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# Energy Conversion

## *Electrical Properties of Organic Compounds*

### SEMIANNUAL TECHNICAL REPORT

*(Period Covering 1 July-31 December 1961)*

**9 FEBRUARY 1962**

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*Prepared for DEPUTY COMMANDER AEROSPACE SYSTEMS*

*AIR FORCE SYSTEMS COMMAND*

*UNITED STATES AIR FORCE*

*Inglewood, California*

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## ABSTRACT

The objective of this program is to determine the mechanism of electronic conduction process in organic compounds to provide data for the development of new solid-state and energy-conversion concepts.

Syntheses of structures related to 7,7,8,8-tetracyanoquinodimethane, whose derivatives have been reported to exhibit extremely high conductivities ( $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$ ), as well as other polycyano and polyhydroxyaromatic compounds, were investigated. Electrical properties, such as conductivity, photoelectric effects, radio frequency loss angle, mobility, and lifetime of charge carriers, will be determined. From such investigations, it should be possible to deduce the nature of the electronic conduction process in organic compounds.

The experimental programs initiated during the past year are:

- (1) the synthesis of organic compounds capable of exhibiting relatively high electrical conductivity, and
- (2) the measurement of their electrical properties.

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## I. INTRODUCTION

The objective of this program is to determine the mechanism of electronic conduction processes in organic compounds to provide data for the development of new solid-state and energy conversion concepts.

Although most organic compounds are insulators, a limited number have electrical properties which place them in the semiconductor class. Perhaps the most interesting is 7,7,8,8-tetracyanoquinodimethane, whose derivatives have been reported to exhibit extremely high conductivities ( $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$ ) and immeasurably low mobilities. This anomalous electrical behaviour is an indication of an electrical conduction mechanism which differs from that of metals or semiconductors such as silicon and germanium.

Organic structures related to 7,7,8,8-tetracyanoquinodimethane, hexacyanobenzene, and polyhydroxy aromatic compounds will be synthesized. Some of the more important electrical properties such as conductivity, photoelectric effects, radio frequency loss angle, mobility, and lifetime of charge carriers will be determined. From such investigations it should be possible to deduce the nature of the electronic conduction process in organic compounds.

The experimental programs initiated during the past year are: (1) the synthesis of organic compounds capable of exhibiting relatively high electrical conductivity, and (2) the measurement of their electrical properties.

## II. BACKGROUND INFORMATION

Only in recent years has a considerable interest in the study of the electrical properties of organic compounds developed, although the photo-conductivity of anthracene was first discovered in 1906 by Pocchettino.<sup>1</sup> An impetus for the current research activity in this field was perhaps provided by the suggestion of Szent-Györgyi<sup>2</sup> in 1941 that the transfer of electrons between molecules may play an important role in many biological processes. Despite the large number of papers which have appeared since then on the electrical properties of organic materials, a full understanding of the semiconducting phenomena has not been obtained.

The resistivity of organic compounds can be described by the following relationship:

$$\rho = \rho_0 \exp ( E/kT ) \quad (1)$$

where  $\rho$  and  $\rho_0$  are resistivities,  $E$  is an energy term,  $k$  is the Boltzman constant, and  $T$  is the absolute temperature at which  $\rho$  is determined. Equation (1) is also frequently expressed in terms of conductivity,  $\sigma$ , which is the reciprocal of resistivity.

The electronic conduction phenomena is a result of a thermal or optical excitation of electrons from a filled valence band to a higher, empty conduction band. An electron, once having reached the conduction band, is free to delocalize and to move freely through the solid under the influence of an electric field. The vacancy or hole left behind in the valence band by the excitation of an electron behaves as a positive charge and also is free to move and contribute to conduction. The energy term,  $E$ , is a measure of the required excitation energy, and is commonly referred to as the "energy gap" between the two bands. The energy gap value influences the conductivity by governing the number of charge carriers, both holes and electrons. Metals, with a zero energy gap, have a large number of charge carriers and a high room

temperature conductivity, generally greater than  $10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$ . Semiconductors have energy gaps ranging from zero to about 2 eV; they contain fewer charge carriers than metals and have conductivities ranging from  $10^3$  to  $10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$ . Insulators are characterized by even larger energy gaps and a consequently negligible concentration of charge carriers. This accounts for their low conductivity, ranging from  $10^{-11}$  to  $10^{-22} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

Conductivity is also a function of carrier mobility, being a product of mobility and carrier concentration. Semiconductors with the same conductivity may have widely different carrier concentration and mobility values.

Although most organic compounds are insulators, a limited number have electrical properties which place them in the semiconductor class. Perhaps the most interesting is the 7,7,8,8-tetracyanoquinodimethane (TCNQ) whose derivatives<sup>3,4</sup> have been reported to exhibit extremely high conductivities ( $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$ ). Included among the compounds which are being studied are the derivatives of TCNQ and related structures as well as the polyhydroxy aromatic compounds which may exhibit relatively high conductivity.

### III. EXPERIMENTAL INVESTIGATION

#### A. Measurement of Electrical Properties

A simple aluminum conductivity cell was built for dc resistivity measurements in which a single crystal or polycrystalline wafer specimen is mounted between two silver strip electrodes and supported by a Teflon block. The electrodes are bonded to the specimen with silver conducting paste. The input terminals are shielded and connected in series with a regulated voltage source and a Keithley electrometer. A schematic diagram of the circuit is shown in Fig. 1. The resistivity is determined by measuring the current through the specimen with the electrometer at several applied voltages ranging from 25 to 500 v. An oven is used to extend the measurements above room temperature. A variac supplies power to heat the oven, and several thermocouples are used to record oven and conductivity cell temperatures. Dry nitrogen is cycled through the cell during the entire measurement period.

