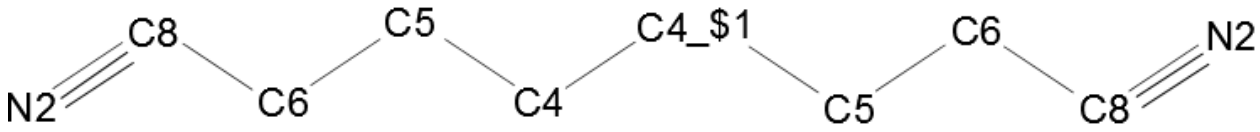


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.174 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.175 for all of the data. R1 was 0.0498 for all 5279 data and 0.0417 for data with $I>2\sigma(I)$; the wR2 value was 0.0997 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	993.14
Crystal color, habit	Clear, prism
Crystal dimensions	600 x 430 x 300 μm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	9941
Lattice parameters	a = 8.0936 (9) Å
	b = 10.8667 (12) Å
	c = 14.2994 (16) Å
	α = 90°
	β = 94.591 (5)°
	γ = 90°
	V = 1253.62 (27) Å^3
Space group	P2(1)/n (#14)
Z value	1
D_{calc}	1.316
F_{000}	532
μ (MoK_α)	0.104 mm^{-1}
Temperature	107 K

B. Intensity measurements

Diffractometer	Bruker Kappa, APEX II CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K_α (λ = 0.71073 Å)
Crystal to detector distance	55 mm
Time per frame	15 s
Temperature	107 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.52°
θ_{max}	35.74°
h k l range	h = -13 to 13
	k = -17 to 17

	l = -21 to 23
No. of reflections measured	Total: 24527
	Unique 5706 (R_{int} = 0.0564)
	I > 2σ(I) = 4873
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	4873
No. variables	235
No. Restraints	27
Reflection:parameter ratio	24.28
For I > 2.00σ(I)	20.74
No. Reflections used in refinement	5706
Final R indices [I > 2σ(I)] R1	0.0417
Final R indices [all data]; R1, wR2	0.0498; 0.0997
Goodness of Fit (s)	1.174
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.461 e/Å^3
Minimum peak in final diff. map	-0.253 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	1.00042 (6)	0.42015 (4)	0.65333 (4)	0.01417 (10)	
O30	−0.02960 (6)	0.08811 (4)	0.65394 (4)	0.01389 (9)	
O10	−0.01119 (6)	0.75152 (4)	0.68234 (3)	0.01383 (9)	
N21	0.81006 (9)	0.52240 (5)	0.73102 (5)	0.02033 (13)	
H21A	0.8641 (15)	0.5906 (10)	0.7225 (8)	0.024*	
H21B	0.7228 (14)	0.5233 (10)	0.7604 (8)	0.024*	
N20	0.78569 (8)	0.31318 (5)	0.70466 (5)	0.01964 (13)	
H20A	0.8305 (14)	0.2461 (10)	0.6860 (8)	0.024*	
H20B	0.7009 (14)	0.3108 (10)	0.7350 (8)	0.024*	
N31	0.19726 (9)	0.19542 (5)	0.70968 (5)	0.01966 (12)	
H31A	0.1533 (14)	0.2617 (10)	0.6839 (8)	0.024*	
H31B	0.2938 (14)	0.1991 (10)	0.7385 (8)	0.024*	
N30	0.17913 (9)	−0.01278 (6)	0.73607 (5)	0.02055 (13)	

H30A	0.1204 (15)	−0.0787 (10)	0.7330 (8)	0.025*	
H30B	0.2634 (15)	−0.0124 (10)	0.7716 (8)	0.025*	
C20	0.86937 (8)	0.41865 (5)	0.69508 (5)	0.01328 (11)	
C30	0.11154 (8)	0.09043 (5)	0.69911 (5)	0.01237 (11)	
N11	−0.03333 (9)	0.85525 (5)	0.54452 (5)	0.01857 (12)	
H11A	−0.0457 (14)	0.9237 (10)	0.5754 (8)	0.022*	
H11B	−0.0162 (14)	0.8586 (10)	0.4860 (8)	0.022*	
C10	−0.00456 (8)	0.75166 (5)	0.59426 (5)	0.01227 (11)	
N10	0.03409 (9)	0.64916 (5)	0.54859 (5)	0.01771 (12)	
H10A	0.0337 (14)	0.5800 (10)	0.5799 (8)	0.021*	
H10B	0.0207 (13)	0.6462 (10)	0.4890 (8)	0.021*	
C3	0.5165 (5)	0.2839 (3)	0.4358 (3)	0.0324 (7)	0.6475
H3A	0.6081	0.3398	0.4221	0.039*	0.6475
H3B	0.4451	0.2729	0.3769	0.039*	0.6475
C2	0.59024 (19)	0.15889 (15)	0.46575 (12)	0.0330 (3)	0.6475
H2A	0.655	0.1272	0.415	0.040*	0.6475
H2B	0.668	0.1707	0.5221	0.040*	0.6475
C1	0.4621 (2)	0.06249 (14)	0.48763 (13)	0.0293 (3)	0.6475
H1A	0.4013	0.0918	0.5407	0.035*	0.6475
H1B	0.381	0.0533	0.4325	0.035*	0.6475
C7	0.4196 (6)	0.3426 (5)	0.5045 (4)	0.0249 (7)	0.6475
N1	0.3416 (8)	0.3875 (11)	0.5575 (6)	0.0388 (8)	0.6475
C5	0.5044 (4)	0.1519 (2)	0.42842 (18)	0.0297 (5)	0.3525
H5A	0.3891	0.148	0.3998	0.036*	0.3525
H5B	0.5779	0.1215	0.3813	0.036*	0.3525
C4	0.5201 (4)	0.0670 (2)	0.5123 (2)	0.0273 (5)	0.3525
H4A	0.4445	0.0957	0.5588	0.033*	0.3525
H4B	0.6347	0.0718	0.5419	0.033*	0.3525
C6	0.5476 (10)	0.2863 (4)	0.4504 (5)	0.0318 (14)	0.3525
H6A	0.6654	0.2909	0.4749	0.038*	0.3525
H6B	0.5356	0.334	0.3912	0.038*	0.3525
C8	0.4466 (10)	0.3436 (9)	0.5178 (7)	0.0219 (10)	0.3525
N2	0.3698 (14)	0.3880 (19)	0.5714 (10)	0.050 (3)	0.3525

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0150 (2)	0.01131 (19)	0.0169 (2)	0.00035 (15)	0.00582 (17)	0.00047 (16)
O30	0.0143 (2)	0.01106 (19)	0.0161 (2)	0.00020 (15)	0.00025 (16)	0.00004 (16)
O10	0.0171 (2)	0.01223 (19)	0.0124 (2)	−0.00031 (15)	0.00252 (16)	0.00011 (15)
N21	0.0227 (3)	0.0106 (2)	0.0297 (3)	0.0004 (2)	0.0146 (3)	−0.0014 (2)
N20	0.0189 (3)	0.0106 (2)	0.0310 (3)	−0.00109 (19)	0.0117 (2)	0.0001 (2)
N31	0.0189 (3)	0.0110 (2)	0.0279 (3)	−0.00260 (19)	−0.0060 (2)	0.0018 (2)
N30	0.0218 (3)	0.0115 (2)	0.0268 (3)	0.0005 (2)	−0.0079 (2)	0.0035 (2)
C20	0.0151 (3)	0.0101 (2)	0.0150 (3)	0.00095 (19)	0.0032 (2)	0.0014 (2)
C30	0.0151 (3)	0.0099 (2)	0.0123 (3)	0.00056 (18)	0.0022 (2)	−0.00042 (19)
N11	0.0309 (3)	0.0108 (2)	0.0140 (3)	0.0014 (2)	0.0018 (2)	0.00151 (19)
C10	0.0126 (3)	0.0102 (2)	0.0141 (3)	−0.00149 (18)	0.0015 (2)	0.00010 (19)
N10	0.0289 (3)	0.0110 (2)	0.0136 (3)	0.0014 (2)	0.0036 (2)	−0.00083 (19)
C3	0.0286 (16)	0.0451 (12)	0.0245 (11)	0.0009 (8)	0.0088 (10)	−0.0071 (8)
C2	0.0199 (6)	0.0471 (8)	0.0330 (7)	−0.0001 (5)	0.0074 (6)	−0.0103 (6)
C1	0.0162 (7)	0.0438 (8)	0.0280 (8)	0.0011 (6)	0.0024 (5)	−0.0114 (6)
C7	0.0158 (14)	0.0373 (10)	0.0214 (15)	−0.0059 (9)	−0.0006 (10)	−0.0070 (9)
N1	0.0313 (11)	0.0458 (14)	0.0414 (18)	−0.0080 (10)	0.0149 (11)	−0.0159 (13)
C5	0.0314 (14)	0.0357 (13)	0.0229 (11)	0.0031 (10)	0.0089 (10)	−0.0050 (10)
C4	0.0241 (15)	0.0376 (13)	0.0198 (12)	0.0029 (11)	−0.0003 (10)	−0.0059 (10)
C6	0.025 (3)	0.040 (2)	0.033 (3)	−0.0036 (14)	0.016 (2)	−0.0037 (16)
C8	0.014 (2)	0.0345 (16)	0.017 (2)	−0.0074 (15)	−0.0038 (16)	−0.0047 (14)
N2	0.063 (6)	0.043 (3)	0.048 (5)	−0.013 (5)	0.032 (5)	−0.016 (4)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2581 (8)	C3—C2	1.532 (4)
O30—C30	1.2668 (8)	C2—C1	1.524 (2)
O10—C10	1.2648 (8)	C1—C1i	1.520 (3)
N21—C20	1.3436 (8)	C7—N1	1.135 (3)
N20—C20	1.3438 (9)	C5—C4	1.511 (4)
N31—C30	1.3376 (9)	C5—C6	1.528 (5)
N30—C30	1.3379 (9)	C4—C4i	1.527 (5)
N11—C10	1.3418 (9)	C6—C8	1.453 (5)
C10—N10	1.3408 (8)	C8—N2	1.133 (5)
C3—C7	1.452 (3)		
O20—C20—N21	120.74 (6)	C7—C3—C2	114.8 (3)
O20—C20—N20	120.68 (6)	C1—C2—C3	114.3 (2)
N21—C20—N20	118.58 (6)	C1i—C1—C2	113.18 (16)
O30—C30—N31	120.86 (6)	N1—C7—C3	178.9 (6)
O30—C30—N30	120.55 (6)	C4—C5—C6	114.7 (3)
N31—C30—N30	118.58 (7)	C5—C4—C4i	113.4 (3)
O10—C10—N10	120.94 (6)	C8—C6—C5	114.5 (5)
O10—C10—N11	120.62 (6)	N2—C8—C6	178.9 (10)
N10—C10—N11	118.43 (6)		
C7—C3—C2—C1	59.2 (4)	C8—C6—C5—C4	−59.4 (7)
C3—C2—C1—C1i	177.1 (2)	C6—C5—C4—C4i	−178.7 (4)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	59.2(4)
C3	C2	C1	C1i	177.1(2)
C8	C6	C5	C4	-59.4(7)
C6	C5	C4	C4i	-178.7(4)

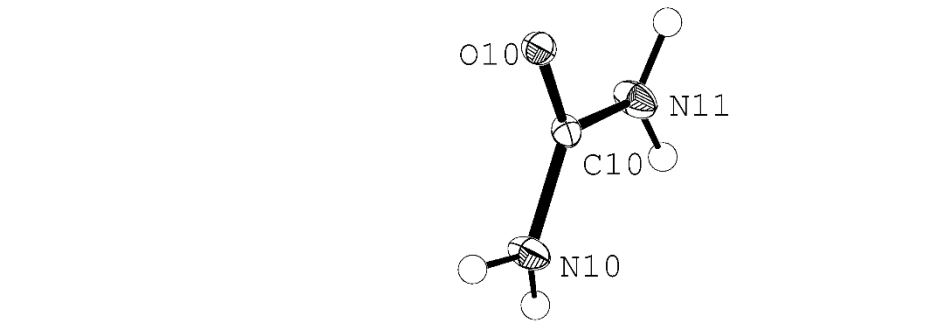
Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.874 (11)	2.121 (11)	2.9896 (8)	172.3 (11)
N21—H21B···O30iii	0.850 (12)	2.179 (12)	2.9944 (8)	160.6 (11)
N20—H20A···O30ii	0.866 (11)	2.127 (11)	2.9860 (8)	171.7 (11)
N20—H20B···O10iv	0.841 (12)	2.112 (12)	2.9276 (8)	163.3 (10)
N31—H31A···O20v	0.872 (11)	2.144 (11)	2.9909 (8)	163.4 (10)
N31—H31B···O10iv	0.855 (12)	2.093 (12)	2.9297 (9)	165.9 (11)
N30—H30A···O10vi	0.859 (11)	2.222 (11)	3.0551 (8)	163.3 (10)
N30—H30B···O20vii	0.817 (12)	2.239 (12)	3.0170 (9)	159.1 (11)
N11—H11A···O30viii	0.875 (11)	2.109 (11)	2.9740 (8)	169.9 (11)
N11—H11B···O30ix	0.860 (11)	2.144 (12)	2.9872 (9)	166.7 (10)
N10—H10A···O20v	0.875 (11)	2.058 (11)	2.9284 (8)	172.6 (10)
N10—H10B···O20x	0.851 (11)	2.153 (12)	2.9755 (9)	162.4 (10)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2 showing part 1 with 40% probability surfaces.



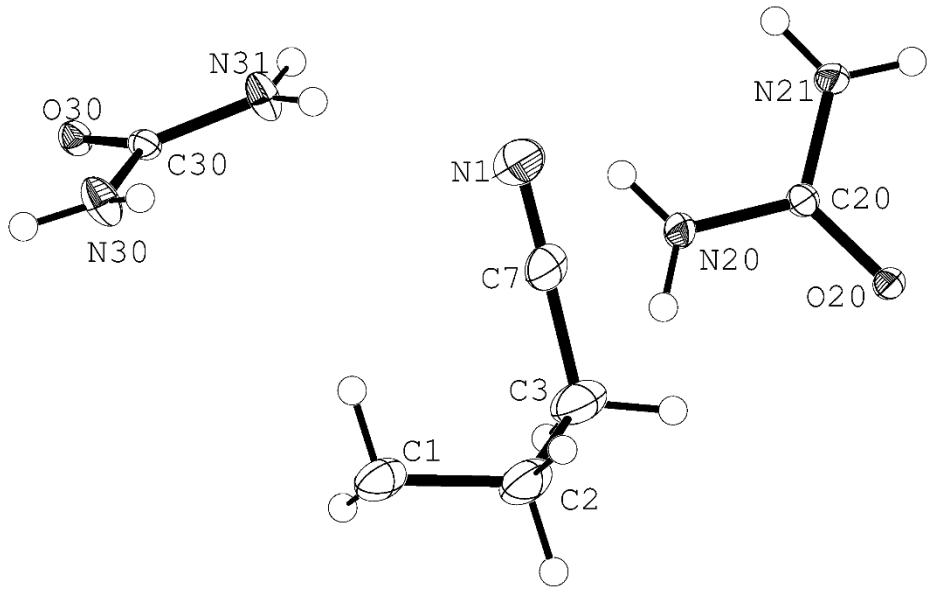
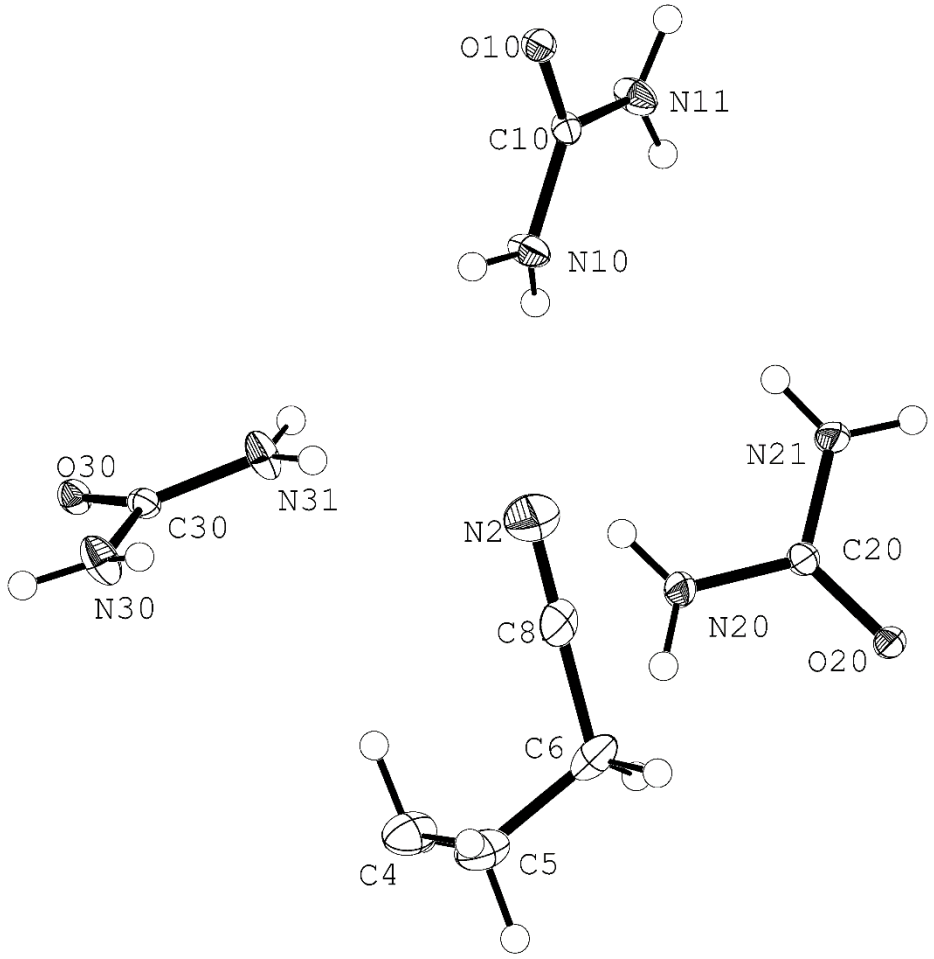


Figure 4: ORTEP rendering by OLEX2 showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 107 K (mh1001d).

2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Data collected using the Bruker APEX2 software package.
4. Bruker SAINT V8.18C
5. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).
6. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
7. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

Structure report for 1,6-dicyanohexane/urea at 124 K[1]

Introduction

The data for this crystal was collected in 2010 by Roman Gajda on the Bruker Kappa diffractometer equipped with an APEX II detector and was originally labeled "mh1001c". (See laboratory notebook RBG A-60-1.) The original crystal was from Christopher J. Nichols (CJN A-78-05). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 62.7% and 37.3%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 78.0°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 600 µm x 430 µm x 300 µm. The crystal was cooled to 124 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 15 seconds and the frame width was 0.25º.[3] The crystal to detector distance was 55.00 mm.

The unit cell parameters were determined[3,4] from 9886 input reflections whose minimum and the maximum 2-theta values were 4.70 and 70.78, respectively. The errors are reported after corrections for the goodness of fit (9.92). The cell volume is 1257.02 (27) Å^3.

a = 8.0968 (9) Å	α = 90°
b = 10.8762 (12) Å	β = 94.605 (5)°
c = 14.3204 (16) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.312 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 25180 reflections of which 647 were rejected. After merging Friedel opposites, there were 5655 unique reflections, of which 4800 had I > 2sigma(I). The R(int) was 0.0565, and the R(sigma) was 0.0390. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.104 mm^{-1}. The absorption correction was made using SADABS.[3, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in mh1001c_06a.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.088 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

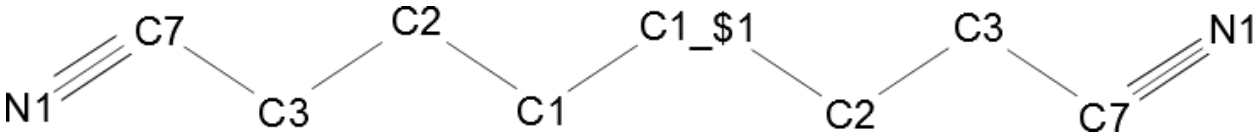


Figure 1: Atomic labeling scheme for part 1 (major part)

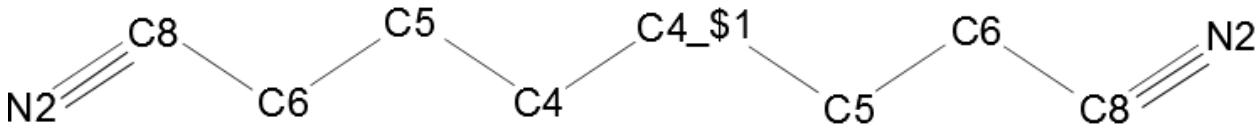


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.199 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.200 for all of the data. R1 was 0.0485 for all 5279 data and 0.0405 for data with $I>2\sigma(I)$; the wR2 value was 0.0980 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5

OMIT 3 2 0
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms. The 3 2 0 reflection was omitted due to the ΔF^2/esd being greater than 10.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	600 x 430 x 300 μm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	9886
Lattice parameters	a = 8.0968 (9) Å
	b = 10.8762 (12) Å
	c = 14.3204 (16) Å
	α = 90°
	β = 94.605 (5)°
	γ = 90°
	V = 1257.02 (27) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.312
F_{000}	532
μ (MoK_α)	0.104 mm^{-1}
Temperature	124 K

B. Intensity measurements

Diffractometer	Bruker Kappa, APEX II CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K_α (λ = 0.71073 Å)
Crystal to detector distance	55 mm
Time per frame	15 s
Temperature	124 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.35°
θ_{max}	35.39°
h k l range	h = -13 to 13
	k = -17 to 17
	l = -21 to 23
No. of reflections measured	Total: 24533
	Unique 5655 (R_{int} = 0.0565)

	$I > 2\sigma(I) = 4800$
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations ($I > 2.00\sigma(I)$)	4800
No. variables	235
No. Restraints	27
Reflection:parameter ratio	24.06
For $I > 2.00\sigma(I)$	20.42
No. Reflections used in refinement	5655
Final R indices [$I > 2\sigma(I)$] R1	0.0405
Final R indices [all data]; R1, wR2	0.0485; 0.0980
Goodness of Fit (s)	1.199
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.414 e/Å^3
Minimum peak in final diff. map	-0.297 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	1.00018 (6)	0.42008 (4)	0.65328 (3)	0.01563 (9)	
O30	−0.02919 (6)	0.08812 (4)	0.65393 (3)	0.01526 (9)	
O10	−0.01123 (6)	0.75147 (4)	0.68225 (3)	0.01520 (9)	
N21	0.80975 (9)	0.52220 (5)	0.73086 (5)	0.02244 (13)	
H21A	0.8614 (14)	0.5894 (10)	0.7226 (8)	0.027*	
H21B	0.7242 (14)	0.5234 (10)	0.7603 (8)	0.027*	
N20	0.78580 (8)	0.31310 (5)	0.70461 (5)	0.02140 (13)	
H20A	0.8288 (14)	0.2466 (10)	0.6858 (8)	0.026*	
H20B	0.6992 (14)	0.3106 (10)	0.7359 (8)	0.026*	
N31	0.19735 (8)	0.19529 (5)	0.70963 (5)	0.02177 (13)	
H31A	0.1526 (14)	0.2612 (10)	0.6838 (8)	0.026*	
H31B	0.2946 (14)	0.1992 (10)	0.7377 (8)	0.026*	
N30	0.17940 (9)	−0.01256 (5)	0.73613 (5)	0.02272 (13)	
H30A	0.1208 (14)	−0.0783 (10)	0.7337 (8)	0.027*	
H30B	0.2641 (14)	−0.0122 (10)	0.7724 (8)	0.027*	

C20	0.86933 (8)	0.41848 (5)	0.69498 (4)	0.01437 (11)	
C30	0.11164 (8)	0.09049 (5)	0.69910 (4)	0.01360 (11)	
N11	−0.03313 (9)	0.85522 (5)	0.54463 (4)	0.02029 (12)	
H11A	−0.0452 (14)	0.9234 (10)	0.5762 (8)	0.024*	
H11B	−0.0199 (13)	0.8577 (10)	0.4875 (8)	0.024*	
C10	−0.00480 (8)	0.75165 (5)	0.59418 (4)	0.01352 (11)	
N10	0.03338 (8)	0.64920 (5)	0.54854 (4)	0.01951 (12)	
H10A	0.0331 (14)	0.5808 (9)	0.5796 (8)	0.023*	
H10B	0.0208 (13)	0.6458 (9)	0.4894 (8)	0.023*	
C3	0.5163 (5)	0.2841 (3)	0.4360 (3)	0.0343 (7)	0.6273
H3A	0.6078	0.3399	0.4223	0.041*	0.6273
H3B	0.4445	0.2733	0.3772	0.041*	0.6273
C2	0.5899 (2)	0.15889 (15)	0.46559 (12)	0.0367 (3)	0.6273
H2A	0.6541	0.1273	0.4147	0.044*	0.6273
H2B	0.668	0.1705	0.5217	0.044*	0.6273
C1	0.4619 (2)	0.06256 (15)	0.48770 (13)	0.0323 (3)	0.6273
H1A	0.4016	0.0918	0.5409	0.039*	0.6273
H1B	0.3805	0.0534	0.4328	0.039*	0.6273
C7	0.4199 (6)	0.3424 (5)	0.5049 (4)	0.0271 (7)	0.6273
N1	0.3429 (8)	0.3883 (11)	0.5576 (6)	0.0428 (9)	0.6273
C5	0.5044 (4)	0.1518 (2)	0.42863 (17)	0.0334 (5)	0.3727
H5A	0.389	0.1484	0.4	0.040*	0.3727
H5B	0.5776	0.1213	0.3815	0.040*	0.3727
C4	0.5198 (4)	0.0667 (2)	0.51236 (19)	0.0306 (5)	0.3727
H4A	0.4438	0.0952	0.5587	0.037*	0.3727
H4B	0.6342	0.0716	0.5422	0.037*	0.3727
C6	0.5484 (9)	0.2857 (4)	0.4510 (5)	0.0370 (14)	0.3727
H6A	0.666	0.2897	0.4758	0.044*	0.3727
H6B	0.5375	0.3335	0.392	0.044*	0.3727
C8	0.4476 (10)	0.3438 (9)	0.5180 (7)	0.0266 (11)	0.3727
N2	0.3703 (14)	0.3854 (19)	0.5722 (10)	0.059 (3)	0.3727

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0165 (2)	0.01252 (19)	0.0186 (2)	0.00047 (15)	0.00621 (16)	0.00056 (16)
O30	0.0155 (2)	0.01213 (19)	0.0179 (2)	0.00011 (14)	0.00003 (16)	0.00015 (16)
O10	0.0190 (2)	0.01322 (19)	0.0136 (2)	−0.00018 (15)	0.00280 (16)	−0.00005 (15)
N21	0.0251 (3)	0.0119 (2)	0.0325 (3)	0.0004 (2)	0.0159 (3)	−0.0014 (2)
N20	0.0210 (3)	0.0114 (2)	0.0334 (3)	−0.00111 (19)	0.0122 (2)	0.0004 (2)
N31	0.0206 (3)	0.0123 (2)	0.0310 (3)	−0.00252 (19)	−0.0069 (2)	0.0020 (2)
N30	0.0245 (3)	0.0125 (2)	0.0293 (3)	0.0004 (2)	−0.0086 (2)	0.0038 (2)
C20	0.0165 (3)	0.0110 (2)	0.0159 (3)	0.00094 (18)	0.0035 (2)	0.00148 (19)
C30	0.0169 (3)	0.0110 (2)	0.0131 (2)	0.00056 (18)	0.0023 (2)	−0.00045 (19)
N11	0.0337 (3)	0.0120 (2)	0.0152 (3)	0.0013 (2)	0.0018 (2)	0.00137 (19)
C10	0.0138 (3)	0.0115 (2)	0.0153 (3)	−0.00179 (18)	0.00133 (19)	0.00013 (19)
N10	0.0318 (3)	0.0119 (2)	0.0151 (3)	0.0012 (2)	0.0039 (2)	−0.00089 (19)
C3	0.0310 (16)	0.0482 (13)	0.0247 (10)	0.0014 (8)	0.0097 (10)	−0.0082 (8)
C2	0.0234 (7)	0.0512 (9)	0.0365 (8)	−0.0008 (6)	0.0092 (6)	−0.0120 (7)
C1	0.0177 (7)	0.0483 (9)	0.0311 (8)	0.0011 (6)	0.0027 (5)	−0.0120 (7)
C7	0.0188 (15)	0.0393 (10)	0.0231 (15)	−0.0078 (10)	0.0006 (11)	−0.0076 (9)
N1	0.0359 (10)	0.0495 (15)	0.0451 (19)	−0.0080 (9)	0.0167 (10)	−0.0163 (15)
C5	0.0345 (13)	0.0422 (13)	0.0250 (11)	0.0028 (10)	0.0103 (10)	−0.0059 (9)
C4	0.0278 (15)	0.0413 (13)	0.0223 (12)	0.0031 (11)	0.0000 (9)	−0.0061 (10)
C6	0.030 (3)	0.047 (2)	0.037 (3)	−0.0051 (14)	0.017 (2)	−0.0026 (16)
C8	0.017 (2)	0.0402 (17)	0.022 (2)	−0.0077 (16)	−0.0028 (16)	−0.0052 (14)
N2	0.081 (7)	0.049 (3)	0.054 (5)	−0.012 (5)	0.040 (5)	−0.016 (4)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2574 (8)	C3—C2	1.533 (4)
O30—C30	1.2653 (8)	C2—C1	1.524 (2)
O10—C10	1.2664 (8)	C1—C1i	1.523 (3)
N21—C20	1.3450 (8)	C7—N1	1.133 (3)
N20—C20	1.3435 (8)	C5—C4	1.512 (3)
N31—C30	1.3367 (8)	C5—C6	1.527 (5)
N30—C30	1.3385 (8)	C4—C4i	1.521 (4)
N11—C10	1.3411 (8)	C6—C8	1.453 (5)
C10—N10	1.3405 (8)	C8—N2	1.130 (5)
C3—C7	1.453 (3)		
O20—C20—N20	120.72 (6)	C7—C3—C2	114.7 (3)
O20—C20—N21	120.77 (6)	C1—C2—C3	114.4 (2)
N20—C20—N21	118.52 (6)	C1i—C1—C2	113.13 (17)
O30—C30—N31	120.89 (6)	N1—C7—C3	178.9 (6)
O30—C30—N30	120.62 (6)	C4—C5—C6	114.5 (3)
N31—C30—N30	118.47 (6)	C5—C4—C4i	113.4 (3)
O10—C10—N10	120.92 (6)	C8—C6—C5	114.7 (5)
O10—C10—N11	120.61 (6)	N2—C8—C6	177.5 (15)
N10—C10—N11	118.46 (6)		
C7—C3—C2—C1	59.1 (4)	C8—C6—C5—C4	−59.7 (7)
C3—C2—C1—C1i	177.2 (2)	C6—C5—C4—C4i	−178.3 (4)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	59.1(4)
C3	C2	C1	C1i	177.2(2)
C8	C6	C5	C4	-59.7(7)
C6	C5	C4	C4i	-178.3(4)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.855 (11)	2.144 (11)	2.9942 (8)	172.3 (10)
N21—H21B···O30iii	0.840 (11)	2.193 (11)	2.9997 (8)	161.2 (10)
N20—H20A···O30ii	0.855 (11)	2.142 (11)	2.9888 (8)	170.6 (10)
N20—H20B···O10iv	0.862 (11)	2.095 (11)	2.9318 (8)	163.3 (10)
N31—H31A···O20v	0.872 (11)	2.148 (11)	2.9951 (8)	163.8 (10)
N31—H31B···O10iv	0.856 (11)	2.095 (12)	2.9321 (9)	165.6 (10)
N30—H30A···O10vi	0.857 (11)	2.234 (11)	3.0616 (8)	162.5 (10)
N30—H30B···O20vii	0.826 (11)	2.234 (12)	3.0192 (9)	158.8 (10)
N11—H11A···O30viii	0.878 (11)	2.107 (11)	2.9764 (8)	170.1 (10)
N11—H11B···O30ix	0.834 (11)	2.176 (11)	2.9917 (9)	165.7 (10)
N10—H10A···O20v	0.866 (11)	2.071 (11)	2.9321 (8)	172.7 (10)
N10—H10B···O20x	0.846 (11)	2.158 (11)	2.9780 (8)	163.0 (10)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2 showing part 1 with 40% probability surfaces.

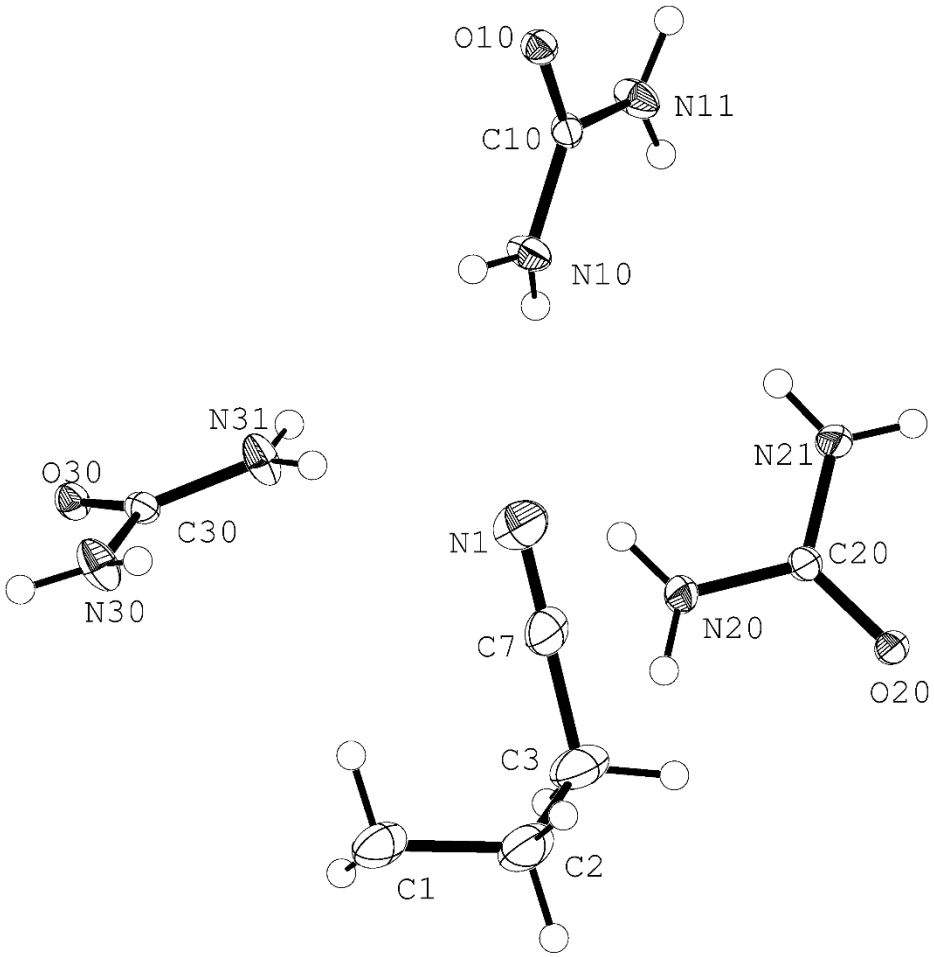
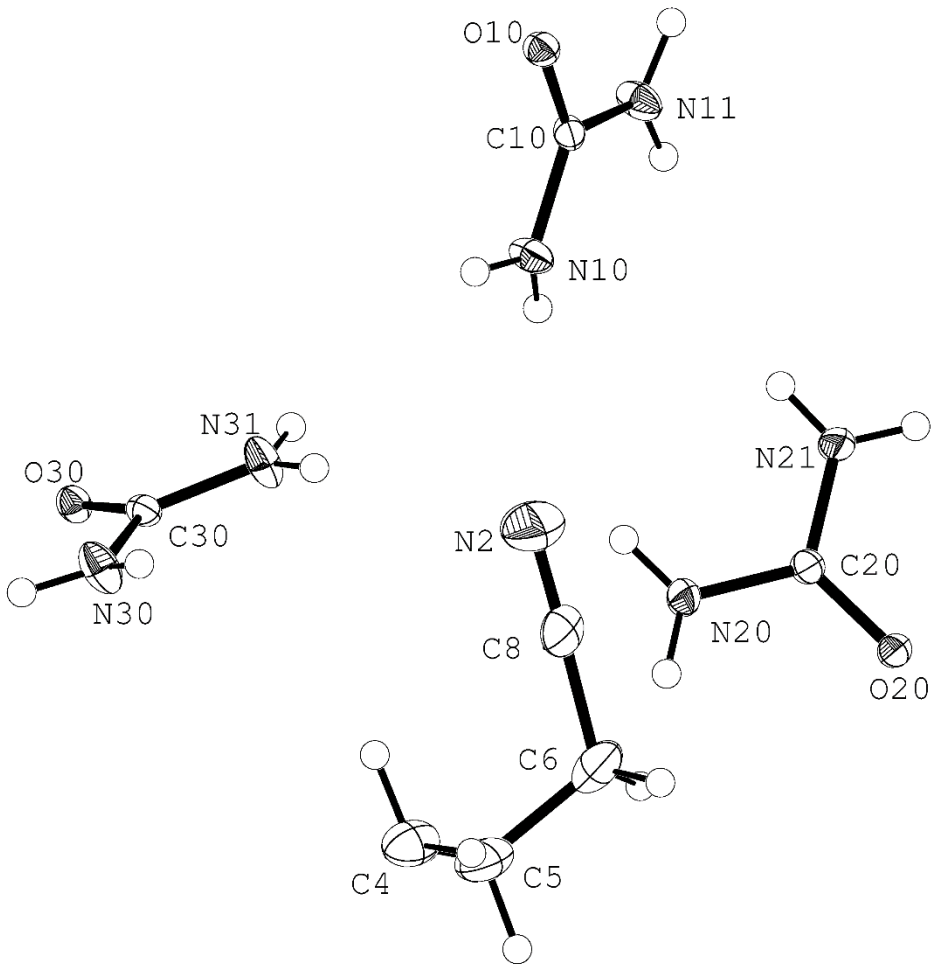


Figure 4: ORTEP rendering by OLEX2 showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 124 K (mh1001c).
2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular

level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Data collected using the Bruker APEX2 software package.
4. Bruker SAINT V8.18C
5. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).
6. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
7. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

Structure report for 1,6-dicyanohexane/urea at 141 K[1]

Introduction

The data for this crystal was collected in 2010 by Roman Gajda on the Bruker Kappa diffractometer equipped with an APEX II detector and was originally labeled "mh1001b". (See laboratory notebook RBG A-60-1.) The original crystal was from CJN A-78-05. As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 61.3% and 38.7%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 78.25°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 600 µm x 430 µm x 300 µm. The crystal was cooled to 141 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 15 seconds and the frame width was 0.25º.[3] The crystal to detector distance was 55.00 mm.

The unit cell parameters were determined[3,4] from 9901 input reflections whose minimum and the maximum 2-theta values were 4.703 and 70.92, respectively. The errors are reported after corrections for the goodness of fit (9.25). The cell volume is 1259.46 (24) Å^3.

a = 8.0994 (8) Å	α = 90°
b = 10.8860 (11) Å	β = 94.641 (5)°
c = 14.3314 (15) Å	γ = 90°

For Z = 2 and F.W. = 496.50, the calculated density is 1.309 g/cm^3. Based on the systematic absences of

$$h00: \ h+l \neq 2n$$
$$0k0: \ k \neq 2n$$
$$h00: \ h \neq 2n$$
$$00l: \ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n \ (\#14).$$

Data Reduction:

The data set contained 25335 reflections of which 676 were rejected. After merging Friedel opposites, there were 5696 unique reflections, of which 4751 had I > 2sigma(I). The R(int) was 0.0502, and the R(sigma) was 0.0366. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.104 mm^{-1}. The absorption correction was made using SADABS.[3, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in mh1001b_06a.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.088 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

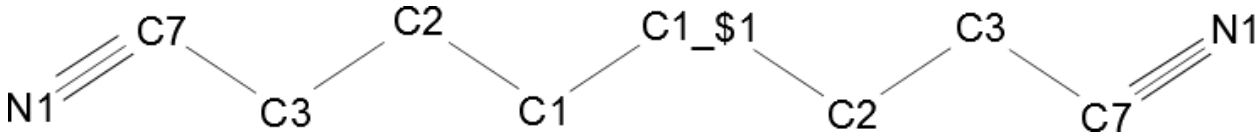


Figure 1: Atomic labeling scheme for part 1 (major part)

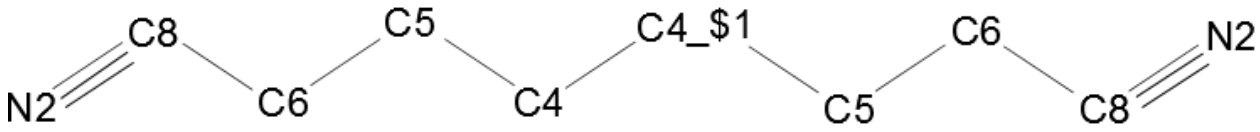


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.207 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.207 for all of the data. R1 was 0.0497 for all 5696 data and 0.0410 for data with $I>2\sigma(I)$; the wR2 value was 0.0946 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	600 x 430 x 300 μm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	9901
Lattice parameters	a = 8.0994 (8) Å
	b = 10.8860 (11) Å
	c = 14.3314 (15) Å
	α = 90°
	β = 94.641 (5)°
	γ = 90°
	V = 1259.46 (24) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.309
F_{000}	532
μ (MoK$_\alpha$)	0.104 mm^{-1}
Temperature	141 K

B. Intensity measurements

Diffractometer	Bruker Kappa, APEX II CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K$_\alpha$ (λ = 0.71073 Å)
Crystal to detector distance	55 mm
Time per frame	15 s
Temperature	141 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.35°
θ_{max}	35.46°
h k l range	h = -13 to 13
	k = -17 to 16
	l = -23 to 23
No. of reflections measured	Total: 24659
	Unique 5696 (R_{int} = 0.0502)

	$I > 2\sigma(I) = 4751$
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations ($I > 2.00\sigma(I)$)	4751
No. variables	235
No. Restraints	27
Reflection:parameter ratio	24.24
For $I > 2.00\sigma(I)$	20.22
No. Reflections used in refinement	5696
Final R indices [$I > 2\sigma(I)$] R1	0.0410
Final R indices [all data]; R1, wR2	0.0497; 0.0946
Goodness of Fit (s)	1.207
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.432 e/Å^3
Minimum peak in final diff. map	-0.282 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99997 (6)	0.42009 (4)	0.65326 (4)	0.01733 (10)	
O30	−0.02879 (6)	0.08812 (4)	0.65397 (4)	0.01704 (10)	
O10	−0.01135 (6)	0.75144 (4)	0.68207 (3)	0.01693 (10)	
N21	0.80958 (9)	0.52194 (5)	0.73078 (5)	0.02487 (14)	
H21A	0.8617 (14)	0.5897 (10)	0.7223 (8)	0.030*	
H21B	0.7229 (14)	0.5224 (10)	0.7597 (8)	0.030*	
N20	0.78586 (8)	0.31312 (5)	0.70463 (5)	0.02376 (13)	
H20A	0.8293 (14)	0.2463 (10)	0.6850 (8)	0.029*	
H20B	0.7011 (14)	0.3100 (10)	0.7352 (8)	0.029*	
N31	0.19740 (9)	0.19527 (6)	0.70964 (5)	0.02444 (13)	
H31A	0.1527 (14)	0.2616 (10)	0.6839 (8)	0.029*	
H31B	0.2926 (15)	0.1974 (10)	0.7379 (8)	0.029*	
N30	0.17949 (9)	−0.01236 (6)	0.73617 (5)	0.02545 (14)	

H30A	0.1186 (15)	−0.0785 (10)	0.7337 (8)	0.031*	
H30B	0.2643 (15)	−0.0107 (10)	0.7713 (8)	0.031*	
C20	0.86923 (8)	0.41837 (5)	0.69487 (5)	0.01599 (12)	
C30	0.11179 (8)	0.09056 (5)	0.69905 (4)	0.01526 (11)	
N11	−0.03288 (9)	0.85512 (5)	0.54465 (5)	0.02274 (13)	
H11A	−0.0460 (14)	0.9219 (10)	0.5758 (8)	0.027*	
H11B	−0.0158 (13)	0.8578 (10)	0.4876 (8)	0.027*	
C10	−0.00495 (8)	0.75165 (5)	0.59429 (5)	0.01491 (11)	
N10	0.03263 (9)	0.64923 (5)	0.54852 (5)	0.02169 (13)	
H10A	0.0303 (14)	0.5804 (9)	0.5803 (8)	0.026*	
H10B	0.0186 (13)	0.6458 (9)	0.4897 (8)	0.026*	
C3	0.5147 (6)	0.2837 (3)	0.4363 (4)	0.0396 (9)	0.6132
H3A	0.6057	0.34	0.4226	0.047*	0.6132
H3B	0.4423	0.2732	0.3778	0.047*	0.6132
C2	0.5891 (2)	0.15878 (17)	0.46523 (14)	0.0409 (4)	0.6132
H2A	0.6524	0.1275	0.4139	0.049*	0.6132
H2B	0.6682	0.1703	0.5209	0.049*	0.6132
C1	0.4622 (2)	0.06262 (16)	0.48776 (15)	0.0358 (4)	0.6132
H1A	0.3802	0.0535	0.4331	0.043*	0.6132
H1B	0.4024	0.0919	0.5411	0.043*	0.6132
C7	0.4190 (5)	0.3407 (5)	0.5061 (5)	0.0303 (7)	0.6132
N1	0.3426 (7)	0.3878 (10)	0.5581 (6)	0.0475 (9)	0.6132
C5	0.5043 (4)	0.1520 (2)	0.42862 (18)	0.0370 (5)	0.3868
H5A	0.3887	0.1487	0.4003	0.044*	0.3868
H5B	0.5769	0.1212	0.3814	0.044*	0.3868
C4	0.5200 (4)	0.0667 (2)	0.51257 (19)	0.0339 (6)	0.3868
H4A	0.4441	0.0951	0.5589	0.041*	0.3868
H4B	0.6344	0.0715	0.5423	0.041*	0.3868
C6	0.5489 (9)	0.2855 (4)	0.4504 (5)	0.0396 (15)	0.3868
H6A	0.6666	0.2891	0.475	0.047*	0.3868
H6B	0.538	0.3327	0.3912	0.047*	0.3868
C8	0.4499 (8)	0.3454 (8)	0.5170 (7)	0.0298 (11)	0.3868
N2	0.3748 (13)	0.3849 (16)	0.5727 (9)	0.066 (3)	0.3868

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0184 (2)	0.01349 (19)	0.0209 (2)	0.00045 (15)	0.00675 (18)	0.00062 (15)
O30	0.0173 (2)	0.01348 (19)	0.0201 (2)	0.00026 (15)	0.00012 (18)	−0.00001 (15)
O10	0.0211 (2)	0.0146 (2)	0.0154 (2)	−0.00033 (15)	0.00320 (17)	0.00002 (15)
N21	0.0281 (3)	0.0130 (2)	0.0360 (4)	0.0007 (2)	0.0172 (3)	−0.0017 (2)
N20	0.0228 (3)	0.0130 (2)	0.0372 (4)	−0.00156 (19)	0.0133 (3)	0.0003 (2)
N31	0.0230 (3)	0.0136 (2)	0.0350 (4)	−0.0027 (2)	−0.0080 (3)	0.0022 (2)
N30	0.0268 (3)	0.0143 (2)	0.0333 (4)	0.0007 (2)	−0.0096 (3)	0.0043 (2)
C20	0.0181 (3)	0.0122 (2)	0.0181 (3)	0.00103 (18)	0.0036 (2)	0.00155 (19)
C30	0.0189 (3)	0.0123 (2)	0.0149 (3)	0.00067 (18)	0.0029 (2)	−0.00049 (18)
N11	0.0376 (4)	0.0135 (2)	0.0171 (3)	0.0014 (2)	0.0021 (2)	0.00178 (19)
C10	0.0153 (3)	0.0125 (2)	0.0170 (3)	−0.00159 (18)	0.0016 (2)	0.00006 (18)
N10	0.0351 (4)	0.0136 (2)	0.0168 (3)	0.0013 (2)	0.0045 (2)	−0.00109 (18)
C3	0.035 (2)	0.0553 (14)	0.0298 (12)	0.0004 (10)	0.0115 (12)	−0.0079 (9)
C2	0.0252 (7)	0.0577 (10)	0.0411 (9)	−0.0008 (7)	0.0108 (7)	−0.0129 (8)
C1	0.0206 (8)	0.0535 (10)	0.0334 (10)	0.0017 (7)	0.0022 (6)	−0.0140 (8)
C7	0.0171 (15)	0.0440 (11)	0.0296 (16)	−0.0097 (11)	0.0014 (13)	−0.0101 (8)
N1	0.0369 (11)	0.0567 (16)	0.052 (2)	−0.0094 (10)	0.0200 (12)	−0.0196 (15)
C5	0.0387 (14)	0.0468 (14)	0.0268 (11)	0.0036 (11)	0.0114 (10)	−0.0058 (10)
C4	0.0321 (16)	0.0480 (14)	0.0210 (13)	0.0042 (12)	−0.0012 (10)	−0.0064 (10)
C6	0.030 (3)	0.050 (2)	0.042 (3)	−0.0051 (14)	0.019 (2)	−0.0044 (16)
C8	0.017 (2)	0.0446 (17)	0.028 (2)	−0.0122 (16)	0.0002 (19)	−0.0080 (13)
N2	0.087 (7)	0.054 (3)	0.062 (5)	−0.014 (5)	0.041 (5)	−0.017 (3)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2568 (8)	C3—C2	1.531 (4)
O30—C30	1.2631 (9)	C2—C1	1.520 (3)
O10—C10	1.2633 (8)	C1—C1i	1.524 (3)
N21—C20	1.3453 (8)	C7—N1	1.130 (3)
N20—C20	1.3430 (8)	C5—C4	1.517 (4)
N31—C30	1.3365 (9)	C5—C6	1.524 (5)
N30—C30	1.3386 (9)	C4—C4i	1.525 (5)
N11—C10	1.3416 (8)	C6—C8	1.450 (5)
C10—N10	1.3411 (8)	C8—N2	1.127 (5)
C3—C7	1.453 (3)		
O20—C20—N20	120.81 (6)	C7—C3—C2	114.4 (4)
O20—C20—N21	120.76 (6)	C1—C2—C3	114.3 (2)
N20—C20—N21	118.43 (6)	C2—C1—C1i	113.49 (19)
O30—C30—N31	120.93 (6)	N1—C7—C3	177.7 (9)
O30—C30—N30	120.59 (6)	C4—C5—C6	114.7 (3)
N31—C30—N30	118.47 (7)	C5—C4—C4i	113.1 (3)
O10—C10—N10	120.99 (6)	C8—C6—C5	115.4 (5)
O10—C10—N11	120.72 (6)	N2—C8—C6	175.2 (14)
N10—C10—N11	118.28 (6)		
C7—C3—C2—C1	58.8 (4)	C8—C6—C5—C4	−59.9 (7)
C3—C2—C1—C1i	177.5 (3)	C6—C5—C4—C4i	−178.0 (4)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	58.8(4)

C3	C2	C1	C1i	177.5(3)
C8	C6	C5	C4	-59.9(7)
C6	C5	C4	C4i	-178.0(4)

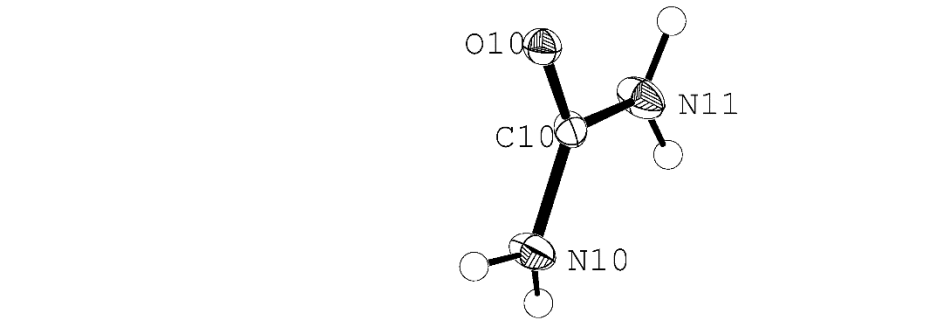
Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.863 (11)	2.142 (11)	2.9994 (8)	172.4 (10)
N21—H21B···O30iii	0.844 (11)	2.197 (12)	3.0044 (8)	160.1 (10)
N20—H20A···O30ii	0.865 (11)	2.137 (11)	2.9928 (8)	170.1 (10)
N20—H20B···O10iv	0.845 (11)	2.113 (11)	2.9351 (8)	164.1 (10)
N31—H31A···O20v	0.876 (11)	2.147 (11)	2.9984 (8)	163.8 (10)
N31—H31B···O10iv	0.841 (12)	2.115 (12)	2.9342 (9)	164.5 (10)
N30—H30A···O10vi	0.872 (11)	2.227 (11)	3.0672 (9)	161.9 (10)
N30—H30B···O20vii	0.818 (12)	2.247 (12)	3.0209 (9)	158.0 (11)
N11—H11A···O30viii	0.864 (11)	2.127 (11)	2.9800 (8)	169.2 (10)
N11—H11B···O30ix	0.841 (11)	2.171 (11)	2.9941 (9)	166.2 (10)
N10—H10A···O20v	0.878 (11)	2.059 (11)	2.9342 (8)	174.4 (10)
N10—H10B···O20x	0.842 (11)	2.165 (11)	2.9796 (9)	162.8 (10)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2 showing part 1 with 40% probability surfaces.



