SYNTHESIS OF CERTAIN NITRILES USEFUL IN THE
FORMATION OF PI COMPLEXES

by

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HISTORICAL BACKGROUND

Complex compounds of certain organic molecules have been known for many years. The most common of these complexes were composed of one to one ratios of phenolic ethers or aromatic hydrocarbons and various aromatic nitro compounds. Andrews[2] has compiled an extensive review of organic molecular complexations, dealing mainly with the above types of compounds.

Certain complexing agents, such as picric acid (2,4,6-trinitrophenol), form high melting, relatively stable, one to one crystalline complexes with phenolic ethers and aromatic hydrocarbons. These characteristics have given it particular value as a means of isolation, identification and purification of aromatic compounds from reaction mixtures.

Each new insight into the nature of chemical bonding has resulted in the postulation of a different type of bonding involved in the complexations. The latest, and most widely accepted, explanation is that the pi electrons of the aromatic nuclei constitute the bonding. Weiss[43,44] was probably the first to specifically mention the role of pi electrons in complexation reactions. From studies of the structures and behavior of certain organic complexes, he concluded that the bonding was ionic in nature, a viewpoint no longer accepted. The visible and ultraviolet absorption study of complexations of inorganic molecules

by various aromatic hydrocarbons led Benesi and Hildebrand to
the conclusion that the reactions were due to an acid-base inter-
action. Mulliken[33] supported this theory from a quantum mechan-
ical standpoint. He was of the opinion that the complexation
represented the interaction of Lewis acid and base molecules.
Mulliken postulated further that the interaction involved
resonance between no-bond and dative structures in which the pi
electrons of the aromatic hydrocarbon (the Lewis base) overlap
available molecular orbitals of the Lewis acid.

With the discovery that certain inorganic molecules could
undergo complexation, in addition to the polynitro aromatic
hydrocarbons, attention was directed to other types of compounds
containing electron-poor multiple bonds. Several low molecular
weight organic compounds, such as oxalyl chloride[40], maleic an-
hydride[9] and tetracyanoethylene[28] were successful complexation
reagents.

Tetracyanoethylene was interesting because it was the first
nitrile reported to undergo a wide variety of complexation re-
actions. Bennett[12,13] had studied 1,3,5-tricyanobenzene much
earlier. Based on the criteria that complexation occurred only
upon intensification of color in solution or formation of a solid
complex, Bennett stated that complexation occurred only with
aromatic amines.

In contrast to ethylene, which is an electron donor, the tetracyanoethylene molecule is an electron acceptor due to the electron deficiency of the double bond caused by the withdrawing effect of the electronegative cyano groups. Tetracyanoethylene is the strongest organic pi acid reported. It undergoes a wide variety of addition reactions with dienes, forming colored pi complexes which disappear upon completion of the addition. Such reactions have led to the postulation that the pi complexes are intermediates in certain addition reactions.

Keefer and Andrews[3,4] have shown that association constants can be calculated for the Lewis acids. They also demonstrated that an increasing number of alkyl substituents on the aromatic hydrocarbon pi base increases the value of the association constant. The extent of the pi complexation appears to be dependent upon the relative Lewis acid-base strengths of the reactants and the nature of the reaction solvent.

STATEMENT OF THE PROBLEM

Aromatic and unsaturated alkyl nitriles, as a group, have only been superficially studied as complexation reagents. The limited work which has been published in this area indicates that the electronegativity of the cyano group is sufficiently strong to impart pi complexation ability to many polycyano aromatic and unsaturated alkyl compounds. A comparison of the

sigma values, which are measures of the electron withdrawing ability of functional groups, shows that the electron withdrawing power of the cyano group is very close to that of the nitro group. Certain nitriles would be expected to possess nearly the same complexing ability as corresponding nitro compounds.

The study of a series of benzenes with an increasing number of cyano substituents and of certain unsaturated alkyl nitriles related to tetracyanoethylene, such as dicyanoacetylene, should provide interesting information in regard to the Lewis acid strengths of these compounds. This study would require the synthesis of several new compounds, such as hexa- and pentacyanobenzene and 1,2,3,4- and 1,2,3,5- isomers of tetracyanobenzene. Synthesis of the 1,2,4,5-tetracyanobenzene was recently described after this work started.

The objectives of this work, briefly summarized, were:

1. to investigate the pi complexation ability of dicyanoacetylene and relate its strength to tetracyanoethylene.

2. to initiate the preparation of a series of polycyanobenzenes which could be expected to form pi complexes and compare the pi acid strength of them with known pi acids such as trinitrobenzene or picric acid.

3. to initiate the synthesis of a series of benzenes fully substituted with cyano and carboxylic ester groups in order to study the effect upon pi complexation ability

of increasing replacement of ester groups with the
cyano group.

DISCUSSION OF EXPERIMENTAL RESULTS

Pi complexation between aromatic hydrocarbons and inorganic
molecules has attracted increasing attention during recent years[8, 11,16,25,26]. A few low molecular weight, unsaturated organic
compounds have also shown pi acid behavior[9,40]. The recent work
of Merrifield and Phillips[28] with tetracyanoethylene indicates
that pi complexation might be expected between aromatic hydro-
carbons and other low molecular weight, unsaturated organic com-
pounds containing electron withdrawing substituents. If such a
generalization were to hold true, dicyanoacetylene might be
expected to undergo pi complexation in the same manner as the
compounds previously cited.

Dicyanoacetylene was first prepared in 1909 by Moureu and
Bongrand[31,32]. The starting material, acetylenedicarboxamide,
II, was prepared by treating dimethyl acetylenedicarboxylate[23],
I, with concentrated, aqueous ammonia or liquid ammonia.

$$CH_3O\overset{O}{\overset{\|}{C}}C\equiv C\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow[\text{or } NH_3, \ -78°]{NH_4OH, \ 0°} NH_2\overset{O}{\overset{\|}{C}}C\equiv C\overset{O}{\overset{\|}{C}}NH_2 + III$$

$$\text{I} \qquad\qquad\qquad\qquad \text{II}$$
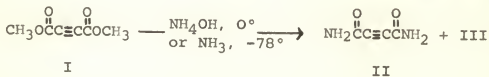
The diamide is only very slightly soluble in the hot, absolute
methanol used to wash the reaction product, however dark brown

crystals of a second compound, III, were recovered from the alcohol wash. Repeated crystallization of this substance from methanol and decolorization with activated charcoal yielded colorless needles melting at 161-2°C. The diamide itself decomposes at 202.5°C. literature, 190-92°[39] and 294°C.[31] Moureu and Bongrand noted the presence of the brown crystals although they made no attempt to identify them.