To calibrate and check the measurement procedure, the resistivity of scintillation grade anthracene crystals was measured. The crystals, obtained from the Harshaw Chemical Company, were 1 cm in diameter and 2 mm thick. The resistivity was measured perpendicular to the cleavage (ab) plane of the crystal. The data obtained from two different samples are presented in Fig. 2. The room temperature resistivity of  $4 \times 10^{15}$  ohm cm was found to be lower than an extrapolation of the higher temperature data would indicate. It is not yet clear if this indicates extrinsic or impurity conduction at room temperature. The linear portion of the log curve gives values of 0.75 ev for the activation energy of conduction and  $\rho_0 = 0.042$  ohm-cm when applied to Eq. (1). These values are in reasonable agreement with those reported in the literature.<sup>5, 6, 7</sup>

Another important semiconductor parameter is the lifetime of the minority charge carriers. The Morton-Haynes method,<sup>8</sup> originally devised for

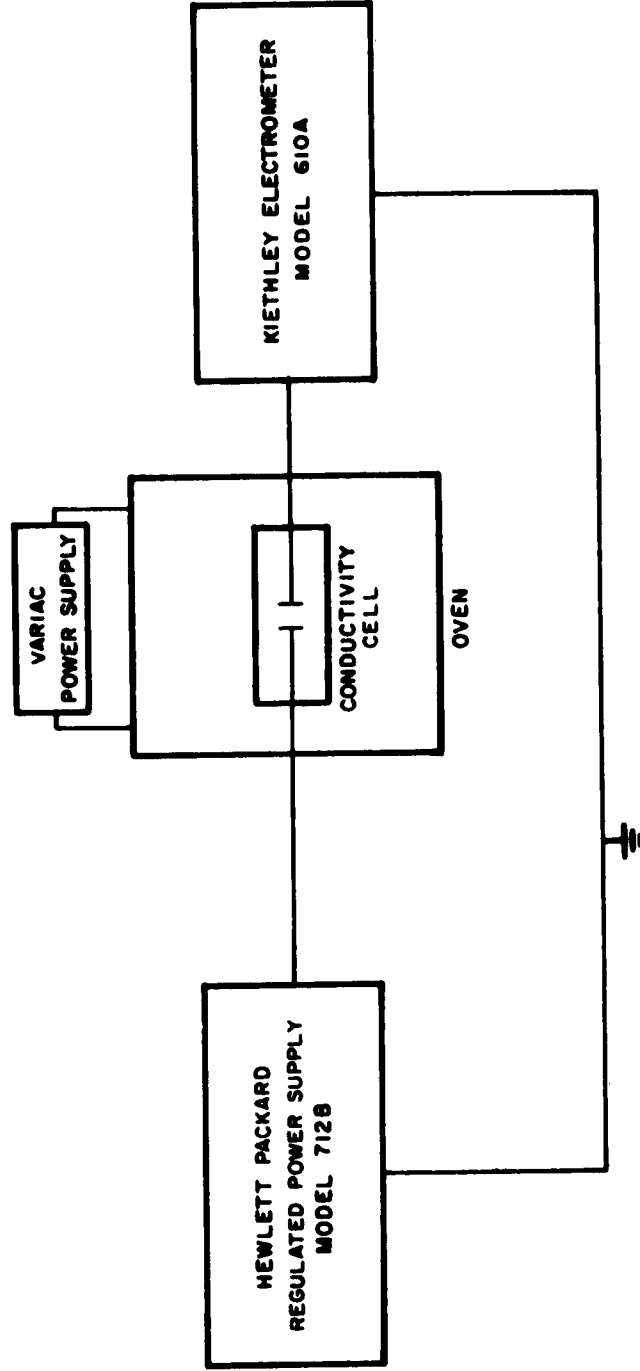


Fig. 1. Schematic Diagram of Measurement Circuit.