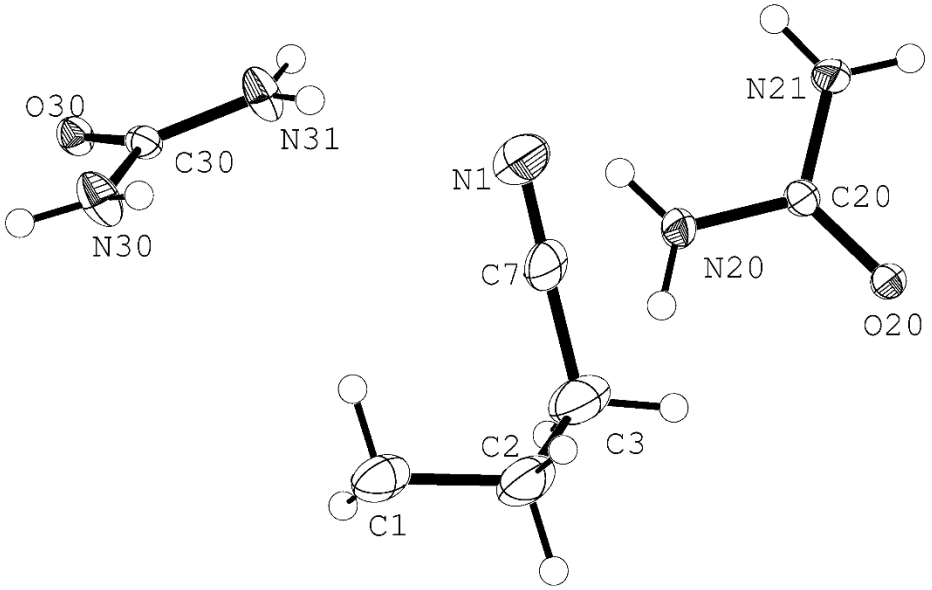
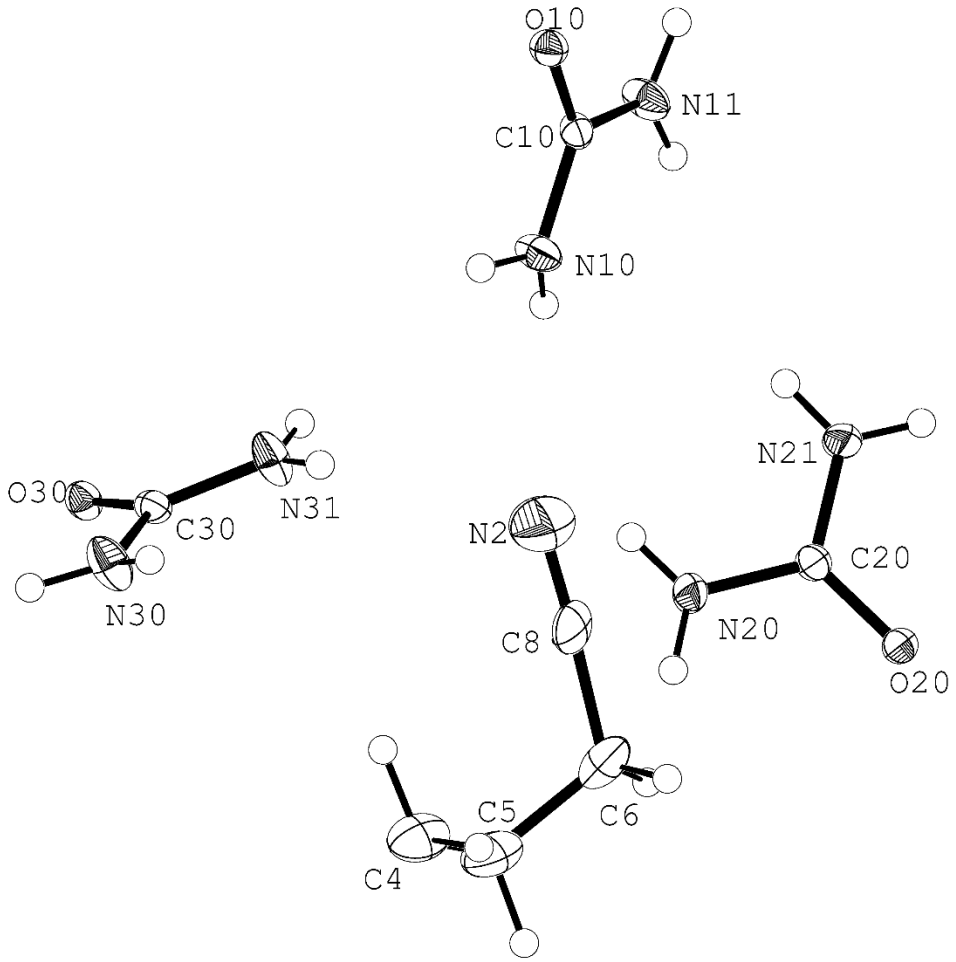


Figure 4: ORTEP rendering by OLEX2 showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 141 K (mh1001b).

2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Data collected using the Bruker APEX2 software package.
4. Bruker SAINT V8.18C
5. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).
6. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
7. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

Structure report for 1,6-dicyanohexane/urea at 158 K[1]

Introduction

The data for this crystal was collected in 2010 by Roman Gajda on the Bruker Kappa diffractometer equipped with an APEX II detector and was originally labeled "mh1001a". (See laboratory notebook RBG A-60-1.) The original crystal was from Christopher J. Nichols (CJN A-78-05). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 60.0% and 40.0%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 78.8°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 600 µm x 430 µm x 300 µm. The crystal was cooled to 158 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 15 seconds and the frame width was 0.25º.[3] The crystal to detector distance was 55.00 mm.

The unit cell parameters were determined[3,4] from 9930 input reflections whose minimum and the maximum 2-theta values were 4.703 and 68.789, respectively. The errors are reported after corrections for the goodness of fit (8.52). The cell volume is 1261.58 (23) Å^3.

a = 8.1050 (8) Å	α = 90°
b = 10.8871 (10) Å	β = 94.601 (4)°
c = 14.3433 (14) Å	γ = 90°

For Z = 2 and F.W. = 496.57, the calculated density is 1.307 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 24546 reflections of which 677 were rejected. After merging Friedel opposites, there were 5279 unique reflections, of which 4481 had I > 2sigma(I). The R(int) was 0.0501, and the R(sigma) was 0.0334. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.103 mm^{-1}. The absorption correction was made using SADABS.[3, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in mh1001a_06a.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.088 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

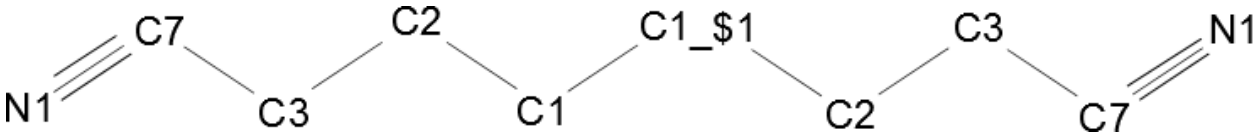


Figure 1: Atomic labeling scheme for part 1 (major part)

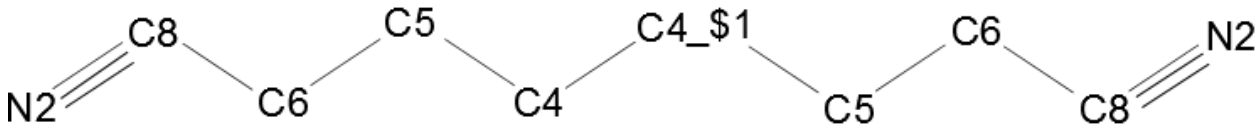


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.186 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.186 for all of the data. R1 was 0.0473 for all 5279 data and 0.0398 for data with $I>2\sigma(I)$; the wR2 value was 0.0859 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	993.14
Crystal color, habit	Clear, prism
Crystal dimensions	600 x 430 x 300 μm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	9930
Lattice parameters	a = 8.1050 (8) Å
	b = 10.8871 (10) Å
	c = 14.3433 (14) Å
	α = 90°
	β = 94.601 (4)°
	γ = 90°
	V = 1261.58(23) Å^3
Space group	P2(1)/n (#14)
Z value	1
D_{calc}	1.307
F_{000}	532
μ (MoK_α)	0.103 mm^{-1}
Temperature	158 K

B. Intensity measurements

Diffractometer	Bruker Kappa, APEX II CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K_α (λ = 0.71073 Å)
Crystal to detector distance	55 mm
Time per frame	15 s
Temperature	158 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.35°
θ_{max}	34.5°
h k l range	h = -12 to 12
	k = -17 to 16

	l = -22 to 22
No. of reflections measured	Total: 23869
	Unique 5279 (R_{int} = 0.050)
	I > 2σ(I) = 4481
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	4481
No. variables	235
No. Restraints	27
Reflection:parameter ratio	22.46
For I > 2.00σ(I)	19.07
No. Reflections used in refinement	5279
Final R indices [I > 2σ(I)] R1	0.0398
Final R indices [all data]; R1, wR2	0.0473; 0.0859
Goodness of Fit (s)	1.186
Mean shift/error in final cycle	0.001
Maximum peak in final diff. map	0.384 e/Å^3
Minimum peak in final diff. map	-0.295 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99978 (6)	0.42007 (4)	0.65328 (4)	0.01916 (10)	
O30	−0.02829 (6)	0.08810 (4)	0.65404 (4)	0.01892 (10)	
O10	−0.01140 (7)	0.75135 (4)	0.68194 (4)	0.01870 (10)	
N21	0.80938 (9)	0.52168 (6)	0.73061 (5)	0.02723 (15)	
H21A	0.8617 (15)	0.5891 (10)	0.7227 (8)	0.033*	
H21B	0.7214 (14)	0.5224 (10)	0.7588 (8)	0.033*	
N20	0.78610 (9)	0.31307 (6)	0.70467 (5)	0.02596 (14)	
H20A	0.8299 (14)	0.2464 (10)	0.6858 (8)	0.031*	
H20B	0.7002 (14)	0.3098 (10)	0.7347 (8)	0.031*	
N31	0.19742 (9)	0.19523 (6)	0.70965 (6)	0.02707 (14)	
H31A	0.1527 (14)	0.2615 (10)	0.6843 (8)	0.032*	
H31B	0.2927 (15)	0.1974 (10)	0.7371 (8)	0.032*	

N30	0.17979 (10)	−0.01215 (6)	0.73617 (6)	0.02807 (15)	
H30A	0.1168 (15)	−0.0781 (10)	0.7335 (8)	0.034*	
H30B	0.2663 (15)	−0.0108 (10)	0.7721 (8)	0.034*	
C20	0.86918 (9)	0.41827 (6)	0.69486 (5)	0.01771 (12)	
C30	0.11209 (9)	0.09065 (6)	0.69907 (5)	0.01668 (12)	
N11	−0.03266 (10)	0.85505 (6)	0.54475 (5)	0.02478 (14)	
H11A	−0.0454 (14)	0.9213 (10)	0.5761 (8)	0.030*	
H11B	−0.0166 (13)	0.8576 (10)	0.4875 (8)	0.030*	
C10	−0.00508 (8)	0.75160 (6)	0.59430 (5)	0.01648 (12)	
N10	0.03214 (9)	0.64928 (6)	0.54850 (5)	0.02403 (13)	
H10A	0.0320 (14)	0.5799 (10)	0.5810 (8)	0.029*	
H10B	0.0192 (13)	0.6457 (10)	0.4897 (8)	0.029*	
C3	0.5150 (7)	0.2834 (3)	0.4363 (4)	0.0441 (10)	0.600
H3A	0.6061	0.3394	0.4226	0.053*	0.600
H3B	0.4428	0.2729	0.3779	0.053*	0.600
C2	0.5890 (2)	0.15865 (18)	0.46510 (15)	0.0449 (4)	0.600
H2A	0.652	0.1273	0.4138	0.054*	0.600
H2B	0.6681	0.1701	0.5207	0.054*	0.600
C1	0.4621 (2)	0.06257 (17)	0.48777 (16)	0.0394 (5)	0.600
H1A	0.3801	0.0533	0.4332	0.047*	0.600
H1B	0.4025	0.0919	0.5411	0.047*	0.600
C7	0.4192 (6)	0.3410 (6)	0.5057 (5)	0.0340 (8)	0.600
N1	0.3430 (7)	0.3882 (11)	0.5572 (6)	0.0526 (12)	0.600
C5	0.5048 (4)	0.1519 (2)	0.42900 (18)	0.0408 (6)	0.400
H5A	0.3897	0.1482	0.4002	0.049*	0.400
H5B	0.5783	0.1216	0.3821	0.049*	0.400
C4	0.5199 (4)	0.0666 (2)	0.5124 (2)	0.0379 (6)	0.400
H4A	0.444	0.095	0.5586	0.045*	0.400
H4B	0.6341	0.0713	0.5422	0.045*	0.400
C6	0.5480 (10)	0.2855 (4)	0.4510 (5)	0.0447 (16)	0.400
H6A	0.6659	0.2897	0.4748	0.054*	0.400
H6B	0.5356	0.3329	0.392	0.054*	0.400
C8	0.4500 (9)	0.3443 (8)	0.5183 (7)	0.0328 (12)	0.400
N2	0.3766 (12)	0.3838 (16)	0.5743 (8)	0.069 (3)	0.400

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0204 (2)	0.0148 (2)	0.0231 (2)	0.00054 (16)	0.00736 (19)	0.00058 (17)
O30	0.0193 (2)	0.0147 (2)	0.0225 (2)	0.00038 (16)	0.00038 (18)	0.00002 (17)
O10	0.0232 (3)	0.0163 (2)	0.0169 (2)	−0.00042 (17)	0.00335 (18)	−0.00011 (16)
N21	0.0303 (4)	0.0144 (3)	0.0395 (4)	0.0006 (2)	0.0190 (3)	−0.0018 (2)
N20	0.0247 (3)	0.0147 (3)	0.0404 (4)	−0.0015 (2)	0.0144 (3)	0.0002 (2)
N31	0.0252 (3)	0.0153 (3)	0.0388 (4)	−0.0030 (2)	−0.0087 (3)	0.0023 (2)
N30	0.0296 (4)	0.0164 (3)	0.0361 (4)	0.0008 (2)	−0.0105 (3)	0.0049 (2)
C20	0.0201 (3)	0.0137 (3)	0.0197 (3)	0.0011 (2)	0.0039 (2)	0.0015 (2)
C30	0.0202 (3)	0.0139 (3)	0.0162 (3)	0.0007 (2)	0.0028 (2)	−0.0005 (2)
N11	0.0405 (4)	0.0151 (3)	0.0188 (3)	0.0016 (2)	0.0023 (3)	0.0019 (2)
C10	0.0168 (3)	0.0139 (3)	0.0187 (3)	−0.0019 (2)	0.0015 (2)	0.0000 (2)
N10	0.0388 (4)	0.0151 (3)	0.0186 (3)	0.0016 (2)	0.0049 (3)	−0.0010 (2)
C3	0.042 (2)	0.0605 (17)	0.0311 (12)	0.0015 (11)	0.0131 (13)	−0.0082 (10)
C2	0.0277 (8)	0.0644 (12)	0.0441 (10)	−0.0001 (8)	0.0111 (8)	−0.0145 (9)
C1	0.0229 (9)	0.0593 (11)	0.0361 (11)	0.0020 (8)	0.0026 (7)	−0.0153 (9)
C7	0.0216 (17)	0.0484 (12)	0.0319 (18)	−0.0099 (12)	0.0016 (14)	−0.0111 (10)
N1	0.0413 (12)	0.063 (2)	0.057 (3)	−0.0094 (11)	0.0205 (13)	−0.021 (2)
C5	0.0421 (15)	0.0519 (15)	0.0298 (12)	0.0036 (12)	0.0119 (11)	−0.0065 (10)
C4	0.0345 (17)	0.0529 (16)	0.0256 (14)	0.0049 (13)	−0.0013 (11)	−0.0073 (11)
C6	0.036 (3)	0.055 (2)	0.046 (3)	−0.0062 (15)	0.020 (2)	−0.0042 (18)
C8	0.021 (2)	0.0490 (19)	0.029 (2)	−0.0125 (17)	−0.0005 (18)	−0.0067 (14)
N2	0.096 (7)	0.058 (3)	0.060 (4)	−0.013 (5)	0.044 (5)	−0.015 (3)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2561 (8)	C3—C2	1.528 (4)
O30—C30	1.2627 (9)	C2—C1	1.520 (3)
O10—C10	1.2623 (8)	C1—C1i	1.524 (4)
N21—C20	1.3436 (9)	C7—N1	1.124 (4)
N20—C20	1.3418 (9)	C5—C4	1.511 (4)
N31—C30	1.3345 (9)	C5—C6	1.523 (5)
N30—C30	1.3379 (9)	C4—C4i	1.521 (5)
N11—C10	1.3408 (9)	C6—C8	1.448 (5)
C10—N10	1.3399 (9)	C8—N2	1.123 (5)
C3—C7	1.453 (4)		
O20—C20—N20	120.81 (6)	C7—C3—C2	114.7 (4)
O20—C20—N21	120.77 (6)	C1—C2—C3	114.3 (2)
N20—C20—N21	118.41 (6)	C2—C1—C1i	113.4 (2)
O30—C30—N31	120.96 (6)	N1—C7—C3	177.7 (9)
O30—C30—N30	120.60 (6)	C4—C5—C6	114.8 (3)
N31—C30—N30	118.44 (7)	C5—C4—C4i	113.5 (3)
O10—C10—N10	121.00 (6)	C8—C6—C5	115.6 (5)
O10—C10—N11	120.75 (6)	N2—C8—C6	175.5 (13)
N10—C10—N11	118.23 (6)		
C7—C3—C2—C1	58.8 (5)	C8—C6—C5—C4	−58.9 (8)
C3—C2—C1—C1i	177.5 (3)	C6—C5—C4—C4i	−178.5 (5)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. **Torsion Angles**

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	58.8(5)

C3	C2	C1	C1i	177.5(3)
C8	C6	C5	C4	-58.9(8)
C6	C5	C4	C4i	-178.5(5)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. **Hydrogen-bond Geometries (in Å)**

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.859 (11)	2.149 (12)	3.0019 (9)	171.8 (11)
N21—H21B···O30iii	0.848 (12)	2.199 (12)	3.0092 (9)	159.8 (10)
N20—H20A···O30ii	0.861 (11)	2.141 (11)	2.9941 (8)	170.9 (11)
N20—H20B···O10iv	0.848 (12)	2.114 (12)	2.9384 (8)	163.8 (10)
N31—H31A···O20v	0.874 (11)	2.151 (12)	3.0007 (9)	164.2 (10)
N31—H31B···O10iv	0.838 (12)	2.123 (12)	2.9381 (9)	164.1 (11)
N30—H30A···O10vi	0.880 (12)	2.226 (12)	3.0729 (9)	161.6 (10)
N30—H30B···O20vii	0.836 (12)	2.232 (12)	3.0238 (10)	158.0 (11)
N11—H11A···O30viii	0.860 (11)	2.132 (11)	2.9812 (9)	169.3 (10)
N11—H11B···O30ix	0.842 (11)	2.173 (12)	2.9972 (9)	166.0 (10)
N10—H10A···O20v	0.888 (11)	2.052 (11)	2.9355 (8)	172.8 (10)
N10—H10B···O20x	0.842 (11)	2.167 (11)	2.9821 (9)	163.1 (10)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by by OLEX2 showing part 1 with 40% probability surfaces.

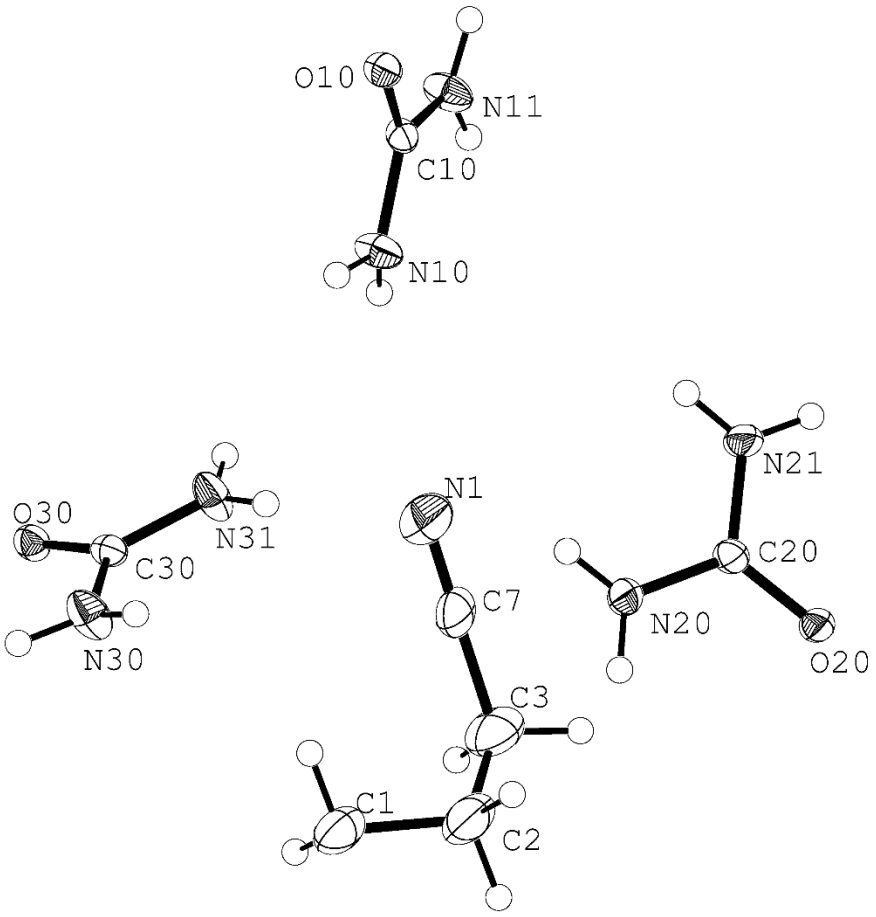
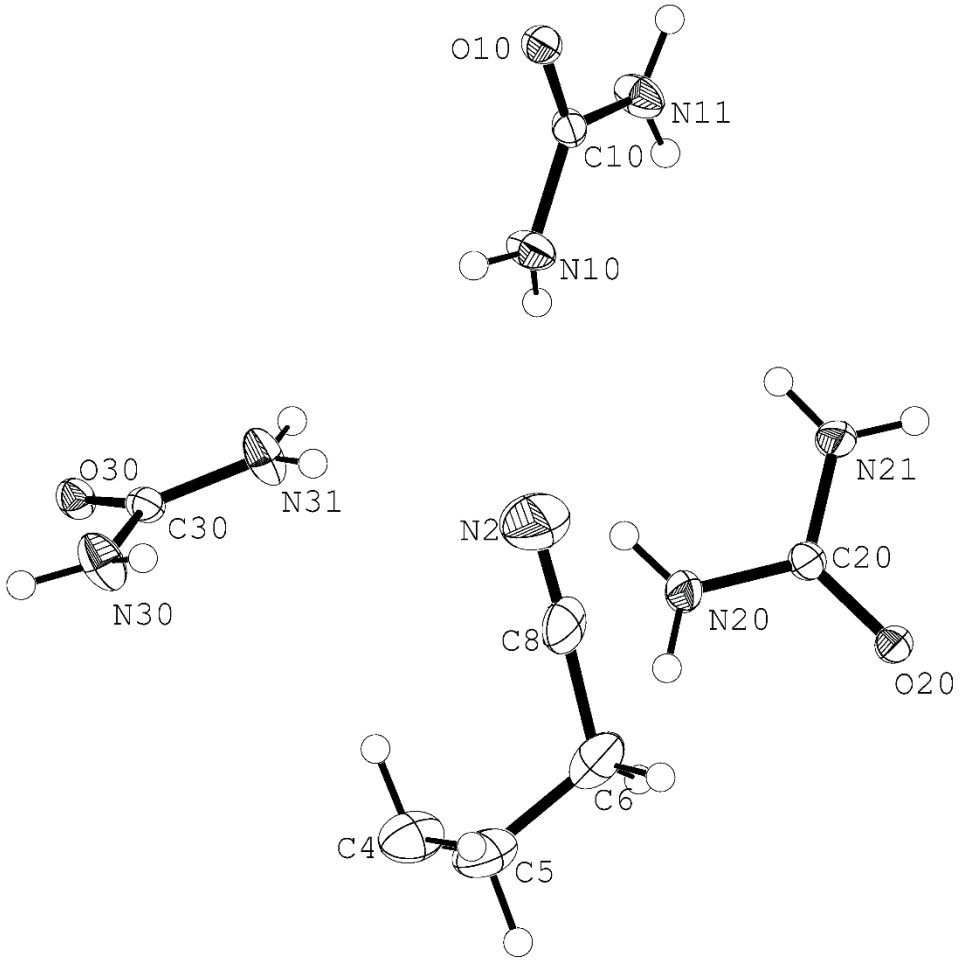


Figure 4: ORTEP rendering by OLEX2 showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 158 K (mh1001a).
2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular

level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Data collected using the Bruker APEX2 software package.
4. Bruker SAINT V8.18C
5. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).
6. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
7. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

Structure report for 1,6-dicyanohexane/urea at 158 K[1]

Introduction

The data for this crystal was collected in 2000 by Kevin Pate on a Siemens P4 diffractometer equipped with a SMART 1000 detector and was originally labeled "KP500". (See laboratory notebook KLP A-34.) The original crystal was from Christopher J. Nichols (CJN A-78-05). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule s disordered between two sites. The ratio of the major to minor sites is found to be 58.8% and 41.2%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 79.8°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 500 µm x 400 µm x 200 µm. The crystal was cooled to 158 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 20 seconds and the frame width was 0.30º. [8] The crystal to detector distance was 49.87 mm.

The unit cell parameters were determined[9,4] from 9930 input reflections whose minimum and the maximum 2-theta values were 4.70 and 54.94, respectively. The errors are reported after corrections for the goodness of fit (1.79). The cell volume is 1267.47(40) Å^3.

a = 8.1241 (9) Å	α = 90°
b = 10.8773 (12) Å	β = 94.5783 (17)°
c = 14.3774 (16) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.302 g/cm^3. Based on the systematic absences of

$$h00: \ h+l \neq 2n$$
$$0k0: \ k \neq 2n$$
$$h00: \ h \neq 2n$$
$$00l: \ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n \ (\#14).$$

Data Reduction:

The data set contained 7572 reflections of which 181 were rejected. After merging Friedel opposites, there were 2797 unique reflections, of which 2445 had I > 2sigma(I). The R(int) was 0.0182, and the R(sigma) was 0.0195. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.103 mm^{-1}. The absorption correction was made using SADABS. [8, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kp500_20.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.832 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

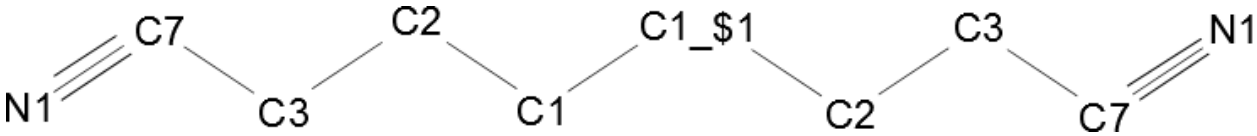


Figure 1: Atomic labeling scheme for part 1 (major part)

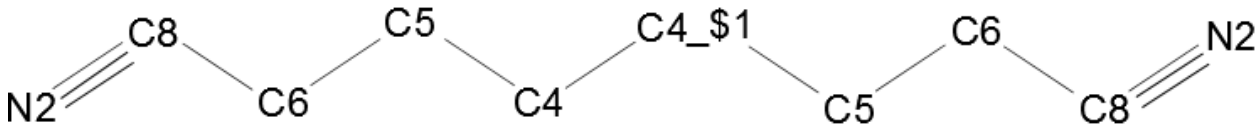


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.236 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.236 for all of the data. R1 was 0.0358 for all 2797 data and 0.0307 for data with $I>2\sigma(I)$; the wR2 value was 0.0718 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	500 x 400 x 200 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	4092
Lattice parameters	a = 8.1241 (9) Å
	b = 10.8773 (12) Å
	c = 14.3774 (16) Å
	α = 90°
	β = 94.5783 (17)°
	γ = 90°
	V = 1267.47(40) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.302
F_{000}	532
μ (MoK$_\alpha$)	0.103 mm^{-1}
Temperature	158 K

B. Intensity measurements

Diffractometer	Siemens P4, SMART 1000 CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K$_\alpha$ (λ = 0.71073 Å)
Crystal to detector distance	49.87 mm
Time per frame	20 s
Temperature	158 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.35°
θ_{max}	27.47°
h k l range	h = -10 to 9
	k = -14 to 14
	l = -17 to 18
No. of reflections measured	Total: 7391
	Unique 2797 (R_{int} = 0.050)

	$I > 2\sigma(I)$ = 2445
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations ($I > 2.00\sigma(I)$)	2445
No. variables	235
No. Restraints	27
Reflection:parameter ratio	11.90
For $I > 2.00\sigma(I)$	10.40
No. Reflections used in refinement	2797
Final R indices [$I > 2\sigma(I)$] R1	0.0307
Final R indices [all data]; R1, wR2	0.0358; 0.0718
Goodness of Fit (s)	1.236
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.148 e/Å^3
Minimum peak in final diff. map	-0.174 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99950 (9)	0.42002 (6)	0.65334 (5)	0.02349 (17)	
O30	−0.02785 (9)	0.08813 (6)	0.65406 (5)	0.02306 (16)	
O10	−0.01142 (9)	0.75126 (6)	0.68179 (5)	0.02302 (16)	
N21	0.80944 (13)	0.52139 (8)	0.73052 (7)	0.0324 (2)	
H21A	0.8628 (17)	0.5898 (12)	0.7216 (9)	0.039*	
H21B	0.7236 (18)	0.5212 (12)	0.7592 (9)	0.039*	
N20	0.78640 (12)	0.31322 (8)	0.70470 (7)	0.0310 (2)	
H20A	0.8304 (17)	0.2453 (12)	0.6850 (9)	0.037*	
H20B	0.6989 (17)	0.3116 (12)	0.7344 (9)	0.037*	
N31	0.19739 (13)	0.19484 (8)	0.70962 (7)	0.0319 (2)	
H31A	0.1543 (17)	0.2619 (12)	0.6847 (9)	0.038*	
H31B	0.2953 (18)	0.1961 (12)	0.7374 (9)	0.038*	
N30	0.17967 (14)	−0.01177 (9)	0.73622 (7)	0.0332 (2)	

H30A	0.1188 (18)	−0.0782 (13)	0.7343 (9)	0.040*	
H30B	0.2661 (19)	−0.0088 (12)	0.7713 (10)	0.040*	
C20	0.86907 (13)	0.41824 (8)	0.69488 (7)	0.0223 (2)	
C30	0.11239 (13)	0.09066 (8)	0.69911 (6)	0.0211 (2)	
N11	−0.03238 (13)	0.85482 (8)	0.54497 (7)	0.0296 (2)	
H11A	−0.0438 (16)	0.9231 (12)	0.5759 (9)	0.036*	
H11B	−0.0165 (16)	0.8572 (11)	0.4878 (10)	0.036*	
C10	−0.00533 (12)	0.75153 (8)	0.59423 (7)	0.0211 (2)	
N10	0.03167 (13)	0.64946 (8)	0.54860 (7)	0.0291 (2)	
H10A	0.0306 (16)	0.5799 (12)	0.5799 (9)	0.035*	
H10B	0.0182 (16)	0.6475 (11)	0.4893 (10)	0.035*	
C3	0.5177 (11)	0.2831 (4)	0.4359 (5)	0.0506 (16)	0.5880
H3A	0.6082	0.3365	0.4174	0.061*	0.5880
H3B	0.4381	0.2723	0.3807	0.061*	0.5880
C2	0.5887 (3)	0.1586 (2)	0.4649 (2)	0.0502 (7)	0.5880
H2A	0.6677	0.17	0.5204	0.060*	0.5880
H2B	0.6515	0.1266	0.4139	0.060*	0.5880
C1	0.4622 (4)	0.0628 (2)	0.4879 (3)	0.0437 (8)	0.5880
H1A	0.38	0.0537	0.4337	0.052*	0.5880
H1B	0.4033	0.0923	0.5413	0.052*	0.5880
C7	0.4350 (12)	0.3439 (7)	0.5090 (7)	0.054 (3)	0.5880
N1	0.3700 (11)	0.3827 (13)	0.5696 (7)	0.084 (3)	0.5880
C5	0.5050 (6)	0.1520 (3)	0.4294 (2)	0.0472 (9)	0.4120
H5A	0.391	0.1466	0.3997	0.057*	0.4120
H5B	0.5805	0.1233	0.3832	0.057*	0.4120
C4	0.5202 (7)	0.0666 (3)	0.5122 (3)	0.0455 (13)	0.4120
H4A	0.4451	0.0952	0.5586	0.055*	0.4120
H4B	0.6344	0.071	0.5416	0.055*	0.4120
C6	0.5435 (15)	0.2861 (5)	0.4521 (7)	0.054 (3)	0.4120
H6A	0.6569	0.2922	0.4825	0.065*	0.4120
H6B	0.5397	0.3339	0.3933	0.065*	0.4120
C8	0.4280 (15)	0.3398 (8)	0.5133 (8)	0.039 (3)	0.4120
N2	0.3401 (13)	0.3900 (18)	0.5571 (10)	0.0520 (19)	0.4120

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0247 (4)	0.0188 (3)	0.0280 (4)	0.0007 (3)	0.0084 (3)	0.0008 (3)
O30	0.0232 (4)	0.0187 (3)	0.0272 (4)	0.0003 (3)	0.0008 (3)	−0.0001 (3)
O10	0.0272 (4)	0.0205 (3)	0.0217 (3)	−0.0005 (3)	0.0042 (3)	0.0000 (3)
N21	0.0347 (6)	0.0199 (4)	0.0454 (6)	0.0000 (4)	0.0210 (5)	−0.0015 (4)
N20	0.0293 (5)	0.0196 (4)	0.0461 (6)	−0.0008 (4)	0.0161 (4)	0.0003 (4)
N31	0.0289 (5)	0.0205 (4)	0.0443 (6)	−0.0025 (4)	−0.0094 (4)	0.0026 (4)
N30	0.0337 (6)	0.0211 (4)	0.0424 (6)	−0.0002 (4)	−0.0112 (4)	0.0049 (4)
C20	0.0245 (5)	0.0197 (4)	0.0231 (5)	0.0016 (4)	0.0034 (4)	0.0026 (4)
C30	0.0249 (5)	0.0194 (4)	0.0195 (4)	0.0016 (4)	0.0049 (4)	−0.0012 (3)
N11	0.0461 (6)	0.0196 (4)	0.0232 (4)	0.0012 (4)	0.0031 (4)	0.0010 (3)
C10	0.0186 (5)	0.0204 (4)	0.0242 (5)	−0.0027 (4)	0.0016 (4)	−0.0001 (4)
N10	0.0455 (6)	0.0198 (4)	0.0224 (4)	0.0010 (4)	0.0060 (4)	−0.0002 (3)
C3	0.055 (3)	0.065 (3)	0.0341 (19)	0.002 (2)	0.0152 (18)	−0.0095 (15)
C2	0.0324 (14)	0.0708 (18)	0.0490 (15)	−0.0007 (13)	0.0128 (12)	−0.0151 (13)
C1	0.026 (2)	0.0654 (18)	0.0397 (18)	0.0024 (12)	0.0024 (13)	−0.0158 (13)
C7	0.042 (4)	0.072 (4)	0.048 (4)	−0.019 (3)	0.010 (3)	0.005 (3)
N1	0.105 (7)	0.071 (3)	0.083 (5)	−0.015 (5)	0.056 (5)	−0.017 (3)
C5	0.050 (2)	0.059 (2)	0.0352 (18)	0.0045 (19)	0.0147 (17)	−0.0075 (16)
C4	0.041 (3)	0.065 (3)	0.030 (2)	0.008 (2)	−0.0010 (19)	−0.0082 (16)
C6	0.051 (4)	0.067 (4)	0.047 (5)	−0.007 (3)	0.026 (4)	−0.005 (3)
C8	0.047 (6)	0.035 (4)	0.038 (5)	−0.001 (3)	0.021 (4)	−0.018 (3)
N2	0.033 (2)	0.064 (4)	0.060 (3)	−0.005 (2)	0.016 (2)	−0.021 (3)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2574 (12)	C3—C2	1.517 (5)
O30—C30	1.2651 (12)	C2—C1	1.518 (4)
O10—C10	1.2639 (12)	C1—C1i	1.527 (5)
N21—C20	1.3401 (13)	C7—N1	1.135 (5)
N20—C20	1.3382 (13)	C5—C4	1.508 (5)
N31—C30	1.3294 (13)	C5—C6	1.522 (6)
N30—C30	1.3335 (13)	C4—C4i	1.520 (6)
N11—C10	1.3369 (13)	C6—C8	1.459 (6)
C10—N10	1.3360 (12)	C8—N2	1.129 (6)
C3—C7	1.451 (5)		
O20—C20—N20	120.82 (9)	C7—C3—C2	113.3 (5)
O20—C20—N21	120.85 (9)	C3—C2—C1	115.1 (4)
N20—C20—N21	118.33 (9)	C2—C1—C1i	113.4 (3)
O30—C30—N31	121.01 (9)	N1—C7—C3	174.6 (11)
O30—C30—N30	120.68 (9)	C4—C5—C6	114.7 (5)
N31—C30—N30	118.31 (10)	C5—C4—C4i	113.7 (4)
O10—C10—N10	121.02 (9)	C8—C6—C5	112.4 (6)
O10—C10—N11	120.78 (9)	N2—C8—C6	174.4 (15)
N10—C10—N11	118.18 (9)		
C7—C3—C2—C1	63.4 (8)	C8—C6—C5—C4	−63.6 (11)
C3—C2—C1—C1i	177.2 (4)	C6—C5—C4—C4i	179.6 (7)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	63.4(8)
C3	C2	C1	C1i	177.2(4)

C8	C6	C5	C4	-63.6(11)
C6	C5	C4	C4i	179.6(7)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.876 (14)	2.133 (14)	3.0039 (12)	172.9 (12)
N21—H21B···O30iii	0.838 (14)	2.221 (14)	3.0199 (12)	159.5 (13)
N20—H20A···O30ii	0.877 (13)	2.128 (14)	2.9962 (12)	170.1 (13)
N20—H20B···O10iv	0.858 (14)	2.120 (14)	2.9480 (12)	161.9 (12)
N31—H31A···O20v	0.873 (14)	2.157 (14)	3.0052 (12)	163.7 (12)
N31—H31B···O10iv	0.861 (15)	2.113 (15)	2.9473 (13)	162.9 (13)
N30—H30A···O10vi	0.875 (14)	2.236 (14)	3.0777 (12)	161.2 (12)
N30—H30B···O20vii	0.832 (15)	2.252 (15)	3.0340 (13)	156.7 (13)
N11—H11A···O30viii	0.874 (13)	2.117 (14)	2.9820 (12)	170.4 (12)
N11—H11B···O30ix	0.842 (14)	2.182 (14)	3.0061 (12)	165.9 (12)
N10—H10A···O20v	0.881 (13)	2.060 (14)	2.9372 (11)	173.5 (12)
N10—H10B···O20x	0.852 (14)	2.172 (14)	2.9912 (12)	161.4 (12)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

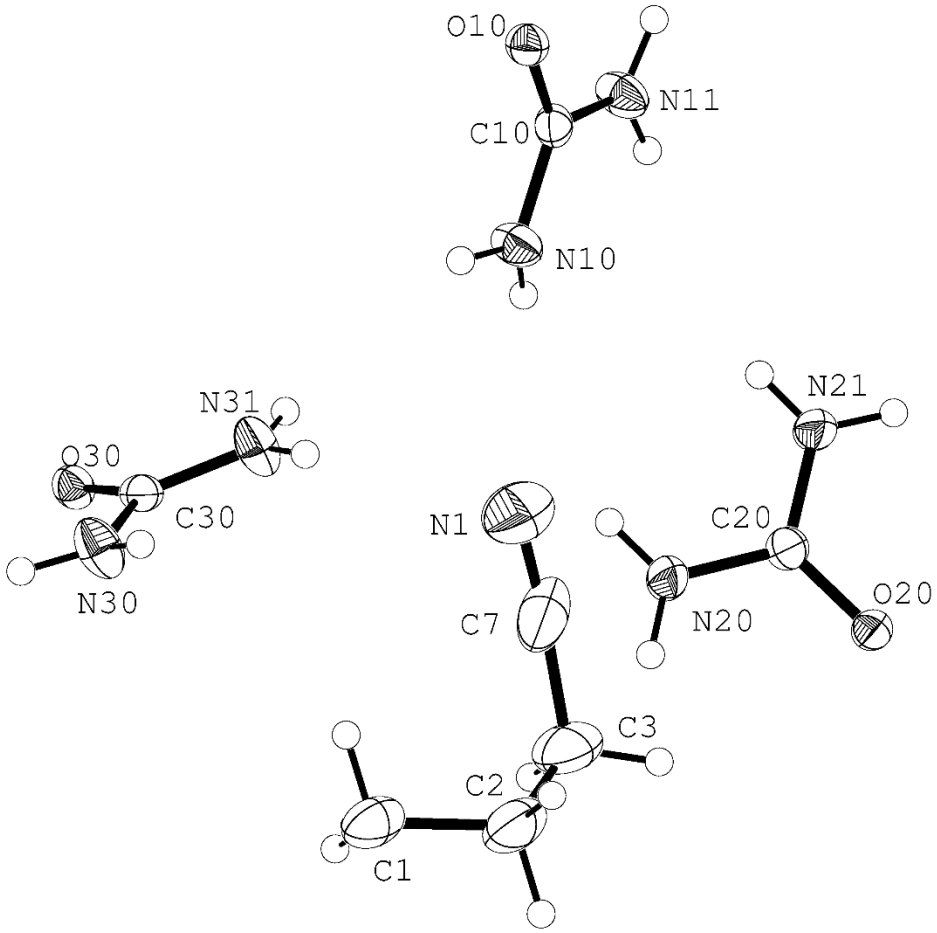
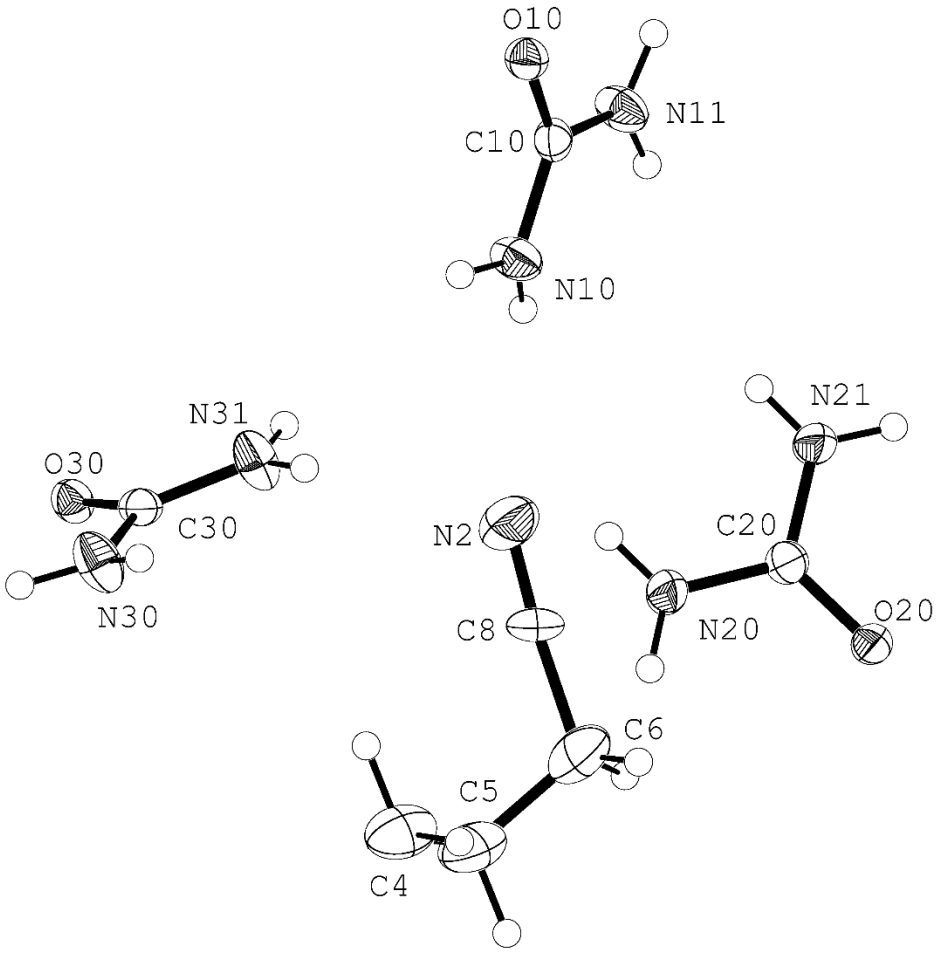


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 158 K (KP500).