The infrared spectrum of substance III indicated the presence of the ester carbonyl function at 5.77μ. Primary amide and the imine absorptions occur very close together. Absorptions occurring at 5.97 and 6.21μ could conceivably be assigned to either function. A single absorption at 3.00μ could likewise be assigned 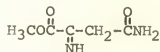to either the amide or imine N-H stretching frequency. Elemental analysis of the compound gave an empirical formula of $C_5H_9O_3N_2$. The possible structure of compound III could be either IIIa or IIIb.

$$H_3COC\text{-}CH_2\text{-}C\text{-}CNH_2 \qquad\qquad H_3COC\text{-}C\text{-}CH_2\text{-}CNH_2$$
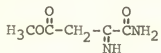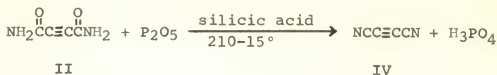
IIIa   IIIb

A compound of this structure has not been reported previously in the literature.

Dicyanoacetylene, IV, was prepared by dehydration of acetylenedicarboxamide, II, with phosphorous pentoxide. The method developed by Moureu and Bongrand[31,32] was followed with

only a few modifications in technique.

$$\underset{\text{II}}{NH_2\overset{O}{\overset{\|}{C}}C\equiv C\overset{O}{\overset{\|}{C}}NH_2} + P_2O_5 \xrightarrow[\text{210-15°}]{\text{silicic acid}} \underset{\text{IV}}{NC\equiv CCN} + H_3PO_4$$

The ultraviolet spectrum of the dicyanoacetylene vapor is similar to the vapor spectrum of benzene in that the absorption peaks are very sharp and well defined except that there are fewer peaks in the dicyanoacetylene spectrum. The absorption spectrum appears as six distinct groups of peaks. The first group, containing twenty-three identifiable peaks, between 287.66 mμ and 277.68 mμ, is of very low relative intensity. The next four groups, each containing nine to eleven peaks or distinct shoulders, are similar in configuration and intensity, although the relative intensity of some of the peaks increases at shorter wavelengths. The sixth, and last, absorption group resembles the preceding four groups although it is lacking in detail and is of lesser intensity. Upon conversion of the absorption wavelengths to reciprocal centimeters it was found that, in the four middle groups, the energy difference from the peaks in one group to the corresponding peaks in the following group was remarkably constant, although the distance was not the same for all groups. The energy difference between the peaks within the groups varied little from group to group.

The infrared spectrum of the liquid dicyanoacetylene agreed closely with the spectrum reported by Saggiomo[39] who attributed

the strong absorption at 4.41μ to the cyano group and the weak absorption at 4.24μ to the carbon-carbon triple bond. The remaining absorptions were regarded as overtones.

A mass spectral cracking pattern[20] established that the parent molecule was C_4N_2 and not a dimer of dicyanoacetylene. The ion abundance data agreed closely with that published recently by Franklin and co-workers[18].

The method most frequently used to detect pi complexation is a comparison of the separate ultraviolet or visible absorption spectra of the aromatic hydrocarbon and pi acid separately with the spectrum of a mixture of the two compounds. Pi complexation is assumed when the spectrum of the mixture differs significantly from the additive spectra of the two individual components, indicating the formation of a new molecular species. The measurements usually are taken with low concentrations of the reactants dissolved in an unreactive solvent.

The spectrum obtained from dicyanoacetylene and naphthalene in spectral grade iso-octane (2,2,4-trimethylpentane) was essentially the sum of the separate spectra, indicating that no pi complex was formed. However, Merrifield and Phillips[28] have shown that the solvent used in the measurements can have a significant effect upon the value of the complex equilibrium constant. They concluded that the effect was due to a competing complex formation between the solvent and the pi acid. A

different solvent might enhance pi complexation.

Measurement of the dicyanoacetylene vapor spectrum in the presence of bromine vapor also showed no change other than being the sum of the separate spectra. Similar results were obtained from 1,3,5-trinitrobenzene and dicyanoacetylene in iso-octane.

Since bromine and trinitrobenzene normally function as pi acids in complex formation and naphthalene functions as a pi base, it was shown that under the conditions employed dicyano-acetylene functioned neither as a pi acid or pi base. The failure of the dicyanoacetylene to function as a pi acid in-dicates that the electron withdrawing power of the two nitrile groups is not sufficient to create a significant electron deficiency within the molecule to permit acceptance of electrons from electron-rich compounds. The electron density of the molecule is, as expected, too low to enable it to act as a pi base and donate electrons to electron-poor centers of pi acids.

Upon standing in contact with bromine vapor for several hours at room temperature, however, crystals of an addition product, V, of bromine and dicyanoacetylene were observed to form. Elemental analysis has shown this compound has the com-position, $C_4Br_2N_2$. Moureu and Bongrand[32] postulated the existence of the same compound on the basis that dicyanoacetylene slowly decolorized a solution of bromine in chloroform and ether,

although no product was isolated and identified. Isolation of
the addition compound, V, has not been previously reported in
the literature.

$$NCC{\equiv}CCN + Br_2 \longrightarrow NCC{=}CCN \text{ (Br, Br)}$$

IV   V
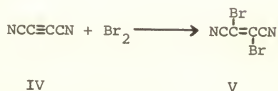
Dicyanoacetylene was of interest not only as a possible pi
complexing reagent but also as a possible starting material in
the synthesis of hexacyanobenzene, a compound unreported in the
literature, which should also be of interest as a pi acid. Diels
and Alder[15] obtained hexamethyl mellitate in 25 per cent yield
from the addition of pyridine to dimethyl acetylenedicarboxylate
in acetic acid. Analogous trimerizations were attempted with
dicyanoacetylene; (1) by addition to a solution of acetic acid
and pyridine, (2) passage of the vapor into a solution of acetic
acid and pyridine and (3) into a solution of benzene, acetic
acid and pyridine, and (4) addition of a solution of acetic acid
and pyridine to a solution of dicyanoacetylene in benzene.

$$NCC{\equiv}CCN \xleftarrow{\quad\text{catalyst}\quad} C_6(CN)_6$$
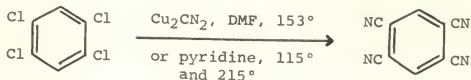
IV   VI
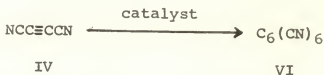
In every case a very fine black solid formed immediately
upon contact of the catalyst solution and the dicyanoacetylene.
The reactions were somewhat exothermic. The fine black solid
which formed defied recrystallization. It appeared to be insoluble

in all solvents tried. It formed a red solution when warmed with nitrobenzene but could not be crystallized from it. An attempt to sublime it at reduced pressure yielded only a very small amount of soft white crystals whose infrared spectrum gave no insight into the identity of the material.

Lawton and McRitchie[27] recently reported the synthesis of pyromellitonitrile (1,2,4,5-tetracyanobenzene) for the first time. Their method of preparation was dehydration of the corresponding tetraamide with an excess of thionyl chloride in DMF. A related compound prepared by the same authors, 2,5-dicyanodimethylterphthalate, was obtained from the corresponding 2,5-dibromodimethylterphthalate via the Friedman modification of the Rosenmund-Von Braun reaction[19], in which the bromo ester and cuprous cyanide were heated together with DMF as the solvent or "complexing intermediate".