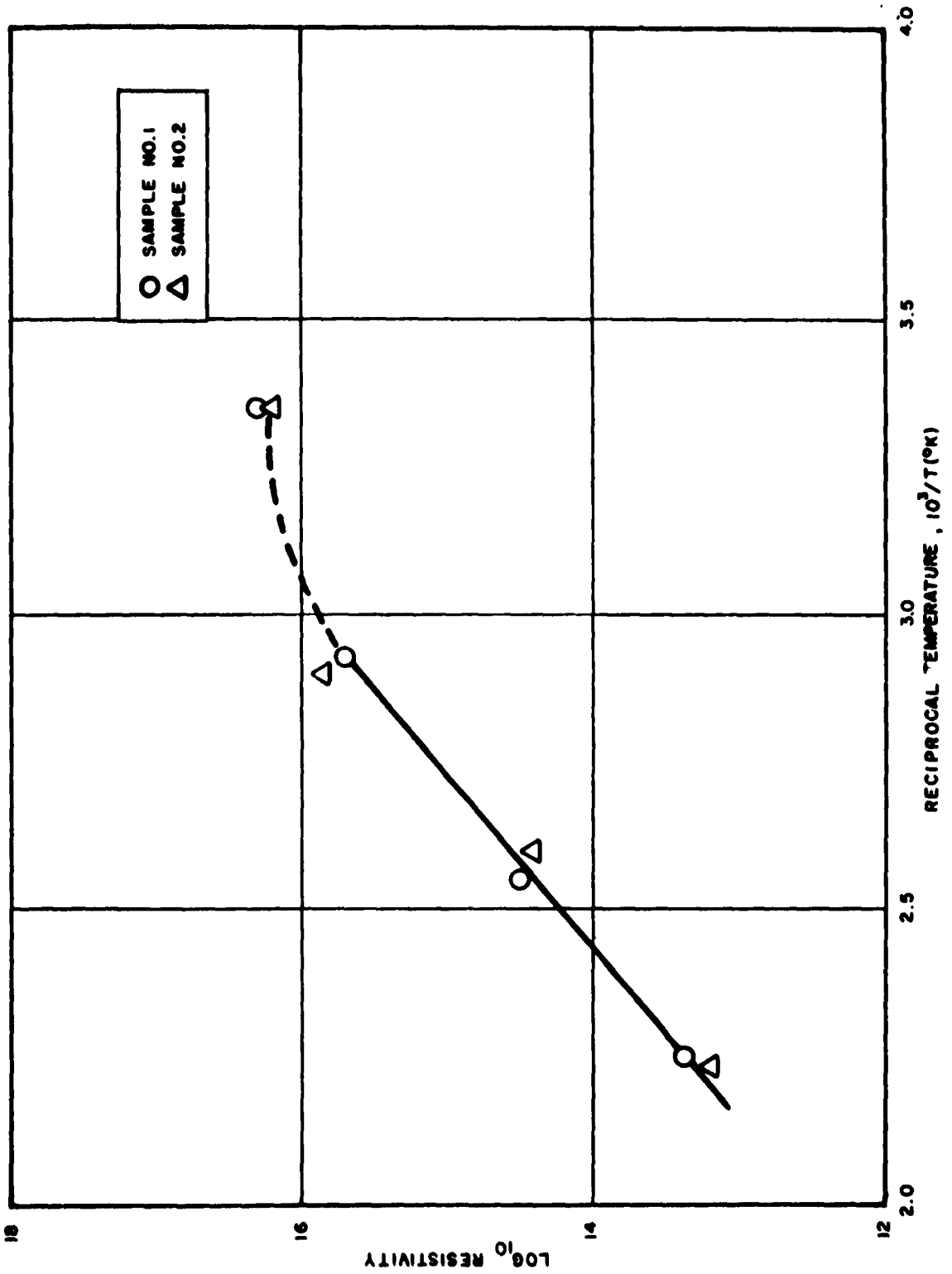


Fig. 2. Resistivity of Anthracene.

germanium, has been selected to measure this parameter in anthracene. Experimentally the method consists of generating hole-electron pairs by light on the surface of the crystal specimen and measuring the concentration of minority carriers as a function of distance from the point where they are liberated. This provides a measure of the diffusion length of the minority carriers, which can be related to the lifetime when the carrier mobility is known. Both hole and electron mobilities in anthracene have been measured and are approximately  $1 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ .<sup>7</sup> This leaves only the diffusion length to be determined to calculate minority carrier lifetime.

Thermoelectric power measurements have indicated that anthracene is characteristically a p-type semiconductor with conducting electrons present as the minority charge carrier.<sup>10</sup> It will be possible to verify the type of charge carrier, noting the polarity of the measured signal developed in the photoconductivity mobility and lifetime experiments.

A schematic diagram of the apparatus is shown in Fig. 3. The light from a 1 kw Xenon-mercury lamp (Hanovia Model No. 537B) passes through an adjustable slit and, by means of a chopping disk driven by a synchronous motor, is interrupted as a 17 cps square wave. A quartz lens and a planar mirror are used to focus an image of the slit on the surface of the anthracene crystal. The position of the lens can be adjusted in a support tube which is provided with a baffle and painted black internally to cut down the scattered light. A microscope stage is used as a micromanipulator to move the crystal and detector probe relative to the center of the stationary illuminated slit line. The detector probe is 36-gauge platinum wire attached to the anthracene crystal by means of a slight spring action and silver conducting paste. The opposite side of the anthracene crystal is attached to a silver strip with silver paste and acts as the reference electrode. The anthracene crystal obtained from Harshaw Chemical Company was 1 in. in diameter and 3 mm thick. A 3-v mercury battery is used to bias the collector point in the reverse direction since the