2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Bruker AXS, Inc. (1998). SMART software Version 5.060. Bruker AXS, Inc., Madison, Wisconsin, USA.
4. Siemens P4 diffractometer equipped with a SMART 1000 CCD Detector.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Structure report for 1,6-dicyanohexane/urea at 173 K[1]

Introduction

The data for this crystal was collected in 2000 by Kevin Pate on a Siemens P4 diffractometer equipped with a SMART 1000 CCD detector and was originally labeled "KP600". (See laboratory notebook KLP A-34.) The original crystal was from Christopher J. Nichols (CJN A-78-05). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 58.92% and 41.08%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 78.76°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 500 µm x 400 µm x 200 µm. The crystal was cooled to 173 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 20 seconds and the frame width was 0.30º. [8] The crystal to detector distance was 49.87 mm.

The unit cell parameters were determined[9,4] from 4258 input reflections whose minimum and the maximum 2-theta values were 4.70 and 54.94, respectively. The errors are reported after corrections for the goodness of fit (1.63). The cell volume is 1267.34 (39) Å^3.

a = 8.1256 (5) Å	α = 90°
b = 10.8796 (7) Å	β = 94.5672 (9)°
c = 14.3816 (9) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.301 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 7862 reflections of which 190 were rejected. After merging Friedel opposites, there were 2798 unique reflections, of which 2446 had I > 2sigma(I). The R(int) was 0.0165, and the R(sigma) was 0.0170. The linear absorption coefficient, μ, for Mo-K_α radiation is 0.103 mm^{-1}. The absorption correction was made using SADABS.[8, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kp600_20.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.866 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

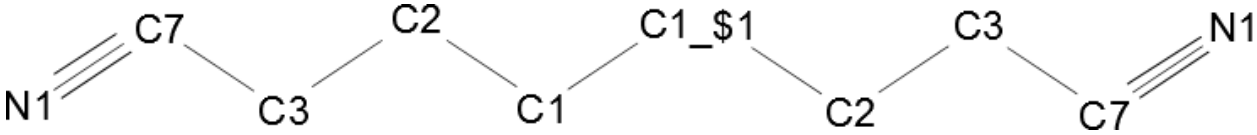


Figure 1: Atomic labeling scheme for part 1 (major part)

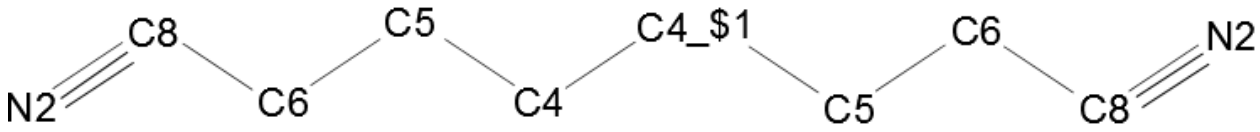


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.270 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.268 for all of the data. R1 was 0.0372 for all 2798 data and 0.0318 for data with $I>2\sigma(I)$; the wR2 value was 0.0728 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	500 x 400 x 200 μm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	4258
Lattice parameters	a = 8.1256 (5) Å b = 10.8796 (7) Å c = 14.3816 (9) Å α = 90° β = 94.5672 (9)° γ = 90° V = 1267.34 (39) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.301
F_{000}	532
μ (MoK_α)	0.103 mm^{-1}
Temperature	173 K

B. Intensity measurements

Diffractometer	Siemens P4, SMART 1000 CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K_α (λ = 0.71073 Å)
Crystal to detector distance	49.87 mm
Time per frame	20 s
Temperature	173 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.35°
θ_{max}	34.5°
h k l range	h = -10 to 10 k = -14 to 14 l = -18 to 18

No. of reflections measured	Total: 7672
	Unique 2798 (R_{int} = 0.0165)
	I > 2σ(I) = 2446
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	2446
No. variables	235
No. Restraints	27
Reflection:parameter ratio	11.91
For I > 2.00σ(I)	10.41
No. Reflections used in refinement	2798
Final R indices [I > 2σ(I)] R1	0.0318
Final R indices [all data]; R1, wR2	0.0372; 0.0728
Goodness of Fit (s)	1.270
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.145 e/Å^3
Minimum peak in final diff. map	-0.167 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99939 (9)	0.42002 (6)	0.65333 (5)	0.02417 (17)	
O30	−0.02770 (9)	0.08810 (6)	0.65412 (5)	0.02384 (17)	
O10	−0.01142 (9)	0.75125 (6)	0.68178 (5)	0.02364 (17)	
N21	0.80937 (13)	0.52129 (9)	0.73047 (7)	0.0333 (2)	
H21A	0.8622 (18)	0.5903 (13)	0.7216 (9)	0.040*	
H21B	0.7232 (18)	0.5207 (13)	0.7589 (10)	0.040*	
N20	0.78645 (13)	0.31319 (8)	0.70476 (7)	0.0316 (2)	
H20A	0.8298 (17)	0.2454 (12)	0.6847 (9)	0.038*	
H20B	0.6983 (18)	0.3117 (12)	0.7349 (9)	0.038*	
N31	0.19749 (14)	0.19486 (9)	0.70964 (7)	0.0328 (2)	

H31A	0.1548 (17)	0.2616 (13)	0.6850 (9)	0.039*	
H31B	0.2960 (19)	0.1961 (13)	0.7372 (10)	0.039*	
N30	0.17975 (14)	−0.01171 (9)	0.73617 (7)	0.0342 (2)	
H30A	0.1188 (18)	−0.0789 (13)	0.7343 (9)	0.041*	
H30B	0.2654 (19)	−0.0085 (13)	0.7711 (10)	0.041*	
C20	0.86895 (13)	0.41822 (9)	0.69486 (7)	0.0230 (2)	
C30	0.11249 (13)	0.09070 (8)	0.69912 (7)	0.0217 (2)	
N11	−0.03224 (13)	0.85485 (8)	0.54501 (7)	0.0304 (2)	
H11A	−0.0450 (17)	0.9228 (12)	0.5760 (9)	0.036*	
H11B	−0.0152 (17)	0.8575 (12)	0.4868 (10)	0.036*	
C10	−0.00533 (12)	0.75156 (9)	0.59429 (7)	0.0216 (2)	
N10	0.03149 (13)	0.64953 (8)	0.54860 (7)	0.0297 (2)	
H10A	0.0294 (17)	0.5798 (12)	0.5799 (9)	0.036*	
H10B	0.0189 (16)	0.6473 (12)	0.4895 (10)	0.036*	
C3	0.5146 (10)	0.2830 (4)	0.4361 (5)	0.0505 (16)	0.5892
H3A	0.6056	0.3388	0.4221	0.061*	0.5892
H3B	0.4431	0.2719	0.3777	0.061*	0.5892
C2	0.5884 (3)	0.1588 (2)	0.4649 (2)	0.0516 (7)	0.5892
H2A	0.6513	0.1272	0.4137	0.062*	0.5892
H2B	0.6675	0.1705	0.5202	0.062*	0.5892
C1	0.4625 (4)	0.0628 (2)	0.4879 (3)	0.0454 (9)	0.5892
H1A	0.3803	0.0536	0.4337	0.055*	0.5892
H1B	0.4034	0.0923	0.5412	0.055*	0.5892
C7	0.4186 (10)	0.3421 (8)	0.5041 (6)	0.0401 (15)	0.5892
N1	0.3437 (10)	0.3864 (11)	0.5570 (7)	0.0573 (14)	0.5892
C5	0.5050 (6)	0.1519 (3)	0.4294 (2)	0.0472 (9)	0.4108
H5A	0.3902	0.1481	0.4007	0.057*	0.4108
H5B	0.5784	0.122	0.3825	0.057*	0.4108
C4	0.5205 (8)	0.0666 (3)	0.5124 (3)	0.0470 (13)	0.4108
H4A	0.4456	0.0953	0.5589	0.056*	0.4108
H4B	0.6348	0.0708	0.5416	0.056*	0.4108
C6	0.5477 (14)	0.2855 (5)	0.4523 (7)	0.052 (2)	0.4108
H6A	0.6657	0.2899	0.4752	0.062*	0.4108
H6B	0.5336	0.334	0.3939	0.062*	0.4108
C8	0.4506 (14)	0.3426 (11)	0.5210 (8)	0.0351 (18)	0.4108
N2	0.3796 (16)	0.3853 (17)	0.5763 (10)	0.086 (4)	0.4108

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0253 (4)	0.0195 (3)	0.0287 (4)	0.0008 (3)	0.0085 (3)	0.0007 (3)
O30	0.0237 (4)	0.0194 (3)	0.0282 (4)	0.0002 (3)	0.0006 (3)	−0.0002 (3)
O10	0.0279 (4)	0.0212 (3)	0.0222 (3)	−0.0006 (3)	0.0039 (3)	−0.0001 (3)
N21	0.0358 (6)	0.0207 (4)	0.0462 (6)	0.0003 (4)	0.0212 (5)	−0.0013 (4)
N20	0.0295 (5)	0.0204 (4)	0.0469 (6)	−0.0011 (4)	0.0160 (4)	0.0002 (4)
N31	0.0294 (5)	0.0215 (4)	0.0455 (6)	−0.0026 (4)	−0.0097 (4)	0.0029 (4)
N30	0.0344 (6)	0.0221 (5)	0.0437 (6)	0.0002 (4)	−0.0117 (4)	0.0051 (4)
C20	0.0247 (5)	0.0203 (5)	0.0242 (5)	0.0016 (4)	0.0034 (4)	0.0026 (4)
C30	0.0253 (5)	0.0199 (4)	0.0204 (4)	0.0016 (4)	0.0050 (4)	−0.0009 (4)
N11	0.0471 (6)	0.0203 (4)	0.0238 (5)	0.0014 (4)	0.0030 (4)	0.0011 (3)
C10	0.0190 (5)	0.0212 (5)	0.0247 (5)	−0.0027 (4)	0.0016 (4)	−0.0003 (4)
N10	0.0463 (6)	0.0206 (4)	0.0228 (4)	0.0009 (4)	0.0058 (4)	−0.0004 (3)
C3	0.050 (3)	0.068 (3)	0.0343 (18)	0.0009 (18)	0.0115 (19)	−0.0071 (15)
C2	0.0334 (15)	0.0730 (19)	0.0498 (16)	−0.0011 (13)	0.0129 (12)	−0.0155 (14)
C1	0.027 (2)	0.0679 (19)	0.0415 (19)	0.0027 (12)	0.0026 (13)	−0.0165 (13)
C7	0.031 (3)	0.056 (2)	0.032 (3)	−0.0116 (18)	−0.004 (2)	−0.0076 (17)
N1	0.0475 (18)	0.068 (2)	0.059 (3)	−0.0092 (16)	0.024 (2)	−0.026 (2)
C5	0.049 (2)	0.059 (2)	0.0347 (18)	0.0042 (19)	0.0128 (17)	−0.0084 (16)
C4	0.044 (4)	0.067 (3)	0.030 (2)	0.008 (2)	−0.0012 (19)	−0.0086 (17)
C6	0.043 (4)	0.066 (4)	0.049 (5)	−0.008 (2)	0.021 (4)	−0.007 (2)
C8	0.023 (4)	0.056 (3)	0.025 (3)	−0.009 (2)	−0.004 (3)	−0.009 (2)
N2	0.118 (10)	0.078 (4)	0.068 (6)	−0.029 (6)	0.044 (6)	−0.022 (4)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2575 (12)	C3—C2	1.523 (5)
O30—C30	1.2647 (13)	C2—C1	1.517 (4)
O10—C10	1.2631 (12)	C1—C1i	1.525 (5)
N21—C20	1.3392 (13)	C7—N1	1.120 (4)
N20—C20	1.3382 (13)	C5—C4	1.509 (5)
N31—C30	1.3295 (13)	C5—C6	1.525 (6)
N30—C30	1.3333 (13)	C4—C4i	1.523 (6)
N11—C10	1.3372 (13)	C6—C8	1.453 (5)
C10—N10	1.3360 (13)	C8—N2	1.120 (6)
C3—C7	1.450 (4)		
O20—C20—N20	120.81 (9)	C7—C3—C2	115.5 (4)
O20—C20—N21	120.84 (9)	C1—C2—C3	114.3 (3)
N20—C20—N21	118.35 (9)	C2—C1—C1i	113.7 (3)
O30—C30—N31	121.05 (9)	N1—C7—C3	179.1 (11)
O30—C30—N30	120.64 (9)	C4—C5—C6	114.3 (4)
N31—C30—N30	118.30 (10)	C5—C4—C4i	113.4 (4)
O10—C10—N10	121.05 (9)	C8—C6—C5	115.3 (6)
O10—C10—N11	120.83 (9)	N2—C8—C6	177.6 (12)
N10—C10—N11	118.11 (9)		
C7—C3—C2—C1	58.6 (7)	C8—C6—C5—C4	−58.0 (11)
C3—C2—C1—C1i	177.3 (4)	C6—C5—C4—C4i	−179.2 (7)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	58.6(7)
C3	C2	C1	C1i	177.3(4)
C8	C6	C5	C4	-58.0(11)

C6	C5	C4	C4i	-179.2(7)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.879 (14)	2.131 (14)	3.0054 (12)	172.6 (12)
N21—H21B···O30iii	0.838 (15)	2.223 (15)	3.0210 (12)	159.0 (13)
N20—H20A···O30ii	0.876 (14)	2.131 (14)	2.9971 (12)	169.4 (13)
N20—H20B···O10iv	0.866 (14)	2.113 (14)	2.9481 (12)	161.8 (12)
N31—H31A···O20v	0.869 (14)	2.163 (14)	3.0067 (13)	163.7 (13)
N31—H31B···O10iv	0.865 (15)	2.111 (15)	2.9474 (13)	162.6 (13)
N30—H30A···O10vi	0.882 (14)	2.231 (15)	3.0793 (13)	161.2 (12)
N30—H30B···O20vii	0.826 (16)	2.260 (16)	3.0356 (13)	156.6 (13)
N11—H11A···O30viii	0.874 (14)	2.119 (14)	2.9824 (12)	169.4 (13)
N11—H11B···O30ix	0.859 (14)	2.167 (14)	3.0078 (12)	166.1 (12)
N10—H10A···O20v	0.882 (14)	2.059 (14)	2.9383 (12)	174.3 (12)
N10—H10B···O20x	0.849 (14)	2.174 (14)	2.9923 (12)	161.7 (12)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2; (iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z; (vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z; (ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

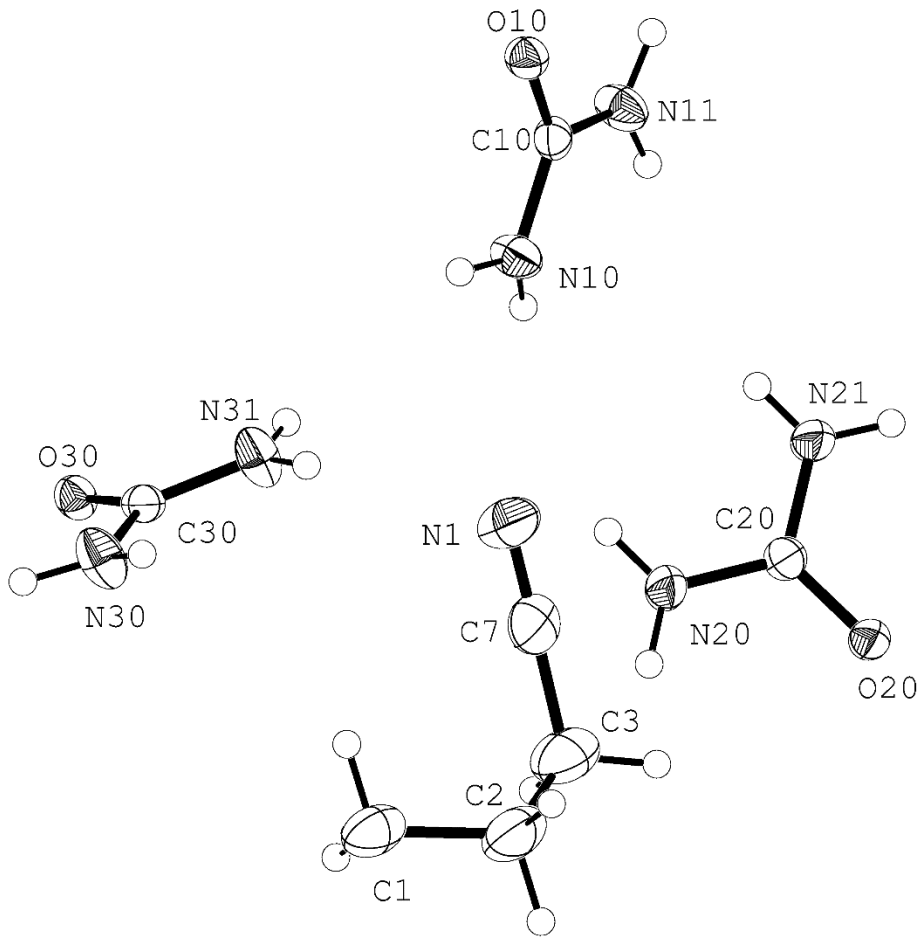
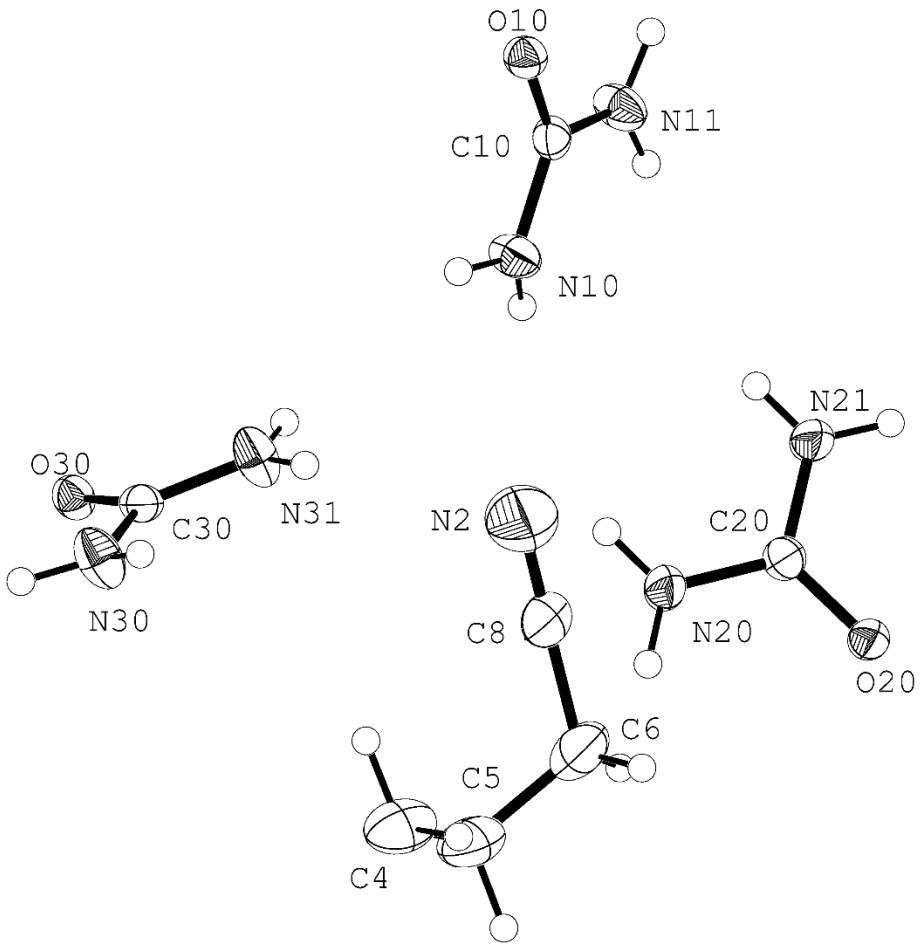


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 173 K (KP600).

2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Bruker AXS, Inc. (1998). SMART software Version 5.060. Bruker AXS, Inc., Madison, Wisconsin, USA.
4. Siemens P4 diffractometer equipped with a SMART 1000 CCD Detector.
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6. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Structure report for 1,6-dicyanohexane/urea at 188 K[1]

Introduction

The data for this crystal was collected in 2000 by Kevin Pate on a Siemens P4 diffractometer equipped with a SMART 1000 CCD detector and was originally labeled "KP800". (See laboratory notebook KLP A-37.) The original crystal was from Christopher J. Nichols (CJN A-78-05). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 58.0% and 42.0%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 79.2°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 500 µm x 400 µm x 200 µm. The crystal was cooled to 188 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 20 seconds and the frame width was 0.30º. [8] The crystal to detector distance was 49.87 mm.

The unit cell parameters were determined[9,4] from 3950 input reflections whose minimum and the maximum 2-theta values were 4.70 and 54.04, respectively. The errors are reported after corrections for the goodness of fit (1.56). The cell volume is 1271.4(2) Å^3.

a = 8.1342(8) Å	α = 90°
b = 10.8885(11) Å	β = 94.5469(15)°
c = 14.3997(14) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.297 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 7623 reflections of which 180 were rejected. After merging Friedel opposites, there were 2813 unique reflections, of which 2445 had I > 2sigma(I). The R(int) was 0.0176, and the R(sigma) was 0.0191. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.103 mm^{-1}. The absorption correction was made using SADABS.[8, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kp800_20.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.859 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

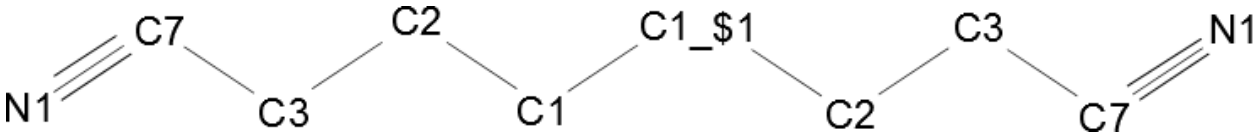


Figure 1: Atomic labeling scheme for part 1 (major part)

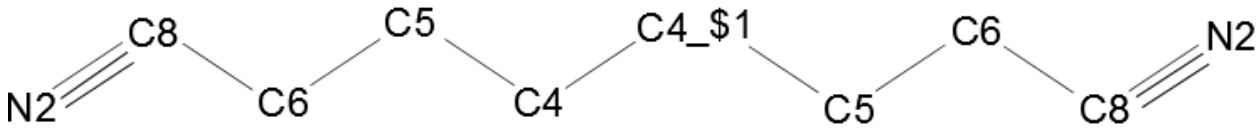


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.151 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.149 for all of the data. R1 was 0.0375 for all 5279 data and 0.0320 for data with $I>2\sigma(I)$; the wR2 value was 0.0790 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	500 x 400 x 200 μm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	9930
Lattice parameters	a = 8.1342(8) Å
	b = 10.8885(11) Å
	c = 14.3997(14) Å
	α = 90°
	β = 94.5469(15)°
	γ = 90°
	V = 1271.4(2) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.297
F_{000}	532
μ (MoK$_\alpha$)	0.103 mm^{-1}
Temperature	188 K

B. Intensity measurements

Diffractometer	Bruker-Siemens P4
	SMART 1000 CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K$_\alpha$ (λ = 0.71073 Å)
Crystal to detector distance	49.87 mm
Time per frame	20 s
Temperature	188 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.35°
θ_{max}	27.52°
h k l range	h = -10 to 9
	k = -14 to 14
	l = -17 to 18
No. of reflections measured	Total: 7443

	Unique 2813 (R_{int} = 0.0176)
	I > 2σ(I) = 2445
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	2445
No. variables	235
No. Restraints	27
Reflection:parameter ratio	11.97
For I > 2.00σ(I)	10.40
No. Reflections used in refinement	2813
Final R indices [I > 2σ(I)] R1	0.0320
Final R indices [all data]; R1, wR2	0.0375; 0.0790
Goodness of Fit (s)	1.149
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.142 e/Å^3
Minimum peak in final diff. map	-0.168 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99916 (9)	0.42001 (6)	0.65336 (5)	0.02613 (17)	
O30	−0.02728 (9)	0.08814 (6)	0.65419 (5)	0.02574 (17)	
O10	−0.01142 (9)	0.75115 (6)	0.68167 (5)	0.02557 (17)	
N21	0.80912 (13)	0.52113 (8)	0.73033 (7)	0.0358 (2)	
H21A	0.8618 (18)	0.5902 (13)	0.7221 (10)	0.043*	
H21B	0.7235 (19)	0.5202 (13)	0.7587 (10)	0.043*	
N20	0.78666 (12)	0.31309 (8)	0.70485 (7)	0.0341 (2)	
H20A	0.8302 (18)	0.2450 (12)	0.6852 (9)	0.041*	
H20B	0.7000 (18)	0.3118 (12)	0.7353 (10)	0.041*	
N31	0.19758 (14)	0.19481 (9)	0.70959 (7)	0.0358 (2)	
H31A	0.1554 (18)	0.2614 (13)	0.6849 (10)	0.043*	
H31B	0.2949 (19)	0.1962 (13)	0.7373 (10)	0.043*	

N30	0.17999 (14)	−0.01149 (9)	0.73625 (7)	0.0370 (2)	
H30A	0.1200 (18)	−0.0785 (13)	0.7345 (10)	0.044*	
H30B	0.266 (2)	−0.0080 (13)	0.7714 (10)	0.044*	
C20	0.86897 (13)	0.41813 (8)	0.69485 (7)	0.0246 (2)	
C30	0.11267 (13)	0.09076 (8)	0.69918 (6)	0.0233 (2)	
N11	−0.03194 (13)	0.85479 (8)	0.54514 (7)	0.0326 (2)	
H11A	−0.0447 (17)	0.9233 (12)	0.5763 (10)	0.039*	
H11B	−0.0174 (17)	0.8577 (12)	0.4878 (10)	0.039*	
C10	−0.00545 (12)	0.75150 (8)	0.59424 (7)	0.0232 (2)	
N10	0.03088 (13)	0.64953 (8)	0.54855 (7)	0.0322 (2)	
H10A	0.0301 (17)	0.5809 (12)	0.5798 (10)	0.039*	
H10B	0.0185 (17)	0.6472 (12)	0.4899 (10)	0.039*	
C3	0.5146 (10)	0.2828 (4)	0.4363 (5)	0.0552 (17)	0.5796
H3A	0.6055	0.3384	0.4221	0.066*	0.5796
H3B	0.4427	0.2717	0.3782	0.066*	0.5796
C2	0.5883 (4)	0.1587 (3)	0.4650 (2)	0.0564 (7)	0.5796
H2A	0.651	0.1273	0.4138	0.068*	0.5796
H2B	0.6673	0.1704	0.5202	0.068*	0.5796
C1	0.4625 (4)	0.0626 (2)	0.4879 (3)	0.0495 (9)	0.5796
H1A	0.3804	0.0535	0.4338	0.059*	0.5796
H1B	0.4034	0.0921	0.5411	0.059*	0.5796
C7	0.4194 (11)	0.3422 (8)	0.5042 (6)	0.0447 (17)	0.5796
N1	0.3440 (10)	0.3865 (11)	0.5567 (6)	0.0622 (15)	0.5796
C5	0.5052 (6)	0.1519 (3)	0.4297 (2)	0.0522 (9)	0.4204
H5A	0.3908	0.1479	0.4007	0.063*	0.4204
H5B	0.5792	0.1222	0.3831	0.063*	0.4204
C4	0.5200 (8)	0.0666 (3)	0.5124 (3)	0.0520 (14)	0.4204
H4A	0.4446	0.0951	0.5586	0.062*	0.4204
H4B	0.6339	0.0711	0.542	0.062*	0.4204
C6	0.5471 (15)	0.2854 (5)	0.4522 (7)	0.058 (3)	0.4204
H6A	0.6652	0.2903	0.4745	0.069*	0.4204
H6B	0.5317	0.3337	0.394	0.069*	0.4204
C8	0.4510 (14)	0.3421 (10)	0.5213 (8)	0.0387 (18)	0.4204
N2	0.3822 (15)	0.3842 (17)	0.5775 (9)	0.091 (4)	0.4204

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0274 (4)	0.0212 (3)	0.0310 (4)	0.0007 (3)	0.0095 (3)	0.0009 (3)
O30	0.0254 (4)	0.0209 (3)	0.0307 (4)	0.0003 (3)	0.0007 (3)	0.0001 (3)
O10	0.0304 (4)	0.0229 (3)	0.0238 (3)	−0.0005 (3)	0.0044 (3)	0.0000 (3)
N21	0.0385 (6)	0.0221 (4)	0.0498 (6)	0.0003 (4)	0.0227 (5)	−0.0016 (4)
N20	0.0323 (5)	0.0218 (4)	0.0504 (6)	−0.0013 (4)	0.0175 (5)	0.0003 (4)
N31	0.0326 (6)	0.0228 (4)	0.0497 (6)	−0.0028 (4)	−0.0109 (4)	0.0030 (4)
N30	0.0379 (6)	0.0238 (4)	0.0468 (6)	0.0000 (4)	−0.0121 (5)	0.0057 (4)
C20	0.0264 (5)	0.0220 (4)	0.0257 (5)	0.0015 (4)	0.0042 (4)	0.0027 (4)
C30	0.0272 (5)	0.0213 (4)	0.0218 (4)	0.0018 (4)	0.0053 (4)	−0.0009 (3)
N11	0.0504 (6)	0.0220 (4)	0.0254 (4)	0.0011 (4)	0.0029 (4)	0.0014 (3)
C10	0.0204 (5)	0.0225 (4)	0.0265 (5)	−0.0031 (4)	0.0018 (4)	−0.0004 (4)
N10	0.0500 (6)	0.0226 (4)	0.0246 (4)	0.0011 (4)	0.0062 (4)	−0.0005 (3)
C3	0.057 (4)	0.073 (3)	0.0370 (18)	0.0010 (19)	0.0139 (19)	−0.0078 (15)
C2	0.0369 (16)	0.079 (2)	0.0549 (17)	−0.0008 (14)	0.0138 (13)	−0.0170 (15)
C1	0.031 (2)	0.073 (2)	0.044 (2)	0.0021 (12)	0.0049 (14)	−0.0185 (14)
C7	0.036 (3)	0.061 (2)	0.036 (3)	−0.0126 (19)	−0.002 (2)	−0.0086 (19)
N1	0.0520 (19)	0.074 (2)	0.064 (3)	−0.0104 (16)	0.027 (2)	−0.028 (3)
C5	0.055 (3)	0.065 (2)	0.0379 (18)	0.004 (2)	0.0156 (17)	−0.0089 (17)
C4	0.051 (4)	0.071 (3)	0.033 (2)	0.007 (2)	0.000 (2)	−0.0089 (17)
C6	0.048 (4)	0.074 (4)	0.054 (5)	−0.008 (2)	0.025 (4)	−0.007 (3)
C8	0.027 (4)	0.060 (3)	0.028 (3)	−0.007 (2)	−0.002 (3)	−0.007 (2)
N2	0.125 (10)	0.085 (4)	0.069 (6)	−0.027 (6)	0.047 (6)	−0.021 (4)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2566 (12)	C3—C2	1.522 (5)
O30—C30	1.2647 (13)	C2—C1	1.517 (4)
O10—C10	1.2638 (12)	C1—C1i	1.524 (5)
N21—C20	1.3399 (13)	C7—N1	1.120 (4)
N20—C20	1.3389 (13)	C5—C4	1.507 (5)
N31—C30	1.3291 (13)	C5—C6	1.522 (6)
N30—C30	1.3335 (13)	C4—C4i	1.523 (6)
N11—C10	1.3368 (13)	C6—C8	1.451 (5)
C10—N10	1.3355 (13)	C8—N2	1.118 (5)
C3—C7	1.447 (4)		
O20—C20—N20	120.83 (9)	C7—C3—C2	115.7 (5)
O20—C20—N21	120.87 (9)	C1—C2—C3	114.4 (4)
N20—C20—N21	118.30 (9)	C2—C1—C1i	113.7 (4)
O30—C30—N31	121.04 (9)	N1—C7—C3	178.8 (11)
O30—C30—N30	120.71 (9)	C4—C5—C6	114.7 (5)
N31—C30—N30	118.25 (10)	C5—C4—C4i	113.5 (4)
O10—C10—N10	121.05 (9)	C8—C6—C5	115.4 (6)
O10—C10—N11	120.80 (9)	N2—C8—C6	176.9 (12)
N10—C10—N11	118.14 (9)		
C7—C3—C2—C1	58.9 (8)	C8—C6—C5—C4	−57.2 (11)
C3—C2—C1—C1i	177.4 (5)	C6—C5—C4—C4i	−179.1 (7)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	58.9(8)
C3	C2	C1	C1i	177.4(5)
C8	C6	C5	C4	-57.2(11)
C6	C5	C4	C4i	-179.1(7)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.878 (14)	2.138 (15)	3.0095 (12)	171.8 (13)
N21—H21B···O30iii	0.835 (15)	2.232 (15)	3.0262 (12)	158.8 (13)
N20—H20A···O30ii	0.878 (14)	2.131 (14)	2.9995 (12)	169.7 (13)
N20—H20B···O10iv	0.859 (14)	2.124 (15)	2.9526 (12)	161.9 (13)
N31—H31A···O20v	0.867 (14)	2.171 (15)	3.0110 (12)	163.3 (13)
N31—H31B···O10iv	0.858 (16)	2.120 (16)	2.9515 (13)	163.0 (13)
N30—H30A···O10vi	0.877 (15)	2.244 (15)	3.0866 (13)	161.1 (12)
N30—H30B···O20vii	0.830 (16)	2.261 (16)	3.0392 (13)	156.2 (13)
N11—H11A···O30viii	0.881 (14)	2.116 (14)	2.9856 (12)	169.5 (13)
N11—H11B···O30ix	0.843 (14)	2.187 (15)	3.0127 (12)	166.3 (12)
N10—H10A···O20v	0.873 (14)	2.073 (14)	2.9414 (12)	173.4 (13)
N10—H10B···O20x	0.843 (14)	2.183 (14)	2.9955 (12)	161.9 (12)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

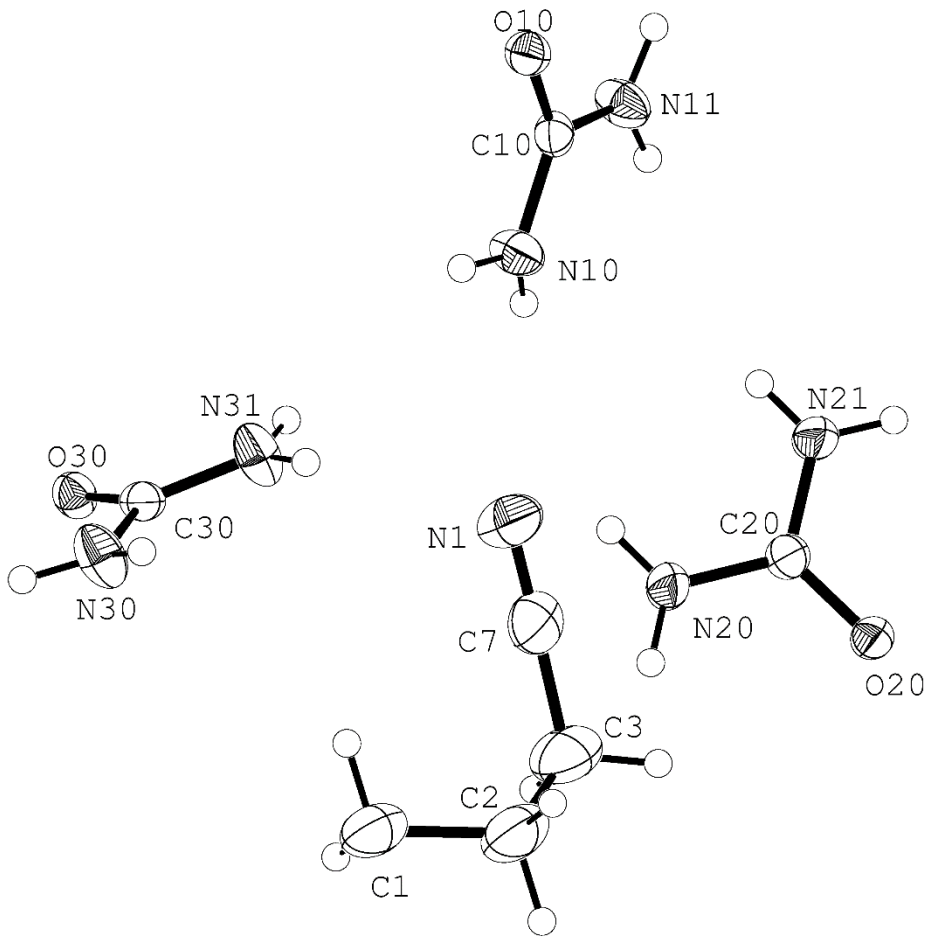
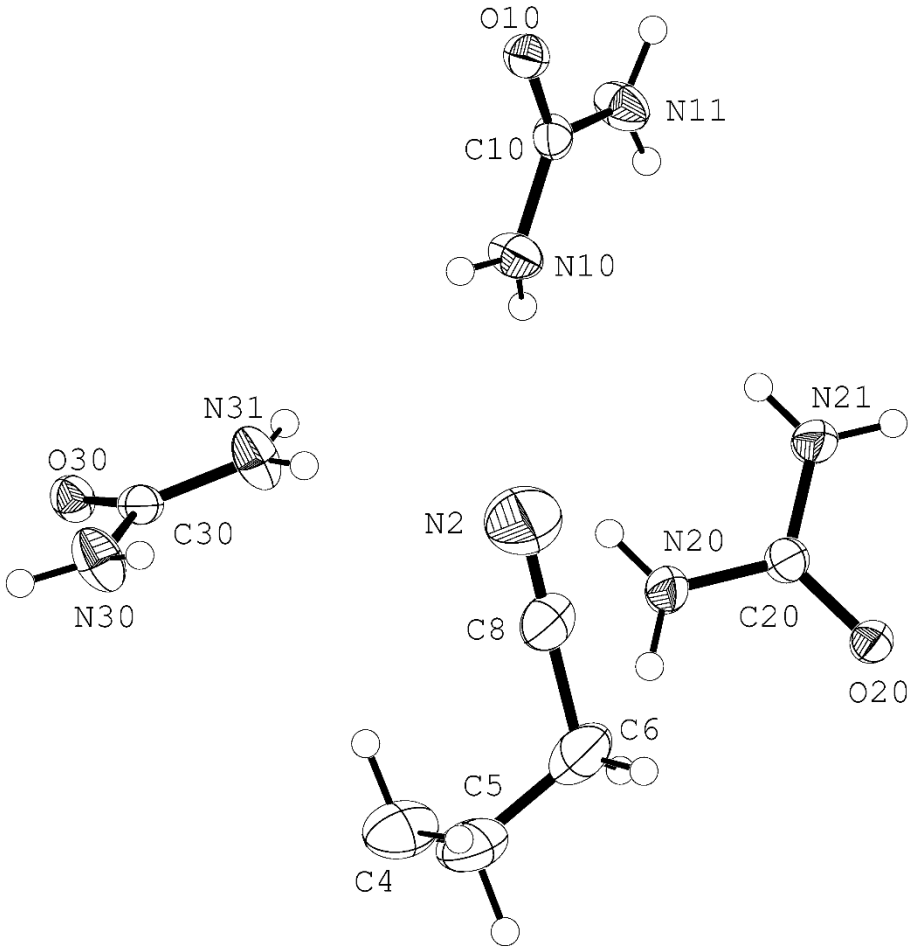


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 188 K (KP800).

2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Bruker AXS, Inc. (1998). SMART software Version 5.060. Bruker AXS, Inc., Madison, Wisconsin, USA.
4. Siemens P4 diffractometer equipped with a SMART 1000 CCD Detector.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **42**, 339–341 (2009).

Structure report for 1,6-dicyanohexane/urea at 203 K[1]

Introduction

The data for this crystal was collected in 2000 by Kevin Pate on a Siemens P4 diffractometer equipped with a SMART 1000 CCD detector and was originally labeled "KP900". (See laboratory notebook KLP A-38.) The original crystal was from Christopher J. Nichols (CJN A-78-05). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 57.9% and 42.1%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 79.26°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 500 µm x 400 µm x 200 µm. The crystal was cooled to 203 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 20 seconds and the frame width was 0.30º. [8] The crystal to detector distance was 49.87 mm.