It was decided to attempt to prepare pyromellitonitrile directly from 1,2,4,5-tetrachlorobenzene via the Friedman modification of the Rosenmund-Von Braun reaction.

$$\text{Cl} \quad \text{Cl} \quad \xrightarrow[\substack{\text{or pyridine, 115°} \\ \text{and 215°}}]{\text{Cu}_2\text{CN}_2,\ \text{DMF, 153°}} \quad \text{NC} \quad \text{CN}$$

VII

Refluxing with DMF (b.p. 153°C.) and with pyridine (b.p. 115-16°C.) for 24 hours yielded only starting material. Increasing

the reaction temperature to 210-15°C. for 24 hours with pyridine solvent still resulted only in recovery of starting material.

In the study of the pi complexation of aromatic nitriles we were hopeful of preparing some of the lower members of a series of compounds steming from hexamethylmellitate (hexamethyl ester of benzene hexacarboxylic acid) in which the ester groups are replaced one by one with a nitrile group through conversion of the ester group to an amide with subsequent dehydration to the nitrile.

The first compound of the series which we attempted to prepare was 3,6-dicyano-1,2,4,5-tetramethylpyromellitate. Mellitic acid is difficult to prepare in good yields with acceptable purity as a starting material, therefore it was decided to attempt to adapt the Friedman modification of the Rosenmund-Von Braun reaction for this first step in the series. Nuclear bromination of a 1,2,4,5-tetraalkylbenzene with subsequent oxidation and esterification seemed to be the most promising method for the preparation of the necessary intermediate.

The method of bromination used in this work was adapted from that of Hopff and Manukian[21] who carried out the dichlorination of durene through introduction of dry chlorine gas with stirring into a solution of durene and a few crystals of iodine in petroleum ether. Their reaction was complete in 15 minutes and the product was isolated in 52 per cent yield. In this work, four equivalents

of bromine were used per mole of durene in place of the chlorine
gas. In view of the ease of the dichlorination of durene demon-
strated by Hopff and Manukian it was felt that dibromination by
this method should proceed with less difficulty than with other
methods available[36,41]. It was found that the use of petroleum
ether as the solvent led to the preferential bromination of the
petroleum ether. This was especially true at elevated temper-
atures. The most satisfactory condition found was the use of
carbon tetrachloride as solvent and addition of the bromine at
room temperature. A few crystals of iodine were dissolved
along with the durene in each reaction to aid as a nuclear
bromination catalyst[38].
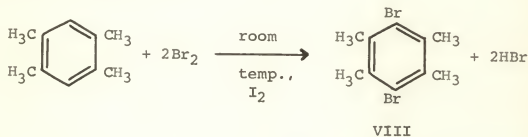
VIII

Stirring for 10 hours at room temperature after the addition
of the bromine gave 3,6-dibromodurene, VIII, (m.p. 201.5-202°C.)
in 80 per cent yield. The melting point of 3,6-dibromodurene
has been reported variously as 199 to 203°C.[10,29,41].

Heating of the reaction at reflux temperature for 2 hours
after the addition of the bromine tended to form only monobromo-
durene, probably due to vaporization of bromine from the reaction
mixture. Treatment of the monobromodurene with additional bromine

at reflux temperature for another hour gave 3,6-dibromodurene in only 41 per cent yield.

Aromatic side chain oxidation is often a difficult procedure requiring rigorous conditions and quite often results in poor yields of the intended product. Phillippi and co-workers[35,36] obtained 3,6-dibromopyromellitic acid in very small yield from the sealed tube oxidation of 2,5-dibromo-3,6-dimethyl-1,4-di-ethylbenzene. Smith and co-workers[42] treated monobromodurene with fuming nitric acid and obtained a product which they postulated was 4-bromo-2,3,5-trimethyl-1-nitrobenzene-6-methylnitrate. Other general methods of side chain oxidation include the use of alkaline permanganate[17] and chromic acid[24] although these reagents apparently have not been used extensively in oxidations of polyalkyl benzenes.

Lack of equipment precluded the use of the more successful method of Hopff and Manukian[21] who oxidized 3,6-dichlorodurene to the corresponding dichloropyromellitic acid in 68 per cent yield with 25 per cent nitric acid in an autoclave or that of Miller[30] and Phillippi[34] who reported yields of polycarboxylic acids as high as 89 per cent with vapor phase oxidations util-izing vanadium oxide catalysts.

Attempts to oxidize the 3,6-dibromodurene, VIII, to the corresponding 3,6-dibromopyromellitic acid, IX, with nitric acid in a glass Carius tube resulted in very poor yields, in
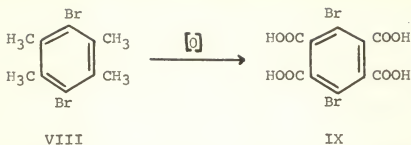
the order of 1-2 per cent of theoretical. Most of the starting
material was recovered from these reactions. The poor results
were due, in part, to an inability to achieve a proper seal,
even though the stainless steel caps were tightened with a wrench.
At temperatures above 110°C. some leakage of pressure was observ-
ed and the passage of gases upward through the liquid compacted
the dibromodurene and forced it above the liquid level in the
tube. Such conditions afforded very little contact between the
dibromodurene and nitric acid. Refluxing dibromodurene with a
two to one mixture of concentrated nitric acid and fuming nitric
acid for periods of 4 to 18 hours gave 1 to 6 per cent yields of
products whose infrared spectra showed the characteristics of
the acid anhydride. The material obtained from a 4 hour reflux-
ing with concentrated nitric acid and a Carius tube oxidation
were combined (the combined products represented 2.6 per cent of
the theoretical yield) and the neutralization equivalent deter-
mination gave a value of 190.6 (calculated for dibromopyro-
mellitic acid dianhydride is 94). A significant amount of
material failed to react with the sodium hydroxide and evidently

was not the acid or acid anhydride.

The neutralization equivalent of the product from the 18 hour refluxing with nitric acid was determined to be 91.2 ± 1.5. Refluxing the dibromodurene with the strong nitric acid solutions evidently completely decomposed most of the starting material since the acid anhydrides were the only products recovered, even after evaporation of the nitric acid.

Refluxing dibromodurene with alkaline potassium permanganate for 4 hours, heating dibromodurene with a weakly acidic solution of potassium permanganate on a steam bath for 7 days and refluxing for 3 hours with acidic potassium dichromate also resulted only in recovery of starting material.