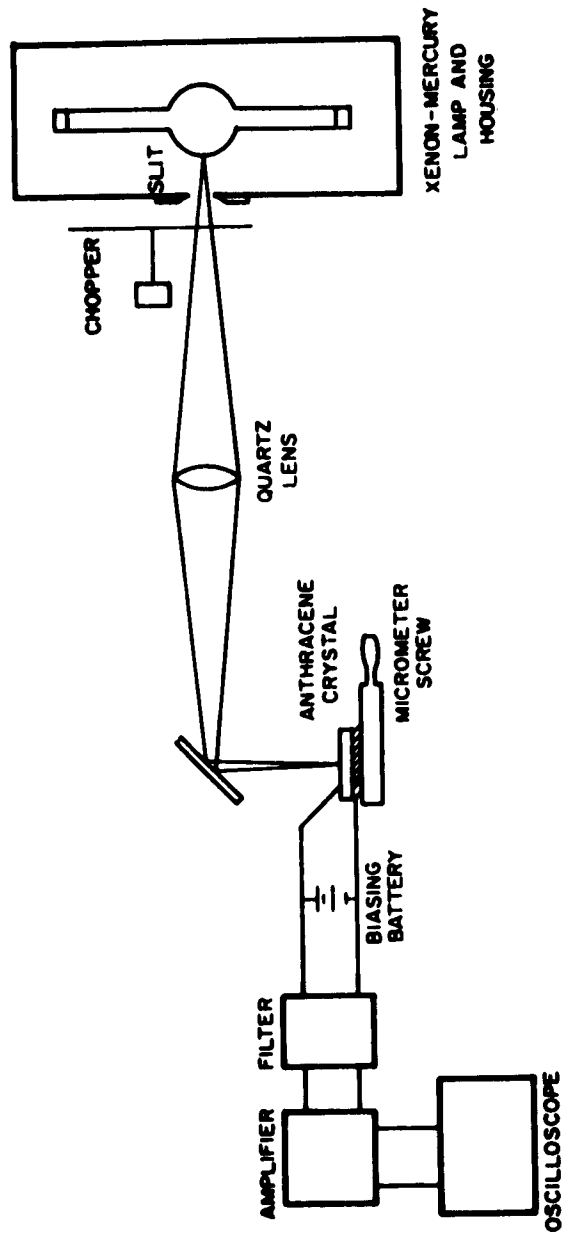


Fig. 3. Schematic Diagram of Carrier Lifetime Apparatus.

current through such a point is linearly related to the minority carrier density. Both the battery and crystal are enclosed in a small shielded box to minimize the pickup of extraneous signals. The rest of the measuring circuit consists of a narrow band-pass filter turned to the frequency of the square wave of chopped light, a sensitive amplifier, and an oscilloscope to display the signal. Thus far, the signal-to-noise ratio has been too low to yield significant results. The experiment will be continued with more emphasis on the method of attaching the collector probe to the anthracene. One technique that will be tried will be to electrically heat the probe and while it is still hot, press it onto the crystal surface. Following attachment of the electrode, a high-voltage-forming pulse will be sent through the electrode contact to further enhance the collection of the minority carriers.

In conjunction with the electrical measurements program, several methods of purifying the organic compounds will be investigated. Sublimation apparatus was built and a Fisher zone refiner was acquired to zone refine substances melting below 300°C. Both pieces of equipment can be used to grow single crystals for electrical property studies.

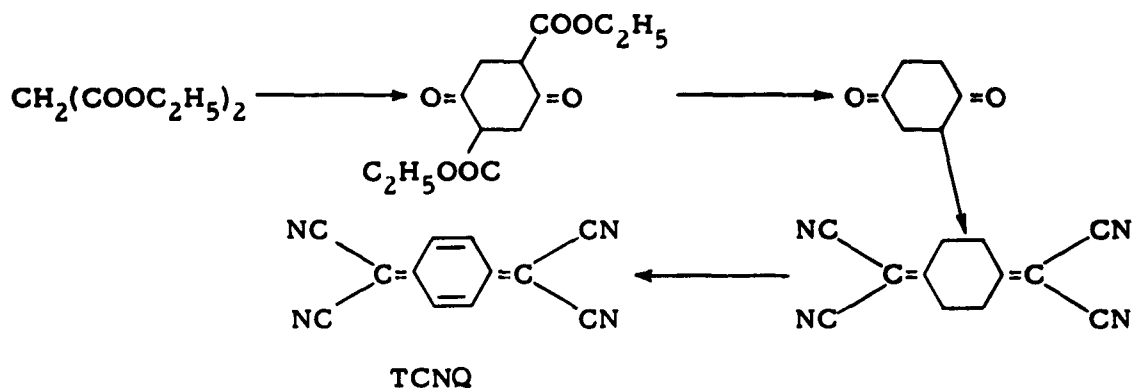
Copper phthalocyanine has been successfully sublimed and recrystallized at 450°C in a nitrogen atmosphere. The resulting crystals, however, were found to be too small for direct measurement. A mold has been built to compress these needle-like crystals into a polycrystalline wafer specimen.

#### B. Chemical Syntheses

A brief discussion of the syntheses of organic compounds, which are of interest in the present program, together with the results of the experimental work is presented in this section. Since in the majority of the cases the reactions discussed are still under study, only a limited amount of conclusions or interpretations can be drawn at this time.

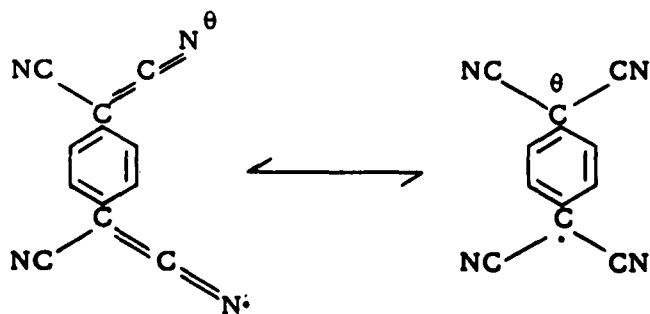
In view of the high conductivities reported for anion radical derivatives of TCNQ,<sup>4</sup> syntheses of these compounds were undertaken to familiarize

ourselves with their chemical and physical properties and to determine electrical properties as a standard of comparison. TCNQ has been prepared by DuPont using the following sequence of reactions:



Although the synthetic route for the successful preparation of TCNQ is given in the literature, neither the description of the experiments nor the properties of the intermediates is mentioned. The above reaction sequence has been carried out in the laboratory with little difficulty except in the last step. This step involving the dehydrogenation of 1,4-bis(dicyanomethylene) cyclohexane appears to be extremely sensitive to the amount of pyridine and bromine used. However, a product melting at the value reported<sup>4</sup> for TCNQ has been obtained.