The unit cell parameters were determined[9,4] from 3839 input reflections whose minimum and the maximum 2-theta values were 4.70 and 54.74, respectively. The errors are reported after corrections for the goodness of fit (1.55). The cell volume is 1272.9(2) Å^3.

a = 8.1374(8) Å	α = 90°
b = 10.8911(11) Å	β = 94.5192(16)°
c = 14.4071(15) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.296 g/cm^3. Based on the systematic absences of

$$h00: \ h+l \neq 2n$$
$$0k0: \ k \neq 2n$$
$$h00: \ h \neq 2n$$
$$00l: \ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n \ (\#14).$$

Data Reduction:

The data set contained 7571 reflections of which 183 were rejected. After merging Friedel opposites, there were 2789 unique reflections, of which 2394 had I > 2sigma(I). The R(int) was 0.0179, and the R(sigma) was 0.0190. The linear absorption coefficient, μ, for Mo-K_α radiation is 0.103 mm^{-1}. The absorption correction was made using SADABS.[8, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kp900_20.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.849 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

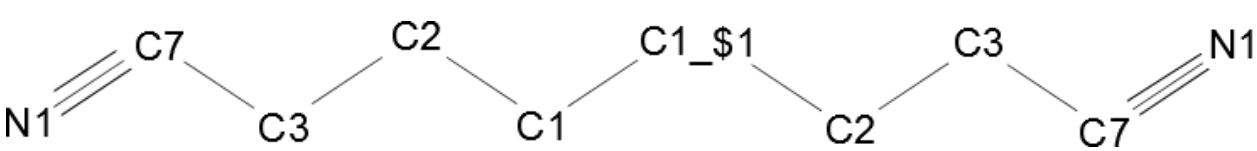


Figure 1: Atomic labeling scheme for part 1 (major part)

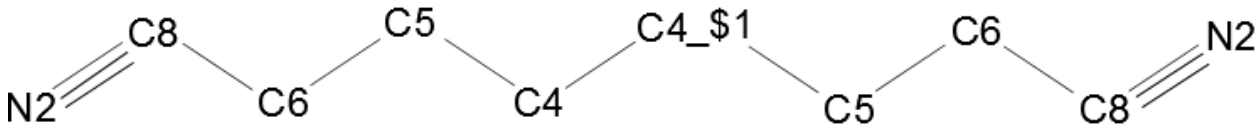


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.118 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.117 for all of the data. R1 was 0.0382 for all 2789 data and 0.0317 for data with $I>2\sigma(I)$; the wR2 value was 0.0777 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	500 x 400 x 200 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	3839
Lattice parameters	a = 8.1374(8) Å
	b = 10.8911(11) Å
	c = 14.4071(15) Å
	α = 90°
	β = 94.5192(16)°
	γ = 90°
	V = 1272.9(2) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.296
F_{000}	532
μ (MoK$_\alpha$)	0.103 mm^{-1}
Temperature	203 K

B. Intensity measurements

Diffractometer	Siemens P4, SMART 1000 CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K$_\alpha$ (λ = 0.71073 Å)
Crystal to detector distance	49.87 mm
Time per frame	20 s
Temperature	203 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.35°
θ_{max}	27.37°
h k l range	h = -10 to 9
	k = -14 to 14
	l = -17 to 18
No. of reflections measured	Total: 7388
	Unique 2789 (R_{int} = 0.0179)

	$I > 2\sigma(I) = 2394$
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations ($I > 2.00\sigma(I)$)	2394
No. variables	235
No. Restraints	27
Reflection:parameter ratio	11.87
For $I > 2.00\sigma(I)$	10.19
No. Reflections used in refinement	2789
Final R indices [$I > 2\sigma(I)$] R1	0.0317
Final R indices [all data]; R1, wR2	0.0382; 0.0777
Goodness of Fit (s)	1.117
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.119 e/Å^3
Minimum peak in final diff. map	-0.152 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99893 (9)	0.41998 (6)	0.65339 (5)	0.02802 (18)	
O30	−0.02675 (9)	0.08809 (6)	0.65431 (5)	0.02768 (17)	
O10	−0.01149 (9)	0.75105 (6)	0.68151 (5)	0.02716 (17)	
N21	0.80891 (13)	0.52087 (9)	0.73023 (7)	0.0382 (3)	
H21A	0.8607 (18)	0.5897 (13)	0.7211 (10)	0.046*	
H21B	0.7236 (19)	0.5202 (13)	0.7584 (10)	0.046*	
N20	0.78689 (13)	0.31307 (8)	0.70494 (8)	0.0366 (2)	
H20A	0.8308 (18)	0.2455 (13)	0.6859 (10)	0.044*	
H20B	0.7007 (18)	0.3114 (12)	0.7346 (10)	0.044*	
N31	0.19780 (14)	0.19472 (9)	0.70959 (8)	0.0383 (2)	
H31A	0.1554 (18)	0.2615 (13)	0.6844 (10)	0.046*	
H31B	0.2945 (19)	0.1963 (13)	0.7374 (10)	0.046*	

N30	0.18020 (15)	−0.01127 (9)	0.73626 (8)	0.0398 (3)	
H30A	0.1202 (19)	−0.0779 (13)	0.7345 (10)	0.048*	
H30B	0.266 (2)	−0.0069 (13)	0.7710 (10)	0.048*	
C20	0.86891 (13)	0.41801 (8)	0.69492 (7)	0.0261 (2)	
C30	0.11297 (13)	0.09077 (8)	0.69924 (7)	0.0248 (2)	
N11	−0.03163 (13)	0.85470 (8)	0.54525 (7)	0.0352 (2)	
H11A	−0.0439 (17)	0.9226 (12)	0.5763 (10)	0.042*	
H11B	−0.0181 (17)	0.8573 (12)	0.4883 (10)	0.042*	
C10	−0.00564 (12)	0.75145 (8)	0.59420 (7)	0.0247 (2)	
N10	0.03038 (13)	0.64953 (8)	0.54854 (7)	0.0345 (2)	
H10A	0.0289 (17)	0.5807 (12)	0.5798 (10)	0.041*	
H10B	0.0178 (17)	0.6475 (12)	0.4902 (10)	0.041*	
C3	0.5132 (11)	0.2827 (4)	0.4374 (6)	0.0596 (18)	0.5790
H3A	0.6029	0.3382	0.4235	0.072*	0.5790
H3B	0.4418	0.2725	0.3799	0.072*	0.5790
C2	0.5875 (4)	0.1585 (3)	0.4646 (2)	0.0610 (8)	0.5790
H2A	0.6479	0.1279	0.4131	0.073*	0.5790
H2B	0.6672	0.1695	0.5186	0.073*	0.5790
C1	0.4625 (4)	0.0627 (2)	0.4882 (3)	0.0536 (10)	0.5790
H1A	0.3804	0.0537	0.4351	0.064*	0.5790
H1B	0.4051	0.0918	0.5413	0.064*	0.5790
C7	0.4186 (10)	0.3409 (8)	0.5058 (7)	0.0457 (15)	0.5790
N1	0.3431 (10)	0.3881 (13)	0.5566 (7)	0.0676 (18)	0.5790
C5	0.5045 (6)	0.1518 (3)	0.4298 (3)	0.0556 (10)	0.4210
H5A	0.3907	0.1486	0.4021	0.067*	0.4210
H5B	0.5761	0.1217	0.3831	0.067*	0.4210
C4	0.5202 (8)	0.0665 (3)	0.5125 (3)	0.0556 (14)	0.4210
H4A	0.4461	0.0946	0.5585	0.067*	0.4210
H4B	0.6332	0.0708	0.5413	0.067*	0.4210
C6	0.5484 (15)	0.2847 (5)	0.4517 (7)	0.062 (3)	0.4210
H6A	0.6656	0.2886	0.4733	0.075*	0.4210
H6B	0.5334	0.3321	0.3939	0.075*	0.4210
C8	0.4549 (14)	0.3431 (11)	0.5207 (9)	0.045 (2)	0.4210
N2	0.3861 (15)	0.3812 (19)	0.5782 (9)	0.091 (4)	0.4210

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0295 (4)	0.0223 (3)	0.0334 (4)	0.0010 (3)	0.0102 (3)	0.0010 (3)
O30	0.0274 (4)	0.0221 (3)	0.0332 (4)	0.0004 (3)	0.0006 (3)	−0.0001 (3)
O10	0.0324 (4)	0.0243 (3)	0.0252 (3)	−0.0006 (3)	0.0048 (3)	0.0000 (3)
N21	0.0411 (6)	0.0239 (4)	0.0529 (6)	0.0007 (4)	0.0241 (5)	−0.0016 (4)
N20	0.0346 (6)	0.0235 (4)	0.0540 (6)	−0.0014 (4)	0.0185 (5)	0.0003 (4)
N31	0.0346 (6)	0.0249 (4)	0.0529 (6)	−0.0034 (4)	−0.0117 (5)	0.0029 (4)
N30	0.0400 (6)	0.0260 (5)	0.0507 (6)	0.0005 (4)	−0.0129 (5)	0.0066 (4)
C20	0.0281 (5)	0.0230 (5)	0.0277 (5)	0.0018 (4)	0.0043 (4)	0.0028 (4)
C30	0.0286 (5)	0.0227 (4)	0.0234 (4)	0.0015 (4)	0.0053 (4)	−0.0008 (3)
N11	0.0546 (7)	0.0235 (4)	0.0273 (5)	0.0015 (4)	0.0030 (4)	0.0018 (3)
C10	0.0223 (5)	0.0237 (5)	0.0279 (5)	−0.0030 (4)	0.0020 (4)	0.0000 (4)
N10	0.0539 (6)	0.0239 (4)	0.0263 (5)	0.0011 (4)	0.0068 (4)	−0.0006 (3)
C3	0.060 (4)	0.079 (3)	0.0412 (18)	0.002 (2)	0.015 (2)	−0.0068 (17)
C2	0.0398 (17)	0.085 (2)	0.0605 (18)	−0.0002 (15)	0.0168 (14)	−0.0187 (16)
C1	0.034 (2)	0.078 (2)	0.048 (2)	0.0038 (13)	0.0046 (15)	−0.0190 (15)
C7	0.032 (3)	0.063 (2)	0.042 (3)	−0.013 (2)	0.001 (3)	−0.0126 (17)
N1	0.053 (2)	0.081 (3)	0.072 (4)	−0.0109 (18)	0.025 (2)	−0.025 (3)
C5	0.057 (3)	0.071 (2)	0.0415 (19)	0.005 (2)	0.0163 (18)	−0.0080 (18)
C4	0.052 (4)	0.078 (3)	0.036 (2)	0.008 (2)	0.000 (2)	−0.0087 (18)
C6	0.049 (4)	0.078 (4)	0.064 (6)	−0.007 (2)	0.029 (4)	−0.008 (3)
C8	0.026 (4)	0.068 (3)	0.040 (4)	−0.013 (3)	−0.003 (3)	−0.007 (2)
N2	0.126 (10)	0.084 (4)	0.071 (6)	−0.013 (8)	0.051 (6)	−0.020 (5)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2560 (12)	C3—C2	1.521 (5)
O30—C30	1.2635 (13)	C2—C1	1.515 (4)
O10—C10	1.2626 (12)	C1—C1i	1.522 (5)
N21—C20	1.3384 (13)	C7—N1	1.116 (4)
N20—C20	1.3371 (13)	C5—C4	1.508 (5)
N31—C30	1.3283 (13)	C5—C6	1.518 (6)
N30—C30	1.3315 (13)	C4—C4i	1.522 (6)
N11—C10	1.3353 (13)	C6—C8	1.446 (5)
C10—N10	1.3346 (13)	C8—N2	1.116 (6)
C3—C7	1.445 (4)		
O20—C20—N20	120.82 (9)	C7—C3—C2	115.9 (5)
O20—C20—N21	120.86 (9)	C1—C2—C3	114.2 (4)
N20—C20—N21	118.31 (9)	C2—C1—C1i	113.8 (4)
O30—C30—N31	121.06 (9)	N1—C7—C3	177.8 (11)
O30—C30—N30	120.71 (9)	C4—C5—C6	114.8 (5)
N31—C30—N30	118.22 (11)	C5—C4—C4i	113.4 (4)
O10—C10—N10	121.01 (9)	C8—C6—C5	115.7 (6)
O10—C10—N11	120.81 (9)	N2—C8—C6	174.8 (16)
N10—C10—N11	118.16 (9)		
C7—C3—C2—C1	58.1 (8)	C8—C6—C5—C4	−57.7 (12)
C3—C2—C1—C1i	177.9 (5)	C6—C5—C4—C4i	−178.4 (8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	58.1(8)
C3	C2	C1	C1i	177.9(5)
C8	C6	C5	C4	-57.7(12)
C6	C5	C4	C4i	-178.4(8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.875 (14)	2.142 (15)	3.0124 (12)	173.1 (13)
N21—H21B···O30iii	0.831 (15)	2.239 (15)	3.0293 (12)	159.0 (13)
N20—H20A···O30ii	0.871 (14)	2.139 (15)	3.0017 (12)	170.5 (13)
N20—H20B···O10iv	0.849 (15)	2.135 (15)	2.9550 (12)	162.2 (13)
N31—H31A···O20v	0.872 (14)	2.170 (15)	3.0144 (13)	162.9 (13)
N31—H31B···O10iv	0.855 (16)	2.124 (16)	2.9535 (13)	163.4 (13)
N30—H30A···O10vi	0.874 (15)	2.252 (15)	3.0923 (13)	161.2 (13)
N30—H30B···O20vii	0.824 (16)	2.273 (16)	3.0417 (14)	155.4 (14)
N11—H11A···O30viii	0.874 (14)	2.123 (14)	2.9869 (12)	169.7 (13)
N11—H11B···O30ix	0.837 (14)	2.197 (15)	3.0159 (12)	166.0 (12)
N10—H10A···O20v	0.875 (14)	2.071 (14)	2.9426 (12)	174.0 (13)
N10—H10B···O20x	0.840 (14)	2.189 (14)	2.9974 (12)	161.6 (12)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

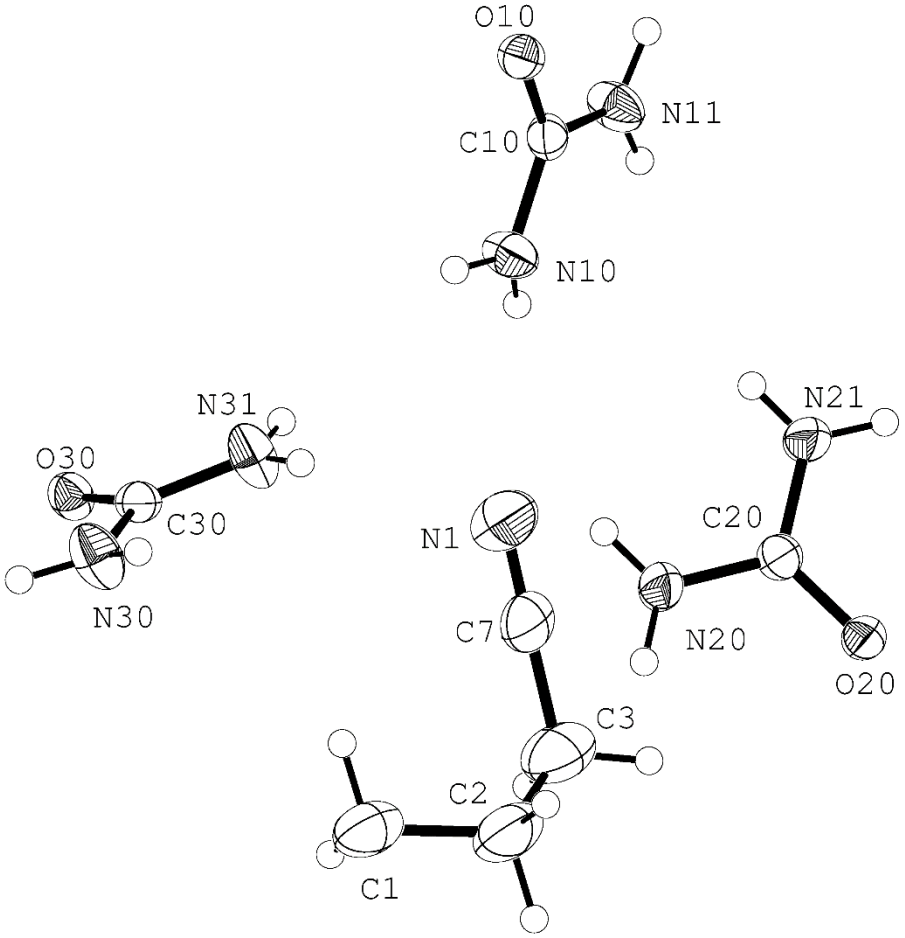
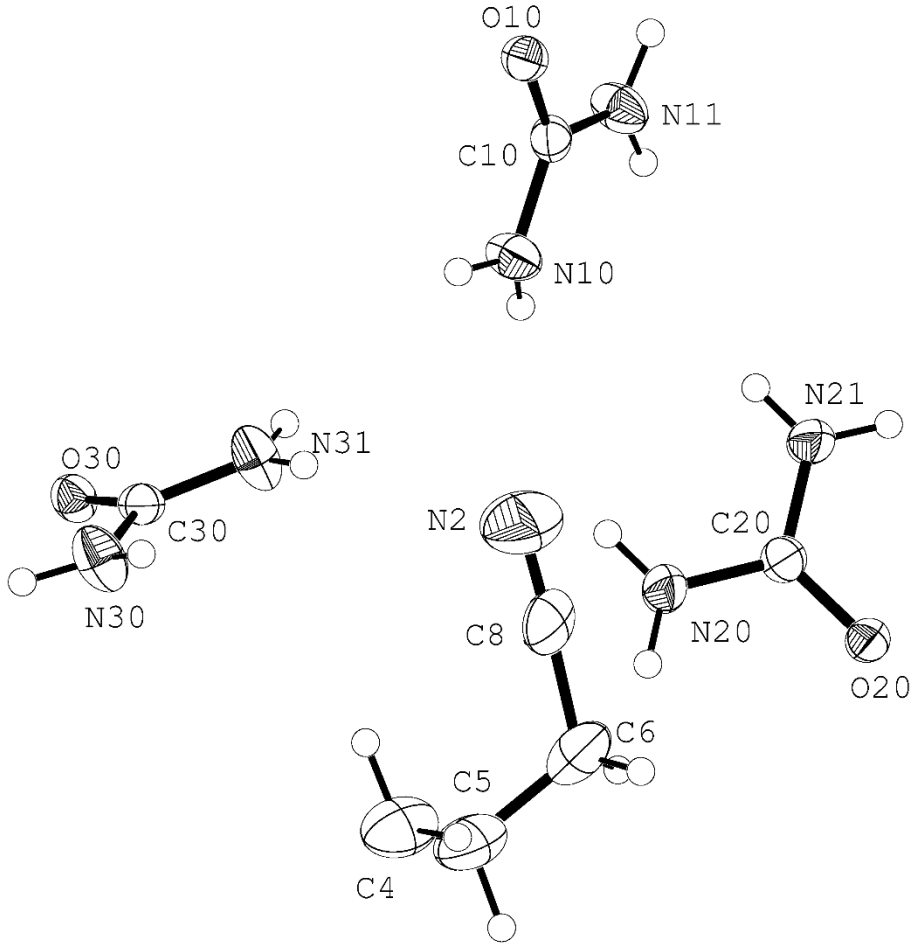


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 203 K (KP900).
2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Bruker AXS, Inc. (1998). SMART software Version 5.060. Bruker AXS, Inc., Madison, Wisconsin, USA.
4. Siemens P4 diffractometer equipped with a SMART 1000 CCD Detector.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. *Acta Crystallogr.*, *A***51**, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Structure report for 1,6-dicyanohexane/urea at 218 K[1]

Introduction

The data for this crystal was collected in 2000 by Kevin Pate on a Siemens P4 diffractometer equipped with a SMART 1000 CCD detector and was originally labeled "KP1000". (See laboratory notebook KLP A-39.) The original crystal was from Christopher J. Nichols (CJN A-78-05). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 56.81% and 43.19%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 79.8°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 500 µm x 400 µm x 200 µm. The crystal was cooled to 218 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 20 seconds and the frame width was 0.30º. [8] The crystal to detector distance was 49.87 mm.

The unit cell parameters were determined[9,4] from 3718 input reflections whose minimum and the maximum 2-theta values were 4.70 and 54.98, respectively. The errors are reported after corrections for the goodness of fit (1.51). The cell volume is 1279.07 (24) Å^3.

a = 8.1482 (8) Å	α = 90°
b = 10.9008 (11) Å	β = 94.4833 (16)°
c = 14.4234 (14) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.291 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 7655 reflections of which 183 were rejected. After merging Friedel opposites, there were 2825 unique reflections, of which 2395 had I > 2sigma(I). The R(int) was 0.0173, and the R(sigma) was 0.0181. The linear absorption coefficient, μ, for Mo-K_α radiation is 0.102 mm^{-1}. The absorption correction was made using SADABS.[8, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kp1000_20.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.853 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

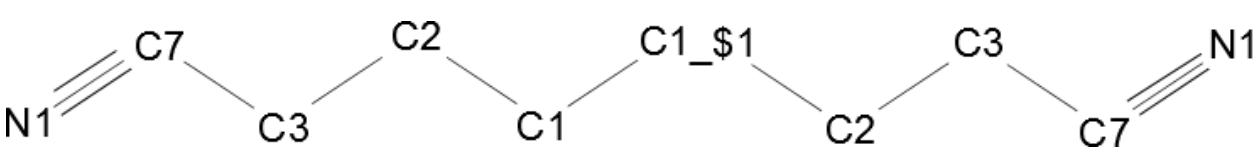


Figure 1: Atomic labeling scheme for part 1 (major part)

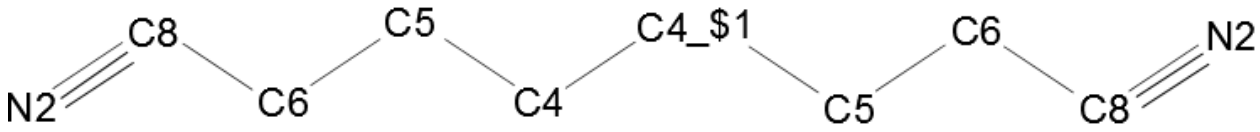


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.272 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.272 for all of the data. R1 was 0.0400 for all 2825 data and 0.0335 for data with $I>2\sigma(I)$; the wR2 value was 0.0819 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	500 x 400 x 200 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	3718
Lattice parameters	a = 8.1482 (8) Å b = 10.9008 (11) Å c = 14.4234 (14) Å α = 90° β = 94.4833 (16)° γ = 90° V = 1279.07 (24) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.291
F_{000}	532
μ (MoK$_\alpha$)	0.102 mm^{-1}
Temperature	218 K

B. Intensity measurements

Diffractometer	Siemens P4, SMART 1000 CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K$_\alpha$ (λ = 0.71073 Å)
Crystal to detector distance	49.87 mm
Time per frame	20 s
Temperature	218 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.35°
θ_{max}	27.49°
h k l range	h = -9 to 10 k = -14 to 14 l = -18 to 17
No. of reflections measured	Total: 7472 Unique 2825 (R_{int} = 0.0173)

	$I > 2\sigma(I) = 2395$
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations ($I > 2.00\sigma(I)$)	2395
No. variables	235
No. Restraints	27
Reflection:parameter ratio	12.02
For $I > 2.00\sigma(I)$	10.19
No. Reflections used in refinement	2825
Final R indices [$I > 2\sigma(I)$] R1	0.0335
Final R indices [all data]; R1, wR2	0.0400; 0.0819
Goodness of Fit (s)	1.272
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.112 e/Å^3
Minimum peak in final diff. map	-0.174 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99862 (9)	0.41994 (6)	0.65347 (5)	0.03016 (18)	
O30	−0.02609 (9)	0.08812 (6)	0.65449 (5)	0.03000 (18)	
O10	−0.01147 (9)	0.75098 (6)	0.68140 (5)	0.02948 (18)	
N21	0.80866 (14)	0.52061 (9)	0.73008 (8)	0.0413 (3)	
H21A	0.8606 (19)	0.5896 (13)	0.7211 (10)	0.050*	
H21B	0.7224 (19)	0.5199 (13)	0.7577 (10)	0.050*	
N20	0.78723 (13)	0.31299 (8)	0.70512 (8)	0.0394 (2)	
H20A	0.8308 (18)	0.2456 (13)	0.6858 (10)	0.047*	
H20B	0.7002 (18)	0.3117 (12)	0.7344 (10)	0.047*	
N31	0.19800 (14)	0.19468 (9)	0.70954 (8)	0.0417 (3)	
H31A	0.1554 (18)	0.2611 (13)	0.6838 (10)	0.050*	
H31B	0.2937 (19)	0.1960 (13)	0.7366 (10)	0.050*	
N30	0.18051 (15)	−0.01093 (9)	0.73636 (8)	0.0432 (3)	
H30A	0.1209 (19)	−0.0771 (13)	0.7342 (10)	0.052*	

H30B	0.264 (2)	−0.0063 (14)	0.7713 (10)	0.052*	
C20	0.86878 (13)	0.41785 (8)	0.69490 (7)	0.0281 (2)	
C30	0.11331 (13)	0.09087 (8)	0.69927 (7)	0.0267 (2)	
N11	−0.03127 (14)	0.85463 (8)	0.54537 (7)	0.0377 (2)	
H11A	−0.0447 (17)	0.9223 (12)	0.5761 (10)	0.045*	
H11B	−0.0177 (17)	0.8570 (12)	0.4889 (10)	0.045*	
C10	−0.00550 (12)	0.75139 (8)	0.59423 (7)	0.0264 (2)	
N10	0.02973 (14)	0.64954 (8)	0.54845 (7)	0.0372 (2)	
H10A	0.0282 (17)	0.5805 (12)	0.5791 (10)	0.045*	
H10B	0.0176 (17)	0.6472 (12)	0.4905 (10)	0.045*	
C3	0.5133 (12)	0.2822 (4)	0.4372 (6)	0.066 (2)	0.5681
H3A	0.6028	0.3372	0.4224	0.079*	0.5681
H3B	0.4416	0.2711	0.38	0.079*	0.5681
C2	0.5877 (4)	0.1584 (3)	0.4651 (3)	0.0666 (9)	0.5681
H2A	0.6494	0.1277	0.4143	0.080*	0.5681
H2B	0.666	0.1698	0.5196	0.080*	0.5681
C1	0.4623 (5)	0.0625 (2)	0.4880 (3)	0.0582 (11)	0.5681
H1A	0.3813	0.0534	0.4345	0.070*	0.5681
H1B	0.4039	0.0915	0.5407	0.070*	0.5681
C7	0.4196 (11)	0.3421 (8)	0.5048 (6)	0.0504 (17)	0.5681
N1	0.3439 (9)	0.3877 (12)	0.5560 (6)	0.0724 (18)	0.5681
C5	0.5062 (6)	0.1514 (3)	0.4300 (3)	0.0610 (10)	0.4319
H5A	0.3935	0.1472	0.401	0.073*	0.4319
H5B	0.58	0.1219	0.3844	0.073*	0.4319
C4	0.5198 (9)	0.0665 (3)	0.5124 (3)	0.0606 (15)	0.4319
H4A	0.4445	0.0947	0.5578	0.073*	0.4319
H4B	0.632	0.071	0.5421	0.073*	0.4319
C6	0.5471 (16)	0.2846 (5)	0.4521 (7)	0.068 (3)	0.4319
H6A	0.6644	0.29	0.4727	0.081*	0.4319
H6B	0.5294	0.3323	0.3947	0.081*	0.4319
C8	0.4540 (15)	0.3408 (11)	0.5222 (8)	0.047 (2)	0.4319
N2	0.3883 (14)	0.3809 (17)	0.5798 (8)	0.098 (4)	0.4319

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0319 (4)	0.0240 (3)	0.0359 (4)	0.0008 (3)	0.0112 (3)	0.0010 (3)
O30	0.0301 (4)	0.0235 (3)	0.0361 (4)	0.0005 (3)	0.0005 (3)	−0.0001 (3)
O10	0.0357 (4)	0.0264 (3)	0.0268 (4)	−0.0007 (3)	0.0051 (3)	0.0000 (3)
N21	0.0449 (6)	0.0256 (4)	0.0570 (6)	0.0009 (4)	0.0263 (5)	−0.0019 (4)
N20	0.0375 (6)	0.0252 (4)	0.0579 (6)	−0.0014 (4)	0.0199 (5)	0.0008 (4)
N31	0.0383 (6)	0.0267 (4)	0.0574 (6)	−0.0039 (4)	−0.0125 (5)	0.0030 (4)
N30	0.0443 (7)	0.0282 (5)	0.0545 (6)	0.0009 (4)	−0.0136 (5)	0.0073 (4)
C20	0.0305 (6)	0.0250 (5)	0.0292 (5)	0.0018 (4)	0.0052 (4)	0.0029 (4)
C30	0.0313 (6)	0.0241 (4)	0.0251 (5)	0.0018 (4)	0.0056 (4)	−0.0011 (3)
N11	0.0589 (7)	0.0250 (4)	0.0292 (5)	0.0018 (4)	0.0035 (4)	0.0019 (3)
C10	0.0243 (5)	0.0250 (4)	0.0299 (5)	−0.0028 (4)	0.0020 (4)	0.0000 (4)
N10	0.0586 (7)	0.0253 (4)	0.0283 (5)	0.0014 (4)	0.0076 (4)	−0.0008 (3)
C3	0.071 (5)	0.084 (4)	0.0450 (19)	0.004 (2)	0.016 (2)	−0.0080 (18)
C2	0.0443 (19)	0.093 (2)	0.064 (2)	−0.0014 (17)	0.0177 (15)	−0.0209 (18)
C1	0.039 (3)	0.084 (2)	0.052 (2)	0.0044 (14)	0.0057 (16)	−0.0199 (16)
C7	0.039 (4)	0.071 (2)	0.041 (3)	−0.012 (2)	0.000 (3)	−0.009 (2)
N1	0.059 (2)	0.088 (3)	0.073 (4)	−0.0123 (19)	0.029 (3)	−0.027 (3)
C5	0.068 (3)	0.074 (3)	0.043 (2)	0.005 (2)	0.0193 (19)	−0.0087 (18)
C4	0.059 (4)	0.083 (3)	0.039 (2)	0.009 (2)	0.001 (2)	−0.0094 (18)
C6	0.055 (4)	0.085 (5)	0.067 (5)	−0.008 (3)	0.032 (4)	−0.008 (3)
C8	0.034 (4)	0.069 (3)	0.037 (4)	−0.009 (2)	−0.003 (3)	−0.007 (2)
N2	0.137 (10)	0.091 (4)	0.073 (6)	−0.015 (7)	0.049 (6)	−0.021 (4)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2553 (12)	C3—C2	1.521 (6)
O30—C30	1.2623 (13)	C2—C1	1.516 (4)
O10—C10	1.2621 (12)	C1—C1i	1.524 (5)
N21—C20	1.3383 (13)	C7—N1	1.115 (4)
N20—C20	1.3361 (13)	C5—C4	1.503 (5)
N31—C30	1.3277 (13)	C5—C6	1.518 (6)
N30—C30	1.3311 (13)	C4—C4i	1.523 (6)
N11—C10	1.3357 (13)	C6—C8	1.447 (5)
C10—N10	1.3344 (13)	C8—N2	1.112 (5)
C3—C7	1.442 (4)		
O20—C20—N20	120.86 (9)	C7—C3—C2	116.3 (5)
O20—C20—N21	120.82 (9)	C1—C2—C3	114.1 (4)
N20—C20—N21	118.32 (10)	C2—C1—C1i	113.6 (4)
O30—C30—N31	121.09 (9)	N1—C7—C3	178.4 (9)
O30—C30—N30	120.75 (10)	C4—C5—C6	114.9 (5)
N31—C30—N30	118.15 (11)	C5—C4—C4i	113.5 (5)
O10—C10—N10	121.10 (9)	C8—C6—C5	115.7 (6)
O10—C10—N11	120.78 (9)	N2—C8—C6	176.0 (12)
N10—C10—N11	118.10 (9)		
C7—C3—C2—C1	59.3 (9)	C8—C6—C5—C4	−55.5 (12)
C3—C2—C1—C1i	177.6 (5)	C6—C5—C4—C4i	−179.2 (8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	59.3(9)
C3	C2	C1	C1i	177.6(5)
C8	C6	C5	C4	-55.5(12)
C6	C5	C4	C4i	-179.2(8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.877 (14)	2.145 (15)	3.0179 (12)	172.9 (13)
N21—H21B···O30iii	0.835 (15)	2.243 (15)	3.0355 (12)	158.5 (13)
N20—H20A···O30ii	0.871 (14)	2.143 (15)	3.0049 (12)	170.1 (13)
N20—H20B···O10iv	0.853 (15)	2.138 (15)	2.9597 (12)	161.5 (13)
N31—H31A···O20v	0.874 (14)	2.176 (15)	3.0195 (13)	162.3 (13)
N31—H31B···O10iv	0.845 (16)	2.139 (16)	2.9575 (14)	163.0 (13)
N30—H30A···O10vi	0.869 (15)	2.264 (15)	3.1012 (13)	161.7 (13)
N30—H30B···O20vii	0.817 (16)	2.287 (16)	3.0462 (14)	154.7 (14)
N11—H11A···O30viii	0.871 (14)	2.132 (14)	2.9911 (12)	168.7 (13)
N11—H11B···O30ix	0.831 (14)	2.209 (15)	3.0214 (12)	165.9 (12)
N10—H10A···O20v	0.873 (14)	2.077 (14)	2.9467 (12)	174.0 (13)
N10—H10B···O20x	0.834 (14)	2.196 (15)	3.0005 (12)	162.0 (12)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

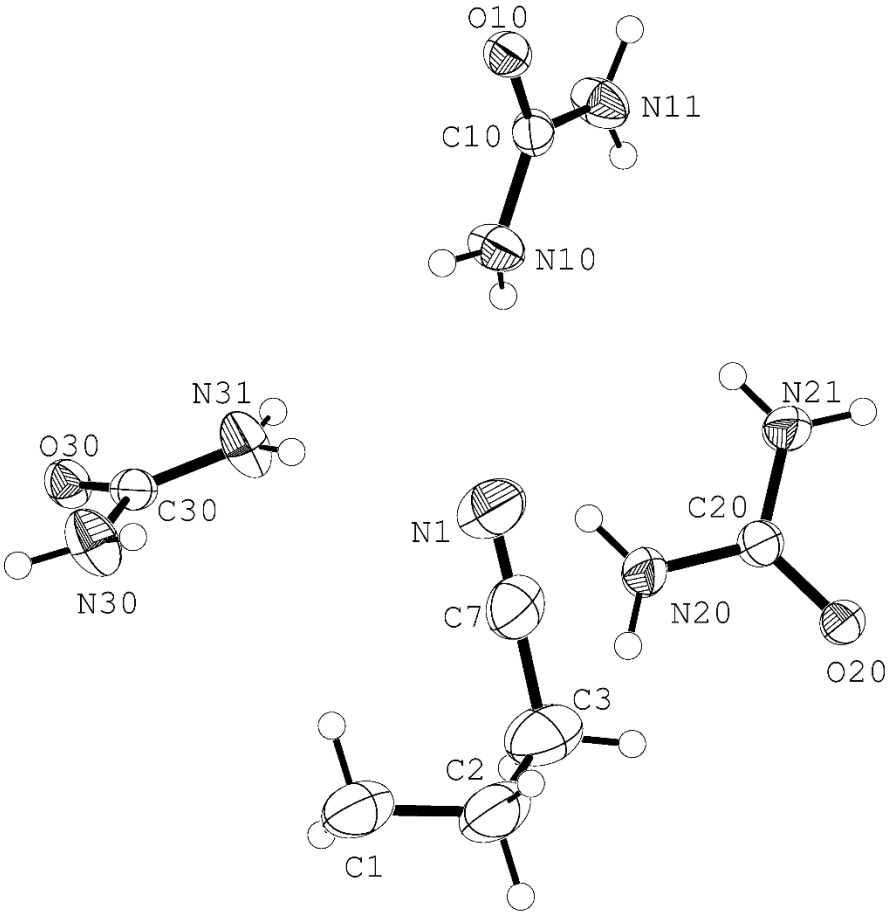
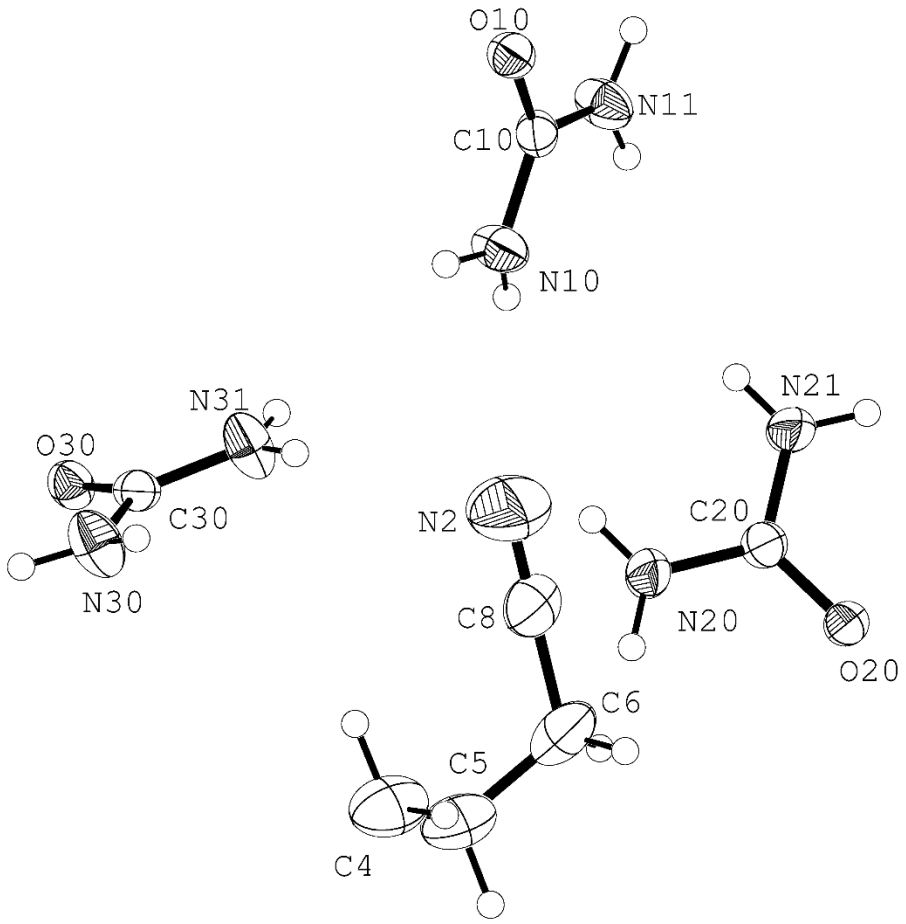


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 218 K (KP1000).
2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Bruker AXS, Inc. (1998). SMART software Version 5.060. Bruker AXS, Inc., Madison, Wisconsin, USA.
4. Siemens P4 diffractometer equipped with a SMART 1000 CCD Detector.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. *Acta Crystallogr. A***51**, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **42**, 339–341 (2009).

Structure report for 1,6-dicyanohexane/urea at 233 K[1]

Introduction

The data for this crystal was collected by Kevin Pate on the P4 CCD diffractometer in 2000 and was originally labeled “KP1100”. (See laboratory notebook KLP A-40.) The original crystal was from Christopher J. Nichols (CJN A-78-05). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 57.18% and 42.82%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 79.85°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 500 µm x 400 µm x 200 µm. The crystal was cooled to 233 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 20 seconds and the frame width was 0.30º. [8] The crystal to detector distance was 49.87 mm.

The unit cell parameters were determined[9,4] from 3593 input reflections whose minimum and the maximum 2-theta values were 4.68 and 55.02, respectively. The errors are reported after corrections for the goodness of fit (1.53). The cell volume is 1286.16 (25) Å^3.

a = 8.1569 (9) Å	α = 90°
b = 10.9083 (11) Å	β = 94.4450 (16)°
c = 14.4377 (15) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.288 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 7701 reflections of which 186 were rejected. After merging Friedel opposites, there were 2845 unique reflections, of which 2372 had I > 2sigma(I). The R(int) was 0.0189, and the R(sigma) was 0.0183. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.102 mm^{-1}. The absorption correction was made using SADABS.[8, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kp1100_20.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.847 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

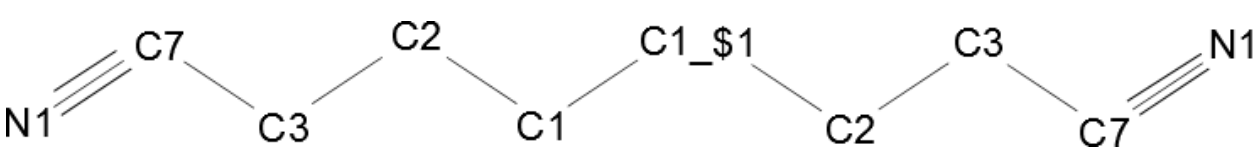


Figure 1: Atomic labeling scheme for part 1 (major part)

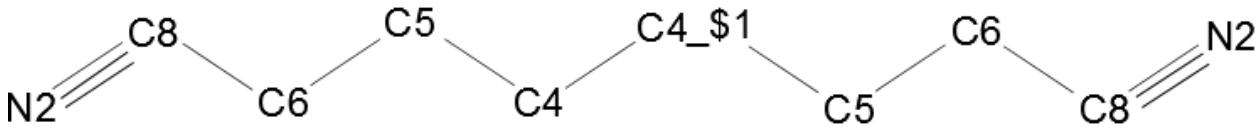


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.249 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.249 for all of the data. R1 was 0.0419 for all 2845 data and 0.0339 for data with $I>2\sigma(I)$; the wR2 value was 0.0821 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	500 x 400 x 200 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	3593
Lattice parameters	a = 8.1569 (9) Å b = 10.9083 (11) Å c = 14.4377 (15) Å α = 90° β = 94.4450 (16)° γ = 90° V = 1286.16 (25) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.288
F_{000}	532
μ (MoK$_\alpha$)	0.102 mm^{-1}
Temperature	233 K

B. Intensity measurements

Diffractometer	Siemens P4, SMART 1000 CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K$_\alpha$ (λ = 0.71073 Å)
Crystal to detector distance	49.87 mm
Time per frame	20 s
Temperature	233 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.34°
θ_{max}	27.51°
h k l range	h = -9 to 10 k = -14 to 14 l = -18 to 17
No. of reflections measured	Total: 7515 Unique 2845 (R_{int} = 0.0189)

	$I > 2\sigma(I)$ = 2372
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations ($I > 2.00\sigma(I)$)	2372
No. variables	235
No. Restraints	27
Reflection:parameter ratio	12.11
For $I > 2.00\sigma(I)$	10.09
No. Reflections used in refinement	2845
Final R indices [$I > 2\sigma(I)$] R1	0.0339
Final R indices [all data]; R1, wR2	0.0419; 0.0821
Goodness of Fit (s)	1.249
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.116 e/Å^3
Minimum peak in final diff. map	-0.180 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99837 (9)	0.41991 (6)	0.65351 (5)	0.03259 (19)	
O30	−0.02553 (9)	0.08808 (6)	0.65460 (5)	0.03234 (18)	
O10	−0.01142 (9)	0.75084 (6)	0.68129 (5)	0.03156 (18)	
N21	0.80837 (14)	0.52037 (9)	0.72995 (8)	0.0442 (3)	
H21A	0.8597 (19)	0.5887 (13)	0.7203 (10)	0.053*	
H21B	0.7232 (19)	0.5194 (13)	0.7578 (10)	0.053*	
N20	0.78747 (13)	0.31298 (9)	0.70526 (8)	0.0422 (3)	
H20A	0.8316 (18)	0.2456 (13)	0.6858 (10)	0.051*	
H20B	0.7014 (19)	0.3117 (13)	0.7345 (10)	0.051*	
N31	0.19817 (15)	0.19456 (9)	0.70953 (8)	0.0448 (3)	
H31A	0.1564 (18)	0.2607 (13)	0.6834 (10)	0.054*	
H31B	0.293 (2)	0.1962 (14)	0.7373 (10)	0.054*	

N30	0.18070 (15)	−0.01071 (9)	0.73653 (8)	0.0465 (3)	
H30A	0.1223 (19)	−0.0766 (13)	0.7341 (10)	0.056*	
H30B	0.265 (2)	−0.0048 (14)	0.7720 (10)	0.056*	
C20	0.86872 (13)	0.41775 (8)	0.69494 (7)	0.0299 (2)	
C30	0.11354 (13)	0.09095 (8)	0.69933 (7)	0.0285 (2)	
N11	−0.03085 (14)	0.85456 (9)	0.54547 (7)	0.0404 (2)	
H11A	−0.0435 (18)	0.9220 (12)	0.5765 (10)	0.048*	
H11B	−0.0192 (17)	0.8568 (12)	0.4894 (10)	0.048*	
C10	−0.00564 (13)	0.75133 (8)	0.59424 (7)	0.0284 (2)	
N10	0.02916 (14)	0.64960 (9)	0.54842 (7)	0.0402 (3)	
H10A	0.0287 (18)	0.5814 (12)	0.5788 (10)	0.048*	
H10B	0.0166 (17)	0.6475 (12)	0.4905 (10)	0.048*	
C3	0.5132 (12)	0.2822 (4)	0.4374 (6)	0.070 (2)	0.5718
H3A	0.6026	0.3371	0.4227	0.084*	0.5718
H3B	0.4411	0.2717	0.3805	0.084*	0.5718
C2	0.5871 (4)	0.1581 (3)	0.4647 (3)	0.0727 (10)	0.5718
H2A	0.6474	0.1274	0.4133	0.087*	0.5718
H2B	0.6665	0.1691	0.5186	0.087*	0.5718
C1	0.4625 (5)	0.0627 (2)	0.4882 (3)	0.0629 (12)	0.5718
H1A	0.3807	0.0538	0.4352	0.076*	0.5718
H1B	0.4051	0.0918	0.5412	0.076*	0.5718
C7	0.4204 (12)	0.3414 (9)	0.5056 (7)	0.0556 (19)	0.5718
N1	0.3445 (10)	0.3876 (12)	0.5561 (6)	0.0786 (19)	0.5718
C5	0.5055 (7)	0.1517 (3)	0.4302 (3)	0.0645 (11)	0.4282
H5A	0.3924	0.148	0.4019	0.077*	0.4282
H5B	0.5782	0.1223	0.3841	0.077*	0.4282
C4	0.5203 (9)	0.0664 (3)	0.5128 (3)	0.0655 (17)	0.4282
H4A	0.446	0.0943	0.5586	0.079*	0.4282
H4B	0.6328	0.0704	0.5418	0.079*	0.4282
C6	0.5477 (16)	0.2844 (5)	0.4529 (7)	0.074 (3)	0.4282
H6A	0.6647	0.289	0.474	0.088*	0.4282
H6B	0.5315	0.3325	0.3956	0.088*	0.4282
C8	0.4546 (16)	0.3410 (12)	0.5224 (9)	0.052 (2)	0.4282
N2	0.3913 (15)	0.3803 (17)	0.5810 (8)	0.104 (4)	0.4282

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0345 (4)	0.0258 (3)	0.0389 (4)	0.0010 (3)	0.0126 (3)	0.0011 (3)
O30	0.0321 (4)	0.0253 (3)	0.0392 (4)	0.0005 (3)	0.0005 (3)	0.0001 (3)
O10	0.0382 (5)	0.0279 (4)	0.0291 (4)	−0.0005 (3)	0.0057 (3)	−0.0001 (3)
N21	0.0476 (7)	0.0274 (5)	0.0612 (7)	0.0009 (4)	0.0283 (5)	−0.0019 (4)
N20	0.0403 (6)	0.0270 (4)	0.0622 (7)	−0.0014 (4)	0.0217 (5)	0.0009 (4)
N31	0.0413 (6)	0.0288 (5)	0.0617 (7)	−0.0045 (4)	−0.0131 (5)	0.0031 (4)
N30	0.0474 (7)	0.0301 (5)	0.0591 (7)	0.0008 (5)	−0.0146 (5)	0.0078 (4)
C20	0.0320 (6)	0.0262 (5)	0.0321 (5)	0.0020 (4)	0.0057 (4)	0.0034 (4)
C30	0.0333 (6)	0.0258 (5)	0.0272 (5)	0.0018 (4)	0.0062 (4)	−0.0010 (4)
N11	0.0625 (7)	0.0270 (4)	0.0317 (5)	0.0017 (4)	0.0036 (5)	0.0021 (4)
C10	0.0265 (5)	0.0266 (5)	0.0321 (5)	−0.0036 (4)	0.0024 (4)	−0.0002 (4)
N10	0.0634 (7)	0.0274 (4)	0.0305 (5)	0.0012 (4)	0.0084 (5)	−0.0011 (4)
C3	0.078 (5)	0.087 (4)	0.049 (2)	0.003 (2)	0.019 (2)	−0.0104 (19)
C2	0.047 (2)	0.102 (3)	0.071 (2)	0.0006 (18)	0.0193 (16)	−0.020 (2)
C1	0.043 (3)	0.091 (3)	0.056 (2)	0.0057 (15)	0.0058 (17)	−0.0208 (17)
C7	0.045 (4)	0.075 (3)	0.046 (4)	−0.014 (2)	0.002 (3)	−0.011 (2)
N1	0.066 (3)	0.095 (3)	0.079 (4)	−0.013 (2)	0.031 (3)	−0.030 (4)
C5	0.068 (3)	0.082 (3)	0.045 (2)	0.006 (2)	0.020 (2)	−0.0083 (19)
C4	0.063 (4)	0.091 (4)	0.041 (3)	0.011 (3)	0.001 (2)	−0.0088 (19)
C6	0.060 (4)	0.094 (5)	0.072 (6)	−0.007 (3)	0.034 (4)	−0.005 (3)
C8	0.038 (5)	0.077 (3)	0.042 (4)	−0.010 (3)	0.001 (3)	−0.008 (3)
N2	0.144 (11)	0.097 (4)	0.077 (6)	−0.015 (8)	0.050 (6)	−0.019 (5)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2549 (12)	C3—C2	1.522 (6)
O30—C30	1.2615 (13)	C2—C1	1.511 (4)
O10—C10	1.2613 (12)	C1—C1i	1.526 (5)
N21—C20	1.3377 (13)	C7—N1	1.113 (4)
N20—C20	1.3353 (13)	C5—C4	1.510 (5)
N31—C30	1.3266 (14)	C5—C6	1.518 (6)
N30—C30	1.3314 (14)	C4—C4i	1.524 (6)
N11—C10	1.3356 (13)	C6—C8	1.443 (5)
C10—N10	1.3338 (13)	C8—N2	1.111 (6)
C3—C7	1.440 (4)		
O20—C20—N20	120.87 (9)	C7—C3—C2	116.2 (5)
O20—C20—N21	120.85 (9)	C1—C2—C3	114.2 (4)
N20—C20—N21	118.28 (10)	C2—C1—C1i	113.7 (4)
O30—C30—N31	121.17 (9)	N1—C7—C3	177.7 (10)
O30—C30—N30	120.76 (10)	C4—C5—C6	114.5 (5)
N31—C30—N30	118.07 (11)	C5—C4—C4i	113.1 (5)
O10—C10—N10	121.10 (9)	C8—C6—C5	115.8 (6)
O10—C10—N11	120.86 (9)	N2—C8—C6	174.5 (14)
N10—C10—N11	118.03 (10)		
C7—C3—C2—C1	58.8 (9)	C8—C6—C5—C4	−56.6 (13)
C3—C2—C1—C1i	177.8 (5)	C6—C5—C4—C4i	−179.1 (8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	58.8(9)
C3	C2	C1	C1i	177.8(5)
C8	C6	C5	C4	-56.6(13)
C6	C5	C4	C4i	-179.1(8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.872 (15)	2.154 (15)	3.0223 (13)	173.8 (13)
N21—H21B···O30iii	0.830 (15)	2.253 (15)	3.0402 (12)	158.6 (14)
N20—H20A···O30ii	0.874 (14)	2.144 (15)	3.0088 (12)	170.3 (13)
N20—H20B···O10iv	0.847 (15)	2.148 (15)	2.9639 (12)	161.7 (13)
N31—H31A···O20v	0.871 (15)	2.186 (15)	3.0247 (13)	161.5 (13)
N31—H31B···O10iv	0.841 (16)	2.144 (16)	2.9607 (14)	163.8 (14)
N30—H30A···O10vi	0.861 (15)	2.277 (15)	3.1086 (14)	162.2 (13)
N30—H30B···O20vii	0.825 (16)	2.291 (16)	3.0499 (14)	153.3 (14)
N11—H11A···O30viii	0.871 (14)	2.134 (14)	2.9937 (12)	169.2 (13)
N11—H11B···O30ix	0.823 (15)	2.221 (15)	3.0253 (13)	165.7 (13)
N10—H10A···O20v	0.864 (14)	2.090 (14)	2.9500 (12)	173.3 (13)
N10—H10B···O20x	0.835 (15)	2.200 (15)	3.0039 (13)	161.7 (12)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

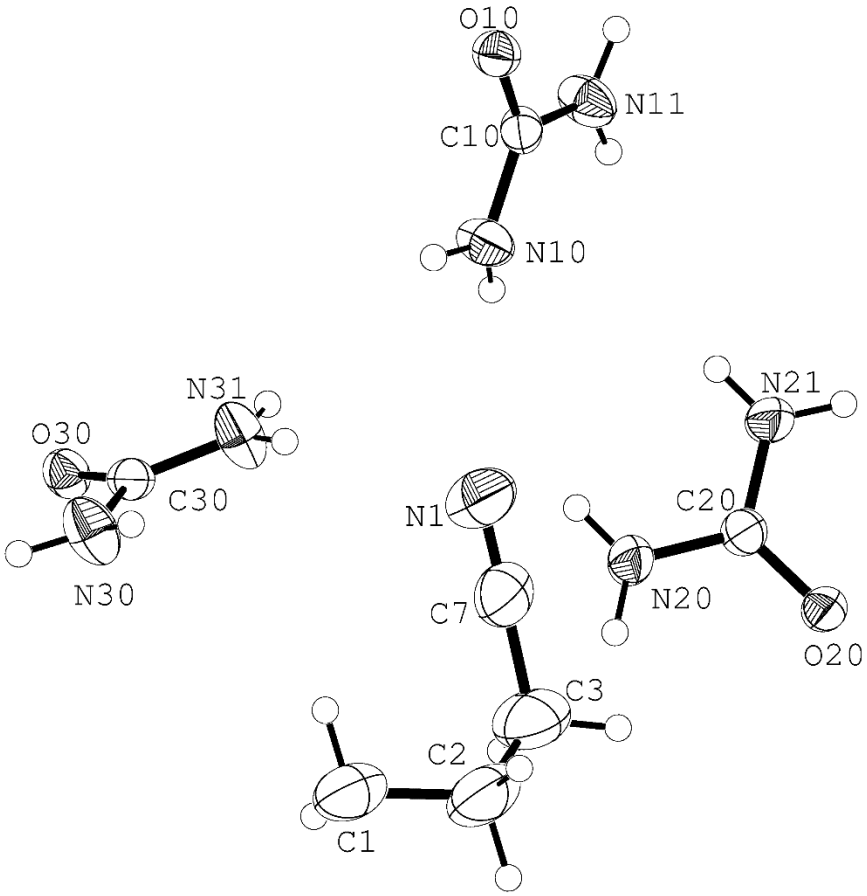
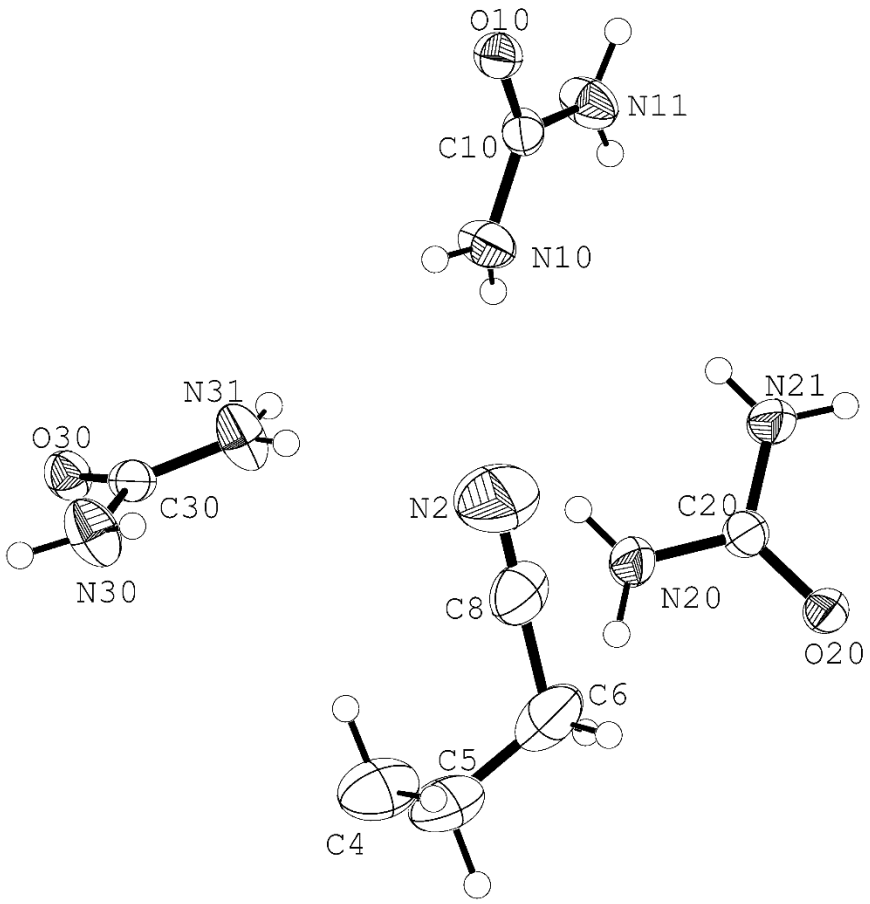


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 233 K (KP1100).
2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular

level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).