An English patent[14] described an improved technique for the preparation of benzene carboxylic acids through oxidation of chloromethyl substituents with 40 per cent nitric acid at atmospheric pressure. By analogy, bromomethyl substituents should also be readily oxidized. Bromination of the methyl substituents in 3,6-dibromodurene was carried out at room temperature by dropwise addition to dibromodurene dissolved in carbon tetrachloride of an excess of bromine required to replace one hydrogen in each methyl group. Sunlight was used as the catalyst. The reaction proceeded smoothly with yields in excess of 90 per cent of the crude product, X.
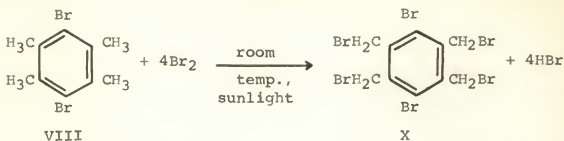
The product, X, was only slightly soluble in the carbon tetra-chloride and most of it precipitated as the reaction progressed. Elemental analysis showed that the compound possessed the empirical formula $C_{10}H_8Br_6$.

Atkinson and Thorpe[5] have demonstrated that substitution of bromine at a side-chain carbon already bearing a bromine atom becomes increasingly difficult and bromination will preferentially take place at an unsubstituted alkyl group. Construction of molecular models shows that substitution of one bromine in each methyl group is sterically possible. On the basis of this evidence the compound, X, was postulated as the 3,6-dibromo-1,2,4,5-tetrakis(bromomethyl)benzene which had been previously unreported in the literature. Subsequently, Hopff and co-workers[22] published an account of the independent synthesis of this compound. They reported a melting point of 262-263°C. compared to 265-266.5°C. noted by this author. No infrared or ultra-violet absorption data was reported.

Oxidation of the 3,6-dibromo-1,2,4,5-tetrakis(bromomethyl)-benzene with 38 per cent nitric acid as described in the English

patent resulted in virtually no reaction other than decomposition after 24 hours of refluxing. Increasing the strength of the acid to 69 per cent gave a 32 per cent yield of dibromopyromellitic acid upon hydrolysis of the mixture of acid and anhydride obtained after 24 hours of refluxing. Solid material, XI, amounting to 25 per cent by weight of the starting material was recovered which has not been identified. The remainder of the starting material was apparently decomposed.
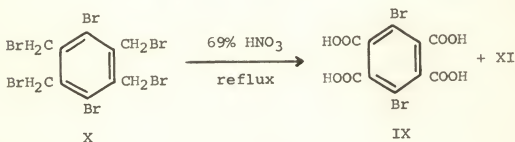
In a continuing attempt to increase the yield of 3,6-dibromopyromellitic acid, IX, less vigorous reaction conditions were desired in order to reduce the losses due to decomposition. The first step of the new sequence was hydrolysis of the bromomethyl groups in 3,6-dibromo-1,2,4,5-tetrakis(bromomethyl)benzene to hydroxymethyl substituents. Oxidation of the resulting 3,6-dibromo-1,2,4,5-tetrakis(hydroxymethyl)benzene should be possible under much milder conditions than those previously employed.

	NaOH	
X	Dioxane reflux	XII
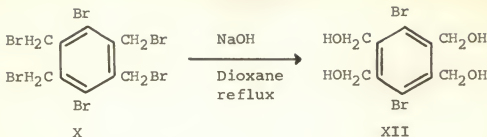
The method of hydrolysis utilized was that of Hopff and
Manukian[21]. The 3,6-dibromo-1,2,4,5-tetrakis(bromomethyl)-
benzene was heated at reflux temperature with dioxane and six
molar sodium hydroxide with vigorous stirring. Ninety per
cent of the product of the reaction was very insoluble in common
solvents and was only very slightly soluble in DMF. The remain-
ing 10 per cent was very soluble in acetone and benzene and dis-
played a marked difference in melting point. The infrared
spectra of these two substances were very similar with the
exception that the -OH absorption of the less soluble portion
was distinctly weaker. The formation of an inter- or intra-
molecular ether was suspected, although it would be difficult to
determine this from the infrared spectrum since the only region
in which the ether absorption occurs is also overlapped by the
absorptions of alcohols, aromatic rings and, in some cases,
alkyl groups. An attempt to cleave the suspected ether with
hydroiodic acid in acetic acid was unsuccessful.

Although it is well known that carboxylic acids and an-
hydride groups deactivate an aromatic nucleus toward electro-

philic substitution[37], it was hoped that under vigorous conditions bromination of the unsubstituted 3,6- positions of pyromellitic acid dianhydride (PMDA) could be induced. Such a reaction, even in small yields, could be helpful in eliminating a number of steps in the preparation of the tetramethyl ester of 3,6-dibromopyromellitic acid, an intermediate desired in the preparation of substituted cyanobenzenes.
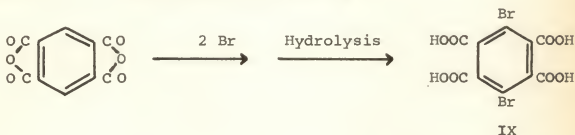
Treatment of PMDA with liquid bromine in a fuming sulfuric acid solvent resulted only in hydrolysis of the anhydride. Such a result would usually be expected since aromatic halogenations are normally considered to be nucleophilic in nature. Protonation of the PMDA by the sulfuric acid would prevent this type of reaction.

The use of dimethylformamide (DMF) would be expected to be more successful since the DMF is a basic, polar solvent which should favor an ionic reaction mechanism. With the use of DMF as a solvent, some soft white crystals were recovered from the reaction in addition to unreacted starting material. The crystals could be readily separated from the PMDA by virtue of

their easy solubility in water. Analysis showed that bromine composed 53.3 per cent of the compound. The calculated bromine content of dimethylformamide in which one hydrogen atom has been replaced by bromine is 52.6 per cent. The postulated structure of this compound is N-methyl-N-bromomethylformamide, XIII.

$$HC\underset{O}{\overset{\parallel}{N}}\begin{matrix} \diagup CH_2Br \\ \diagdown CH_3 \end{matrix}$$

XIII

The possible bromination of DMF is supported by the work of Adams and Braun[1] who have reported that the use of DMF in chlorination reactions not only enhances the formation of polychlorinated products not obtained using ordinary solvents but that the DMF was also chlorinated. Bigelow and co-workers[6,7] have isolated the completely fluorinated fragments of DMF from low temperature reaction with elemental fluorine.

Low energy free radical bromination of PMDA was also unsuccessful. Reaction with N-bromosuccinimide catalyzed by benzoyl peroxide failed. The transition state of the free radical may be too bulky to permit reaction with the single aromatic hydrogen between the anhydride groups. Bromination with elemental bromine in a Carius tube at 150° was unsuccessful, possibly because the free radicals were not energetic enough at that temperature.

EXPLANATION OF PLATE I

INFRARED SPECTRA

Fig. 1. 1,2-Dicyanoacetylene. Neat. 0.10 mm NaCl cavity cell.

Fig. 2. 1,2-Dibromo-1,2-dicyanoacetylene. KBr pellet.