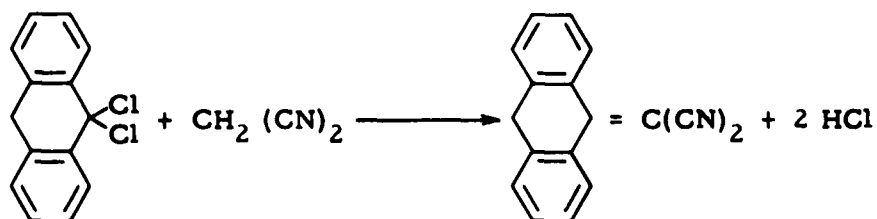
TCNQ undergoes a one-electron reduction to form an anion radical whose structure may be illustrated as:



The highest conductivity ( $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$ ) has been reported for the anion radical complex containing a quinolinium cation, TCNQ anion radical, and a neutral molecule of TCNQ. Several anion radical derivatives of TCNQ will be prepared, and measurements of their electrical properties will be carried out.

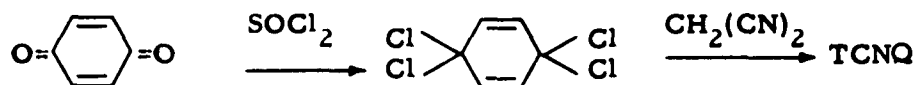
Other methods of syntheses of TCNQ and related structures are also being explored.

It has been reported<sup>11</sup> that the condensation of 9,9-dichloroxanthene with malonitrile produced an almost quantitative yield of xanthenemalononitrile, whereas when xanthone, itself, was reacted with the above dinitrile, a very poor yield of the product was obtained:



In view of the fact that the direct condensation of p-benzoquinone with malonitrile results<sup>12</sup> in ring substitution, this gem dichloride approach toward the synthesis of TCNQ appeared promising.

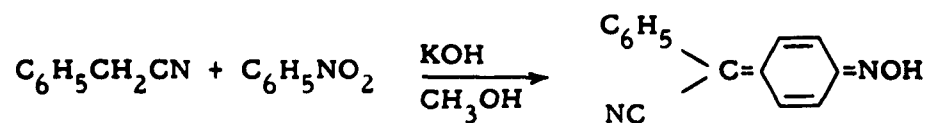
The reaction of p-benzoquinone with thionyl chloride was carried out. The resulting product upon heating with malonitrile produced a vigorous reaction with an evolution of hydrogen chloride:



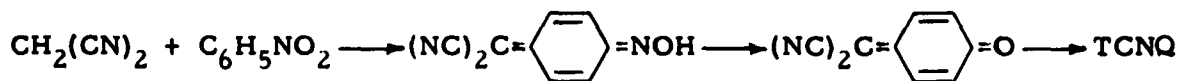
Although the product has not yet been definitely identified, the preliminary observations made on the above reaction sequence closely parallel that reported for the conversion of xanthone to 9,9-dichloroxanthene and finally to xanthenemalononitrile.

In addition to p-benzoquinone, other quinones such as chloranil and anthraquinone are also being investigated. The successful replacement of the oxygens of quinones with the dicyanomethylene structure would make possible the synthesis of a wide variety of compounds related to TCNQ.

Davis et al.<sup>13</sup> have reported that phenylacetonitrile condensed readily with a wide variety of substituted nitrobenzenes to yield phenylcyanomethylenequinone oximes. The para position was the preferred position of attack producing the quinone-like structures. For example, phenylacetonitrile was reacted with nitrobenzene in alcoholic potassium hydroxide to yield phenylcyanomethylenequinone oxime:



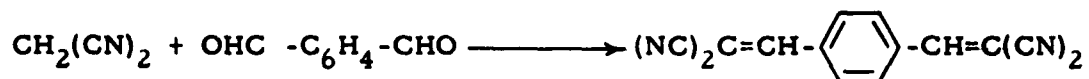
The above reaction provides a potential route to the synthesis of TCNQ and related compounds. If malononitrile can be condensed with nitrobenzene, the resulting compound would be dicyanomethylenequinone oxime. The hydrolysis of this oxime and the subsequent condensation with another molecule of malononitrile would produce TCNQ. The reactions may be expected to proceed as follows:



It may be possible to hydrolyze the oxime directly, or, alternatively, to convert it to the ketone by trans-oximation with a more reactive ketone, such as formaldehyde. Similarly, the ketone may be condensed directly with malononitrile, or initially reacted with thionyl chloride to yield the dichloro compound, and then converted to TCNQ.

In the preliminary experiments, the desired oxime has not been obtained. The condensation of malononitrile with nitrobenzene appeared to proceed in alcoholic potassium hydroxide in that the expected color changes were observed. A solid was obtained which is believed to be the potassium salt of the expected oxime (or the isomeric nitroso derivative). However, upon acidification of this salt, a considerable evolution of gas identified as hydrocyanic acid was observed. Although the dicyanomethylenequinone oxime has not yet been obtained, this reaction is being investigated further. The reactions of other active methylene compounds with nitrobenzene are also being studied to yield compounds having the quinone-like structure which may exhibit interesting electrical properties.