3. Bruker AXS, Inc. (1998). SMART software Version 5.060. Bruker AXS, Inc., Madison, Wisconsin, USA.
4. Siemens P4 diffractometer equipped with a SMART 1000 CCD Detector.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. *Acta Crystallogr. A***51**, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **42**, 339–341 (2009).

Structure report for 1,6-dicyanohexane/urea at 293 K[1]

Introduction

The data for this crystal was collected in 2010 by Roman Gajda on the Bruker Kappa diffractometer equipped with an APEX II detector and was originally labeled "mh1013b". (See laboratory notebook RBG A-60-1.) The original crystal was from Christopher J. Nichols (CJN A-78-05). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 56.9% and 43.1%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 81.78°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 600 µm x 430 µm x 300 µm. The crystal was cooled to 293 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 10 seconds and the frame width was 0.10º.[3] The crystal to detector distance was 65.00 mm.

The unit cell parameters were determined[3,4] from 6021 input reflections whose minimum and the maximum 2-theta values were 4.68 and 57.00, respectively. The errors are reported after corrections for the goodness of fit (4.51). The cell volume is 1291.24(14) Å^3.

a = 8.1958(5) Å	α = 90°
b = 10.9173(7) Å	β = 94.244(4)°
c = 14.4708(9) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.277 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 18795 reflections of which 513 were rejected. After merging Friedel opposites, there were 3323 unique reflections, of which 2447 had I > 2sigma(I). The R(int) was 0.0609, and the R(sigma) was 0.0339. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.101 mm^{-1}. The absorption correction was made using SADABS.[3, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-dicyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in mh1013b_06a.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.088 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

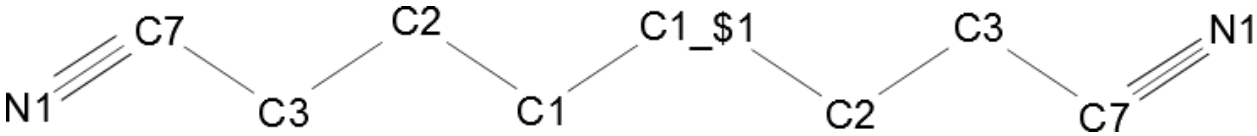


Figure 1: Atomic labeling scheme for part 1 (major part)

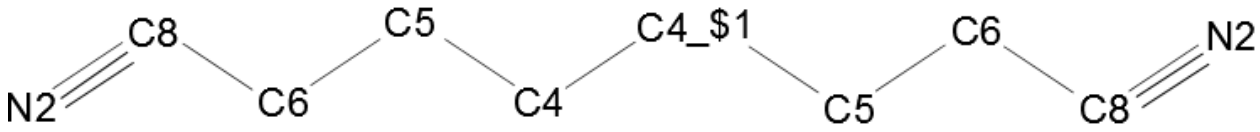


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.234 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.237 for all of the data. R1 was 0.0672 for all 3323 data and 0.0487 for data with $I>2\sigma(I)$; the wR2 value was 0.0967 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5

DELU C2 C3
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms. The DELU command was used to make the U_{ij} of C2 and C3 similar.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	600 x 430 x 300 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	6021
Lattice parameters	a = 8.1958 (5) Å
	b = 10.9173(7) Å
	c = 14.4708(9) Å
	α = 90°
	β = 94.244(4)°
	γ = 90°
	V = 1291.24(14) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.277
F_{000}	532
μ (MoK$_\alpha$)	0.101 mm^{-1}
Temperature	293 K

B. Intensity measurements

Diffractometer	Bruker Kappa, APEX II CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K$_\alpha$ (λ = 0.71073 Å)
Crystal to detector distance	65 mm
Time per frame	10 s
Temperature	293 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.34°
θ_{max}	28.50°
h k l range	h = -11 to 11
	k = -13 to 14
	l = -19 to 19
No. of reflections measured	Total: 18282
	Unique 3323 (R_{int} = 0.0609)

	$I > 2\sigma(I) = 2447$
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations ($I > 2.00\sigma(I)$)	2447
No. variables	236
No. Restraints	28
Reflection:parameter ratio	14.08
For $I > 2.00\sigma(I)$	10.37
No. Reflections used in refinement	3323
Final R indices [$I > 2\sigma(I)$] R1	0.0487
Final R indices [all data]; R1, wR2	0.0672; 0.0967
Goodness of Fit (s)	1.234
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.158 e/Å^3
Minimum peak in final diff. map	-0.147 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-dicyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99762 (12)	0.41968 (9)	0.65389 (7)	0.0408 (3)	
O30	−0.02322 (12)	0.08807 (9)	0.65529 (7)	0.0410 (3)	
O10	−0.01118 (13)	0.75038 (9)	0.68082 (7)	0.0396 (3)	
N21	0.8076 (2)	0.51946 (14)	0.72976 (12)	0.0544 (4)	
H21A	0.856 (3)	0.589 (2)	0.7211 (14)	0.065*	
H21B	0.720 (3)	0.5192 (19)	0.7584 (14)	0.065*	
N20	0.78838 (19)	0.31260 (14)	0.70573 (12)	0.0524 (4)	
H20A	0.832 (2)	0.2431 (19)	0.6860 (14)	0.063*	
H20B	0.704 (3)	0.3092 (18)	0.7366 (14)	0.063*	
N31	0.1987 (2)	0.19444 (14)	0.70924 (12)	0.0559 (4)	
H31A	0.157 (3)	0.2611 (19)	0.6841 (14)	0.067*	
H31B	0.295 (3)	0.1960 (19)	0.7371 (14)	0.067*	

N30	0.1818 (2)	−0.00969 (15)	0.73693 (13)	0.0586 (4)	
H30A	0.122 (3)	−0.075 (2)	0.7362 (14)	0.070*	
H30B	0.266 (3)	−0.0051 (19)	0.7744 (15)	0.070*	
C20	0.86877 (18)	0.41727 (13)	0.69497 (10)	0.0369 (3)	
C30	0.11480 (18)	0.09138 (13)	0.69945 (10)	0.0360 (3)	
N11	−0.0295 (2)	0.85423 (14)	0.54587 (11)	0.0499 (4)	
H11A	−0.036 (2)	0.9219 (18)	0.5773 (14)	0.060*	
H11B	−0.019 (2)	0.8572 (17)	0.4876 (14)	0.060*	
C10	−0.00554 (17)	0.75104 (13)	0.59431 (10)	0.0352 (3)	
N10	0.0278 (2)	0.64956 (13)	0.54804 (11)	0.0499 (4)	
H10A	0.024 (2)	0.5843 (18)	0.5769 (14)	0.060*	
H10B	0.015 (2)	0.6489 (17)	0.4874 (14)	0.060*	
C3	0.5151 (17)	0.2811 (5)	0.4396 (8)	0.093 (3)	0.5694
H3A	0.6004	0.3325	0.4172	0.111*	0.5694
H3B	0.4305	0.2717	0.3896	0.111*	0.5694
C2	0.5859 (6)	0.1570 (4)	0.4647 (5)	0.0941 (19)	0.5694
H2A	0.6427	0.1266	0.4129	0.113*	0.5694
H2B	0.6663	0.1665	0.5169	0.113*	0.5694
C1	0.4627 (7)	0.0629 (3)	0.4893 (6)	0.086 (2)	0.5694
H1A	0.3798	0.0552	0.4382	0.103*	0.5694
H1B	0.4091	0.0912	0.543	0.103*	0.5694
C7	0.447 (2)	0.3412 (10)	0.5166 (10)	0.090 (5)	0.5694
N1	0.3928 (13)	0.3779 (14)	0.5801 (7)	0.130 (4)	0.5694
C5	0.5060 (10)	0.1512 (5)	0.4311 (4)	0.084 (2)	0.4306
H5A	0.395	0.1464	0.4029	0.101*	0.4306
H5B	0.5787	0.123	0.3856	0.101*	0.4306
C4	0.5211 (14)	0.0662 (3)	0.5127 (5)	0.089 (3)	0.4306
H4A	0.4491	0.0941	0.5586	0.106*	0.4306
H4B	0.6324	0.0694	0.5406	0.106*	0.4306
C6	0.545 (2)	0.2834 (6)	0.4531 (11)	0.099 (6)	0.4306
H6A	0.6531	0.2886	0.4846	0.119*	0.4306
H6B	0.5457	0.3292	0.3957	0.119*	0.4306
C8	0.428 (3)	0.3388 (13)	0.5107 (13)	0.073 (5)	0.4306
N2	0.3411 (12)	0.3905 (16)	0.5526 (9)	0.090 (3)	0.4306

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0437 (6)	0.0310 (6)	0.0496 (6)	0.0009 (4)	0.0163 (5)	0.0012 (4)
O30	0.0408 (6)	0.0310 (6)	0.0507 (6)	0.0005 (4)	−0.0009 (5)	−0.0002 (5)
O10	0.0493 (6)	0.0342 (6)	0.0357 (5)	−0.0010 (4)	0.0065 (4)	−0.0004 (4)
N21	0.0585 (10)	0.0331 (8)	0.0758 (11)	0.0028 (6)	0.0332 (8)	−0.0023 (7)
N20	0.0511 (9)	0.0328 (8)	0.0763 (11)	−0.0022 (6)	0.0252 (7)	0.0012 (7)
N31	0.0541 (9)	0.0346 (8)	0.0758 (11)	−0.0061 (7)	−0.0157 (8)	0.0037 (7)
N30	0.0598 (10)	0.0383 (9)	0.0743 (11)	0.0024 (7)	−0.0174 (8)	0.0112 (7)
C20	0.0403 (8)	0.0308 (8)	0.0402 (8)	0.0029 (6)	0.0068 (6)	0.0033 (6)
C30	0.0424 (8)	0.0299 (7)	0.0362 (7)	0.0031 (6)	0.0066 (6)	−0.0009 (5)
N11	0.0762 (10)	0.0329 (8)	0.0406 (8)	0.0015 (7)	0.0034 (7)	0.0033 (6)
C10	0.0360 (7)	0.0306 (7)	0.0392 (7)	−0.0041 (6)	0.0030 (6)	0.0000 (6)
N10	0.0790 (11)	0.0317 (8)	0.0399 (8)	0.0011 (7)	0.0099 (7)	−0.0018 (6)
C3	0.103 (7)	0.111 (8)	0.066 (4)	0.004 (4)	0.025 (4)	−0.010 (4)
C2	0.063 (3)	0.132 (6)	0.090 (4)	0.001 (3)	0.025 (3)	−0.022 (4)
C1	0.059 (4)	0.121 (6)	0.078 (4)	0.011 (3)	0.011 (3)	−0.024 (4)
C7	0.090 (8)	0.112 (9)	0.070 (7)	−0.024 (6)	0.026 (5)	0.000 (6)
N1	0.169 (10)	0.129 (6)	0.100 (6)	0.000 (8)	0.061 (7)	−0.017 (5)
C5	0.084 (5)	0.108 (6)	0.062 (4)	0.011 (4)	0.021 (3)	−0.011 (3)
C4	0.088 (7)	0.118 (8)	0.061 (5)	0.023 (5)	0.011 (4)	−0.004 (4)
C6	0.088 (7)	0.123 (12)	0.094 (9)	−0.014 (6)	0.051 (7)	−0.011 (6)
C8	0.061 (6)	0.080 (9)	0.080 (9)	−0.010 (5)	0.020 (5)	−0.025 (6)
N2	0.067 (4)	0.110 (7)	0.098 (7)	−0.013 (4)	0.030 (4)	−0.033 (6)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2498 (17)	C3—C2	1.508 (7)
O30—C30	1.2579 (18)	C2—C1	1.502 (6)
O10—C10	1.2562 (17)	C1—C1i	1.526 (6)
N21—C20	1.3368 (19)	C7—N1	1.123 (6)
N20—C20	1.334 (2)	C5—C4	1.501 (7)
N31—C30	1.321 (2)	C5—C6	1.507 (8)
N30—C30	1.330 (2)	C4—C4i	1.524 (7)
N11—C10	1.3337 (19)	C6—C8	1.445 (7)
C10—N10	1.3333 (19)	C8—N2	1.123 (7)
C3—C7	1.442 (7)		
O20—C20—N20	121.03 (14)	C7—C3—C2	112.8 (7)
O20—C20—N21	121.02 (14)	C1—C2—C3	114.7 (6)
N20—C20—N21	117.95 (14)	C2—C1—C1i	113.4 (6)
O30—C30—N31	121.36 (14)	N1—C7—C3	173.8 (14)
O30—C30—N30	120.81 (15)	C4—C5—C6	115.0 (7)
N31—C30—N30	117.83 (15)	C5—C4—C4i	113.1 (7)
O10—C10—N10	121.32 (14)	C8—C6—C5	112.6 (8)
O10—C10—N11	120.92 (14)	N2—C8—C6	174.5 (19)
N10—C10—N11	117.75 (14)		
C7—C3—C2—C1	65.9 (14)	C8—C6—C5—C4	−66.2 (18)
C3—C2—C1—C1i	177.7 (8)	C6—C5—C4—C4i	179.3 (12)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. **Torsion Angles**

Atom	Atom	Atom	Atom	Angle/°
C7	C3	C2	C1	65.9(14)
C3	C2	C1	C1i	177.7(8)
C8	C6	C5	C4	-66.2(18)
C6	C5	C4	C4i	179.3(12)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. **Hydrogen-bond Geometries (in Å)**

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O10ii	0.87 (2)	2.18 (2)	3.0363 (19)	171.6 (19)
N21—H21B···O30iii	0.86 (2)	2.24 (2)	3.0550 (18)	158.9 (19)
N20—H20A···O30ii	0.90 (2)	2.13 (2)	3.0154 (19)	169.1 (18)
N20—H20B···O10iv	0.85 (2)	2.15 (2)	2.9782 (18)	164.6 (19)
N31—H31A···O20v	0.87 (2)	2.19 (2)	3.035 (2)	162.0 (19)
N31—H31B···O10iv	0.86 (2)	2.14 (2)	2.9766 (19)	163 (2)
N30—H30A···O10vi	0.87 (2)	2.31 (2)	3.136 (2)	159.5 (19)
N30—H30B···O20vii	0.85 (2)	2.28 (2)	3.062 (2)	153 (2)
N11—H11A···O30viii	0.87 (2)	2.13 (2)	3.0024 (19)	174.0 (18)
N11—H11B···O30ix	0.85 (2)	2.20 (2)	3.0403 (19)	166.0 (18)
N10—H10A···O20v	0.83 (2)	2.13 (2)	2.9601 (18)	176.3 (19)
N10—H10B···O20x	0.88 (2)	2.17 (2)	3.0105 (18)	159.9 (17)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2 showing part 1 with 40% probability surfaces.

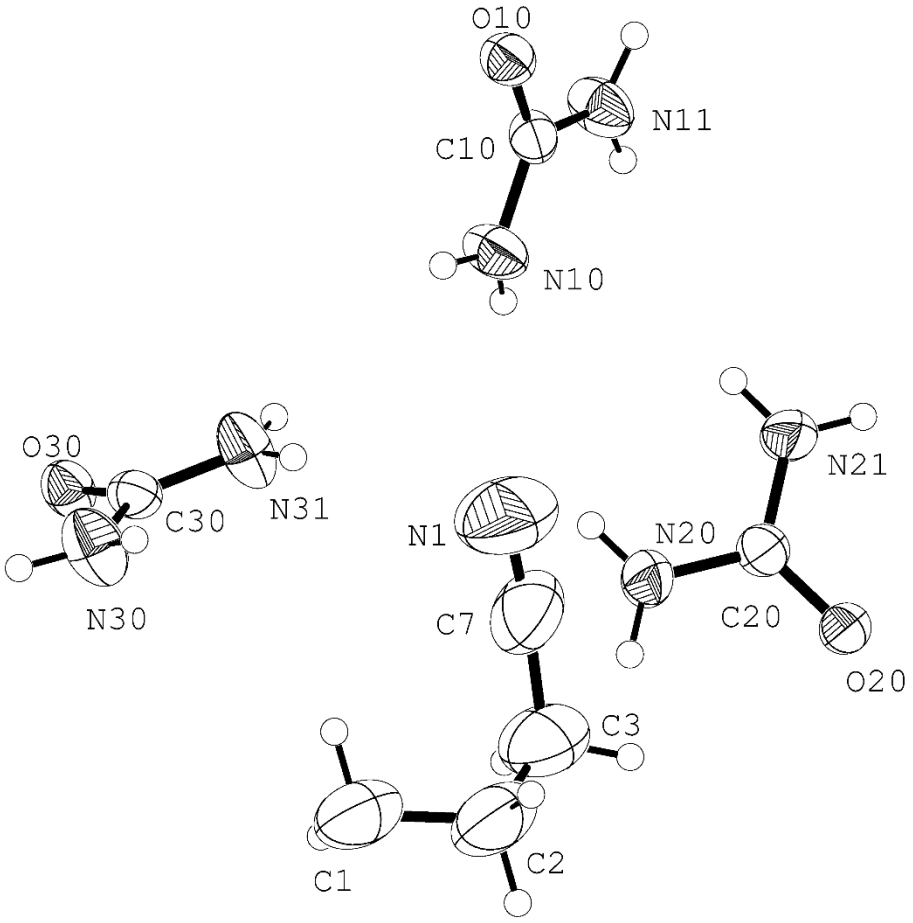
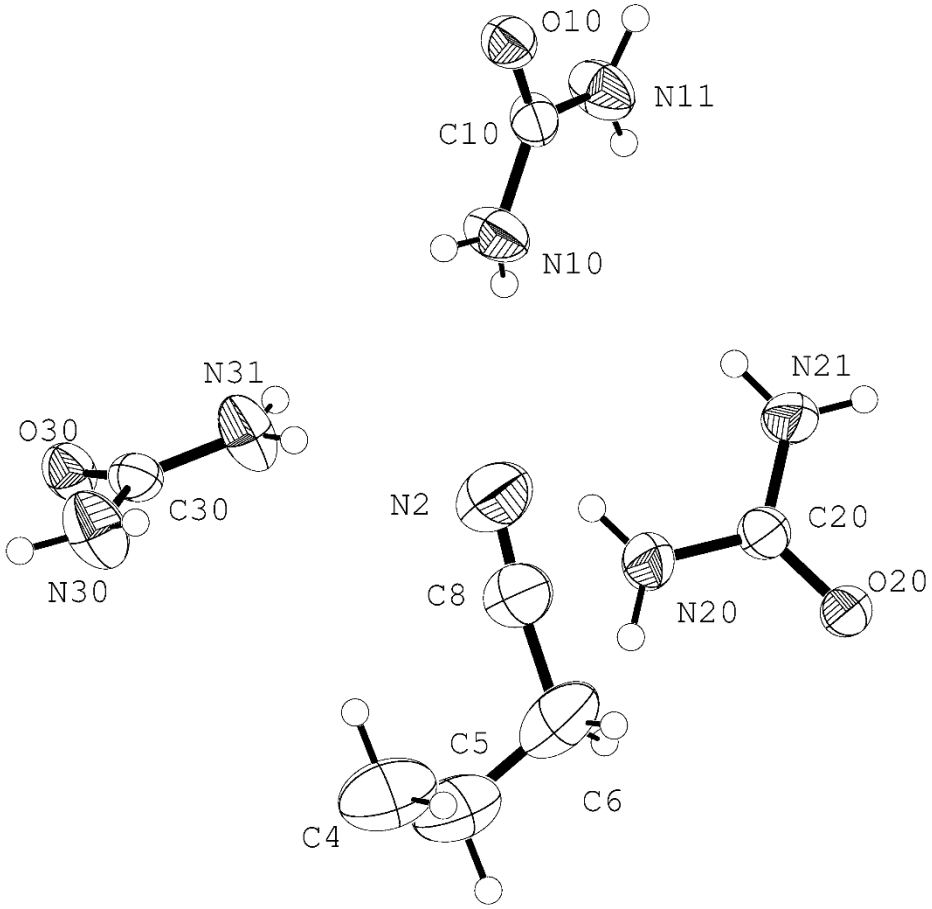


Figure 4: ORTEP rendering by OLEX2 showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at 293 K (mh1013b).

2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999); (DOI: 10.1021/ja9919534).
3. Data collected using the Bruker APEX2 software package.
4. Bruker SAINT V8.18C
5. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).
6. Sheldrick, G. M., A short history of SHELX. *Acta Crystallographica Section A* **64**, 112-122 (2008); (DOI: 10.1107/s0108767307043930).
7. Standard deviation of an observation of unit weight:

$$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$$

where n is the number of reflections and p is the total number of parameters refined.

$$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$$

where P is

$$P = [2Fc^2 + \max(Fo^2,0)]/3.$$

Structure report for 1,6-diisocyanohexane/urea at 140 K[1]

Introduction

This data set was collected in 2012 by Keith Alquist using a Bruker P4 diffractometer equipped with an APEX II detector.[11] (See laboratory notebook KEA-C-289.) The crystal was a fragment from a crystal grown by Mark Hollingsworth (MDH-K-150-19). This is the low temperature form and, like 1,6-dibromohexane/urea at 109 K, exhibits no disorder in the guest.[2]

Molecular replacement was used to determine the atomic sites using similar structures. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 300 µm x 200 µm x 60 µm. The crystal was cooled to 140 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 5 seconds and the frame width was 0.30º.[3] The crystal to detector distance was 80.00 mm.

The unit cell parameters were determined[11,4] from 1348 input reflections whose minimum and the maximum 2-theta values were 4.84 and 44.32, respectively. The errors are reported after corrections for the goodness of fit (3.63). The cell volume is 1230.0 (3) Å^3.

a = 8.5036 (12) Å	α = 90°
b = 10.7843 (15) Å	β = 93.884 (8)°
c = 13.443 (2) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.341 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 4157 reflections of which 173 were rejected. After merging Friedel opposites, there were 1510 unique reflections, of which 1130 had I > 2sigma(I). The R(int) was 0.0351, and the R(sigma) was 0.0514. The linear absorption coefficient, μ, for Mo-K_α radiation is 0.106 mm^{-1}. The absorption correction was made using SADABS.[3, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6]

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kea_C_289_iso.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.880 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

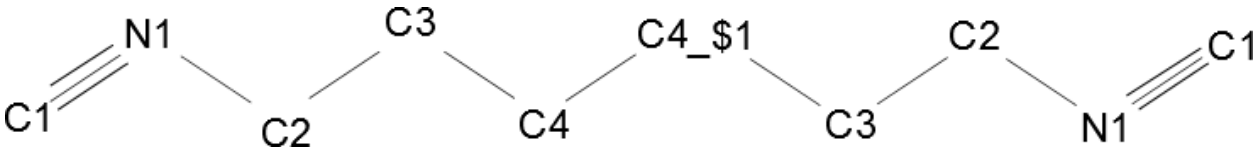


Figure 1: Atomic labeling scheme for the low temperature form of 1,6-diisocyanohexane/urea.

EQIV $1 1-x, 1-y, 1-z

SADI C2 C3 C3 C4 C4 C4_$1
SADI C2 C4 C3 C4_$1
SADI C3 N1 C6 N2
SADI C3 C7 C6 C8

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely.

The goodness of fit[7] was 1.201 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.259 for all of the data. R1 was 0.0939 for all 1510 data and 0.0675 for data with $I>2\sigma(I)$; the wR2 value was 0.1713 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
DEFS 0.01
SADI C2 C3 C3 C4 C4 C4_$1
SADI C2 C4 C3 C4_$1

FLAT C2 C3 N1 C1

ISOR 0.001 N10 N11 N20 N21 N30 N31
```

The FLAT commands were used to insure that the overlapping isocyano carbons were connected to the correct atoms. The ISOR restraints were used to set the U_{ij} parameters to be more isotropic. This was done because urea nitrogen atoms were approaching a prolate thermal parameter shape (a "discus" shape rather than the more realistic "bean" shape.)

The following reflections were omitted due to their ΔF^2/esd being greater than 10.

```
OMIT 0 2 0
OMIT 0 4 0
OMIT 7 5 4
```

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	300 x 200 x 60 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	1348
Lattice parameters	a = 8.5036 (12) Å
	b = 10.7843 (15) Å
	c = 13.443 (2) Å
	α = 90°
	β = 93.884 (8) °
	γ = 90°
	V = 1230.0 (3) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.341

F_{000}	532
μ (MoK_α)	0.106 mm^{-1}
Temperature	140 K

B. Intensity measurements

Diffractometer	Siemens P4 CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K_α (λ = 0.71073 Å)
Crystal to detector distance	80.00 mm
Time per frame	5 s
Temperature	140 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.42°
θ_{max}	22.16°
h k l range	h = -8 to 9
	k = -8 to 11
	l = -14 to 7
No. of reflections measured	Total: 3984
	Unique 1510 (R_{int} = 0.0354)
	I > 2σ(I) = 1130
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	1130
No. variables	154
No. Restraints	41
Reflection:parameter ratio	9.81
For I > 2.00σ(I)	7.33
No. Reflections used in refinement	1510
Final R indices [I > 2σ(I)] R1	0.0675
Final R indices [all data]; R1, wR2	0.0939; 0.1713
Goodness of Fit (s)	1.201
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.322 e/Å^3
Minimum peak in final diff. map	-0.344 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-diisocyanohexane/urea.

	x	y	z	Uiso*/Ueq
O10	−0.0122 (3)	0.7528 (2)	0.6861 (2)	0.0201 (8)
C10	−0.0113 (4)	0.7522 (4)	0.5929 (3)	0.0186 (11)
N10	−0.0510 (4)	0.8527 (3)	0.5398 (3)	0.0237 (10)
H10A	−0.0784	0.921	0.57	0.028*
H10B	−0.0498	0.851	0.4744	0.028*
N11	0.0278 (4)	0.6504 (3)	0.5444 (3)	0.0231 (10)
H11A	0.0535	0.5823	0.5777	0.028*
H11B	0.028	0.6511	0.4789	0.028*
O20	1.0145 (3)	0.4175 (2)	0.6663 (2)	0.0214 (8)
N20	0.8113 (4)	0.3146 (3)	0.7250 (2)	0.0222 (9)
H20A	0.8453	0.2441	0.7014	0.027*
H20B	0.7246	0.3161	0.7572	0.027*
C20	0.8905 (5)	0.4184 (4)	0.7122 (3)	0.0180 (11)
N21	0.8342 (4)	0.5235 (3)	0.7466 (2)	0.0236 (10)
H21A	0.8838	0.5938	0.7375	0.028*
H21B	0.7473	0.523	0.7786	0.028*
O30	−0.0319 (3)	0.0845 (2)	0.6690 (2)	0.0210 (8)
C30	0.1002 (5)	0.0833 (4)	0.7165 (3)	0.0179 (11)
N30	0.1581 (4)	−0.0200 (3)	0.7589 (2)	0.0210 (9)
H30A	0.1035	−0.0893	0.7539	0.025*
H30B	0.2511	−0.0191	0.7919	0.025*
N31	0.1853 (4)	0.1862 (3)	0.7270 (3)	0.0251 (10)
H31A	0.1491	0.2561	0.7005	0.030*
H31B	0.2779	0.1845	0.7604	0.030*
C1	0.3367 (7)	0.8870 (5)	0.5557 (5)	0.0573 (17)
N1	0.4298 (5)	0.8421 (3)	0.5105 (3)	0.0339 (11)
C2	0.5488 (5)	0.7877 (4)	0.4567 (4)	0.0321 (12)
H2A	0.642	0.843	0.4599	0.039*
H2B	0.5102	0.7797	0.3859	0.039*
C3	0.5976 (5)	0.6616 (3)	0.4964 (3)	0.0299 (12)
H3A	0.6907	0.6337	0.4621	0.036*
H3B	0.6301	0.6695	0.5682	0.036*
C4	0.4712 (5)	0.5634 (2)	0.4838 (3)	0.0295 (12)

H4A	0.3818	0.5871	0.5233	0.035*
H4B	0.432	0.5599	0.4128	0.035*

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O10	0.0254 (17)	0.0123 (17)	0.0231 (19)	−0.0020 (12)	0.0047 (13)	−0.0002 (14)
C10	0.010 (2)	0.011 (2)	0.036 (3)	−0.0011 (18)	0.006 (2)	0.001 (2)
N10	0.0283 (16)	0.0168 (16)	0.0260 (16)	0.0036 (13)	0.0016 (13)	−0.0011 (14)
N11	0.0272 (16)	0.0156 (16)	0.0267 (16)	0.0030 (13)	0.0024 (13)	−0.0010 (14)
O20	0.0180 (16)	0.0127 (18)	0.0339 (19)	−0.0028 (13)	0.0064 (14)	−0.0012 (13)
N20	0.0227 (15)	0.0139 (16)	0.0310 (17)	0.0003 (13)	0.0086 (13)	−0.0020 (13)
C20	0.019 (2)	0.007 (2)	0.028 (3)	0.000 (2)	0.002 (2)	0.001 (2)
N21	0.0238 (16)	0.0163 (16)	0.0313 (17)	−0.0016 (13)	0.0072 (13)	0.0004 (14)
O30	0.0165 (17)	0.0140 (17)	0.0323 (19)	0.0001 (13)	−0.0006 (14)	0.0012 (13)
C30	0.025 (3)	0.006 (2)	0.024 (3)	0.001 (2)	0.009 (2)	−0.0016 (19)
N30	0.0229 (15)	0.0141 (16)	0.0256 (16)	−0.0026 (13)	−0.0015 (13)	0.0029 (13)
N31	0.0236 (15)	0.0181 (16)	0.0330 (17)	−0.0005 (13)	−0.0022 (13)	0.0029 (14)
C1	0.049 (4)	0.040 (4)	0.086 (5)	−0.006 (3)	0.021 (4)	−0.009 (3)
N1	0.032 (2)	0.023 (2)	0.048 (3)	−0.004 (2)	0.012 (2)	0.003 (2)
C2	0.029 (3)	0.025 (3)	0.043 (3)	−0.002 (2)	0.010 (2)	0.000 (2)
C3	0.029 (3)	0.025 (3)	0.036 (3)	0.001 (2)	−0.001 (2)	0.000 (2)
C4	0.025 (3)	0.027 (3)	0.037 (3)	0.003 (2)	0.003 (2)	0.001 (2)

Table 3. Geometric parameters (Å, °)

O10—C10	1.254 (5)	C30—N31	1.327 (5)
C10—N10	1.329 (5)	C30—N30	1.331 (5)
C10—N11	1.331 (5)	C1—N1	1.138 (6)
O20—C20	1.257 (5)	N1—C2	1.410 (6)
N20—C20	1.324 (5)	C2—C3	1.509 (5)
C20—N21	1.326 (5)	C3—C4	1.510 (5)

O30—C30	1.254 (5)	C4—C4i	1.506 (6)
O10—C10—N10	121.0 (4)	O30—C30—N30	121.3 (4)
O10—C10—N11	120.8 (4)	N31—C30—N30	118.1 (4)
N10—C10—N11	118.2 (4)	C1—N1—C2	178.3 (5)
O20—C20—N20	120.6 (4)	N1—C2—C3	112.5 (4)
O20—C20—N21	120.8 (4)	C4—C3—C2	114.6 (3)
N20—C20—N21	118.6 (4)	C4i—C4—C3	112.9 (4)
O30—C30—N31	120.6 (4)		
N1—C2—C3—C4	66.1 (5)	C3—C4—C4i—C3i	180.000 (1)
C2—C3—C4—C4i	175.0 (5)		

Symmetry code: (i) −x+1, −y+1,−z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
N1	C2	C3	C4	66.1(5)
C2	C3	C4	C4i	175.0(5)

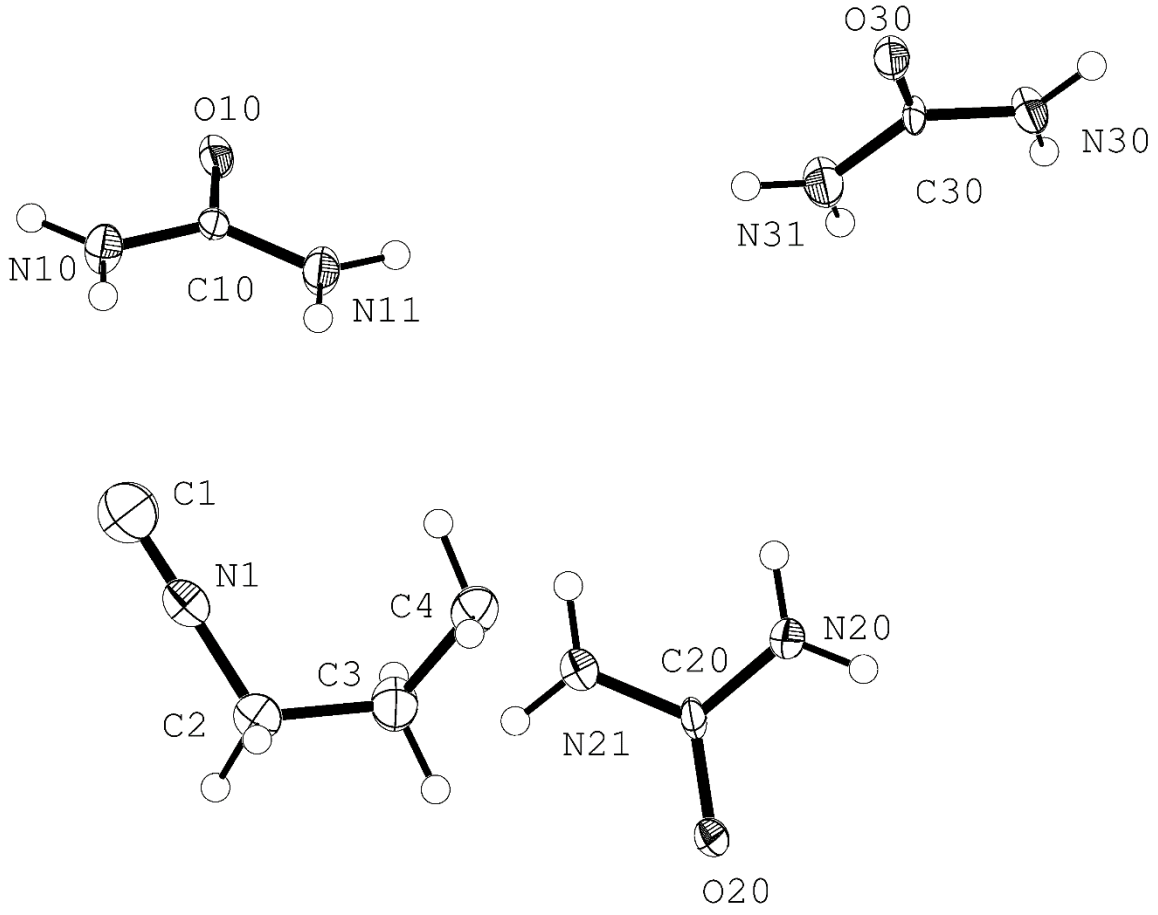
Symmetry code: (i) −x+1, −y+1,−z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···A	*D—H*	H···A	*D···A*	*D—H···A*
N10—H10A···O30ii	0.88	2.23	3.042 (4)	154
N10—H10B···O30iii	0.88	2.21	3.017 (5)	153
N11—H11A···O20iv	0.88	2.18	3.005 (4)	157
N11—H11B···O20i	0.88	2.1	2.924 (4)	156
N20—H20A···O30v	0.88	2.07	2.939 (4)	167
N20—H20B···O10vi	0.88	2.12	2.958 (4)	159
N21—H21A···O10v	0.88	2.07	2.936 (4)	169
N21—H21B···O30vii	0.88	2.11	2.954 (4)	160
N30—H30A···O10viii	0.88	2.14	2.978 (4)	159
N30—H30B···O20ix	0.88	2.15	2.972 (4)	156
N31—H31A···O20iv	0.88	2.12	2.973 (4)	164
N31—H31B···O10vi	0.88	2.2	3.028 (4)	157

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-diisocyanohexane/urea at 140 K (KEA-C-289).
2. Siemens P4 diffractometer equipped with a Bruker APEX II CCD detector
3. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
4. Data collected using the Bruker APEX2 software package.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. *Acta Crystallogr. A***51**, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$$

where n is the number of reflections and p is the total number of parameters refined.

$$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$$

where P is

$$P = [2Fc^2 + \max(Fo^2,0)]/3.$$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **42**, 339–341 (2009).

Structure report for 1,6-diisocyanohexane/urea at 150 K[1]

Introduction

This data set was collected in 2012 by Keith Alquist using a Siemens P4 diffractometer equipped with an APEX II detector.[11] (See laboratory notebook KEA-C-271.) The crystal was a fragment from a crystal grown by Mark Hollingsworth (MDH-K-150-19). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the end groups to be disordered between major and minor sites. The model shown here allows the isocyano end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 68.9% and 31.1%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 78.8°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 240 µm x 200 µm x 60 µm. The crystal was cooled to 150 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 20 seconds and the frame width was 0.20º.[3] The crystal to detector distance was 80.00 mm.

The unit cell parameters were determined[11,4] from 1937 input reflections whose minimum and the maximum 2-theta values were 5.70 and 31.34, respectively. The errors are reported after corrections for the goodness of fit (5.05). The cell volume is 1260.6 (2) Å^3.

a = 8.1122 (8) Å	α = 90°
b = 10.8595 (12) Å	β = 95.317 (5)°
c = 14.3714 (16) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.308 g/cm^3. Based on the systematic absences of

$$h00: \ h+l \neq 2n$$
$$0k0: \ k \neq 2n$$
$$h00: \ h \neq 2n$$
$$00l: \ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n \ (\#14).$$

Data Reduction:

The data set contained 10994 reflections of which 357 were rejected. After merging Friedel opposites, there were 4790 unique reflections, of which 2884 had I > 2sigma(I). The R(int) was 0.0491, and the R(sigma) was 0.0582. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.104 mm^{-1}. The absorption correction was made using SADABS.[3, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-diisocyanohexane/urea refined the dinitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kea_271_iso.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.889 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

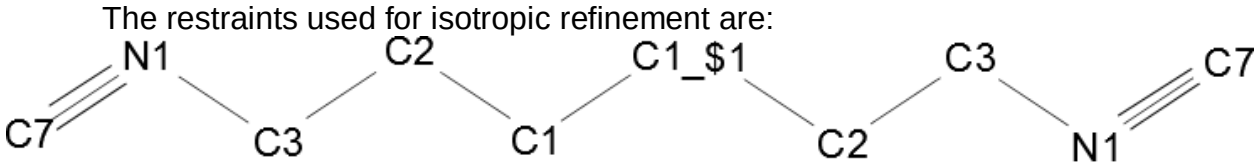


Figure 1: Atomic labeling scheme for part 1 (major part)

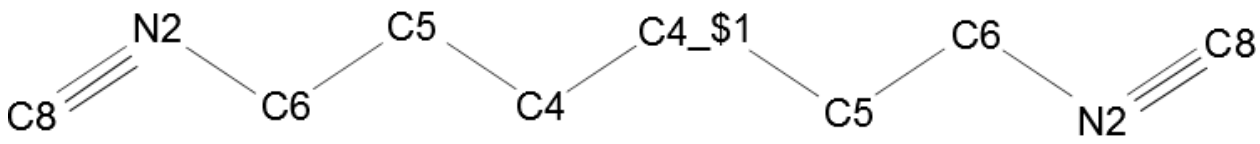


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, -y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 N1 C6 N2
SADI C3 C7 C6 C8
SADI N1 C2 N2 C5
FLAT C2 C3 N1 C7
FLAT C5 C6 N2 C8
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was refined to 0.0026 (7).

The goodness of fit[7] was 1.118 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.119 for all of the data. R1 was 0.0932 for all 5279 data and 0.0500 for data with $I>2\sigma(I)$; the wR2 value was 0.0838 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 N1 C6 N2
SADI C3 C7 C6 C8
SADI N1 C2 N2 C5

FLAT C2 C3 N1 C7
FLAT C5 C6 N2 C8
```

(All but two EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping isocyano carbons were connected to the correct atoms. The following EADP constraints were used to set the U_{ij} parameters of the minor guest's isocyano group to match the major guest's isocyano atoms. This was done because the minor guest isocyano atoms were approaching a prolate thermal parameter shape (a "discus" shape rather than the more realistic "bean" shape.)

```
EADP N1 N2
EADP C8 C7
```

The following reflections were omitted due to their ΔF^2/esd being greater than 10.

```
OMIT 0 3 6
OMIT -4 0 6
OMIT 0 3 5
OMIT 0 1 1
```

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	240 x 200 x 60 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	1937
Lattice parameters	a = 8.1122 (8) Å
	b = 10.8595 (12) Å
	c = 14.3714 (16) Å
	α = 90°
	β = 95.317 (5)°
	γ = 90°
	V = 1260.6 (2) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.308
F_{000}	532
μ (MoK$_\alpha$)	0.104 mm^{-1}