Fig. 3. Product sublimed from attempted trimerization of 1,2-
         Dicyanoacetylene. KBr pellet.
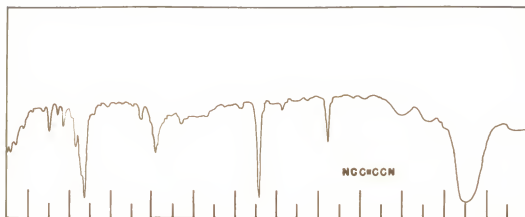
Fig. 1
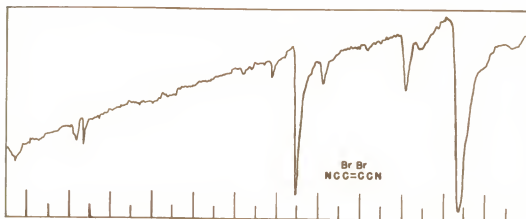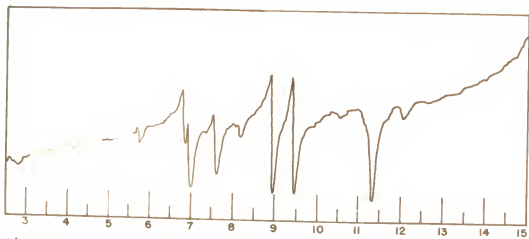
Fig. 2

Fig. 3

EXPLANATION OF PLATE II

INFRARED SPECTRA

Fig. 1. Product from reaction of dimethyl acetylenedicarboxylate
         and liquid ammonia. KBr pellet.

Fig. 2. 3,6-Dibromo-1,2,4,5-tetrakis(bromomethyl)benzene. KBr
         pellet.

Fig. 3. Product from reaction of 3,6-Dibromo-1,2,4,5-tetrakis-
         (bromomethyl)benzene and 10 per cent sodium hydroxide
         in refluxing dioxane. KBr pellet.

Fig. 1

Fig. 2

Fig. 3

Table 1. Ultraviolet Absorption Spectrum of Dicyanoacetylene.

Group No. 1				Group No. 3		
Peak No.	Absorption mμ	cm^{-1}	Relative Intensity	Peak No.	Absorption mμ	cm^{-1}	Relative Intensity
1	287.66	34763	0.14	1	256.65	38963	0.3
2	287.46	34787	0.14	2	253.05	39518	1.9
3	286.86	34860	0.15	3	251.43	39772	2.7
4	286.70	34879	0.16	4	250.00	40000	1.5
5	286.45	34910	0.16	5	248.17	40295	10.0
6	286.34	34923	0.17	6	246.97	40491	9.0
7	286.23	34937	0.17	7	246.09	40635	1.3
8	286.04	34960	0.15	8	245.82	40680	1.3
9	284.86	35104	0.16	9	244.60	40883	2.1
10	282.82	35358	0.24	10	243.66	41040	0.7
11	282.46	35403	0.22	11	243.00	41152	0.7
12	281.43	35532	0.43				
13	281.32	35546	0.37		Group No. 4		
14	280.14	35696	0.45				
15	280.00	35714	0.43	1	241.69	41375	1.0
16	279.80	35739	0.42	2	239.80	41701	2.3
17	279.61	35771	0.41	3	238.30	41964	3.0
18	279.50	35778	0.44	4	237.20	42159	2.2
19	279.39	35792	0.45	5	235.44	42474	10.0
20	279.27	35808	0.45	6	234.35	42671	9.4
21	278.73	35877	0.44	7	233.64	42801	2.2
22	278.64	35888	0.43	8	233.36	42852	2.2
23	277.68	36012	0.22	9	232.20	43066	2.8
				10	231.32	43230	1.7
	Group No. 2						
					Group No. 5		
1	peak obscured						
2	268.03	37309	1.8	1	229.73	43529	1.8
3	266.25	37559	2.6	2	227.90	43879	2.8
4	264.70	37779	1.6	3	226.60	44130	3.3
5	262.59	38082	10.0	4	225.60	44326	3.0
6	261.24	38279	8.2	5	224.11	44621	10.0
7	260.03	38448	1.1	6	223.11	44821	9.6
8	259.75	38498	1.0	7	shoulder		3.4
9	258.50	38685	1.6	8	shoulder		3.3
10	257.93	38770	0.9	9	221.16	45216	4.3
				10	220.26	45401	3.1

Table 1 (concl.).

Group No. 6

Peak No.	Absorption mμ cm^{-1}	Relative Intensity
1	218.90 45682	2.6
2	217.40 45998	3.7
3	216.20 46253	3.8
4	shoulder	---
5	214.00 46729	10.0
6	213.20 46904	9.0
7	211.40 47303	4.9
8	obscured	---
9	obscured	---

EXPERIMENTAL

All infrared spectra were taken with a Perkin-Elmer Infracord, Model 138. All samples were prepared as potassium bromide pellets unless otherwise noted.

All ultraviolet spectral measurements were conducted with a Cary Model 11 ultraviolet spectrometer. Vapor measurements were made using a 10 cm. quartz cell. Solution measurements were made using a 1 cm. quartz cell.

Mass spectral measurements were obtained using a Bendix model 12-100 time-of-flight mass spectrometer.

Elemental analyses were made by Dr. G. Weiler and Dr. F. B. Strauss, Microanalytical Laboratory, Oxford, England and by Galbraith Laboratories, Inc., Knoxville, Tennessee.

All melting points are uncorrected and were taken on a Fisher-Johns melting point apparatus.

Dimethyl Acetylenedicarboxylate

The ester was prepared from the corresponding acid by the method of Huntress and co-workers[23] with the exception that the esterification was allowed 17 days reaction time instead of 4 or 5 days. The reaction yielded 65.5 per cent of the theoretical quantity of ester distilling at 130°C. and 57-58 mm, n_D^{20} 1.4465.

Acetylenedicarboxamide

(A). The diamide was prepared from the corresponding dimethyl ester by the method of Moureu and Bongrand[32] in 70 per cent yield of a tan powder decomposing at 202-203°C.

(B). In a slight modification of the method of Moureu and Bongrand, liquid NH_3 was used in place of concentrated aqueous ammonia. The reaction system was immersed in an insulated n-propanol-dry ice bath. Slow dropwise addition of 10 g. (0.07 mole) of dimethyl acetylenedicarboxylate was carried out with vigorous stirring to prevent the reaction from becoming too vigorous. When addition was completed, 15 ml. of absolute methanol was added and the reaction mixture was allowed to warm to room temperature while stirring. The flesh-colored precipitate of the diamide was then treated as in the previous method,

yielding 5.89 g. (74.6 per cent of theoretical) of tan colored
product, decomposing at 202.5°C. Some brown crystals were re-
covered from the methanol washes of the crude diamide in pro-
cedures A and B. Treatment of the crystals three times with
activated charcoal and recrystallization from methanol yielded
long white needles melting at 161-2°C.

Anal. calcd. for $C_5H_8O_3N_2$: C,41.62; H,5.59; N,19.44.

Found: C,41.71; H,5.96; N,18.85.