The condensation of terephthalaldehyde with malononitrile will result in a compound having a structure related to TCNQ.

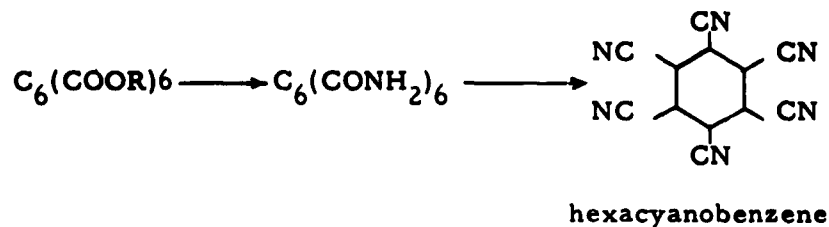


This compound has been prepared in methanol using piperidine as a catalyst. It is conceivable that this tetracyano compound may also undergo a one-electron reduction to form the anion radical.

A percyano compound which is of particular interest in the present program is the heretofore-unreported hexacyanobenzene. The presence of six cyano groups on a benzene nucleus would impart an even greater deficiency of electrons in the ring than is obtained with TCNQ which has four cyano groups, and should complex readily with electron donors and also form anion radical derivatives. Because the mechanism of electronic conduction is closely related to the electron acceptor-donor quality of the molecule, the properties of hexacyanobenzene should be interesting.

Hexacyanobenzene is, at first glance, a simple compound in the sense that it is a benzene molecule in which the hydrogens are replaced by cyano

groups. The most obvious route to the synthesis of hexacyanobenzene is through (1) mellitic acid, ester, (2) its conversion to the amide, and, finally, (3) dehydration to the nitrile:



This is a conventional method for preparing organonitriles. The fact that hexacyanobenzene has not been prepared would indicate that this route may not be as simple as it appears.

Hexamethyl mellitate, the starting material for the above synthesis, was prepared by the trimerization of dicarbomethoxyacetylene in acetic acid and pyridine according to the method of Diels.<sup>14</sup> Although the trimerization reaction was accompanied by a considerable amount of polymer formation, the ready availability of dicarbomethoxyacetylene made this method a convenient route to the mellitic acid ester. On the other hand, the acetic acid-pyridine trimerization of dicarbomethoxyacetylene resulted in an extremely poor yield of hexamethyl mellitate.

In addition to the method described above, hexamethyl mellitate was obtained using dimesitylnickel as a trimerization catalyst. This organonickel compound has been reported by Tsutsui and Zeiss<sup>15</sup> as an effective catalyst for the aromatization of 2-butyne and tolane.

Perhaps the best possible method for obtaining hexacyanobenzene is through the trimerization of dicyanoacetylene:

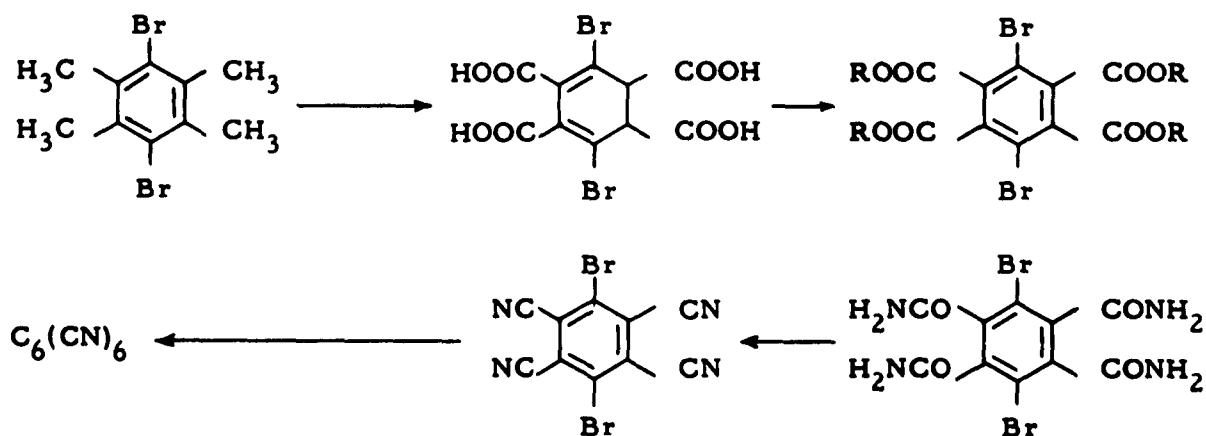


A variety of catalysts for the trimerization of acetylenic derivatives have been reported, including the dimesitylnickel mentioned earlier. Many of them give relatively good yields, and the reaction offers a convenient one-step route to the hexa-substituted benzene derivatives.

In preparation for the attempted synthesis of hexacyanobenzene by the trimerization of dicyanoacetylene, this compound was prepared by the procedure of Blomquist and Winslow.<sup>16</sup> Dicarbomethoxyacetylene was converted by ammonolysis to dicarbonamidoacetylene. The diamide, thus obtained, melted considerably lower ( $\sim 215^\circ\text{C}$ ) than that reported in the literature ( $\sim 290^\circ\text{C}$ ), but the dehydration of this relatively low melting diamide with phosphorus pentoxide yielded dicyanoacetylene.