Temperature	150 K

B. Intensity measurements

Diffractometer	Siemens P4, APEX II CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K_α (λ = 0.71073 Å)
Crystal to detector distance	80.00 mm
Time per frame	20 s
Temperature	150 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.85°
θ_{max}	30.67°
h k l range	h = -12 to 13
	k = -16 to 16
	l = -23 to 20
No. of reflections measured	Total: 10637
	Unique 4790 (R_{int} = 0.0491)
	I > 2σ(I) = 2884
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	2884
No. variables	224
No. Restraints	27
Reflection:parameter ratio	21.38
For I > 2.00σ(I)	12.88
No. Reflections used in refinement	4790
Final R indices [I > 2σ(I)] R1	0.0500
Final R indices [all data]; R1, wR2	0.0932; 0.0838
Goodness of Fit (s)	1.118
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.252 e/Å^3
Minimum peak in final diff. map	-0.240 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-diisocyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99722 (10)	0.42009 (8)	0.65317 (6)	0.02250 (18)	
O30	−0.03006 (9)	0.08843 (8)	0.65384 (6)	0.02199 (18)	
O10	−0.01213 (10)	0.75143 (8)	0.68142 (5)	0.02218 (17)	
N21	0.80948 (14)	0.52203 (10)	0.73048 (8)	0.0298 (3)	
H21A	0.862 (2)	0.5921 (17)	0.7241 (11)	0.036*	
H21B	0.726 (2)	0.5223 (16)	0.7593 (11)	0.036*	
N20	0.78561 (13)	0.31383 (10)	0.70526 (8)	0.0278 (2)	
H20A	0.8290 (19)	0.2451 (17)	0.6843 (11)	0.033*	
H20B	0.701 (2)	0.3109 (16)	0.7372 (11)	0.033*	
N31	0.19492 (14)	0.19616 (11)	0.70984 (8)	0.0290 (2)	
H31A	0.1488 (19)	0.2642 (17)	0.6832 (11)	0.035*	
H31B	0.291 (2)	0.1988 (16)	0.7400 (11)	0.035*	
N30	0.18101 (15)	−0.01160 (11)	0.73427 (9)	0.0309 (3)	
H30A	0.113 (2)	−0.0792 (17)	0.7332 (11)	0.037*	
H30B	0.265 (2)	−0.0094 (17)	0.7736 (11)	0.037*	
C20	0.86783 (13)	0.41886 (11)	0.69496 (8)	0.0203 (2)	
C30	0.11148 (13)	0.09121 (11)	0.69851 (8)	0.0202 (2)	
N11	−0.03154 (14)	0.85504 (10)	0.54457 (8)	0.0269 (2)	
H11A	−0.0501 (18)	0.9244 (16)	0.5747 (11)	0.032*	
H11B	−0.0148 (19)	0.8567 (16)	0.4855 (11)	0.032*	
C10	−0.00491 (13)	0.75179 (11)	0.59400 (8)	0.0198 (2)	
N10	0.03287 (14)	0.64955 (11)	0.54905 (8)	0.0270 (2)	
H10A	0.0330 (19)	0.5792 (17)	0.5788 (11)	0.032*	
H10B	0.0216 (18)	0.6452 (16)	0.4895 (11)	0.032*	
C3	0.5174 (7)	0.2808 (3)	0.4328 (4)	0.0451 (12)	0.689
H3A	0.6087	0.3359	0.4179	0.054*	0.689
H3B	0.4427	0.2697	0.3749	0.054*	0.689
C2	0.5887 (3)	0.1576 (3)	0.4632 (2)	0.0481 (7)	0.689
H2A	0.6685	0.17	0.5188	0.058*	0.689
H2B	0.6511	0.1245	0.4127	0.058*	0.689
C1	0.4625 (3)	0.0623 (2)	0.4868 (2)	0.0426 (7)	0.689
H1A	0.3798	0.052	0.4323	0.051*	0.689
H1B	0.4036	0.0933	0.5394	0.051*	0.689
N1	0.4277 (6)	0.3386 (5)	0.5016 (4)	0.0390 (8)	0.689
C7	0.3473 (4)	0.3859 (6)	0.5520 (3)	0.0523 (9)	0.689

C5	0.5070 (8)	0.1505 (4)	0.4276 (3)	0.0456 (13)	0.311
H5A	0.5786	0.1178	0.3812	0.055*	0.311
H5B	0.3914	0.148	0.3988	0.055*	0.311
C4	0.5211 (9)	0.0667 (3)	0.5116 (4)	0.0440 (16)	0.311
H4A	0.4462	0.097	0.5571	0.053*	0.311
H4B	0.6357	0.0708	0.5418	0.053*	0.311
C6	0.5536 (16)	0.2828 (6)	0.4473 (8)	0.057 (4)	0.311
H6A	0.6714	0.2866	0.4723	0.068*	0.311
H6B	0.5417	0.3296	0.3879	0.068*	0.311
N2	0.4550 (18)	0.3402 (13)	0.5124 (11)	0.0390 (8)	0.311
C8	0.3944 (11)	0.3817 (15)	0.5733 (8)	0.0523 (9)	0.311

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0237 (4)	0.0191 (4)	0.0257 (4)	0.0006 (3)	0.0073 (3)	0.0011 (3)
O30	0.0221 (4)	0.0184 (4)	0.0252 (4)	0.0004 (3)	0.0006 (3)	−0.0002 (3)
O10	0.0265 (4)	0.0194 (4)	0.0210 (4)	−0.0006 (3)	0.0040 (3)	0.0003 (4)
N21	0.0321 (5)	0.0197 (5)	0.0405 (6)	0.0010 (4)	0.0179 (5)	−0.0013 (5)
N20	0.0269 (5)	0.0195 (5)	0.0387 (6)	−0.0010 (4)	0.0127 (4)	0.0007 (5)
N31	0.0270 (5)	0.0192 (5)	0.0388 (6)	−0.0020 (4)	−0.0069 (4)	0.0020 (5)
N30	0.0319 (6)	0.0210 (5)	0.0375 (6)	0.0005 (5)	−0.0090 (5)	0.0035 (5)
C20	0.0218 (5)	0.0184 (5)	0.0208 (5)	0.0011 (4)	0.0031 (4)	0.0018 (5)
C30	0.0234 (5)	0.0184 (5)	0.0193 (5)	0.0014 (4)	0.0039 (4)	−0.0005 (4)
N11	0.0395 (6)	0.0195 (5)	0.0218 (5)	0.0021 (4)	0.0037 (4)	0.0013 (4)
C10	0.0186 (4)	0.0191 (5)	0.0217 (5)	−0.0026 (4)	0.0020 (4)	−0.0002 (5)
N10	0.0411 (6)	0.0191 (5)	0.0212 (5)	0.0016 (4)	0.0055 (4)	−0.0001 (4)
C3	0.042 (2)	0.060 (3)	0.0343 (14)	−0.0012 (13)	0.0117 (14)	−0.0071 (14)
C2	0.0332 (12)	0.069 (2)	0.0437 (14)	−0.0015 (12)	0.0113 (10)	−0.0136 (14)
C1	0.0261 (12)	0.0630 (19)	0.0390 (15)	0.0001 (11)	0.0047 (10)	−0.0173 (13)
N1	0.028 (2)	0.0524 (9)	0.0367 (16)	−0.0083 (12)	0.0067 (14)	−0.0087 (9)
C7	0.042 (2)	0.0642 (14)	0.053 (2)	−0.011 (2)	0.0153 (15)	−0.018 (2)
C5	0.049 (3)	0.059 (4)	0.031 (3)	0.003 (3)	0.014 (2)	−0.012 (3)
C4	0.038 (3)	0.061 (4)	0.032 (3)	0.002 (3)	−0.004 (2)	−0.012 (3)
C6	0.041 (5)	0.076 (8)	0.059 (7)	−0.002 (4)	0.029 (5)	−0.004 (5)
N2	0.028 (2)	0.0524 (9)	0.0367 (16)	−0.0083 (12)	0.0067 (14)	−0.0087 (9)
C8	0.042 (2)	0.0642 (14)	0.053 (2)	−0.011 (2)	0.0153 (15)	−0.018 (2)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2567 (13)	C3—C2	1.507 (5)
O30—C30	1.2628 (13)	C2—C1	1.516 (4)
O10—C10	1.2631 (13)	C1—C1i	1.518 (5)
N21—C20	1.3360 (16)	N1—C7	1.141 (3)
N20—C20	1.3364 (16)	C5—C6	1.505 (7)
N31—C30	1.3279 (16)	C5—C4	1.508 (6)
N30—C30	1.3323 (16)	C4—C4i	1.519 (6)
N11—C10	1.3341 (16)	C6—N2	1.430 (6)
C10—N10	1.3345 (16)	N2—C8	1.136 (6)
C3—N1	1.427 (3)		
O20—C20—N20	120.63 (11)	N1—C3—C2	113.3 (4)
O20—C20—N21	120.99 (11)	C3—C2—C1	115.0 (3)
N20—C20—N21	118.38 (10)	C2—C1—C1i	113.6 (3)
O30—C30—N31	120.79 (11)	C7—N1—C3	175.3 (6)
O30—C30—N30	120.57 (11)	C6—C5—C4	115.2 (6)
N31—C30—N30	118.63 (11)	C5—C4—C4i	113.7 (5)
O10—C10—N11	120.80 (11)	N2—C6—C5	113.1 (7)
O10—C10—N10	120.85 (11)	C8—N2—C6	170.4 (15)
N11—C10—N10	118.33 (11)		
N2—C6—C5—C4	−59.4 (13)	N1—C3—C2—C1	59.7 (6)
C6—C5—C4—C4i	−178.0 (8)	C3—C2—C1—C1i	177.5 (4)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
N2	C6	C5	C4	-59.4 (13)
C6	C5	C4	C4i	-178.0(8)
N1	C3	C2	C1	59.7(6)
C3	C2	C1	C1i	177.5(4)

Symmetry code: (i) −x+1, −y,

−z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N21—H21*A*···O10^{ii}	0.881 (19)	2.128 (19)	2.9977 (14)	169.0 (15)
N21—H21*B*···O30^{iii}	0.826 (17)	2.229 (17)	3.0199 (14)	160.4 (16)
N20—H20*A*···O30^{ii}	0.889 (18)	2.118 (18)	2.9963 (14)	169.2 (14)
N20—H20*B*···O10^{iv}	0.859 (16)	2.115 (17)	2.9500 (13)	164.0 (16)
N31—H31*A*···O20^{v}	0.898 (18)	2.113 (18)	2.9844 (15)	163.3 (14)
N31—H31*B*···O10^{iv}	0.854 (16)	2.111 (17)	2.9460 (14)	165.8 (16)
N30—H30*A*···O10^{vi}	0.916 (19)	2.199 (19)	3.0714 (15)	159.0 (14)
N30—H30*B*···O20^{vii}	0.842 (17)	2.247 (18)	3.0328 (14)	155.3 (16)
N11—H11*A*···O30^{viii}	0.889 (17)	2.111 (18)	2.9810 (15)	165.8 (14)
N11—H11*B*···O30^{ix}	0.873 (16)	2.152 (17)	3.0036 (14)	165.1 (16)
N10—H10*A*···O20^{v}	0.875 (18)	2.067 (18)	2.9346 (15)	171.3 (14)
N10—H10*B*···O20^{x}	0.854 (16)	2.161 (17)	2.9909 (14)	163.9 (16)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2; (iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z; (vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z; (ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

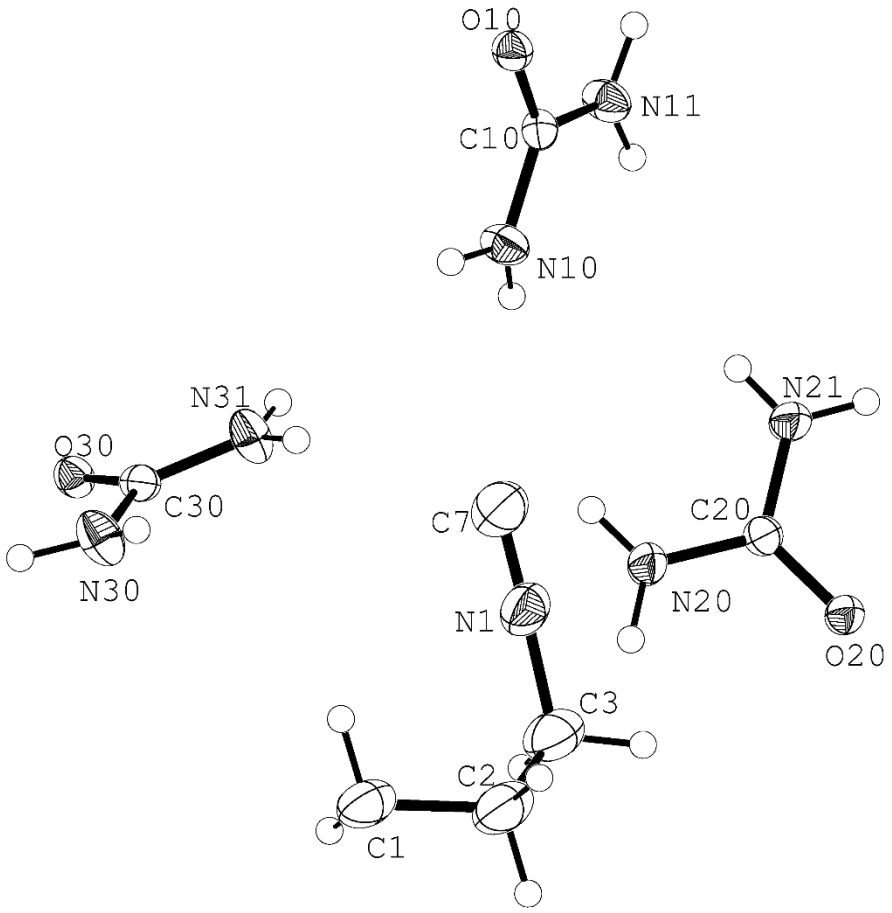
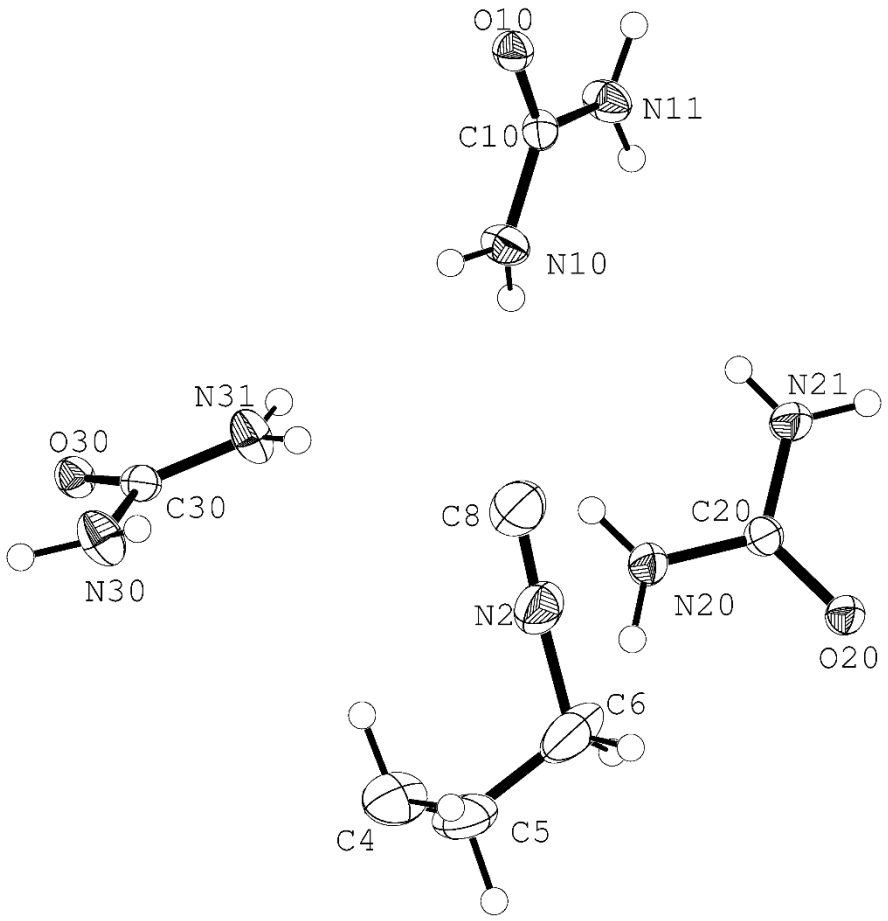


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-diisocyanohexane/urea at 150 K (KEA-C-271).

2. Siemens P4 diffractometer equipped with a Bruker APEX II CCD detector
3. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
4. Data collected using the Bruker APEX2 software package.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **42**, 339–341 (2009).

Structure report for 1,6-diisocyanohexane/urea at 165 K[1]

Introduction

This data set was collected in 2012 by Keith Alquist using a Siemens P4 diffractometer equipped with an APEX II detector.[11] (See laboratory notebook KEA-C-283.) The crystal was a fragment collected from MDH-K-150-19. As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the end groups to be disordered between major and minor sites. The model shown here allows the isocyano end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 66.6% and 33.4%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 78.52°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 300 µm x 260 µm x 80 µm. The crystal was cooled to 165 K using an Oxford Cryosystems cryostream using liquid nitrogen. The requested frame exposure was 10 seconds and the frame width was 0.20º.[3] The crystal to detector distance was 80.00 mm.

The unit cell parameters were determined[11,4] from 3631 input reflections whose minimum and the maximum 2-theta values were 5.70 and 60.48, respectively. The errors are reported after corrections for the goodness of fit (4.44). The cell volume is 1260.53 (16) Å^3.

a = 8.1036 (6) Å	α = 90°
b = 10.8591 (7) Å	β = 95.236 (3)°
c = 14.3846 (11) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.308 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 12090 reflections of which 351 were rejected. After merging Friedel opposites, there were 3830 unique reflections, of which 2806 had I > 2sigma(I). The R(int) was0.0518, and the R(sigma) was 0.0418. The linear absorption coefficient, μ, for Mo-K_α radiation is 0.104 mm^{-1}. The absorption correction was made using SADABS.[3, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-diisocyanohexane/urea refined the dinitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kea_283_iso.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.853 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

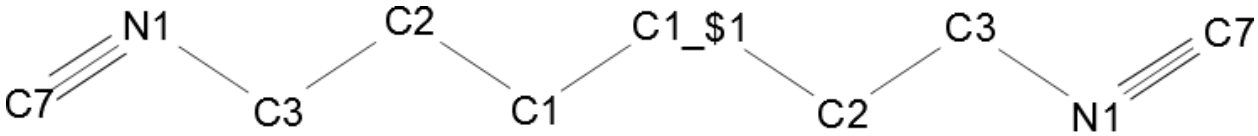


Figure 1: Atomic labeling scheme for part 1 (major part)

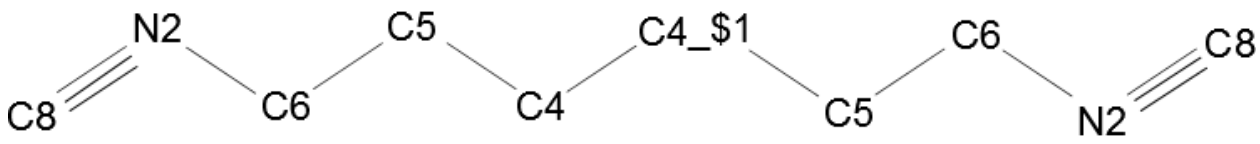


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, -y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 N1 C6 N2
SADI C3 C7 C6 C8
SADI N1 C2 N2 C5
FLAT C2 C3 N1 C7
FLAT C5 C6 N2 C8
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was refined to 0.0108 (14).

The goodness of fit[7] was 1.118 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.119 for all of the data. R1 was 0.0932 for all 5279 data and 0.0500 for data with $I>2\sigma(I)$; the wR2 value was 0.0838 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 N1 C6 N2
SADI C3 C7 C6 C8
SADI N1 C2 N2 C5

FLAT C2 C3 N1 C7
FLAT C5 C6 N2 C8
```

(All but two EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping isocyano carbons were connected to the correct atoms.

The following reflections were omitted due to their ΔF^2/esd being greater than 10.

OMIT -4 6 4

OMIT -7 7 4

OMIT 1 5 5

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	300 x 260 x 80 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	3631
Lattice parameters	a = 8.1036 (6) Å
	b = 10.8591 (7) Å
	c = 14.3846 (11) Å
	α = 90°
	β = 95.236 (3)°
	γ = 90°
	V = 1260.53 (16) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.308
F_{000}	532
μ (MoK_α)	0.104 mm^{-1}
Temperature	165 K

B. Intensity measurements

Diffractometer	Siemens P4, APEX II CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K_α (λ = 0.71073 Å)
Crystal to detector distance	80.00 mm
Time per frame	10 s
Temperature	165 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.35°
θ_{max}	30.24°
h k l range	h = -11 to 11

	k = -15 to 15
	l = -19 to 20
No. of reflections measured	Total: 11739
	Unique 3830 (R_{int} = 0.0518)
	I > 2σ(I) = 2806
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	2806
No. variables	236
No. Restraints	27
Reflection:parameter ratio	16.23
For I > 2.00σ(I)	11.89
No. Reflections used in refinement	3830
Final R indices [I > 2σ(I)] R1	0.0415
Final R indices [all data]; R1, wR2	0.0608; 0.0809
Goodness of Fit (s)	1.167
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.231 e/Å^3
Minimum peak in final diff. map	-0.269 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-diisocyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99703 (9)	0.42005 (7)	0.65310 (5)	0.02241 (17)	
O30	−0.02958 (9)	0.08835 (7)	0.65384 (5)	0.02236 (17)	
O10	−0.01208 (9)	0.75145 (7)	0.68124 (5)	0.02206 (17)	
N21	0.80931 (13)	0.52175 (9)	0.73049 (8)	0.0308 (2)	
H21A	0.8593 (18)	0.5912 (13)	0.7222 (10)	0.037*	
H21B	0.7216 (18)	0.5218 (13)	0.7605 (10)	0.037*	
N20	0.78556 (12)	0.31375 (9)	0.70539 (8)	0.0289 (2)	
H20A	0.8266 (17)	0.2456 (13)	0.6863 (10)	0.035*	
H20B	0.7004 (17)	0.3122 (13)	0.7360 (10)	0.035*	

N31	0.19551 (13)	0.19596 (9)	0.71004 (8)	0.0302 (2)	
H31A	0.1524 (18)	0.2630 (13)	0.6874 (10)	0.036*	
H31B	0.2920 (18)	0.1988 (13)	0.7399 (10)	0.036*	
N30	0.18143 (13)	−0.01122 (10)	0.73434 (8)	0.0320 (2)	
H30A	0.1239 (18)	−0.0812 (13)	0.7311 (10)	0.038*	
H30B	0.2696 (18)	−0.0080 (13)	0.7733 (10)	0.038*	
C20	0.86765 (12)	0.41842 (9)	0.69499 (7)	0.0209 (2)	
C30	0.11178 (12)	0.09128 (9)	0.69862 (7)	0.0204 (2)	
N11	−0.03124 (13)	0.85482 (9)	0.54477 (7)	0.0277 (2)	
H11A	−0.0457 (17)	0.9243 (13)	0.5751 (10)	0.033*	
H11B	−0.0149 (17)	0.8555 (12)	0.4888 (10)	0.033*	
C10	−0.00517 (12)	0.75159 (10)	0.59408 (7)	0.0202 (2)	
N10	0.03252 (13)	0.64952 (9)	0.54907 (7)	0.0280 (2)	
H10A	0.0313 (17)	0.5806 (13)	0.5795 (10)	0.034*	
H10B	0.0211 (16)	0.6445 (12)	0.4901 (11)	0.034*	
C3	0.5155 (7)	0.2803 (3)	0.4329 (4)	0.0480 (12)	0.666
H3A	0.6064	0.3356	0.4179	0.058*	0.666
H3B	0.4409	0.2688	0.3751	0.058*	0.666
C2	0.5883 (3)	0.1570 (2)	0.46298 (19)	0.0502 (7)	0.666
H2A	0.6688	0.1695	0.5182	0.060*	0.666
H2B	0.65	0.124	0.4121	0.060*	0.666
C1	0.4625 (3)	0.0623 (2)	0.4870 (2)	0.0450 (7)	0.666
H1A	0.3792	0.052	0.4327	0.054*	0.666
H1B	0.4041	0.0934	0.5398	0.054*	0.666
N1	0.4254 (6)	0.3380 (6)	0.5008 (5)	0.0376 (10)	0.666
C7	0.3500 (6)	0.3856 (9)	0.5522 (4)	0.0531 (13)	0.666
C5	0.5070 (7)	0.1501 (4)	0.4281 (3)	0.0469 (11)	0.335
H5A	0.3912	0.1479	0.3995	0.056*	0.335
H5B	0.5786	0.1177	0.3815	0.056*	0.335
C4	0.5214 (8)	0.0664 (3)	0.5116 (3)	0.0455 (14)	0.335
H4A	0.4469	0.0968	0.5574	0.055*	0.335
H4B	0.6363	0.0702	0.5415	0.055*	0.335
C6	0.5541 (14)	0.2823 (6)	0.4487 (7)	0.056 (3)	0.335
H6A	0.6727	0.2856	0.4721	0.068*	0.335
H6B	0.5401	0.3299	0.3898	0.068*	0.335
N2	0.4596 (12)	0.3394 (11)	0.5152 (9)	0.0346 (18)	0.335
C8	0.3971 (14)	0.3801 (19)	0.5748 (8)	0.065 (3)	0.335

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0236 (3)	0.0185 (4)	0.0262 (4)	0.0010 (3)	0.0078 (3)	0.0011 (3)
O30	0.0220 (3)	0.0184 (4)	0.0264 (4)	−0.0001 (3)	0.0003 (3)	0.0006 (3)
O10	0.0263 (4)	0.0199 (4)	0.0202 (4)	−0.0003 (3)	0.0033 (3)	0.0002 (3)
N21	0.0334 (5)	0.0190 (5)	0.0428 (6)	0.0003 (4)	0.0193 (4)	−0.0018 (4)
N20	0.0269 (5)	0.0192 (5)	0.0426 (6)	−0.0009 (4)	0.0145 (4)	0.0005 (4)
N31	0.0280 (5)	0.0191 (5)	0.0416 (6)	−0.0021 (4)	−0.0079 (4)	0.0015 (4)
N30	0.0336 (5)	0.0213 (5)	0.0386 (6)	0.0018 (4)	−0.0099 (4)	0.0040 (4)
C20	0.0225 (5)	0.0185 (5)	0.0220 (5)	0.0017 (4)	0.0031 (4)	0.0018 (4)
C30	0.0233 (5)	0.0193 (5)	0.0191 (5)	0.0013 (4)	0.0039 (4)	−0.0013 (4)
N11	0.0414 (5)	0.0200 (5)	0.0217 (5)	0.0020 (4)	0.0028 (4)	0.0015 (4)
C10	0.0187 (4)	0.0200 (5)	0.0219 (5)	−0.0025 (4)	0.0016 (3)	0.0002 (4)
N10	0.0436 (6)	0.0196 (5)	0.0214 (5)	0.0020 (4)	0.0056 (4)	−0.0006 (4)
C3	0.043 (3)	0.067 (3)	0.0347 (15)	−0.0002 (14)	0.0121 (15)	−0.0088 (14)
C2	0.0325 (11)	0.0735 (19)	0.0465 (14)	−0.0005 (12)	0.0132 (10)	−0.0149 (13)
C1	0.0243 (12)	0.071 (2)	0.0398 (16)	0.0045 (11)	0.0028 (10)	−0.0157 (13)
N1	0.026 (2)	0.0537 (16)	0.033 (2)	−0.0075 (15)	0.0015 (15)	−0.0099 (13)
C7	0.045 (2)	0.063 (2)	0.053 (3)	−0.010 (2)	0.0176 (18)	−0.016 (3)
C5	0.055 (3)	0.054 (3)	0.033 (2)	0.001 (3)	0.013 (2)	−0.008 (2)
C4	0.037 (3)	0.067 (4)	0.032 (3)	0.010 (3)	−0.001 (2)	−0.009 (2)
C6	0.039 (5)	0.078 (6)	0.057 (6)	−0.007 (3)	0.029 (4)	−0.007 (4)
N2	0.017 (3)	0.056 (3)	0.030 (4)	−0.010 (2)	−0.002 (2)	−0.006 (2)
C8	0.076 (8)	0.077 (5)	0.045 (5)	−0.009 (7)	0.024 (5)	−0.011 (5)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2561 (12)	C3—C2	1.510 (4)
O30—C30	1.2623 (12)	C2—C1	1.510 (3)
O10—C10	1.2601 (12)	C1—C1i	1.517 (4)
N21—C20	1.3369 (14)	N1—C7	1.126 (3)
N20—C20	1.3323 (14)	C5—C4	1.502 (5)
N31—C30	1.3264 (14)	C5—C6	1.507 (6)
N30—C30	1.3299 (14)	C4—C4i	1.513 (6)
N11—C10	1.3330 (14)	C6—N2	1.421 (6)
C10—N10	1.3331 (14)	N2—C8	1.125 (6)
C3—N1	1.418 (3)		
O20—C20—N20	120.87 (10)	N1—C3—C2	114.0 (4)
O20—C20—N21	120.74 (10)	C3—C2—C1	114.5 (3)
N20—C20—N21	118.39 (10)	C2—C1—C1i	113.6 (2)
O30—C30—N31	120.99 (10)	C7—N1—C3	177.5 (7)
O30—C30—N30	120.62 (10)	C4—C5—C6	114.8 (5)
N31—C30—N30	118.37 (10)	C5—C4—C4i	113.7 (5)
O10—C10—N11	120.75 (10)	N2—C6—C5	113.9 (6)
O10—C10—N10	121.00 (10)	C8—N2—C6	172.7 (12)
N11—C10—N10	118.23 (10)		
N2—C6—C5—C4	−58.2 (11)	N1—C3—C2—C1	59.2 (5)
C6—C5—C4—C4i	−178.2 (7)	C3—C2—C1—C1i	177.6 (4)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
N2	C6	C5	C4	-58.2(11)
C6	C5	C4	C4i	-178.2(7)
N1	C3	C2	C1	59.2(5)
C3	C2	C1	C1i	177.6(4)

Symmetry code: (i) −x+1, −y,

$-z+1$.

Table 5. Hydrogen-bond Geometries (in Å)

D—*H*···*A*	*D*—*H*	H···A	*D*···*A*	*D*—*H*···*A*
N21—H21A···O10ii	0.869 (15)	2.139 (15)	3.0009 (13)	171.3 (13)
N21—H21B···O30iii	0.865 (14)	2.194 (15)	3.0197 (12)	159.7 (13)
N20—H20A···O30ii	0.866 (14)	2.143 (15)	2.9980 (13)	169.1 (13)
N20—H20B···O10iv	0.853 (14)	2.124 (15)	2.9476 (12)	162.3 (13)
N31—H31A···O20v	0.859 (15)	2.150 (15)	2.9898 (13)	165.6 (13)
N31—H31B···O10iv	0.858 (15)	2.104 (15)	2.9424 (13)	165.8 (13)
N30—H30A···O10vi	0.890 (15)	2.211 (15)	3.0767 (13)	164.1 (13)
N30—H30B···O20vii	0.867 (15)	2.223 (15)	3.0329 (13)	155.2 (13)
N11—H11A···O30viii	0.885 (14)	2.108 (14)	2.9813 (13)	168.8 (13)
N11—H11B···O30ix	0.827 (15)	2.202 (15)	3.0071 (13)	164.4 (13)
N10—H10A···O20v	0.867 (14)	2.072 (15)	2.9342 (13)	172.8 (13)
N10—H10B···O20x	0.847 (15)	2.168 (15)	2.9930 (13)	164.7 (13)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2; (iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z; (vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z; (ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

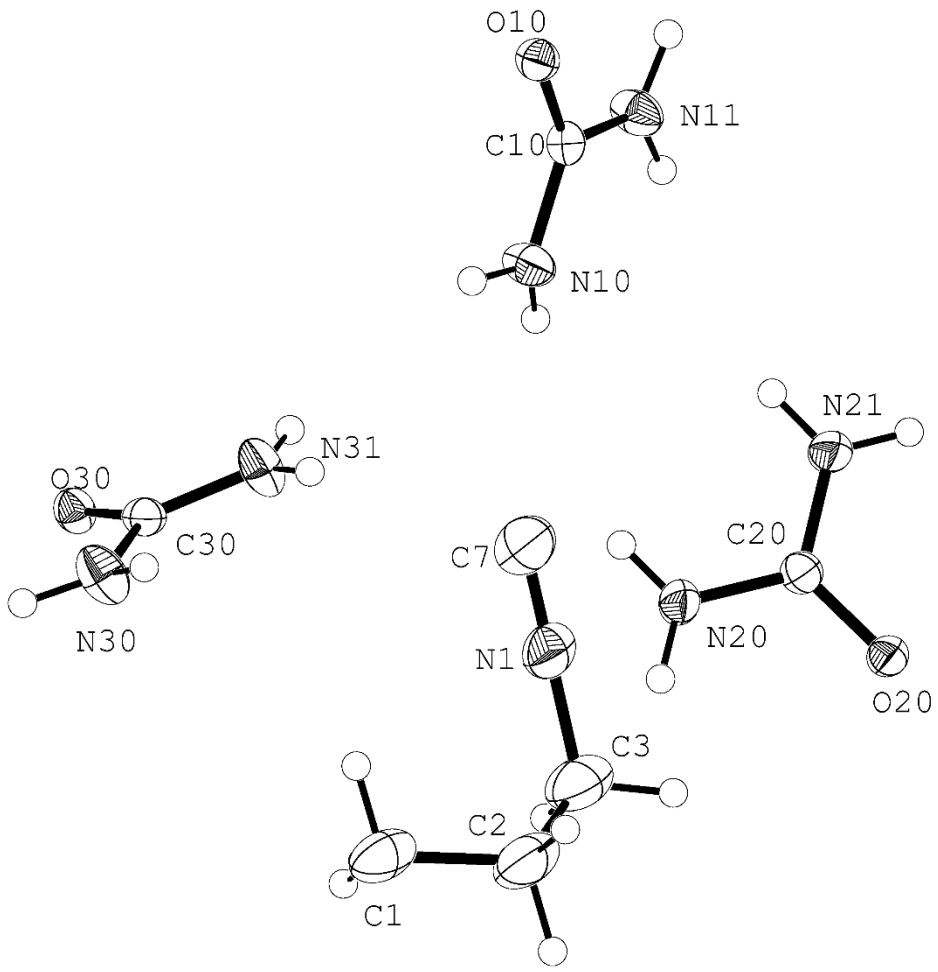
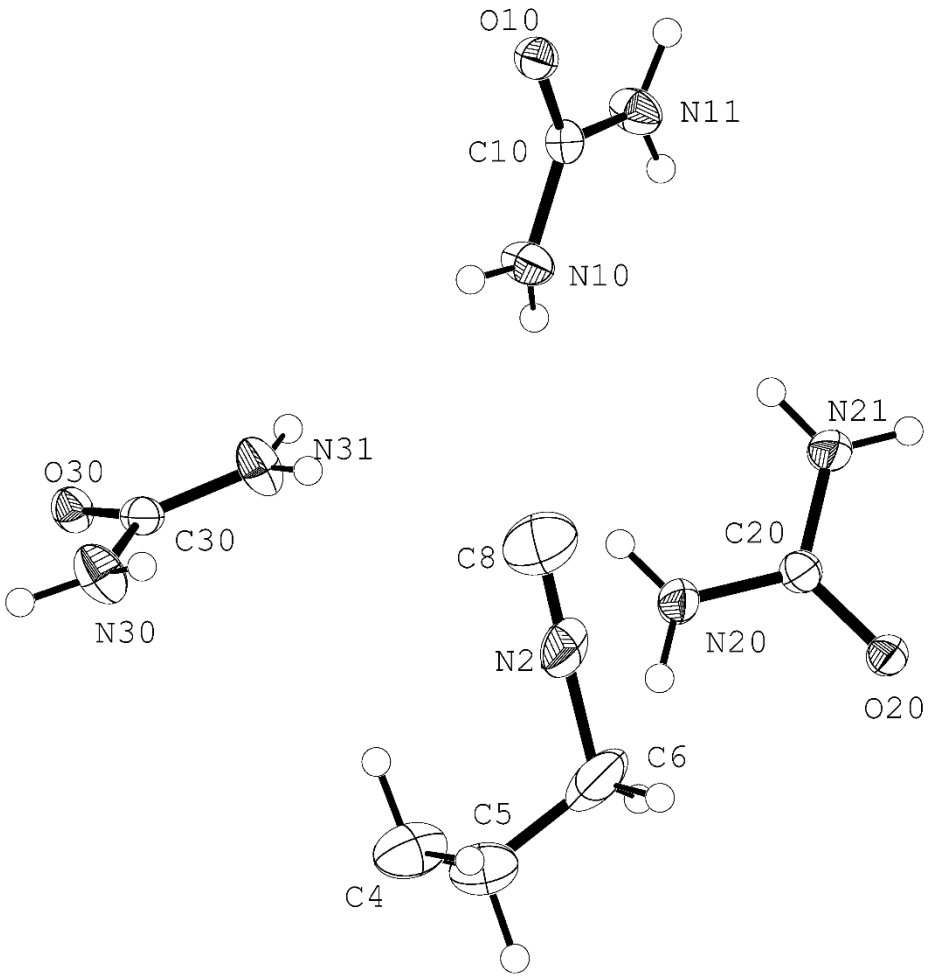


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-diisocyanohexane/urea at 165 K (KEA-C-283).
2. Siemens P4 diffractometer equipped with a Bruker APEX II CCD detector
3. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
4. Data collected using the Bruker APEX2 software package.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. *Acta Crystallogr. A***51**, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **42**, 339–341 (2009).

Structure report for 1,6-diisocyanohexane/urea at 183 K[1]

Introduction

The data for this crystal was collected by Kevin Pate on the P4 CCD diffractometer in 2000 and was originally labeled "KP2400". (See laboratory notebook KLP A-155.) The original crystal was from Mark Hollingsworth (MDH-K-150-18). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 66.2% and 33.8%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 76.8°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 500 µm x 400 µm x 200 µm. The crystal was cooled to 183 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 10 seconds and the frame width was 0.30º. [8] The crystal to detector distance was 49.87 mm.

The unit cell parameters were determined[9,4] from 1665 input reflections whose minimum and the maximum 2-theta values were 5.66 and 48.80, respectively. The errors are reported after corrections for the goodness of fit (1.50). The cell volume is 1277.4 (4) Å^3.

a = 8.1422 (13) Å	α = 90°
b = 10.9048 (17) Å	β = 95.163 (3)°
c = 14.445 (2) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.291 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 7572 reflections of which 181 were rejected. After merging Friedel opposites, there were 2797 unique reflections, of which 2445 had I > 2sigma(I). The R(int) was 0.0182, and the R(sigma) was 0.0195. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.102 mm^{-1}. The absorption correction was made using SADABS. [8, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-diisocyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kp2400_iso.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.880 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

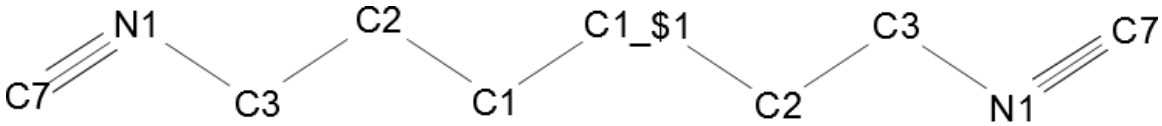


Figure 1: Atomic labeling scheme for part 1 (major part)

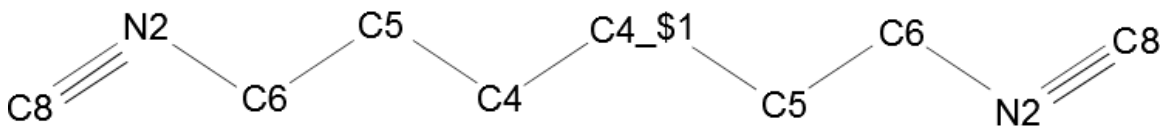


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.287 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.280 for all of the data. R1 was 0.0570 for all 2797 data and 0.0410 for data with $I>2\sigma(I)$; the wR2 value was 0.0993 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	500 x 400 x 200 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	1665
Lattice parameters	a = 8.1422 (13) Å b = 10.9048 (17) Å c = 14.445 (2) Å α = 90° β = 95.163 (3)° γ = 90° V = 1277.4 (4) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.291
F_{000}	532
μ (MoK_α)	0.102 mm^{-1}
Temperature	183 K

B. Intensity measurements

Diffractometer	Siemens P4, APEX II CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K_α (λ = 0.71073 Å)
Crystal to detector distance	49.87 mm
Time per frame	10 s
Temperature	183 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.83°
θ_{max}	24.40°
h k l range	h = -9 to 9 k = -12 to 11 l = -15 to 16
No. of reflections measured	Total: 6108 Unique 2112 (R_{int} = 0.0236) I > 2σ(I) = 1608

Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	1608
No. variables	199
No. Restraints	27
Reflection:parameter ratio	10.61
For I > 2.00σ(I)	8.08
No. Reflections used in refinement	2112
Final R indices [I > 2σ(I)] R1	0.0410
Final R indices [all data]; R1, wR2	0.0570; 0.0993
Goodness of Fit (s)	1.280
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.197 e/Å^3
Minimum peak in final diff. map	-0.200 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-diisocyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99652 (14)	0.41991 (10)	0.65316 (9)	0.0273 (3)	
O30	−0.02856 (14)	0.08844 (10)	0.65412 (9)	0.0275 (3)	
O10	−0.01229 (15)	0.75121 (10)	0.68108 (9)	0.0265 (3)	
N21	0.8086 (2)	0.52120 (14)	0.73001 (12)	0.0373 (5)	
H21A	0.8606	0.5912	0.7243	0.045*	
H21B	0.7181	0.5189	0.759	0.045*	
N20	0.78609 (19)	0.31364 (14)	0.70569 (12)	0.0347 (4)	
H20A	0.823	0.2447	0.6836	0.042*	
H20B	0.6958	0.3136	0.7349	0.042*	
N31	0.1958 (2)	0.19561 (14)	0.70980 (12)	0.0360 (4)	
H31A	0.1532	0.264	0.6859	0.043*	

H31B	0.2937	0.1964	0.741	0.043*	
N30	0.1817 (2)	−0.01055 (14)	0.73497 (12)	0.0376 (5)	
H30A	0.1294	−0.0810	0.728	0.045*	
H30B	0.2798	−0.0075	0.7659	0.045*	
C20	0.8672 (2)	0.41846 (15)	0.69480 (13)	0.0245 (4)	
C30	0.1125 (2)	0.09142 (15)	0.69877 (13)	0.0237 (4)	
N11	−0.0303 (2)	0.85457 (13)	0.54499 (12)	0.0337 (4)	
H11A	−0.0518	0.9236	0.573	0.040*	
H11B	−0.0251	0.8534	0.4844	0.040*	
C10	−0.0055 (2)	0.75155 (16)	0.59440 (14)	0.0244 (4)	
N10	0.0305 (2)	0.64960 (13)	0.54883 (12)	0.0345 (4)	
H10A	0.0499	0.5806	0.5795	0.041*	
H10B	0.0347	0.6515	0.4882	0.041*	
C3	0.5130 (12)	0.2799 (4)	0.4337 (7)	0.057 (2)	0.663
H3A	0.601	0.3347	0.4148	0.069*	0.663
H3B	0.4312	0.2685	0.3795	0.069*	0.663
C2	0.5868 (5)	0.1573 (4)	0.4628 (4)	0.0609 (15)	0.663
H2A	0.6685	0.1699	0.5169	0.073*	0.663
H2B	0.6465	0.1247	0.4113	0.073*	0.663
C1	0.4627 (5)	0.0624 (3)	0.4881 (6)	0.0567 (19)	0.663
H1A	0.3773	0.053	0.4353	0.068*	0.663
H1B	0.4076	0.0927	0.542	0.068*	0.663
N1	0.4342 (17)	0.3364 (8)	0.5080 (9)	0.051 (4)	0.663
C7	0.3776 (16)	0.3832 (19)	0.5681 (11)	0.093 (5)	0.663
C5	0.5054 (13)	0.1502 (6)	0.4277 (5)	0.053 (2)	0.337
H5A	0.5718	0.117	0.3793	0.064*	0.337
H5B	0.3885	0.15	0.4021	0.064*	0.337
C4	0.5238 (17)	0.0660 (4)	0.5113 (6)	0.055 (4)	0.337
H4A	0.4541	0.0972	0.5589	0.066*	0.337
H4B	0.6399	0.0682	0.5384	0.066*	0.337
C6	0.558 (2)	0.2812 (7)	0.4482 (13)	0.059 (6)	0.337
H6A	0.6693	0.2817	0.4819	0.071*	0.337
H6B	0.5637	0.326	0.389	0.071*	0.337
N2	0.444 (3)	0.3423 (18)	0.5033 (19)	0.057 (9)	0.337
C8	0.349 (2)	0.384 (3)	0.5471 (19)	0.051 (5)	0.337

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0301 (7)	0.0231 (7)	0.0301 (8)	0.0011 (5)	0.0108 (6)	0.0013 (6)
O30	0.0286 (7)	0.0225 (7)	0.0312 (9)	0.0002 (5)	0.0014 (6)	0.0003 (6)
O10	0.0334 (7)	0.0247 (7)	0.0220 (8)	0.0001 (5)	0.0053 (6)	0.0006 (6)
N21	0.0407 (9)	0.0246 (9)	0.0500 (13)	0.0008 (7)	0.0224 (9)	−0.0017 (8)
N20	0.0330 (9)	0.0241 (8)	0.0494 (12)	−0.0011 (7)	0.0170 (8)	0.0006 (8)
N31	0.0350 (9)	0.0233 (8)	0.0477 (13)	−0.0027 (7)	−0.0071 (8)	0.0026 (8)
N30	0.0388 (9)	0.0249 (9)	0.0466 (13)	0.0020 (7)	−0.0097 (8)	0.0045 (8)
C20	0.0278 (9)	0.0237 (10)	0.0224 (11)	0.0032 (7)	0.0038 (8)	0.0046 (8)
C30	0.0260 (9)	0.0249 (10)	0.0205 (11)	0.0015 (8)	0.0046 (8)	−0.0015 (8)
N11	0.0531 (11)	0.0238 (9)	0.0241 (10)	0.0029 (7)	0.0024 (8)	0.0017 (7)
C10	0.0229 (9)	0.0233 (10)	0.0271 (12)	−0.0032 (7)	0.0030 (8)	−0.0004 (8)
N10	0.0556 (11)	0.0241 (9)	0.0246 (10)	0.0034 (7)	0.0080 (9)	0.0007 (7)
C3	0.048 (5)	0.080 (5)	0.046 (4)	0.000 (2)	0.014 (3)	−0.011 (3)
C2	0.042 (3)	0.086 (4)	0.056 (4)	−0.003 (2)	0.018 (2)	−0.020 (3)
C1	0.036 (3)	0.083 (5)	0.051 (4)	0.0065 (19)	0.006 (3)	−0.017 (3)
N1	0.052 (8)	0.050 (5)	0.053 (9)	−0.007 (5)	0.018 (6)	−0.012 (5)
C7	0.133 (11)	0.082 (6)	0.073 (8)	−0.028 (8)	0.054 (8)	−0.021 (6)
C5	0.054 (6)	0.074 (6)	0.034 (6)	−0.002 (5)	0.012 (5)	−0.014 (4)
C4	0.053 (7)	0.070 (8)	0.041 (7)	0.015 (5)	0.008 (6)	−0.001 (4)
C6	0.037 (8)	0.087 (10)	0.057 (11)	0.002 (5)	0.028 (7)	−0.001 (6)
N2	0.042 (12)	0.093 (17)	0.039 (15)	−0.012 (11)	0.021 (10)	−0.002 (11)
C8	0.030 (4)	0.074 (9)	0.050 (10)	−0.004 (5)	0.012 (6)	−0.024 (8)

Table 3. Geometric parameters (Å, °)

O20—C20	1.259 (2)	C3—C2	1.510 (6)
O30—C30	1.266 (2)	C2—C1	1.514 (5)
O10—C10	1.258 (2)	C1—C1i	1.516 (6)
N21—C20	1.336 (2)	N1—C7	1.140 (6)
N20—C20	1.337 (2)	C5—C6	1.513 (8)
N31—C30	1.325 (2)	C5—C4	1.513 (7)
N30—C30	1.332 (2)	C4—C4i	1.520 (8)
N11—C10	1.337 (2)	C6—N2	1.437 (8)
C10—N10	1.338 (2)	N2—C8	1.142 (8)
C3—N1	1.437 (6)		
O20—C20—N21	120.94 (15)	N1—C3—C2	111.4 (6)
O20—C20—N20	120.69 (16)	C3—C2—C1	114.5 (5)
N21—C20—N20	118.37 (16)	C2—C1—C1i	114.0 (5)
O30—C30—N31	120.94 (16)	C7—N1—C3	177.3 (14)
O30—C30—N30	120.73 (16)	C6—C5—C4	114.2 (8)
N31—C30—N30	118.32 (18)	C5—C4—C4i	113.4 (8)
O10—C10—N11	121.05 (16)	N2—C6—C5	111.2 (9)
O10—C10—N10	121.23 (17)	C8—N2—C6	176 (3)
N11—C10—N10	117.71 (18)		
N2—C6—C5—C4	−70.3 (18)	N1—C3—C2—C1	62.5 (11)
C6—C5—C4—C4i	−178.0 (14)	C3—C2—C1—C1i	176.8 (8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
N2	C6	C5	C4	-70.3(18)

				-
C6	C5	C4	C4i	178.0(14)
N1	C3	C2	C1	62.5(11)
C3	C2	C1	C1i	176.8(8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—*H*···*A*	*D*—*H*	H···A	*D*···*A*	*D*—*H*···*A*
N21—H21A···O10ii	0.88	2.15	3.017 (2)	168
N21—H21B···O30iii	0.88	2.21	3.0374 (19)	157
N20—H20A···O30ii	0.88	2.15	3.0109 (19)	165
N20—H20B···O10iv	0.88	2.12	2.9606 (19)	160
N31—H31A···O20v	0.88	2.15	3.008 (2)	164
N31—H31B···O10iv	0.88	2.1	2.960 (2)	164
N30—H30A···O10vi	0.88	2.24	3.103 (2)	169
N30—H30B···O20vii	0.88	2.22	3.048 (2)	157
N11—H11A···O30viii	0.88	2.14	2.998 (2)	163
N11—H11B···O30ix	0.88	2.18	3.023 (2)	160
N10—H10A···O20v	0.88	2.12	2.949 (2)	158
N10—H10B···O20x	0.88	2.18	3.004 (2)	156

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

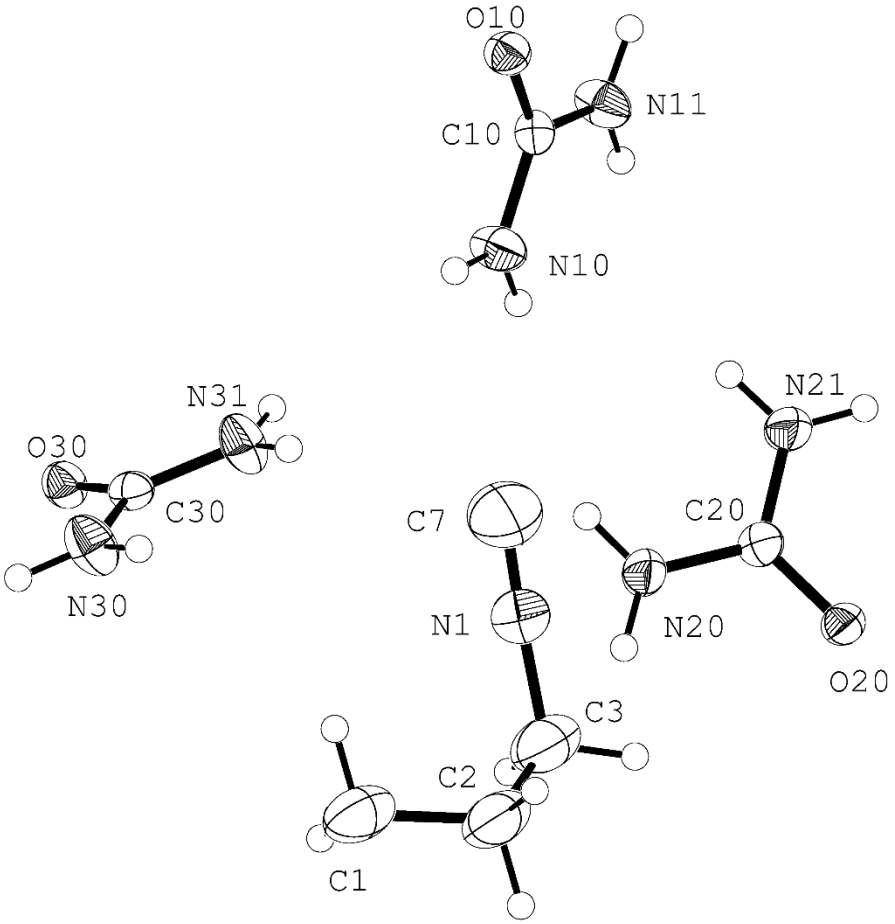
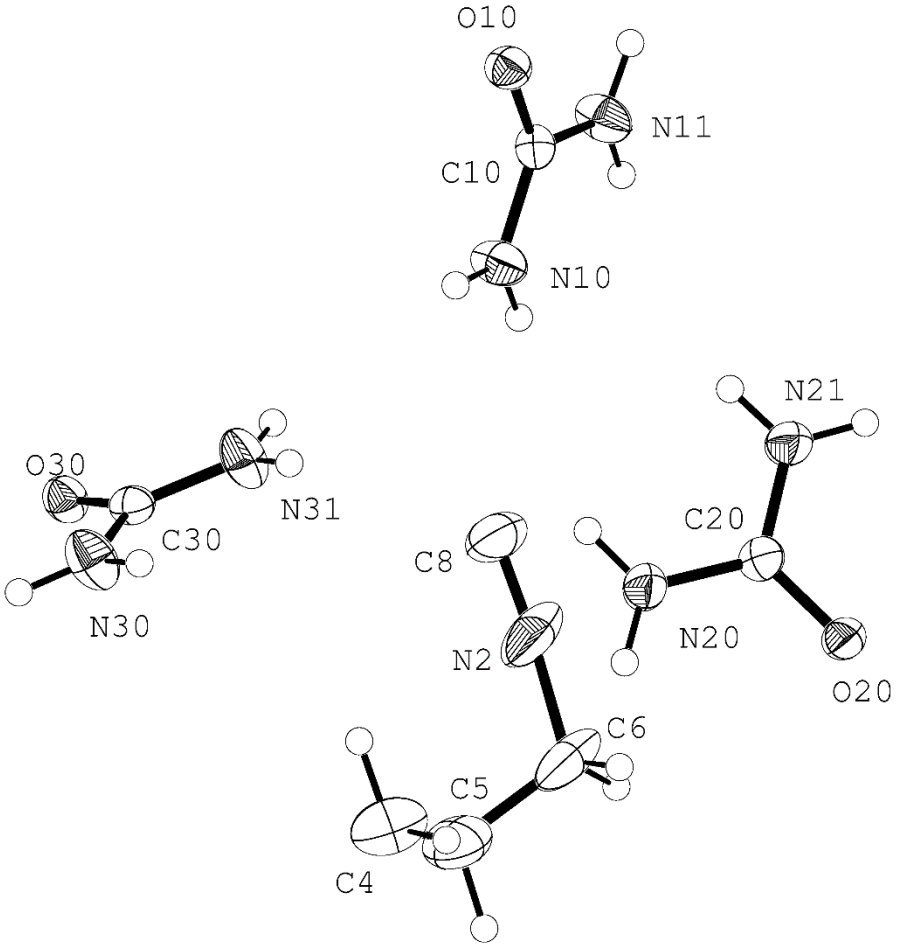


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-diisocyanohexane/urea at 183 K (KP2400).
2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Siemens (1995). SMART software. Version 4.044. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
4. Siemens P4 diffractometer equipped with a CCD Detector.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **42**, 339–341 (2009).

Structure report for 1,6-diisocyanohexane/urea at 200 K[1]

Introduction

This data set was collected in 2012 by Keith Alquist using a Bruker P4 diffractometer equipped with an APEX II detector.[11] (See laboratory notebook KEA-C-277.) The crystal was a fragment from a crystal grown by Mark Hollingsworth (MDH-K-150-19). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the end groups to be disordered between major and minor sites. The model shown here allows the isocyano end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 63.6% and 36.4%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 78.2°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 340 µm x 200 µm x 80 µm. The crystal was cooled to 200 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 20 seconds and the frame width was 0.10º.[3] The crystal to detector distance was 80.00 mm.

The unit cell parameters were determined[11,4] from 3107 input reflections whose minimum and the maximum 2-theta values were 5.70 and 51.96, respectively. The errors are reported after corrections for the goodness of fit (4.48). The cell volume is 1267.2 (2) Å^3.

a = 8.1143 (8) Å	α = 90°
b = 10.8714 (11) Å	β = 95.108 (4)°
c = 14.4223 (12) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.301 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 11320 reflections of which 297 were rejected. After merging Friedel opposites, there were 2704 unique reflections, of which 1899 had I > 2sigma(I). The R(int) was 0.0728, and the R(sigma) was 0.0537. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.103 mm^{-1}. The absorption correction was made using SADABS.[3, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-diisocyanohexane/urea refined the dinitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kea_C277_iso.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.868 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

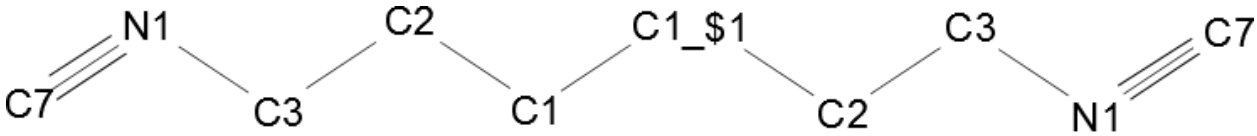


Figure 1: Atomic labeling scheme for part 1 (major part)

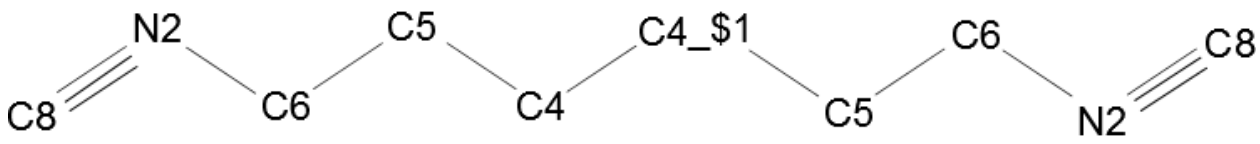


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, -y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 N1 C6 N2
SADI C3 C7 C6 C8
SADI N1 C2 N2 C5
FLAT C2 C3 N1 C7
FLAT C5 C6 N2 C8
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. At this stage, the hydrogens on the urea molecules were allowed to refine freely. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was refined to 0.030(2).

The goodness of fit[7] was 1.156 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.154 for all of the data. R1 was 0.0648 for all 2704 data and 0.0437 for data with $I>2\sigma(I)$; the wR2 value was 0.0780 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 N1 C6 N2
SADI C3 C7 C6 C8
SADI N1 C2 N2 C5

FLAT C2 C3 N1 C7
FLAT C5 C6 N2 C8
```