Dicyanoacetylene

The essential principles of the method reported by Moureu
and Bongrand[32] were followed with some minor modifications. An
inert atmosphere was prepared by allowing solid carbon dioxide
to sublime in a dry box. Moisture in the atmosphere was removed
with calcium chloride. An intimate mixture of 17 g. (0.119
mole) of phosphorous pentoxide and 34 g. of calcined silicic
acid was obtained by shaking them vigorously together in a
250 ml. distilling flask. The silicic acid had no direct part
in the chemical reaction but was used as a diluent to prevent
to some extent the self-condensation of the product. Addition
of 2 g. (0.017 mole) of acetylenedicarboxamide to the flask was
followed by shaking as before. A loose glass wool plug was
placed in the side arm of the flask to prevent the carry-over
of solid material. A 50 ml. distilling flask receiver was

fitted to the side arm of the reaction flask and the side arm of
the receiver was connected to the vacuum system. The system was
cleaned by repeated flooding and evacuation of nitrogen. The
receiver was then immersed in a dry ice-n-propanol bath and a
slow stream of nitrogen passed through the system with pumping
to maintain the pressure at 1-2 mm while the reaction flask was
heated rapidly in an oil bath to a temperature of 215-220°C.
The reaction was essentially complete after 15 minutes but the
conditions were maintained for another 15-20 minutes to insure
as complete a reaction as possible. The receiver was disconnect-
ed, tightly stoppered and stored at dry ice temperature. The
dicyanoacetylene can be stored indefinitely at this temperature
under an inert atmosphere.

1,2-Dibromo-1,2-dicyanoacetylene

A small amount of dicyanoacetylene was sublimed at atmos-
pheric pressure from a storage flask into a 25 ml. Erlenmeyer
flask at dry ice temperature assisted by a stream of nitrogen.
The vaporization of the dicyanoacetylene was aided by warming
the storage flask with heat from the hand. A few drops of bro-
mine were added to the condensed dicyanoacetylene, the flask was
tightly stoppered and allowed to come to room temperature slowly.
After 2 to 3 hours a few orange-red crystals began to form on
the walls of the flask. The reactants were left in contact for

a week although the reaction appeared to reach completion in 2
to 3 days. Excess bromine was removed by vaporization at re-
duced pressure. The crystals were dissolved in methanol, warm-
ed on the steam bath and water was added until the solution be-
came cloudy. Just enough methanol was added to clear the solu-
tion. Cooling to 0°C. produced light yellow crystals of crude
1,2-dibromodicyanoacetylene. Sublimation three times yielded
white crystals, melting at 111-111.5°C.

Anal. calcd. for $C_4Br_2N_2$: C,20.36; Br,67.75; N,11.87.

Found: C,20.69; Br,67.50; N,11.65.

Ultraviolet Spectrometry of Dicyanoacetylene

To obtain the vapor spectrum of dicyanoacetylene the 10 cm.
cell was cooled to dry ice temperature and dicyanoacetylene was
sublimed into it assisted by a stream of gaseous nitrogen. The
cell was stoppered and allowed to come to equilibrium at the
temperature of the cell chamber of the instrument (approximately
23°C.). The spectrum was scanned initially from 340 to 210 mμ.
The first absorption appeared at 287.66 mμ. Subsequent spectra
were scanned from 290 to 210 mμ. The absorption wavelengths
and relative intensities are recorded in Table 1.

The spectra of dicyanoacetylene in iso-octane was measured
with the 1 cm. quartz cell. The dicyanoacetylene was introduced
by the method described previously. Iso-octane was added to fill

the cell and the spectrum was recorded after the cell reached
thermal equilibrium with the cell chamber. The extinction co-
efficient could not be determined due to the difficulty of
accurately measuring the amount of dicyanoacetylene introduced
into the cell. The dicyanoacetylene vapor pressure at room
temperature is 140 mm which made it impossible to open the cell
to admit solvent without losing a significant amount of sample.

The vapor spectrum of bromine-dicyanoacetylene was measur-
ed by placing a few drops of bromine in the 10 cm. cell and re-
cording the spectrum of bromine vapor at equilibrium with liquid
bromine. The cell was cleaned and dicyanoacetylene was added in
the manner previously described. After the equilibrium vapor
spectrum was recorded, the cell was cooled to dry ice temper-
ature, a few drops of liquid bromine introduced and the spectrum
was recorded again after the cell and its contents reached equil-
ibrium.

The spectral measurements to determine pi complexation
with 1,3,5-trinitrobenzene and naphthalene were carried out by
making a solution of dicyanoacetylene in iso-octane as described
previously. After recording the solvent spectrum of dicyano-
acetylene, a few crystals of the naphthalene or 1,3,5-trinitro-
benzene were added, dissolved and the spectrum of the mixture
recorded between 340 and 210 mμ. The spectra of the naphthalene
and 1,3,5-trinitrobenzene alone in iso-octane were recorded and

compared with the preceding spectra.

Mass Spectrometry of Dicyanoacetylene

The ion abundance and appearance potentials were measured using techniques developed at Kansas State University by Dr. R. W. Kiser and co-workers[20]. The spectra showed the parent molecule possessed a mass of 72, proving that the dicyano-acetylene exists as a monomer. The electron impact data obtained agreed favorably with that of Franklin and co-workers[18].

1,2,4,5-Tetracyanobenzene

(A). A mixture of 10 g. (0.0466 mole) of 1,2,4,5-tetra-chlorobenzene and 17.9 g. (0.20 mole) of cuprous cyanide was mixed intimately by shaking and heated in a sand bath with 10 ml. (approximately 0.137 mole) of dimethylformamide. The reaction was refluxed for 24 hours and then poured into 20 ml. of a solution prepared by dissolving 3.0 g. of ferric chloride and 1 ml. of concentrated hydrochloric acid for each 4.0 ml. of water used. The resulting mixture was warmed on a steam bath for 10 minutes and filtered. The residue was extracted twice with hot acetic acid and dissolved in boiling ethanol. Pale yellow crystals separated which were identical with starting material (m.p. 139-140°C.).

(B). A mixture of 5 g. (0.0233 mole) of 1,2,4,5-tetra-chlorobenzene and 9.0 g. (0.100 mole) of cuprous cyanide was prepared by the preceding method except that 20 ml. (approx-imately 0.290 mole) of pyridine was added in place of DMF. The reaction was refluxed for 24 hours, cooled and extracted twice with 100 ml. portions of concentrated, aqueous ammonia. The remaining residue and solution was dissolved in 100 ml. of benzene, then washed successively with 100 ml. portions of water, dilute hydrochloric acid, water and, finally, a saturated solu-tion of sodium chloride. Evaporation of the benzene layer re-sulted only in recovery of starting material.