Due to the difficulty in carrying out large-scale dehydration of dicarbonamidoacetylene by Blomquist's procedure, other methods of syntheses of dicyanoacetylene were investigated. These methods include the attempted dehydration of the diamide with thionyl chloride and also with lithium aluminum hydride, as well as dehydrobromination of the dibromide of fumaronitrile. These reactions were not successful.

Another possible route to hexacyanobenzene may be schematically represented as follows:

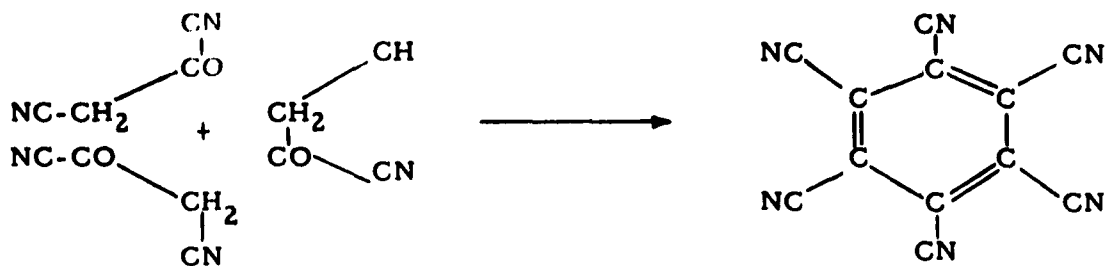


Although most of the intermediates involved in this synthesis have not been reported in the literature, procedures described for analogous compounds can be applied to the present reaction scheme. For example, the preparation of 3,3',4,4'-tetracyanodiphenyl ether following a similar series of reactions has been reported.<sup>17</sup> A potential difficulty in this sequence may be the loss of the substituent group attached to the benzene ring during the conversion of the methyl groups to nitriles. As a first step in the above synthesis scheme, the bromination of durene was carried out in chloroform. Permanganate oxidation of dibromodurene, thus obtained, in a pyridine-water solution has resulted in an unidentified compound. This reaction does not appear to be promising, for, upon acidification of the oxidation mixture, an evolution of gas, believed to be carbon dioxide, was observed. This would indicate that the desired dibromopyromellitic acid was not obtained.

Analogous to the use of dibromodurene outlined above, a sequence of reactions for the synthesis of hexacyanobenzene may be carried out starting with tribromomesitylene. The lability of the substituents attached to the phenyl ring will differ in the two cases, and this route may prove superior to the other.

Although it is well known that halogenation of the benzene ring containing electronegative groups is extremely difficult, it has been reported that pyridine,<sup>18</sup> aromatic aldehydes, ketones<sup>19</sup> and nitriles can be halogenated by using a large excess of aluminum chloride; this method is known as the "swamping catalyst" effect. Since 1,2,4,5-tetracyanobenzene was available, a bromination of this compound to obtain 3,6-dibromo-1,2,4,5-tetracyanobenzene was attempted under the swamping catalyst conditions. In addition to the starting material, a product not yet identified was obtained.

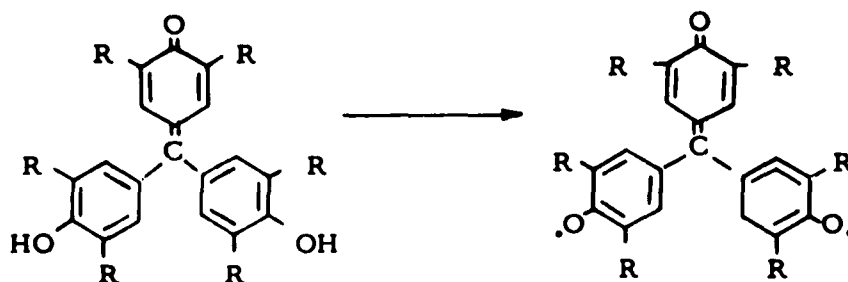
It is possible that hexacyanobenzene may be prepared by a condensation reaction of appropriate starting materials. A number of condensation reactions to yield the desired product may be visualized. For example, self-condensation of  $\alpha$ -ketosuccinonitrile should proceed as follows:



One attempt to prepare  $\alpha$ -ketosuccinonitrile by reacting cuprous cyanide with the product of cyanoacetic acid and thionyl chloride was not successful.

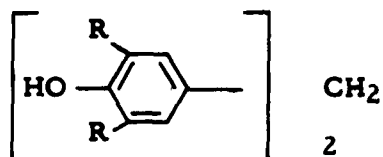
From the vastly different methods of approach mentioned for the synthesis hexacyanobenzene, at least one should lead to the successful synthesis of the desired product. It is believed that hexacyanobenzene and its derivative should exhibit unique chemical and electrical properties which would warrant intensive synthetic effort.