(All but two EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping isocyano carbons were connected to the correct atoms.

The following reflections were omitted due to their ΔF^2/esd being greater than 10.

OMIT -7 0 3

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	340 x 200 x 80 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	3107
Lattice parameters	a = 8.1143 (8)Å b = 10.8714 (11) Å c = 14.4223 (12) Å α = 90° β = 95.108 (4)° γ = 90° V = 1267.2 (2) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.301
F_{000}	532
μ (MoK$_\alpha$)	0.103 mm^{-1}
Temperature	200 K

B. Intensity measurements

Diffractometer	Bruker P4 CCD, APEX II detector
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K$_\alpha$ (λ = 0.71073 Å)
Crystal to detector distance	80.00 mm
Time per frame	10 s
Temperature	200 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.85°
θ_{max}	25.98°
h k l range	h = -10 to 10 k = -13 to 13

	l = -18 to 18
No. of reflections measured	Total: 11023
	Unique 2704 (R_{int} = 0.0728)
	I > 2σ(I) = 1899
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	2704
No. variables	237
No. Restraints	27
Reflection:parameter ratio	11.41
For I > 2.00σ(I)	8.01
No. Reflections used in refinement	2704
Final R indices [I > 2σ(I)] R1	0.0437
Final R indices [all data]; R1, wR2	0.0648; 0.0780
Goodness of Fit (s)	1.156
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.236 e/Å^3
Minimum peak in final diff. map	-0.208 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-diisocyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99636 (12)	0.41994 (8)	0.65313 (7)	0.0288 (3)	
O30	−0.02839 (12)	0.08840 (8)	0.65409 (7)	0.0288 (3)	
O10	−0.01241 (12)	0.75110 (8)	0.68095 (6)	0.0283 (3)	
N21	0.80871 (19)	0.52092 (13)	0.72988 (10)	0.0391 (4)	
H21A	0.860 (2)	0.5902 (16)	0.7241 (12)	0.047*	
H21B	0.720 (2)	0.5195 (16)	0.7595 (12)	0.047*	
N20	0.78670 (18)	0.31347 (12)	0.70553 (10)	0.0360 (4)	
H20A	0.829 (2)	0.2427 (16)	0.6849 (11)	0.043*	
H20B	0.702 (2)	0.3100 (15)	0.7317 (12)	0.043*	

N31	0.19636 (19)	0.19564 (13)	0.70987 (10)	0.0381 (4)	
H31A	0.152 (2)	0.2627 (17)	0.6869 (12)	0.046*	
H31B	0.296 (2)	0.1950 (15)	0.7397 (12)	0.046*	
N30	0.1820 (2)	−0.01033 (13)	0.73468 (10)	0.0398 (4)	
H30A	0.123 (2)	−0.0775 (16)	0.7333 (12)	0.048*	
H30B	0.272 (2)	−0.0073 (16)	0.7712 (12)	0.048*	
C20	0.86705 (18)	0.41831 (12)	0.69493 (10)	0.0267 (3)	
C30	0.11216 (19)	0.09142 (12)	0.69853 (9)	0.0256 (3)	
N11	−0.03036 (18)	0.85431 (12)	0.54501 (10)	0.0348 (3)	
H11A	−0.043 (2)	0.9216 (15)	0.5732 (12)	0.042*	
H11B	−0.014 (2)	0.8583 (15)	0.4871 (12)	0.042*	
C10	−0.00514 (17)	0.75134 (13)	0.59397 (9)	0.0257 (3)	
N10	0.03080 (18)	0.64973 (12)	0.54896 (10)	0.0353 (4)	
H10A	0.033 (2)	0.5809 (16)	0.5793 (12)	0.042*	
H10B	0.016 (2)	0.6454 (15)	0.4884 (12)	0.042*	
C3	0.5148 (12)	0.2797 (4)	0.4327 (6)	0.059 (2)	0.636
H3A	0.6051	0.3347	0.4166	0.070*	0.636
H3B	0.4391	0.2676	0.3757	0.070*	0.636
C2	0.5880 (5)	0.1571 (3)	0.4628 (3)	0.0639 (12)	0.636
H2A	0.6683	0.1699	0.5177	0.077*	0.636
H2B	0.6497	0.124	0.4121	0.077*	0.636
C1	0.4618 (5)	0.0623 (3)	0.4871 (4)	0.0561 (14)	0.636
H1A	0.3785	0.0519	0.4332	0.067*	0.636
H1B	0.4038	0.0933	0.5399	0.067*	0.636
N1	0.4266 (13)	0.3382 (8)	0.5009 (7)	0.0460 (18)	0.636
C7	0.3542 (16)	0.3876 (16)	0.5518 (7)	0.068 (3)	0.636
C5	0.5070 (11)	0.1508 (5)	0.4286 (4)	0.0593 (19)	0.364
H5A	0.5782	0.119	0.3817	0.071*	0.364
H5B	0.3912	0.1486	0.4004	0.071*	0.364
C4	0.5222 (14)	0.0662 (3)	0.5119 (5)	0.058 (3)	0.364
H4A	0.4489	0.0965	0.5583	0.070*	0.364
H4B	0.6374	0.0692	0.5409	0.070*	0.364
C6	0.554 (2)	0.2825 (7)	0.4499 (10)	0.070 (5)	0.364
H6A	0.6726	0.2858	0.4724	0.084*	0.364
H6B	0.5385	0.3309	0.3916	0.084*	0.364
N2	0.461 (2)	0.3384 (15)	0.5174 (13)	0.046 (3)	0.364
C8	0.395 (3)	0.374 (3)	0.5768 (13)	0.086 (7)	0.364

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0307 (6)	0.0235 (5)	0.0338 (6)	0.0008 (4)	0.0108 (4)	0.0013 (4)
O30	0.0280 (6)	0.0239 (5)	0.0342 (6)	0.0010 (4)	0.0015 (5)	0.0002 (4)
O10	0.0344 (6)	0.0256 (5)	0.0253 (5)	−0.0004 (4)	0.0055 (4)	0.0001 (4)
N21	0.0428 (9)	0.0241 (7)	0.0539 (9)	0.0005 (6)	0.0243 (7)	−0.0018 (6)
N20	0.0344 (9)	0.0246 (7)	0.0515 (9)	−0.0015 (6)	0.0176 (7)	0.0012 (6)
N31	0.0347 (9)	0.0242 (7)	0.0530 (9)	−0.0026 (6)	−0.0089 (7)	0.0025 (6)
N30	0.0402 (10)	0.0256 (7)	0.0509 (9)	0.0016 (6)	−0.0105 (7)	0.0058 (6)
C20	0.0291 (9)	0.0245 (8)	0.0268 (7)	0.0015 (6)	0.0042 (6)	0.0031 (6)
C30	0.0298 (9)	0.0240 (8)	0.0237 (7)	0.0021 (6)	0.0057 (6)	−0.0004 (5)
N11	0.0532 (9)	0.0235 (7)	0.0277 (7)	0.0019 (6)	0.0045 (6)	0.0019 (5)
C10	0.0241 (8)	0.0241 (8)	0.0289 (7)	−0.0027 (6)	0.0032 (6)	−0.0005 (6)
N10	0.0566 (10)	0.0232 (7)	0.0268 (7)	0.0025 (6)	0.0080 (6)	−0.0007 (5)
C3	0.062 (5)	0.074 (4)	0.042 (2)	−0.001 (2)	0.017 (3)	−0.012 (2)
C2	0.045 (3)	0.088 (3)	0.061 (3)	0.000 (2)	0.0197 (19)	−0.020 (2)
C1	0.037 (3)	0.079 (3)	0.053 (3)	0.0043 (16)	0.006 (2)	−0.021 (2)
N1	0.036 (4)	0.063 (3)	0.039 (3)	−0.011 (2)	0.003 (3)	−0.009 (2)
C7	0.065 (4)	0.077 (5)	0.066 (5)	−0.011 (3)	0.026 (4)	−0.015 (5)
C5	0.070 (6)	0.073 (5)	0.038 (4)	0.000 (4)	0.017 (3)	−0.007 (3)
C4	0.056 (6)	0.080 (6)	0.039 (4)	0.008 (4)	0.003 (4)	−0.008 (3)
C6	0.045 (6)	0.107 (9)	0.063 (9)	0.001 (4)	0.028 (6)	−0.005 (5)
N2	0.026 (6)	0.077 (5)	0.036 (6)	−0.006 (4)	0.000 (4)	−0.010 (4)
C8	0.129 (18)	0.074 (7)	0.063 (9)	−0.009 (11)	0.047 (10)	−0.006 (8)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2558 (16)	C3—C2	1.507 (6)
O30—C30	1.2579 (17)	C2—C1	1.515 (5)
O10—C10	1.2612 (16)	C1—C1i	1.523 (5)
N21—C20	1.3286 (18)	N1—C7	1.118 (4)
N20—C20	1.3286 (18)	C5—C6	1.506 (7)
N31—C30	1.3256 (19)	C5—C4	1.510 (6)
N30—C30	1.3283 (19)	C4—C4i	1.516 (7)
N11—C10	1.3297 (18)	C6—N2	1.420 (6)
C10—N10	1.3268 (18)	N2—C8	1.119 (7)
C3—N1	1.418 (4)		
O20—C20—N20	120.46 (13)	N1—C3—C2	114.0 (5)
O20—C20—N21	120.76 (13)	C3—C2—C1	114.2 (4)
N20—C20—N21	118.79 (14)	C2—C1—C1i	113.2 (4)
O30—C30—N31	121.28 (13)	C7—N1—C3	177.1 (12)
O30—C30—N30	120.94 (14)	C6—C5—C4	114.5 (6)
N31—C30—N30	117.77 (15)	C5—C4—C4i	113.4 (6)
O10—C10—N10	121.11 (13)	N2—C6—C5	114.0 (7)
O10—C10—N11	120.76 (13)	C8—N2—C6	173 (2)
N10—C10—N11	118.12 (13)		
N2—C6—C5—C4	−57.7 (16)	N1—C3—C2—C1	60.0 (9)
C6—C5—C4—C4i	−178.8 (12)	C3—C2—C1—C1i	177.4 (6)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
N2	C6	C5	C4	-57.7(16)
C6	C5	C4	C4i	-178.8(12)
N1	C3	C2	C1	60.0(9)
C3	C2	C1	C1i	177.4(6)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—H···A	*D—H*	H···A	*D···A*	*D—H···A*
N21—H21A···O10ii	0.868 (18)	2.153 (18)	3.0082 (18)	168.5 (16)
N21—H21B···O30iii	0.870 (18)	2.208 (18)	3.0315 (17)	157.9 (16)
N20—H20A···O30ii	0.903 (18)	2.109 (18)	2.9978 (18)	168.1 (15)
N20—H20B···O10iv	0.816 (18)	2.168 (18)	2.9568 (17)	162.6 (17)
N31—H31A···O20v	0.866 (18)	2.155 (19)	3.0021 (18)	165.9 (16)
N31—H31B···O10iv	0.884 (19)	2.097 (19)	2.9496 (18)	161.8 (15)
N30—H30A···O10vi	0.874 (18)	2.258 (18)	3.0982 (18)	161.4 (16)
N30—H30B···O20vii	0.862 (19)	2.23 (2)	3.0415 (18)	156.3 (16)
N11—H11A···O30viii	0.848 (17)	2.153 (17)	2.9912 (17)	169.3 (17)
N11—H11B···O30ix	0.858 (17)	2.174 (18)	3.0173 (16)	167.5 (15)
N10—H10A···O20v	0.866 (17)	2.084 (18)	2.9413 (17)	170.3 (16)
N10—H10B···O20x	0.872 (17)	2.155 (18)	3.0006 (16)	163.2 (15)

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2; (iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z; (vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z; (ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

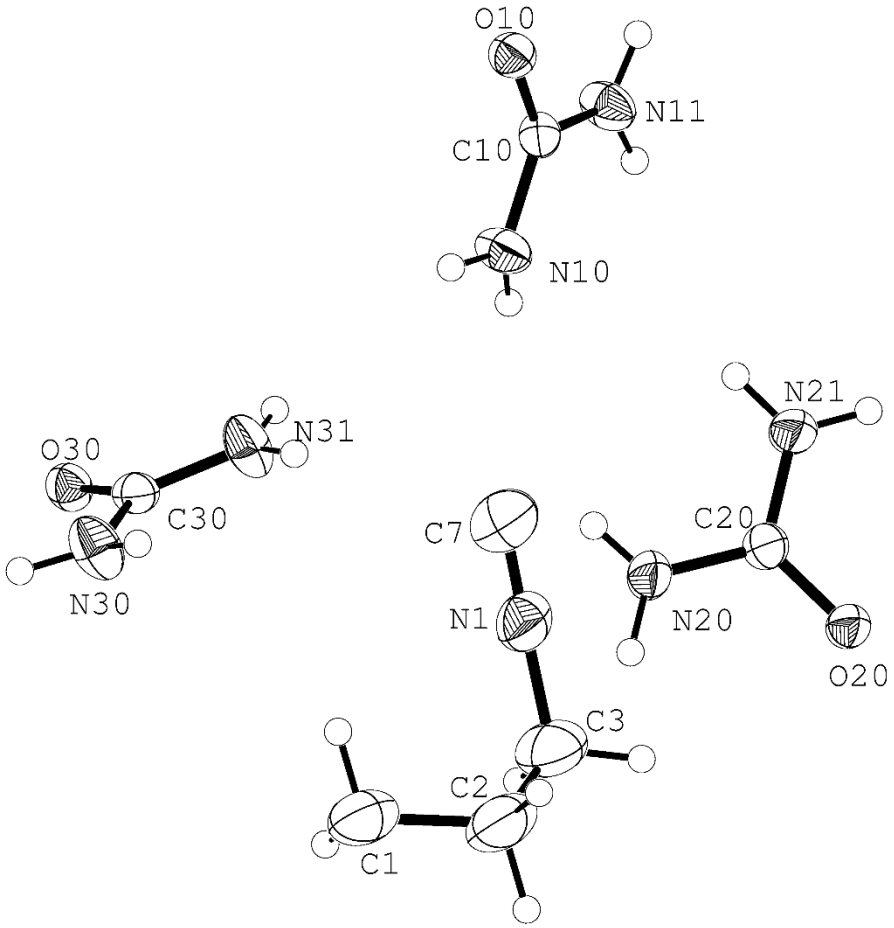
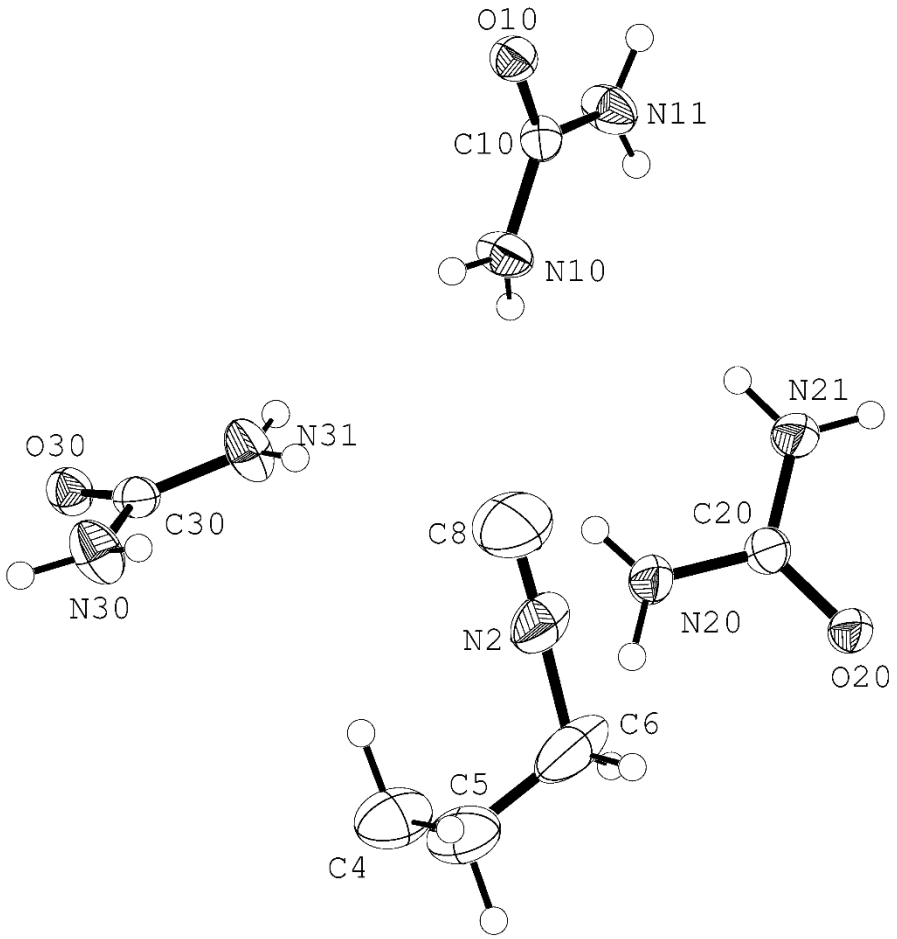


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-diisocyanohexane/urea at 200 K (KEA-C-277).
2. Bruker P4 diffractometer equipped with an APEX II CCD detector
3. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999); (DOI: 10.1021/ja9919534).
4. Data collected using the Bruker APEX2 software package.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallographica Section A* **64**, 112-122 (2008); (DOI: 10.1107/s0108767307043930).
8. Standard deviation of an observation of unit weight:

$$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$$

where n is the number of reflections and p is the total number of parameters refined.

$$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$$

where P is

$$P = [2Fc^2 + \max(Fo^2,0)]/3.$$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.

Structure report for 1,6-diisocyanohexane/urea at 203 K[1]

Introduction

The data for this crystal was collected in 2000 by Kevin Pate on a Siemens P4 diffractometer equipped with a SMART 1000 CCD detector and was originally labeled "KP2300". (See laboratory notebook KLP A-154.) The original crystal was from Mark Hollingsworth (MDH-K-150-18). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 64.65% and 35.35%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 77.93°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 500 µm x 400 µm x 200 µm. The crystal was cooled to 203 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 10 seconds and the frame width was 0.30º. [8] The crystal to detector distance was 49.87 mm.

The unit cell parameters were determined[9,4] from 1597 input reflections whose minimum and the maximum 2-theta values were 5.66 and 47.44, respectively. The errors are reported after corrections for the goodness of fit (1.52). The cell volume is 1281.6(4) Å^3.

a = 8.1494 (13) Å	α = 90°
b = 10.9152 (18) Å	β = 95.110 (3)°
c = 14.465 (2) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.287 g/cm^3. Based on the systematic absences of

$$h00: \ h+l \neq 2n$$
$$0k0: \ k \neq 2n$$
$$h00: \ h \neq 2n$$
$$00l: \ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n \ (\#14).$$

Data Reduction:

The data set contained 6041 reflections of which 164 were rejected. After merging Friedel opposites, there were 2000 unique reflections, of which 1557 had I > 2sigma(I). The R(int) was 0.0233, and the R(sigma) was 0.0262. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.102 mm^{-1}. The absorption correction was made using SADABS. [8, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-diisocyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kp2300_iso.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.870 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

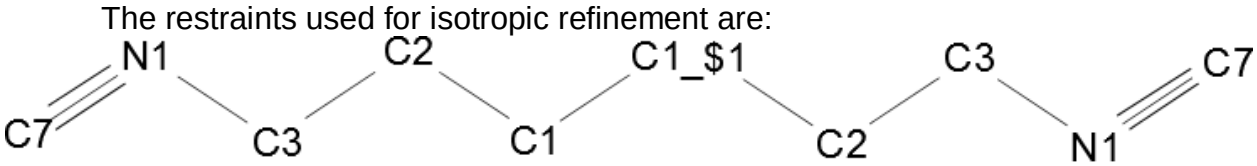


Figure 1: Atomic labeling scheme for part 1 (major part)

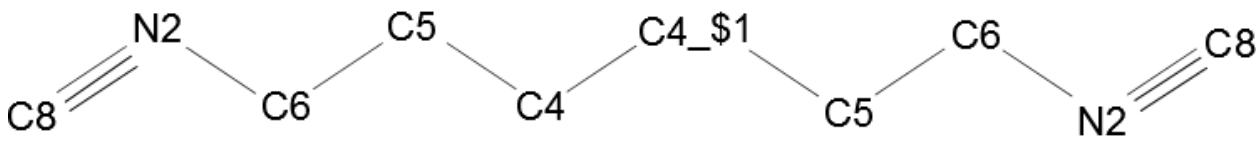


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 N1 C7
FLAT C5 C6 N2 C8
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.271 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.263 for all of the data. R1 was 0.0555 for all 2000 data and 0.0409 for data with $I>2\sigma(I)$; the wR2 value was 0.0979 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 N1 C7
FLAT C5 C6 N2 C8
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 N1 C6 N2
SADI C3 C7 C6 C8
SADI N1 C2 N2 C5
```

Also, the following EADP constraint was used:

```
EADP N1 N2
```

The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	500 x 400 x 200 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	1597
Lattice parameters	a = 8.1494 (13) Å b = 10.9152 (18) Å c = 14.465 (2) Å α = 90° β = 95.110 (3)° γ = 90° V = 1281.6 (4) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.287
F_{000}	532
μ (MoK_α)	0.102 mm^{-1}
Temperature	203 K

B. Intensity measurements

Diffractometer	Siemens P4, SMART 1000 CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K_α (λ = 0.71073 Å)
Crystal to detector distance	49.87 mm
Time per frame	20 s
Temperature	203 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.83°
θ_{max}	23.72°
h k l range	h = -9 to 9 k = -12 to 11 l = -15 to 16
No. of reflections measured	Total: 5877 Unique 2000 (R_{int} = 0.0233)

	$I > 2\sigma(I)$ = 1557
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations ($I > 2.00\sigma(I)$)	1557
No. variables	193
No. Restraints	27
Reflection:parameter ratio	10.36
For $I > 2.00\sigma(I)$	8.07
No. Reflections used in refinement	2000
Final R indices [$I > 2\sigma(I)$] R1	0.0409
Final R indices [all data]; R1, wR2	0.0555; 0.0979
Goodness of Fit (s)	1.263
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.167 e/Å^3
Minimum peak in final diff. map	-0.192 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-diisocyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99621 (15)	0.41983 (10)	0.65320 (9)	0.0299 (4)	
O30	−0.02791 (15)	0.08825 (10)	0.65425 (9)	0.0303 (4)	
O10	−0.01227 (15)	0.75108 (11)	0.68088 (9)	0.0289 (3)	
N21	0.8084 (2)	0.52076 (14)	0.72991 (12)	0.0402 (5)	
H21A	0.8597	0.5899	0.7242	0.048*	
H21B	0.719	0.5185	0.7585	0.048*	
N20	0.78649 (19)	0.31348 (14)	0.70572 (12)	0.0377 (5)	
H20A	0.8231	0.2454	0.684	0.045*	
H20B	0.6973	0.3133	0.7346	0.045*	
N31	0.1959 (2)	0.19543 (14)	0.70972 (13)	0.0399 (5)	
H31A	0.1539	0.2629	0.686	0.048*	

H31B	0.2925	0.1962	0.7406	0.048*	
N30	0.1819 (2)	−0.01021 (14)	0.73496 (13)	0.0414 (5)	
H30A	0.1304	−0.0799	0.728	0.050*	
H30B	0.2787	−0.0070	0.7655	0.050*	
C20	0.8671 (2)	0.41817 (16)	0.69481 (14)	0.0268 (5)	
C30	0.1127 (2)	0.09135 (16)	0.69885 (13)	0.0257 (5)	
N11	−0.0298 (2)	0.85435 (14)	0.54504 (12)	0.0366 (4)	
H11A	−0.0509	0.9226	0.5728	0.044*	
H11B	−0.0247	0.8532	0.4852	0.044*	
C10	−0.0054 (2)	0.75132 (16)	0.59435 (14)	0.0257 (4)	
N10	0.0297 (2)	0.64957 (14)	0.54888 (12)	0.0374 (5)	
H10A	0.0483	0.5813	0.5791	0.045*	
H10B	0.0339	0.6515	0.489	0.045*	
C3	0.5139 (14)	0.2800 (5)	0.4339 (8)	0.062 (3)	0.6465
H3A	0.6012	0.3336	0.4147	0.074*	0.6465
H3B	0.4322	0.2691	0.3806	0.074*	0.6465
C2	0.5864 (6)	0.1573 (4)	0.4628 (5)	0.0679 (18)	0.6465
H2A	0.6671	0.1695	0.5164	0.082*	0.6465
H2B	0.6457	0.1251	0.412	0.082*	0.6465
C1	0.4625 (6)	0.0623 (3)	0.4880 (6)	0.062 (2)	0.6465
H1A	0.3785	0.0528	0.4356	0.075*	0.6465
H1B	0.4074	0.0922	0.5411	0.075*	0.6465
N1	0.437 (2)	0.3368 (11)	0.5083 (12)	0.0586 (10)	0.6465
C7	0.3805 (18)	0.3813 (18)	0.5689 (13)	0.104 (6)	0.6465
C5	0.5059 (13)	0.1506 (6)	0.4282 (6)	0.057 (2)	0.3535
H5A	0.3909	0.15	0.4017	0.068*	0.3535
H5B	0.5735	0.1183	0.381	0.068*	0.3535
C4	0.5221 (18)	0.0662 (4)	0.5113 (7)	0.062 (4)	0.3535
H4A	0.4507	0.0962	0.5574	0.074*	0.3535
H4B	0.636	0.0694	0.5395	0.074*	0.3535
C6	0.557 (3)	0.2818 (8)	0.4491 (14)	0.070 (6)	0.3535
H6A	0.6667	0.2831	0.4825	0.084*	0.3535
H6B	0.5616	0.3269	0.3909	0.084*	0.3535
N2	0.441 (4)	0.340 (2)	0.504 (2)	0.0586 (10)	0.3535
C8	0.351 (2)	0.386 (3)	0.549 (2)	0.059 (5)	0.3535

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0328 (7)	0.0246 (7)	0.0339 (9)	0.0012 (5)	0.0116 (6)	0.0010 (6)
O30	0.0308 (7)	0.0245 (7)	0.0351 (9)	0.0004 (5)	0.0011 (6)	0.0001 (6)
O10	0.0357 (7)	0.0264 (7)	0.0250 (9)	0.0001 (5)	0.0052 (6)	0.0001 (6)
N21	0.0433 (10)	0.0258 (9)	0.0551 (13)	0.0006 (7)	0.0244 (9)	−0.0020 (8)
N20	0.0365 (9)	0.0253 (9)	0.0537 (13)	−0.0014 (7)	0.0176 (9)	0.0008 (8)
N31	0.0384 (9)	0.0258 (9)	0.0530 (13)	−0.0030 (7)	−0.0097 (9)	0.0030 (8)
N30	0.0428 (10)	0.0263 (9)	0.0524 (14)	0.0021 (8)	−0.0109 (9)	0.0047 (8)
C20	0.0300 (10)	0.0251 (10)	0.0256 (12)	0.0032 (8)	0.0046 (9)	0.0044 (8)
C30	0.0298 (10)	0.0236 (10)	0.0242 (12)	0.0021 (8)	0.0060 (9)	−0.0009 (8)
N11	0.0565 (11)	0.0248 (9)	0.0285 (11)	0.0036 (8)	0.0029 (9)	0.0011 (8)
C10	0.0246 (9)	0.0244 (10)	0.0283 (12)	−0.0027 (8)	0.0034 (8)	0.0002 (9)
N10	0.0609 (11)	0.0251 (9)	0.0272 (11)	0.0038 (8)	0.0099 (9)	0.0002 (8)
C3	0.054 (6)	0.083 (5)	0.050 (4)	−0.004 (3)	0.015 (3)	−0.011 (3)
C2	0.045 (3)	0.099 (5)	0.062 (5)	−0.001 (3)	0.018 (3)	−0.025 (3)
C1	0.042 (3)	0.090 (5)	0.056 (4)	0.007 (2)	0.006 (3)	−0.022 (3)
N1	0.0557 (17)	0.0705 (17)	0.052 (2)	−0.0097 (13)	0.0195 (14)	−0.0094 (15)
C7	0.148 (13)	0.091 (7)	0.083 (9)	−0.028 (8)	0.058 (9)	−0.018 (6)
C5	0.060 (6)	0.080 (7)	0.031 (6)	−0.001 (5)	0.013 (5)	−0.010 (4)
C4	0.060 (8)	0.074 (8)	0.051 (8)	0.010 (5)	0.006 (6)	−0.003 (5)
C6	0.052 (9)	0.096 (11)	0.068 (12)	0.008 (6)	0.034 (8)	−0.006 (7)
N2	0.0557 (17)	0.0705 (17)	0.052 (2)	−0.0097 (13)	0.0195 (14)	−0.0094 (15)
C8	0.037 (5)	0.084 (10)	0.061 (10)	−0.005 (5)	0.021 (6)	−0.031 (8)

Table 3. Geometric parameters (Å, °)

O20—C20	1.258 (2)	C3—C2	1.508 (7)
O30—C30	1.264 (2)	C2—C1	1.515 (5)
O10—C10	1.258 (2)	C1—C1i	1.518 (6)
N21—C20	1.335 (2)	N1—C7	1.134 (7)
N20—C20	1.334 (2)	C5—C4	1.512 (7)
N31—C30	1.325 (2)	C5—C6	1.514 (8)
N30—C30	1.330 (2)	C4—C4i	1.517 (8)
N11—C10	1.337 (2)	C6—N2	1.436 (8)
C10—N10	1.335 (2)	N2—C8	1.134 (8)
C3—N1	1.434 (6)		
O20—C20—N20	120.69 (16)	N1—C3—C2	111.2 (6)
O20—C20—N21	120.85 (16)	C3—C2—C1	114.9 (5)
N20—C20—N21	118.46 (16)	C2—C1—C1i	113.9 (5)
O30—C30—N31	120.96 (16)	C7—N1—C3	177.9 (15)
O30—C30—N30	120.78 (16)	C4—C5—C6	114.5 (8)
N31—C30—N30	118.25 (18)	C5—C4—C4i	114.0 (9)
O10—C10—N10	121.28 (17)	N2—C6—C5	110.7 (9)
O10—C10—N11	120.98 (17)	C8—N2—C6	179 (3)
N10—C10—N11	117.73 (18)		
N2—C6—C5—C4	−69 (2)	N1—C3—C2—C1	63.1 (13)
C6—C5—C4—C4i	−177.5 (15)	C3—C2—C1—C1i	177.0 (8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
N2	C6	C5	C4	-69(2)
C6	C5	C4	C4i	-177.5(15)
N1	C3	C2	C1	63.1(13)

C3	C2	C1	C1i	177.0(8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—*H*···*A*	*D*—*H*	H···A	*D*···*A*	*D*—*H*···*A*
N21—H21A···O10ii	0.87	2.17	3.024 (2)	169
N21—H21B···O30iii	0.87	2.22	3.043 (2)	157
N20—H20A···O30ii	0.87	2.17	3.014 (2)	165
N20—H20B···O10iv	0.87	2.13	2.967 (2)	160
N31—H31A···O20v	0.87	2.17	3.013 (2)	164
N31—H31B···O10iv	0.87	2.12	2.965 (2)	164
N30—H30A···O10vi	0.87	2.25	3.112 (2)	169
N30—H30B···O20vii	0.87	2.24	3.054 (2)	157
N11—H11A···O30viii	0.87	2.16	3.002 (2)	163
N11—H11B···O30ix	0.87	2.19	3.027 (2)	160
N10—H10A···O20v	0.87	2.13	2.952 (2)	158
N10—H10B···O20x	0.87	2.19	3.009 (2)	156

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2; (iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z; (vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z; (ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

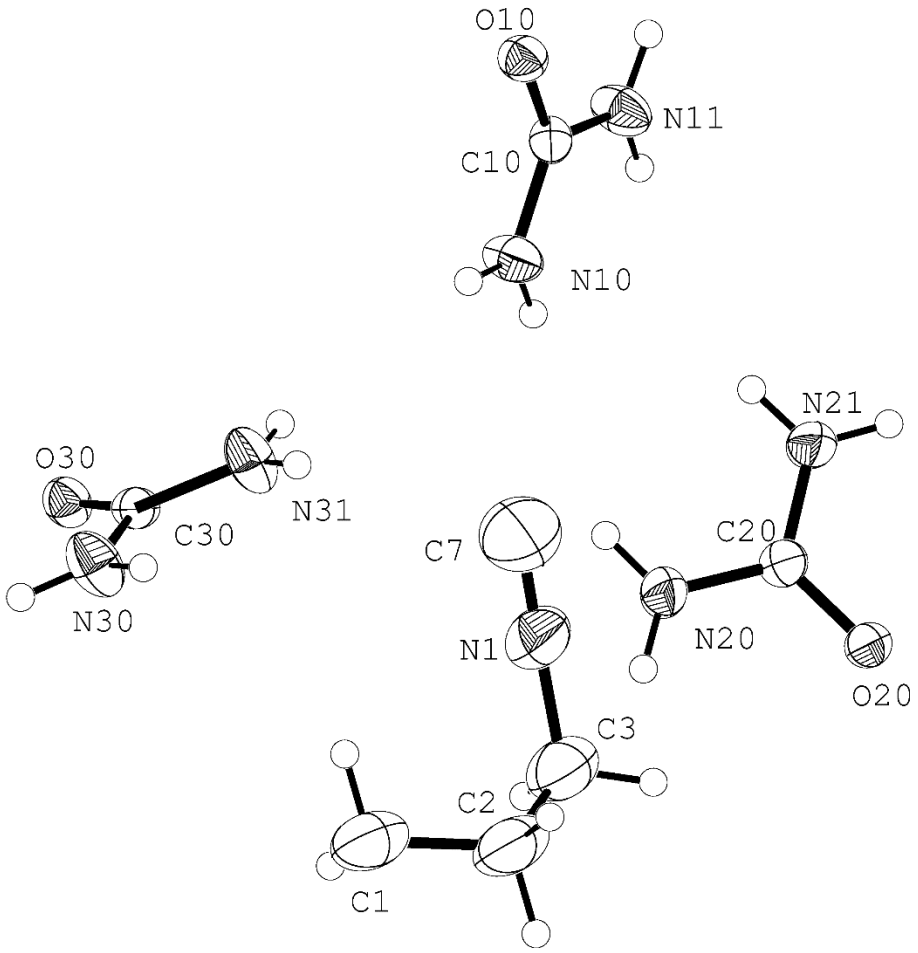
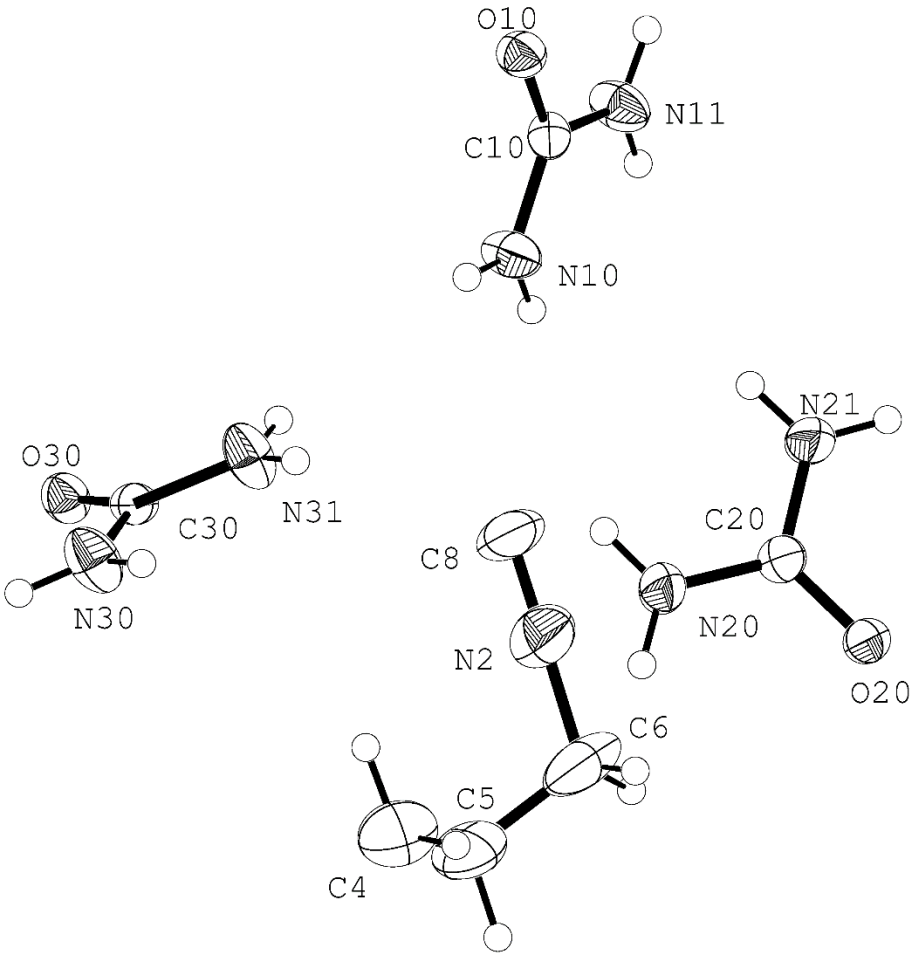


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-diisocyanohexane/urea at 203 K (KP2300).
2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular

level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).

3. Bruker AXS, Inc. (1998). SMART software Version 5.060. Bruker AXS, Inc., Madison, Wisconsin, USA.
4. Siemens P4 diffractometer equipped with a Bruker SMART 1000 CCD Detector.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. *Acta Crystallogr. A***51**, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. J. Appl. Cryst. 42, 339–341 (2009).

Structure report for 1,6-diisocyanohexane/urea at 223 K[1]

Introduction

The data for this crystal was collected in 2000 by Kevin Pate on a Siemens P4 diffractometer equipped with Bruker SMART 1000 CCD detector and was originally labeled "kp2200". (See laboratory notebook KLP A-153.) The original crystal was from Mark Hollingsworth (MDH-K-150-18). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 66.26% and 33.74%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 78.82°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 500 µm x 400 µm x 200 µm. The crystal was cooled to 223 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 10 seconds and the frame width was 0.30º. [8] The crystal to detector distance was 49.87 mm.

The unit cell parameters were determined[9,4] from 2119 input reflections whose minimum and the maximum 2-theta values were 5.00 and 48.70, respectively. The errors are reported after corrections for the goodness of fit (1.54). The cell volume is 1287.3 (3) Å^3.

a = 8.1634 (12) Å	α = 90°
b = 10.9273 (16) Å	β = 95.022 (2)°
c = 14.486 (2) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.281 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 6398 reflections of which 168 were rejected. After merging Friedel opposites, there were 2161 unique reflections, of which 1726 had I > 2sigma(I). The R(int) was 0.0194, and the R(sigma) was 0.0216. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.101 mm^{-1}. The absorption correction was made using SADABS. [8, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea where the bromines are not disordered. Previous models of 1,6-diisocyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kp2200_iso.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.870 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

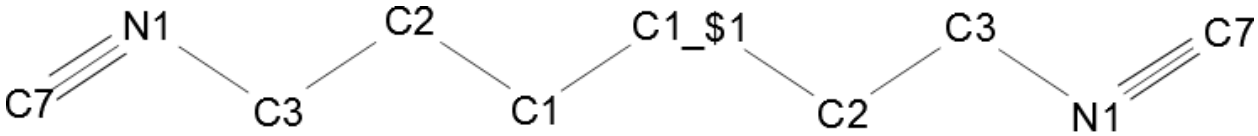


Figure 1: Atomic labeling scheme for part 1 (major part)

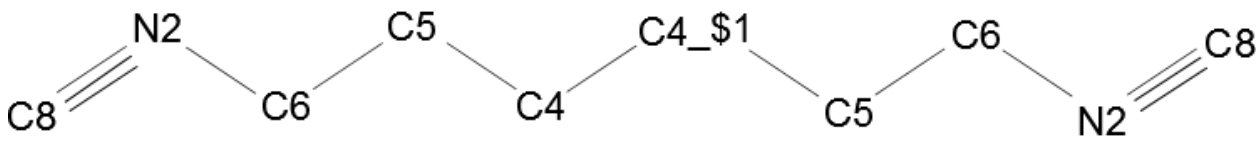


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, -y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 N1 C6 N2
SADI C3 C7 C6 C8
SADI N1 C2 N2 C5
FLAT C2 C3 N1 C7
FLAT C5 C6 N2 C8
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.228 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.226 for all of the data. R1 was 0.0504 for all 2161 data and 0.0383 for data with $I>2\sigma(I)$; the wR2 value was 0.0797 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 N1 C7
FLAT C5 C6 N2 C8
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 N1 C6 N2
SADI C3 C7 C6 C8
SADI N1 C2 N2 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	500 x 400 x 200 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	2119
Lattice parameters	a = 8.1634 (12) Å
	b = 10.9273 (16) Å
	c = 14.486 (2) Å
	α = 90°
	β = 95.022 (2)°
	γ = 90°
	V = 1287.3 (3) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.281
F_{000}	532
μ (MoK$_\alpha$)	0.101 mm^{-1}
Temperature	223 K

B. Intensity measurements

Diffractometer	Siemens P4, SMART 1000 CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K$_\alpha$ (λ = 0.71073 Å)
Crystal to detector distance	49.87 mm
Time per frame	20 s
Temperature	223 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.50°
θ_{max}	24.35°
h k l range	h = -9 to 9
	k = -12 to 11
	l = -15 to 17
No. of reflections measured	Total: 6230

	Unique 2161 (R_{int} = 0.0194)
	I > 2σ(I) = 1726
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	1726
No. variables	199
No. Restraints	27
Reflection:parameter ratio	10.86
For I > 2.00σ(I)	8.67
No. Reflections used in refinement	2161
Final R indices [I > 2σ(I)] R1	0.0383
Final R indices [all data]; R1, wR2	0.0504; 0.0797
Goodness of Fit (s)	1.226
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.192 e/Å^3
Minimum peak in final diff. map	-0.181 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-diisocyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99601 (13)	0.41970 (9)	0.65334 (8)	0.0334 (3)	
O30	−0.02699 (13)	0.08830 (9)	0.65447 (8)	0.0336 (3)	
O10	−0.01218 (13)	0.75083 (10)	0.68079 (8)	0.0325 (3)	
N21	0.80799 (18)	0.52047 (13)	0.72948 (11)	0.0445 (4)	
H21A	0.8585	0.5897	0.7234	0.053*	
H21B	0.7187	0.518	0.7581	0.053*	
N20	0.78694 (17)	0.31345 (13)	0.70589 (11)	0.0419 (4)	
H20A	0.8235	0.2454	0.6842	0.050*	
H20B	0.6979	0.3134	0.7348	0.050*	

N31	0.19630 (18)	0.19539 (13)	0.70969 (11)	0.0448 (4)	
H31A	0.1546	0.2629	0.6861	0.054*	
H31B	0.2927	0.196	0.7404	0.054*	
N30	0.18224 (18)	−0.00995 (13)	0.73516 (11)	0.0468 (4)	
H30A	0.1307	−0.0795	0.7285	0.056*	
H30B	0.2789	−0.0067	0.7656	0.056*	
C20	0.86749 (19)	0.41798 (14)	0.69482 (12)	0.0294 (4)	
C30	0.11306 (19)	0.09166 (14)	0.69876 (11)	0.0287 (4)	
N11	−0.02935 (18)	0.85434 (12)	0.54528 (10)	0.0404 (4)	
H11A	−0.0499	0.9225	0.573	0.048*	
H11B	−0.0243	0.8532	0.4855	0.048*	
C10	−0.00546 (18)	0.75133 (14)	0.59442 (12)	0.0289 (4)	
N10	0.02885 (18)	0.64954 (12)	0.54886 (10)	0.0411 (4)	
H10A	0.047	0.5813	0.579	0.049*	
H10B	0.033	0.6515	0.4891	0.049*	
C3	0.5149 (14)	0.2794 (4)	0.4340 (8)	0.069 (2)	0.6304
H3A	0.6045	0.3333	0.4187	0.082*	0.6304
H3B	0.4407	0.2687	0.3777	0.082*	0.6304
C2	0.5865 (5)	0.1566 (4)	0.4626 (4)	0.0761 (17)	0.6304
H2A	0.6676	0.1683	0.5159	0.091*	0.6304
H2B	0.6449	0.1241	0.4116	0.091*	0.6304
C1	0.4624 (5)	0.0624 (3)	0.4881 (6)	0.068 (2)	0.6304
H1A	0.3781	0.0531	0.4361	0.082*	0.6304
H1B	0.408	0.0925	0.5413	0.082*	0.6304
N1	0.4272 (14)	0.3378 (9)	0.5020 (9)	0.053 (2)	0.6304
C7	0.3526 (14)	0.383 (2)	0.5531 (11)	0.084 (3)	0.6304
C5	0.5070 (11)	0.1501 (6)	0.4291 (5)	0.064 (2)	0.3696
H5A	0.3926	0.1484	0.4021	0.077*	0.3696
H5B	0.5758	0.1187	0.3823	0.077*	0.3696
C4	0.5234 (15)	0.0659 (4)	0.5119 (6)	0.069 (3)	0.3696
H4A	0.4532	0.0961	0.5584	0.083*	0.3696
H4B	0.6374	0.0679	0.5393	0.083*	0.3696
C6	0.555 (2)	0.2814 (7)	0.4503 (12)	0.086 (7)	0.3696
H6A	0.672	0.2842	0.4718	0.103*	0.3696
H6B	0.5393	0.3292	0.393	0.103*	0.3696
N2	0.464 (2)	0.3373 (17)	0.5182 (16)	0.060 (5)	0.3696
C8	0.403 (3)	0.381 (3)	0.5756 (17)	0.096 (7)	0.3696

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0361 (6)	0.0266 (6)	0.0393 (7)	0.0010 (5)	0.0129 (5)	0.0013 (5)
O30	0.0332 (6)	0.0263 (6)	0.0409 (8)	0.0004 (5)	0.0011 (5)	−0.0003 (5)
O10	0.0401 (6)	0.0289 (6)	0.0292 (7)	−0.0004 (5)	0.0062 (5)	0.0002 (5)
N21	0.0490 (9)	0.0280 (8)	0.0605 (11)	0.0013 (7)	0.0278 (8)	−0.0016 (7)
N20	0.0398 (8)	0.0288 (8)	0.0598 (11)	−0.0011 (6)	0.0201 (8)	0.0012 (7)
N31	0.0420 (8)	0.0290 (8)	0.0608 (12)	−0.0034 (7)	−0.0101 (8)	0.0024 (7)
N30	0.0478 (9)	0.0290 (8)	0.0610 (12)	0.0028 (7)	−0.0110 (8)	0.0059 (8)
C20	0.0322 (8)	0.0268 (8)	0.0297 (10)	0.0030 (7)	0.0053 (7)	0.0043 (7)
C30	0.0336 (9)	0.0268 (9)	0.0265 (10)	0.0022 (7)	0.0064 (7)	−0.0010 (7)
N11	0.0608 (10)	0.0284 (8)	0.0318 (9)	0.0032 (7)	0.0033 (7)	0.0023 (7)
C10	0.0278 (8)	0.0267 (8)	0.0325 (10)	−0.0025 (7)	0.0038 (7)	−0.0008 (7)
N10	0.0646 (10)	0.0274 (8)	0.0324 (9)	0.0036 (7)	0.0099 (8)	0.0005 (6)
C3	0.072 (6)	0.088 (5)	0.049 (3)	0.000 (3)	0.018 (3)	−0.013 (3)
C2	0.052 (3)	0.106 (4)	0.073 (4)	0.001 (3)	0.022 (3)	−0.026 (3)
C1	0.043 (3)	0.096 (5)	0.066 (4)	0.009 (2)	0.008 (3)	−0.023 (3)
N1	0.040 (5)	0.072 (3)	0.048 (4)	−0.008 (3)	0.006 (4)	−0.013 (3)
C7	0.068 (4)	0.096 (5)	0.091 (8)	−0.018 (4)	0.028 (5)	−0.028 (6)
C5	0.066 (5)	0.087 (6)	0.041 (5)	0.003 (5)	0.017 (4)	−0.006 (4)
C4	0.064 (7)	0.093 (8)	0.050 (6)	0.010 (5)	0.006 (5)	−0.003 (4)
C6	0.063 (8)	0.118 (12)	0.083 (13)	−0.001 (6)	0.043 (8)	−0.006 (7)
N2	0.036 (7)	0.093 (7)	0.051 (9)	−0.012 (4)	0.000 (5)	−0.005 (5)
C8	0.119 (16)	0.102 (9)	0.074 (11)	−0.025 (14)	0.056 (13)	−0.023 (9)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2540 (18)	C3—C2	1.507 (6)
O30—C30	1.2616 (19)	C2—C1	1.512 (5)
O10—C10	1.2572 (19)	C1—C1i	1.523 (6)
N21—C20	1.336 (2)	N1—C7	1.116 (5)
N20—C20	1.335 (2)	C5—C4	1.509 (7)
N31—C30	1.324 (2)	C5—C6	1.512 (8)
N30—C30	1.333 (2)	C4—C4i	1.521 (8)
N11—C10	1.337 (2)	C6—N2	1.420 (7)
C10—N10	1.335 (2)	N2—C8	1.115 (7)
C3—N1	1.419 (5)		
O20—C20—N20	120.80 (14)	N1—C3—C2	114.7 (6)
O20—C20—N21	120.96 (14)	C3—C2—C1	114.9 (5)
N20—C20—N21	118.23 (14)	C2—C1—C1i	113.5 (5)
O30—C30—N31	121.24 (15)	C7—N1—C3	177.2 (12)
O30—C30—N30	120.70 (15)	C4—C5—C6	114.4 (7)
N31—C30—N30	118.06 (16)	C5—C4—C4i	113.3 (8)
O10—C10—N10	121.17 (15)	N2—C6—C5	114.1 (8)
O10—C10—N11	121.10 (15)	C8—N2—C6	175.0 (19)
N10—C10—N11	117.72 (15)		
N2—C6—C5—C4	−57.9 (19)	N1—C3—C2—C1	58.7 (12)
C6—C5—C4—C4i	−179.2 (13)	C3—C2—C1—C1i	177.1 (8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
N2	C6	C5	C4	-57.9(19)
C6	C5	C4	C4i	-179.2(13)
N1	C3	C2	C1	58.7(12)

C3	C2	C1	C1i	177.1(8)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—*H*···*A*	*D*—*H*	H···A	*D*···*A*	*D*—*H*···*A*
N21—H21A···O10ii	0.87	2.17	3.0282 (18)	169
N21—H21B···O30iii	0.87	2.23	3.0517 (18)	157
N20—H20A···O30ii	0.87	2.17	3.0188 (18)	165
N20—H20B···O10iv	0.87	2.14	2.9730 (17)	160
N31—H31A···O20v	0.87	2.17	3.0189 (18)	164
N31—H31B···O10iv	0.87	2.12	2.9694 (19)	164
N30—H30A···O10vi	0.87	2.27	3.1231 (19)	168
N30—H30B···O20vii	0.87	2.24	3.0587 (19)	156
N11—H11A···O30viii	0.87	2.16	3.0055 (19)	164
N11—H11B···O30ix	0.87	2.2	3.0348 (19)	160
N10—H10A···O20v	0.87	2.13	2.9566 (18)	159
N10—H10B···O20x	0.87	2.2	3.0149 (19)	156

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

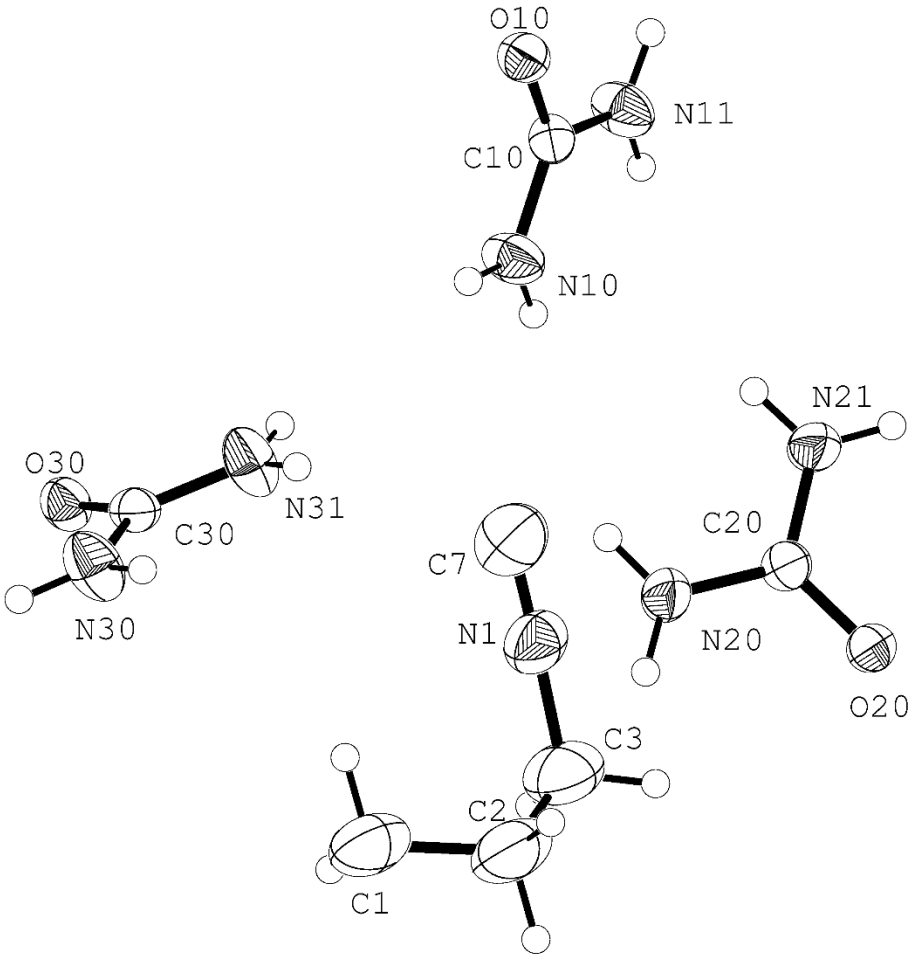
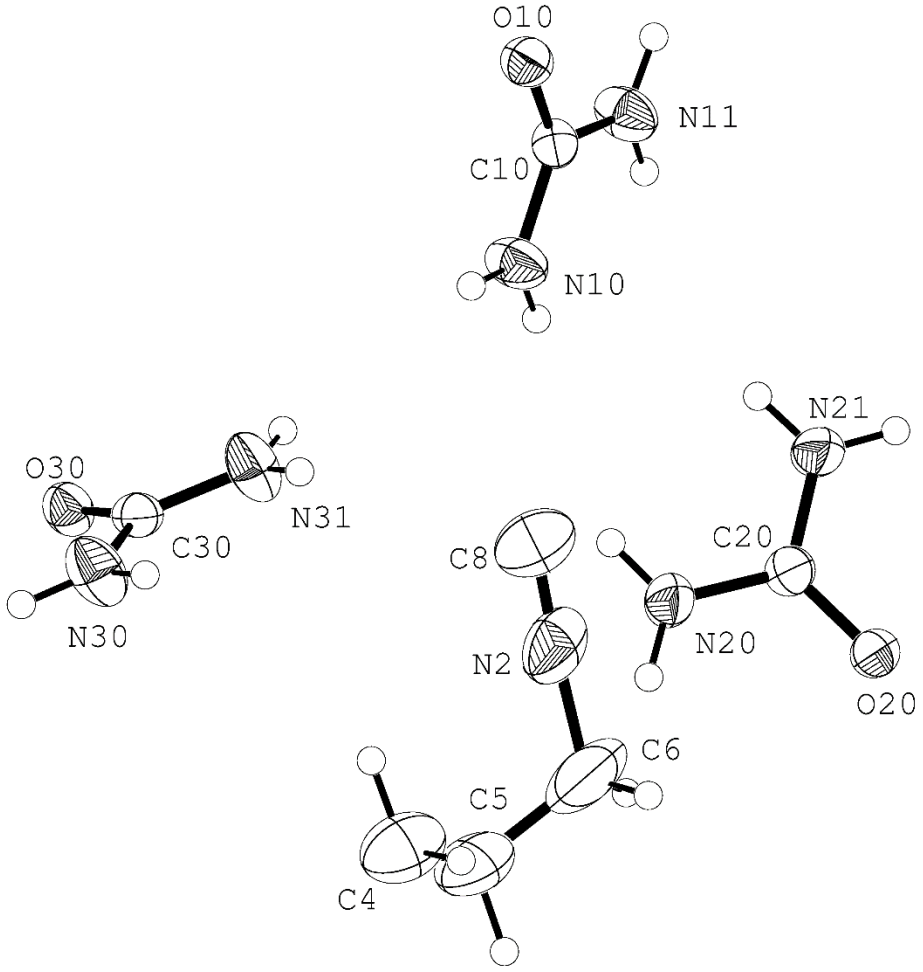


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-diisocyanohexane/urea at 223 K (KP2200).
2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).
3. Bruker AXS, Inc. (1998). SMART software Version 5.060. Bruker AXS, Inc., Madison, Wisconsin, USA.
4. Siemens P4 diffractometer equipped with a Bruker APEX II CCD Detector.
5. Bruker SAINT V8.18C
6. The SADABS program is based on the method of Blessing; see Blessing, R. H. *Acta Crystallogr. A***51**, 33, (1995).
7. Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. A***64**, 112-122 (2008).
8. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

9. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **42**, 339–341 (2009).

Structure report for 1,6-diisocyanohexane/urea at 243 K[1]

Introduction

The data for this crystal was collected in 2000 by Kevin Pate on a Siemens P4 diffractometer equipped with Bruker SMART 1000 CCD detector and was originally labeled "kp2100". (See laboratory notebook KLP A-152.) The original crystal was from Mark Hollingsworth (MDH-K-150-18). As with the bromines in 1,6-dibromohexane/urea,[2] the original model for disorder for this crystal did not allow the cyano end groups to be disordered between major and minor sites. The model shown here allows the end groups to be fully disordered.

The guest molecule is disordered between two sites. The ratio of the major to minor sites is found to be 62.7% and 37.3%. This ratio was refined during isotropic refinement and was subsequently fixed throughout the anisotropic refinements. (See below for details.) The jump angle between the methylene chains of the disordered pair was found to be 78.7°; this angle was taken as that between the mean planes made by the methylene carbons of the disordered parts. Molecular replacement was used to determine the atomic sites using previous models of similar systems. The space group is $P2_1/n$.

Experimental

Data Collection:

The crystal fragment had the approximate dimensions of 500 µm x 450 µm x 200 µm. The crystal was cooled to 243 K using an Oxford Cryosystems crystream using liquid nitrogen. The requested frame exposure was 10 seconds and the frame width was 0.30º. [8] The crystal to detector distance was 49.87 mm.

The unit cell parameters were determined[9,4] from 1972 input reflections whose minimum and the maximum 2-theta values were 5.00 and 47.30, respectively. The errors are reported after corrections for the goodness of fit (1.75). The cell volume is 1292.9 (4) Å^3.

a = 8.1788 (14) Å	α = 90°
b = 10.9387 (18) Å	β = 94.923 (3)°
c = 14.504 (3) Å	γ = 90°

For Z = 2 and F.W. = 496.56, the calculated density is 1.276 g/cm^3. Based on the systematic absences of

$$h00:\ h+l \neq 2n$$
$$0k0:\ k \neq 2n$$
$$h00:\ h \neq 2n$$
$$00l:\ l \neq 2n,$$

a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was uniquely determined to be

$$P2_1/n\ (\#14).$$

Data Reduction:

The data set contained 5864 reflections of which 159 were rejected. After merging Friedel opposites, there were 1913 unique reflections, of which 1533 had I > 2sigma(I). The R(int) was 0.0216, and the R(sigma) was 0.0228. The linear absorption coefficient, μ, for Mo-K$_\alpha$ radiation is 0.101 mm^{-1}. The absorption correction was made using SADABS. [8, 5]

Structure Solution and Refinement:

The atomic positions were found using molecular replacement techniques from similar crystal systems. These structures had been solved by direct methods and expanded using Fourier techniques.[6] The whole guest molecule is disordered, which is different from 1,6-dibromohexane/urea, where the bromines are not disordered. Previous models of 1,6-diisocyanohexane/urea refined the nitrile groups without disorder.

Using Shelx-97,[6] isotropic refinements were used to find the occupancies for the guest molecule. The isotropic refinement is found in kp2100_iso.res.

In the model used to determine site occupancy factors for the guest conformers, the hydrogens on the urea molecules were treated with a riding model (AFIX 93), in which the hydrogens were held in the plane of the urea molecule and the N-H distances were fixed at 0.870 Å. The isotropic Uij for each hydrogen was set to be 1.2 times the isotropic Uij value for atom to which it was attached.

The restraints used for isotropic refinement are:

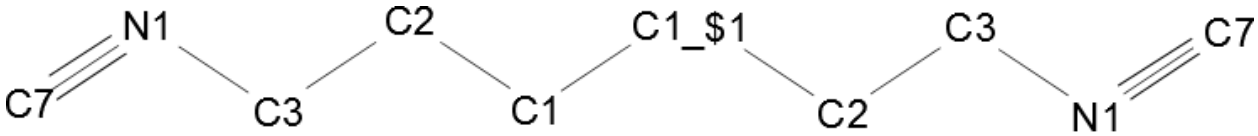


Figure 1: Atomic labeling scheme for part 1 (major part)

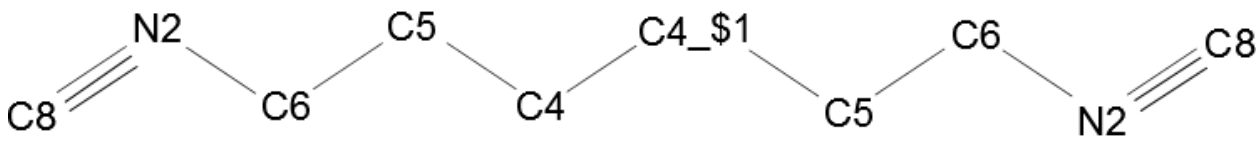


Figure 2: Atomic labeling scheme for part 2 (minor part)

```
DEFS 0.01
EQIV $1 1-x, 2-y, 1-z

SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
```

The EADP constraints were as follows:

```
EADP C3 C6
EADP C2 C5
EADP C1 C4
EADP C7 C8
EADP N1 N2
```

Anisotropic refinements were used to for all non-hydrogen atoms thereafter. In the final cycles of refinement, the weighting scheme was optimized by minimizing the summed esds of the atomic positions while keeping appropriate R1, wR2 and S values. The weighting scheme also gave a flat analysis of variance as a function of resolution. The hydrogens on the guest were treated with a riding model (AFIX 23), which fixes the C-H distances at idealized positions for a CH_2 group. The extinction parameter was not included because it refined to a value of zero.

The goodness of fit[7] was 1.262 for the data with Fo > 4sigma(Fo) and the goodness of fit was 1.263 for all of the data. R1 was 0.0360 for all 1913 data and 0.0467 for data with $I>2\sigma(I)$; the wR2 value was 0.0774 in the final refinement.

In the final cycles of anisotropic refinement, the following restraints were used:

```
FLAT C2 C3 C7 N1
FLAT C5 C6 C8 N2
SADI C3 C2 C2 C1 C1 C1_$1 C6 C5 C5 C4 C4 C4_$1
SADI C3 C1 C2 C1_$1 C6 C4 C5 C4_$1
SADI C7 N1 C8 N2
SADI C3 C7 C6 C8
SADI C3 N1 C6 N2
SADI C7 C2 C8 C5
```

(The EADP constraints were removed at this stage.) The FLAT commands were used to insure that the overlapping cyano carbons were connected to the correct atoms.

EXPERIMENTAL DETAILS

A. Crystal data

Empirical formula	$C_{28}H_{72}N_{28}O_{12}$
Formula weight	496.56
Crystal color, habit	Clear, prism
Crystal dimensions	500 x 450 x 200 µm
Crystal system	Monoclinic
Lattice type	Primitive
No. of reflections used for unit cell determination	1972
Lattice parameters	a = 8.1788 (14) Å
	b = 10.9387 (18) Å
	c = 14.504 (3) Å
	α = 90°
	β = 94.923 (3)°
	γ = 90°
	V = 1292.9 (4) Å^3
Space group	P2(1)/n (#14)
Z value	2
D_{calc}	1.276
F_{000}	532
μ (MoK$_\alpha$)	0.101 mm^{-1}
Temperature	243 K

B. Intensity measurements

Diffractometer	Siemens P4, SMART 1000 CCD
Radiation (graphite monochromated normal-focus sealed tube)	Mo-K$_\alpha$ (λ = 0.71073 Å)
Crystal to detector distance	49.87 mm
Time per frame	20 s
Temperature	243 K
Scan Type	ω and ϕ scan
ω and ϕ angle	2.50°
θ_{max}	23.65°
h k l range	h = -9 to 9
	k = -12 to 11
	l = -14 to 16
No. of reflections measured	Total: 5705

	Unique 1913 (R_{int} = 0.0216)
	I > 2σ(I) = 1533
Corrections	multi-scan absorption correction

C. Structure solution and refinement

Structure solution	Molecular replacement
Refinement	Full-matrix least-squares
Function minimized	Σ w (|Fo| - |Fc|)^2
Least squares weights	1 / σ^2(Fo)
Anomalous dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	1533
No. variables	199
No. Restraints	27
Reflection:parameter ratio	9.61
For I > 2.00σ(I)	7.70
No. Reflections used in refinement	1913
Final R indices [I > 2σ(I)] R1	0.0360
Final R indices [all data]; R1, wR2	0.0467; 0.0774
Goodness of Fit (s)	1.262
Mean shift/error in final cycle	0.000
Maximum peak in final diff. map	0.179 e/Å^3
Minimum peak in final diff. map	-0.152 e/Å^3

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for 1,6-diisocyanohexane/urea. The far right column denotes occupancy if less than 1.

	x	y	z	Uiso*/Ueq	Occ. (<1)
O20	0.99565 (13)	0.41954 (9)	0.65348 (8)	0.0373 (3)	
O30	−0.02581 (14)	0.08816 (10)	0.65477 (9)	0.0380 (3)	
O10	−0.01198 (13)	0.75056 (10)	0.68057 (8)	0.0364 (3)	
N21	0.80736 (18)	0.51991 (13)	0.72934 (11)	0.0498 (5)	
H21A	0.8577	0.5892	0.7234	0.060*	
H21B	0.718	0.5172	0.7578	0.060*	
N20	0.78740 (18)	0.31325 (13)	0.70620 (11)	0.0468 (4)	
H20A	0.8244	0.2452	0.6849	0.056*	

H20B	0.6983	0.3132	0.7349	0.056*	
N31	0.19656 (18)	0.19517 (13)	0.70944 (12)	0.0500 (4)	
H31A	0.155	0.2625	0.6857	0.060*	
H31B	0.2927	0.196	0.7401	0.060*	
N30	0.18266 (19)	−0.00953 (13)	0.73538 (12)	0.0525 (5)	
H30A	0.1315	−0.0791	0.7289	0.063*	
H30B	0.279	−0.0060	0.7657	0.063*	
C20	0.8672 (2)	0.41768 (14)	0.69471 (12)	0.0329 (4)	
C30	0.1136 (2)	0.09157 (14)	0.69889 (12)	0.0323 (4)	
N11	−0.02877 (19)	0.85415 (13)	0.54554 (11)	0.0453 (4)	
H11A	−0.0487	0.9223	0.5734	0.054*	
H11B	−0.0240	0.8531	0.4859	0.054*	
C10	−0.00558 (19)	0.75114 (15)	0.59433 (12)	0.0322 (4)	
N10	0.02794 (19)	0.64952 (13)	0.54872 (11)	0.0462 (4)	
H10A	0.0458	0.5813	0.5787	0.055*	
H10B	0.0319	0.6515	0.489	0.055*	
C3	0.5141 (15)	0.2787 (5)	0.4349 (8)	0.082 (3)	0.6275
H3A	0.6036	0.3324	0.4192	0.098*	0.6275
H3B	0.4396	0.2682	0.3788	0.098*	0.6275
C2	0.5854 (6)	0.1559 (5)	0.4627 (5)	0.087 (2)	0.6275
H2A	0.6675	0.1673	0.5153	0.104*	0.6275
H2B	0.6422	0.1233	0.4113	0.104*	0.6275
C1	0.4620 (6)	0.0625 (3)	0.4891 (7)	0.078 (2)	0.6275
H1A	0.3761	0.0541	0.4381	0.094*	0.6275
H1B	0.4102	0.0921	0.5433	0.094*	0.6275
N1	0.4277 (14)	0.3375 (9)	0.5023 (8)	0.057 (2)	0.6275
C7	0.3531 (14)	0.3879 (14)	0.5513 (8)	0.090 (3)	0.6275
C5	0.5061 (13)	0.1495 (6)	0.4291 (5)	0.071 (3)	0.3725
H5A	0.3913	0.148	0.4034	0.086*	0.3725
H5B	0.5733	0.1181	0.3816	0.086*	0.3725
C4	0.5248 (17)	0.0655 (4)	0.5116 (6)	0.077 (4)	0.3725
H4A	0.4572	0.0964	0.5592	0.092*	0.3725
H4B	0.6395	0.0667	0.5375	0.092*	0.3725
C6	0.555 (3)	0.2806 (7)	0.4503 (12)	0.099 (8)	0.3725
H6A	0.6727	0.2831	0.4696	0.119*	0.3725
H6B	0.5365	0.3288	0.3934	0.119*	0.3725
N2	0.469 (2)	0.3359 (16)	0.5197 (16)	0.068 (5)	0.3725
C8	0.406 (3)	0.372 (2)	0.5797 (13)	0.096 (6)	0.3725

Table 2. Atomic displacement parameters (Å^2)

	U11	U22	U33	U12	U13	U23
O20	0.0399 (7)	0.0292 (6)	0.0448 (8)	0.0016 (5)	0.0146 (6)	0.0017 (5)
O30	0.0370 (7)	0.0293 (6)	0.0471 (8)	0.0007 (5)	0.0010 (6)	0.0001 (6)
O10	0.0447 (7)	0.0322 (6)	0.0329 (8)	−0.0001 (5)	0.0068 (6)	0.0000 (5)
N21	0.0536 (10)	0.0309 (8)	0.0694 (13)	0.0015 (7)	0.0308 (9)	−0.0023 (8)
N20	0.0446 (9)	0.0309 (8)	0.0677 (12)	−0.0020 (7)	0.0214 (8)	0.0011 (8)
N31	0.0470 (9)	0.0319 (8)	0.0683 (13)	−0.0036 (7)	−0.0117 (8)	0.0026 (8)
N30	0.0529 (10)	0.0335 (9)	0.0679 (13)	0.0036 (7)	−0.0129 (9)	0.0072 (8)
C20	0.0356 (9)	0.0298 (9)	0.0338 (11)	0.0033 (7)	0.0056 (8)	0.0043 (8)
C30	0.0374 (10)	0.0282 (9)	0.0319 (11)	0.0026 (8)	0.0067 (8)	−0.0014 (7)
N11	0.0685 (11)	0.0306 (8)	0.0368 (10)	0.0032 (7)	0.0038 (8)	0.0029 (7)
C10	0.0302 (9)	0.0302 (9)	0.0363 (11)	−0.0028 (7)	0.0034 (8)	−0.0005 (8)
N10	0.0727 (11)	0.0305 (8)	0.0365 (10)	0.0038 (7)	0.0115 (8)	−0.0002 (7)
C3	0.085 (6)	0.106 (7)	0.056 (4)	−0.001 (4)	0.021 (4)	−0.009 (4)
C2	0.057 (3)	0.123 (5)	0.084 (5)	0.001 (3)	0.024 (3)	−0.029 (4)
C1	0.049 (3)	0.111 (6)	0.075 (4)	0.011 (2)	0.010 (3)	−0.024 (4)
N1	0.038 (4)	0.084 (3)	0.052 (5)	−0.009 (3)	0.007 (4)	−0.014 (3)
C7	0.077 (5)	0.104 (7)	0.091 (8)	−0.012 (4)	0.026 (5)	−0.012 (6)
C5	0.078 (6)	0.096 (7)	0.043 (6)	0.007 (5)	0.017 (5)	−0.008 (4)
C4	0.064 (7)	0.104 (10)	0.063 (7)	0.012 (5)	0.010 (6)	−0.001 (5)
C6	0.076 (9)	0.124 (14)	0.107 (16)	−0.001 (6)	0.061 (10)	−0.016 (9)
N2	0.045 (9)	0.100 (7)	0.059 (9)	−0.014 (5)	−0.003 (6)	−0.001 (6)
C8	0.128 (17)	0.095 (8)	0.071 (10)	0.013 (11)	0.044 (11)	−0.001 (8)

Table 3. Geometric parameters (Å, °)

O20—C20	1.2527 (18)	C3—C2	1.506 (7)
O30—C30	1.259 (2)	C2—C1	1.507 (5)
O10—C10	1.256 (2)	C1—C1i	1.525 (6)
N21—C20	1.336 (2)	N1—C7	1.120 (5)
N20—C20	1.333 (2)	C5—C4	1.506 (7)
N31—C30	1.323 (2)	C5—C6	1.513 (8)
N30—C30	1.331 (2)	C4—C4i	1.520 (8)
N11—C10	1.335 (2)	C6—N2	1.412 (7)
C10—N10	1.334 (2)	N2—C8	1.120 (7)
C3—N1	1.409 (5)		
O20—C20—N20	120.87 (15)	N1—C3—C2	115.3 (6)
O20—C20—N21	121.02 (15)	C3—C2—C1	114.8 (5)
N20—C20—N21	118.11 (15)	C2—C1—C1i	113.0 (5)
O30—C30—N31	121.15 (15)	C7—N1—C3	175.5 (13)
O30—C30—N30	120.83 (15)	C4—C5—C6	114.2 (8)
N31—C30—N30	118.01 (17)	C5—C4—C4i	113.1 (8)
O10—C10—N10	121.16 (15)	N2—C6—C5	114.3 (8)
O10—C10—N11	121.04 (15)	C8—N2—C6	174 (2)
N10—C10—N11	117.79 (16)		
N2—C6—C5—C4	−57 (2)	N1—C3—C2—C1	58.2 (14)
C6—C5—C4—C4i	−179.9 (14)	C3—C2—C1—C1i	176.4 (9)

Symmetry code: (i) −x+1, −y, −z+1.

Table 4. Torsion Angles

Atom	Atom	Atom	Atom	Angle/°
N2	C6	C5	C4	-57(2)
C6	C5	C4	C4_$1	-179.9(14)
N1	C3	C2	C1	58.2(14)
C3	C2	C1	C1_$1	176.4(9)

Symmetry code: (i) −x+1, −y, −z+1.

Table 5. Hydrogen-bond Geometries (in Å)

D—*H*···*A*	*D*—*H*	H···A	*D*···*A*	*D*—*H*···*A*
N21—H21A···O10ii	0.87	2.18	3.0379 (19)	169
N21—H21B···O30iii	0.87	2.24	3.0577 (18)	156
N20—H20A···O30ii	0.87	2.18	3.0247 (18)	165
N20—H20B···O10iv	0.87	2.15	2.9794 (18)	160
N31—H31A···O20v	0.87	2.18	3.0254 (19)	163
N31—H31B···O10iv	0.87	2.13	2.9768 (19)	164
N30—H30A···O10vi	0.87	2.28	3.1362 (19)	168
N30—H30B···O20vii	0.87	2.25	3.065 (2)	156
N11—H11A···O30viii	0.87	2.16	3.0094 (19)	164
N11—H11B···O30ix	0.87	2.21	3.043 (2)	161
N10—H10A···O20v	0.87	2.13	2.9625 (19)	159
N10—H10B···O20x	0.87	2.2	3.019 (2)	156

Symmetry codes: (ii) x+1, y, z; (iii) −x+1/2, y+1/2, −z+3/2;
(iv) −x+1/2, y−1/2, −z+3/2; (v) x−1, y, z; (vi) x, y−1, z;
(vii) −x+3/2, y−1/2, −z+3/2; (viii) x, y+1, z;
(ix) −x, −y+1, −z+1; (x) −x+1, −y+1, −z+1.

Figure 3: ORTEP rendering by OLEX2[10] showing part 1 with 40% probability surfaces.

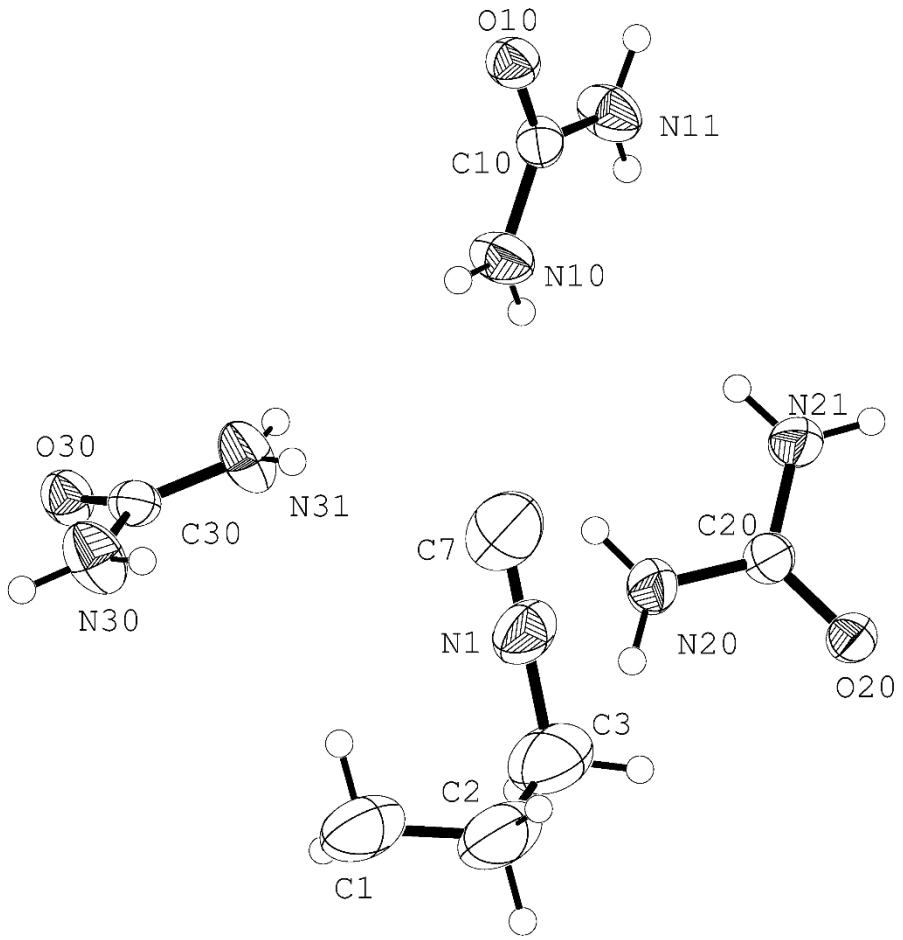
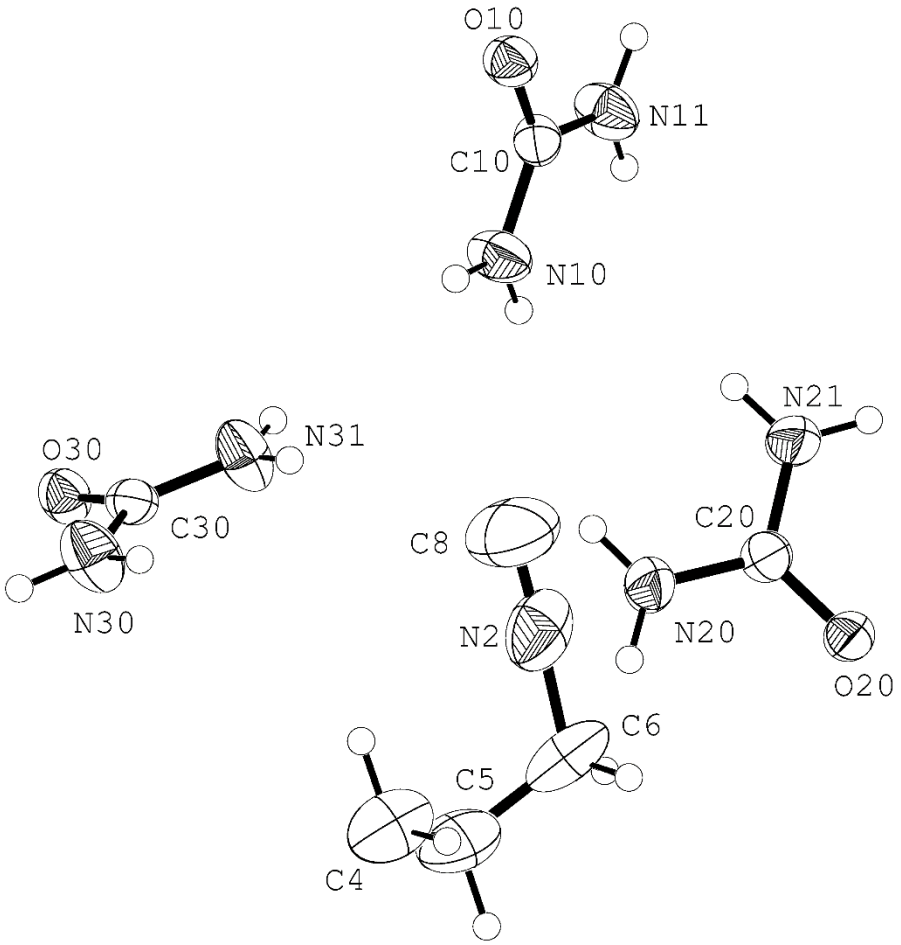


Figure 4: ORTEP rendering by OLEX2[10] showing part 2 with 40% probability surfaces.



References and Notes

References

1. Inquiries regarding the crystallographic results should be directed to Prof. M. D. Hollingsworth at the Chemistry Department, Kansas State University, quoting structure 1,6-dicyanohexane/urea at –115 ⌗C (mh1001a).

2. Hollingsworth, M. D., Werner-Zwanziger, U., Brown, M. E., Chaney, J. D., Huffman, J. C., Harris, K. D. M., Smart, S. P., Spring-loading at the molecular level: Relaxation of guest-induced strain in channel inclusion compounds. *J. Am. Chem. Soc.* **121**, 9732-9733 (1999).

3. Data collected using the Bruker APEX-II software package.

4. Bruker SAINT V8.18C

5. The SADABS program is based on the method of Blessing; see Blessing, R. H. Acta Crystallogr., A51, 33, (1995).

6. Sheldrick, G. M., A short history of SHELX. *Acta Crystallographica Section A* **64**, 112-122 (2008).

7. Standard deviation of an observation of unit weight:

$GooF = S = \{\Sigma[w(Fo^2 - Fc^2)^2/(n-p)]\}^{1/2}$

where n is the number of reflections and p is the total number of parameters refined.

$w = 1/(\sigma^2(Fo^2) + (aP)^2 + bP$

where P is

$P = [2Fc^2 + \max(Fo^2,0)]/3.$

8. Siemens (1995). SMART software. Version 4.044. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

9. Siemens P4 diffractometer equipped with a CCD Detector.

10. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.

11. Bruker P4 diffractometer equipped with a CCD detector