(C). Another mixture of 5 g. (0.0233 mole) of 1,2,4,5-tetrachlorobenzene, 9 g. (0.100 mole) of cuprous cyanide and 5 ml. (approximately 0.072 mole) of pyridine was prepared by the preceding technique. The temperature was maintained at 300-325°C. for 24 hours in the sand bath and 210-215°C. in the re-action flask. Upon cooling, the reaction mixture solidified into a dark glass-like mass which necessitated breaking the flask to remove it. The mass was ground up and extracted twice with 100 ml. portions of concentrated aqueous ammonia. The sol-id remaining was boiled with benzene to extract the organic por-tion. Evaporation of the benzene extract yielded light yellow-brown crystals of starting material (m.p. 138-140°C.).

Nuclear Bromination of Durene

(A). A solution of 68.6 g. (0.43 mole) of bromine in 100 ml. of redistilled carbon tetrachloride was added dropwise, with stirring, to a solution of 25 g. (0.186 mole) of crude durene (1,2,4,5-tetramethylbenzene, Shell Chemical Co.), a few crystals of iodine to act as a catalyst and 50 ml. of redistilled carbon tetrachloride. After the addition was completed the reaction was stirred at room temperature for 10 hours. The solid product was filtered and dried in air. The carbon tetrachloride filtrate was evaporated, leaving more solid residue. The two products were combined and crystallized from petroleum ether yielding 43.2 g. (0.148 mole) of crude 3,6-dibromodurene (80 per cent of theoretical). Two additional recrystallizations from petroleum ether yielded fine white needles, m.p. 201.5-202°C.

(B). A procedure similar to that in part A, except that 1 to 2 hours of refluxing instead of 10 hours at room temperature, gave only a 41 per cent yield of dibromodurene. A 50 per cent theoretical excess of bromine was required for the reaction.

Oxidation of Dibromodurene

(A). A Carius pressure tube containing 2 g. (0.0067 mole)

of 3,6-dibromodurene and 30 ml. of 38 per cent nitric acid was heated to 180°C. for 3 hours. An additional 20 ml. of 100 per cent nitric acid was added and heating continued for 8 more hours. The insoluble material remaining was filtered and the filtrate evaporated to dryness, yielding a very small amount of product. The residue, less than 0.1 g., was combined with the product from part B without further purification. The infrared spectrum of the insoluble material from the reaction was identical with starting material.

(B). A mixture of 1 g. (0.0034 mole) of 3,6-dibromodurene and 40 ml. of 100 per cent nitric acid was heated under reflux for 3 hours with two additions, each of 10 ml., of fuming nitric acid. After 3 hours all the starting material appeared to have dissolved. Evaporation of the acid yielded a small amount of fine white crystals which were dissolved in dilute aqueous sodium hydroxide and reprecipitated with hydrochloric acid. Combination of this product with the product from part A and recrystallization from benzene yielded 0.11 g. (2.6 per cent of theoretical of the combined reactions) of material melting at 228-230°C. with slow decomposition. The neutralization equivalent was 190.6. The calculated neutralization equivalent was 94. The infrared spectrum was similar to authentic pyromellitic acid dianhydride.

(C). A mixture of 1 g. (0.0034 mole) of 3,6-dibromodurene

and 40 ml. of 5 per cent alkaline potassium permanganate was re-
fluxed for 4 hours. The mixture was then cooled, acidified with
3 molar sulfuric acid, heated gently for 1 hour, cooled and 40
per cent sodium hydrogen sulfite added to dissolve the manganese
dioxide. The fine white crystals obtained were filtered, washed
with water and crystallized from petroleum ether. The infrared
spectrum was identical with starting material.

(D). A mixture of 2 g. (0.0067 mole) of 3,6-**dibromo**odurene,
150 ml. of 5 per cent potassium permanganate and 10 ml. of con-
centrated acetic acid was warmed on a steam bath for 7 days.
The insoluble material remaining was filtered, slurried with
water, acidified with 3 molar sulfuric acid and treated with 40
per cent sodium hydrogen sulfite to dissolve the manganese di-
oxide. The white crystals remaining were filtered, washed with
ethanol and recrystallized from petroleum ether. The infrared
spectrum was identical with the starting material.

(E). Refluxing of 5 g. (0.0171 mole) of 3,6-dibromodurene
with 40 ml. of 100 per cent nitric acid was carried out for 18
hours with two additional portions of 10 ml. each of fuming ni-
tric acid added. Cooling and filtration yielded a small quant-
ity of fine white crystals melting at 246-49°C. Recrystalli-
zation from petroleum ether yielded 0.37 g. (5.7 per cent of
theoretical) of white crystals melting at 242-244°C. The in-
frared spectrum showed a strong doublet absorption at 5.40 and

5.55µ characteristic of acid anhydrides. The neutralization equivalent was 91.2 $\pm$ 1.5. The calculated neutralization equivalent was 94. Evaporation of the nitric acid filtrate yielded no further product.

(F). A mixture of 2 g. (0.0067 mole) of 3,6-dibromo-durene, 8 g. (0.0243 mole) of potassium dichromate dissolved in 30 ml. of water and 10 ml. of concentrated sulfuric acid was refluxed for 3 hours, cooled and poured into 100 ml. of water. The solution was then made basic with an excess of aqueous sodium hydroxide, precipitating chromium hydroxide and some white crystals which were filtered, yielding 1.4 g. of mixture, and then washed twice with benzene. The white crystals obtained from evaporation of the benzene were recrystallized from petroleum ether yielding 1.2 g. of material whose infrared spectrum was identical with starting material. Acidification of the filtrate from the reaction with dilute sulfuric acid yielded no further product.

Bromination of Dibromodurene

A solution of 62.4 g. (0.39 mole) of bromine in 100 ml. of redistilled carbon tetrachloride was added dropwise with stirring to a solution of 25 g. (0.085 mole) of 3,6-dibromodurene in 200 ml. of redistilled carbon tetrachloride while the reaction flask was exposed to sunlight. The stirring was continued in

sunlight after the addition until the evolution of hydrogen bro-
mide appeared to cease (3-4 hours). The large amount of pre-
cipitate which formed during the reaction was filtered, yield-
ing 18.8 g. of crude product. Partial evaporation of the car-
bon tetrachloride solvent yielded an additional 28.5 g. of
crude product which, combined with the initial precipitate,
gave a total of 47.3 g. (0.0778 mole) of crude 3,6-dibromo-1,-
2,4,5-tetrakis(bromomethyl)benzene (91.7 per cent of theoretical).
Recrystallization 3 times from bromobenzene yielded very fine
white crystals, m.p. 255-257°C. Recrystallization 3 more times
from benzene and two sublimations at reduced pressure yield-
ed fine white crystals melting at 265-266.5°C.

Anal. calcd. for $C_{10}H_8Br_6$: C,19.76; H,1.32; Br,78.91.
Found: C,20.03; H,1.16; Br,79.12.

<div align="center">

Oxidation of 3,6-Dibromo-1,2,4,5-tetrakis-
(bromomethyl)benzene

</div>

A mixture of 20 g. (0.033 mole) of 3,6-dibromo-1,2,4,5-
tetrakis(bromomethyl)benzene and 100 ml. of 70 per cent nitric
acid was refluxed for 18 hours while passing a stream of air
into the mixture. The solid material remaining was filtered
and the filtrate was evaporated, yielding a small quantity of
product. The solid material and 150 ml. of 70 per cent nitric
acid were refluxed for 24 hours without passing air into the

solution. The solid remaining was then filtered, yielding 4 g. of material insoluble in dilute sodium hydroxide, water or benzene. The infrared spectrum was not identical with the starting material, although the carbonyl absorption of a car-boxylic acid or anhydride were not present. The substance was not identified. The acid filtrate was evaporated on a steam bath and the residue was combined with the residue from the first evaporation yielding a total of 4.32 g. of crude 3,6-dibromopyromellitic acid (32 per cent of theoretical). The acid was purified by dissolving it in aqueous sodium hydroxide and reprecipitation upon acidification with dilute hydrochloric acid.

Hydrolysis of 3,6-Dibromo-1,2,4,5-tetrakis-(bromomethyl)benzene

A mixture of 10 g. (0.0164 mole) of 3,6-dibromo-1,2,4,5-tetrakis(bromomethyl)benzene, 100 ml. of dioxane and 40 ml. of 25 per cent aqueous sodium hydroxide was refluxed with vigorous stirring for 8 hours. Upon cooling, 4.56 g. of solid material was obtained by filtration. Evaporation of the dioxane yield-ed an additional 1.08 g. The two products were combined and extracted with 50 ml. of boiling acetone. Evaporation of the acetone yielded 0.72 g. of product melting at 145-47°C. whose infrared spectrum contained a strong -OH absorption at 2.85μ.

In other respects the spectrum was quite similar to that of the
starting material. The spectrum of the product which was in-
soluble in acetone was almost identical with the acetone-sol-
uble product with the exception that the -OH absorption was much
weaker. The insoluble product did not melt below 300°C., al-
though it began to undergo slow decomposition in the region of
240-260°C. Recrystallization from common solvents was not poss-
ible because of the limited solubility of the compound. It was
very sparingly soluble in DMF and after one recrystallization
still showed a melting point greater than 300°C.

Bromination of Pyromellitic Acid Dianhydride

(A). To a mixture of 5 g. of PMDA (0.023 mole) and 50 ml.
of fuming sulfuric acid (about 20 per cent SO_3) 0.5 g. (0.009
mole) of iron powder was added. Upon warming the mixture with
stirring the PMDA dissolved and 32 g. (0.20 mole) of bromine
was added dropwise, a reflux condenser being attached to the
flask. Heating was continued for 2 hours with stirring. Upon
cooling, a gray precipitate was obtained which was insoluble in
benzene, petroleum ether (b.p. 65-70°C.) or carbon tetrachloride.
Fusion with potassium carbonate-magnesium resulted in a nega-
tive test for halogen. The infrared spectrum was identical
with the spectrum of authentic pyromellitic acid (1,2,4,5-tetra-
carboxybenzene).

(B). A solution of 2 g. (0.0091 mole) of PMDA, 35 ml. of trichloroethylene, 2 g. (0.0112 mole) of N-bromosuccinimide and 0.1 g. of benzoyl peroxide catalyst was heated at reflux temperature for 4 hours. After removal of the solvent by evaporation, the residue was extracted with acetone to remove the NBS and fused with potassium carbonate-magnesium in order to test for halogen (negative). The infrared spectrum of the residue was identical with the starting material.

(C). A Carius pressure tube containing 2 g. (0.0091 mole) of PMDA and 15.6 g. (0.195 mole) of liquid bromine was heated to 150°C. over a 6 hour period. After cooling, the excess bromine was extracted with carbon tetrachloride. The residue was crystallized from hot acetone and fused with potassium carbonate-magnesium to test for halogen (negative). The infrared spectrum was identical with authentic pyromellitic acid.

(D). Refluxing a solution of 2 g. (0.0091 mole) of PMDA and 45 ml. of dimethylformamide with 17.16 g. (0.214 mole) of bromine for 3 hours resulted in a very dark solution. The dimethylformamide solvent was removed by distillation at 20 mm pressure, leaving a dark colored residue which was extracted several times with water. The extracts were combined and evaporated, leaving a brown residue which, after treatment with activated charcoal, yielded white crystals that decomposed slowly upon heating. Attempted sublimation yielded, instead, a copious

amount of white gas, sparingly soluble in water, odorless and acidic to moist litmus paper. Analysis for bromine by fusion and precipitation of the water soluble portion with silver nitrate revealed that the compound contained 53.3 per cent bromine. The residue remaining after the water extraction was recrystallized from acetone, yielding fine white crystals whose infrared spectrum was identical with authentic pyromellitic acid dianhydride.

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SYNTHESIS OF CERTAIN NITRILES USEFUL IN THE
FORMATION OF PI COMPLEXES

by

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AN ABSTRACT OF

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Recent research in pi complexations with tetracyanoethylene and other low molecular weight unsaturated compounds indicates that other unsaturated alkyl nitriles and polycyanobenzenes might be expected to demonstrate pi complexation ability. Few compounds of this nature have been previously studied.

The pi complexing ability and ultraviolet absorption spectrum of dicyanoacetylene was studied. The dicyanoacetylene did not display any tendency to undergo pi complexation, either as a pi acid with naphthalene, or as a pi base with bromine and tri-nitrobenzene. Upon extended contact with bromine, however, an addition compound, $C_4N_2Br_2$, was formed which had not previously been isolated. The attempt to trimerize dicyanoacetylene to form hexacyanobenzene yielded no positive results.

The feasibility of applying the Friedman modification of the Rosenmund-Von Braun method of nitrile synthesis from halogens was investigated briefly. 1,2,4,5-tetrachlorobenzene failed to react under a variety of conditions in the attempt to find an alternate synthesis for the recently reported 1,2,4,5-tetracyano-benzene.

The pilot work in the preparation of a series of fully sub-stituted polycyanobenzenes is described. The 3,6-positions of 1,2,4,5-tetramethylbenzene (durene) were readily brominated under mild conditions with good yields. However, oxidation of the methyl groups to the corresponding 3,6-dibromopyromellitic acid

resulted mainly in decomposition with very low yields. Further
bromination of the methyl groups yielded 3,6-dibromo-1,2,4,5-tetra-
kis(bromomethyl)benzene, a new compound synthesized independently
by Hopff and Manukian. Oxidation of this compound with strong
nitric acid yielded the desired carboxylic acid in fair yield.
Hydrolysis of the bromomethyl groups to hydroxymethyl groups in
order to facilitate easier oxidation resulted in a product the
major portion of which was apparently an inter- or intramolecular
ether.

Direct bromination of pyromellitic acid dianhydride by ionic
and free radical reactions was unsuccessful.