Electrical properties of organic compounds other than those containing polycyano groups merit investigation. The preparation of a stable biradical has recently been reported<sup>20</sup> by the following reaction:

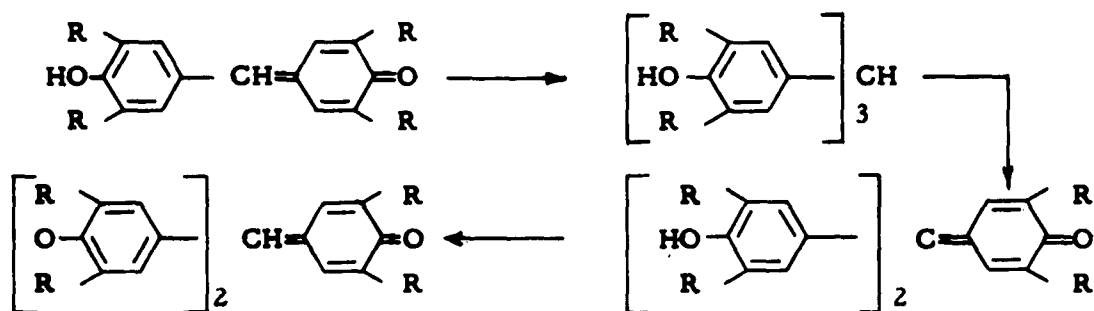


where R is a tertiary butyl group. In addition, certain polyhydroxy aromatic compounds readily undergo one-electron oxidation with the formation of a radical. In view of the high conductivities exhibited by certain charge-transfer complexes having a radical structure, it is of interest to study a series of compounds capable of being converted into relatively stable radicals.

For this study, a 4,4'-dihydroxydiphenylmethane derivative having the structure given below was prepared by the reaction of 2,6-di-*t*-butylphenol with formaldehyde, by the procedure of Kharasch and Joshi<sup>21</sup>:

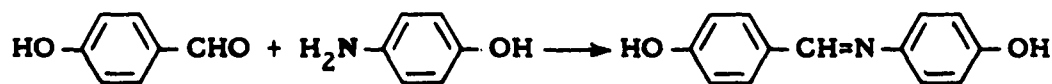


This compound is available commercially, but can readily be prepared in the laboratory. It was converted to the dihydroxydiphenylbromomethane derivative by bromination in acetic acid and then dehydrobrominated to the quinone-like structure in sodium hydroxide. Attempts will be made to effect the condensation of this quinone with another molecule of a phenol derivative to obtain compounds capable of forming a biradical.

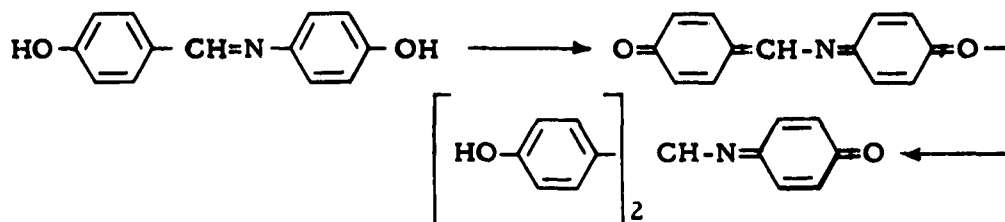


The substituent groups, R, should be varied to study the effect of the structure on conductivity properties.

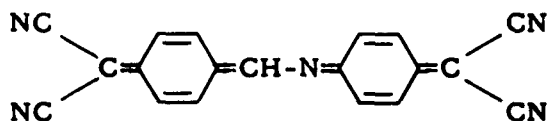
It was also of interest to prepare nitrogen-containing polyhydroxy aromatic compounds. For example, *p*-aminophenol was reacted with *p*-hydroxybenzaldehyde to yield a Schiff base product:



The oxidation of the above Schiff base to the quinoid structure is currently being investigated. If the compound having the quinoid structure can be obtained, it may be possible to condense it with a phenolic derivative to give a product as follows:



Whether the radical formed from this type of compound would exhibit high conductivity remains to be seen. Perhaps more interesting is the possibility of condensing dicyanomethylene groups with the various quinone compounds of this series. An example of such a structure is the following analogue of TCNQ:



Although one of the major objectives of the present program is the correlation of chemical structures with electrical properties, an investigation of certain polymers is worthy of consideration. A study of polymers is made more complex by the fact that in most cases the exact nature of their structures is not known with any degree of certainty. Thus, the interpretation of the conductivity data and especially their application to any theoretical model is extremely difficult. Nevertheless, a knowledge of the number of charge carriers and of their mobilities and the correlation of data with the gross structure of the molecule will be informative. Polymeric materials may realize certain device applications, although the exact mechanism of the conduction may not be well understood.

A class of polymers which may be investigated is the polymeric phthalocyanine derivatives. Phthalocyanine has a completely conjugated double bond system, a structure which appears to facilitate electronic conduction in organic compounds. In preparation for the synthesis of polymeric phthalocyanine, 1,2,4,5-tetracyanobenzene was prepared by the ammonolysis of pyromellitic dianhydride which yielded 1,2,4,5-tetracarboxamidobenzene. The tetra-amide was then dehydrated with thionyl chloride by the procedure described by Lawton and McRitchie.<sup>22</sup>

Several preliminary runs were made in the preparation of polymeric phthalocyanines using 1:1, 2:1, and 3:1 ratios of o-phthalocyanine to tetracyanobenzene, respectively. The yields in these reactions were low. It appears that the reaction conditions must be modified for further studies.

### C. Synthetic Reactions

#### Diethyl Succinoylsuccinate

A procedure similar to that described by Roberts et al.<sup>23</sup> was used.

In a dry, three-necked, one-liter flask equipped with a reflux condenser, a mechanical stirrer, and a dropping funnel and containing a nitrogen atmosphere, were placed 30.6 g (0.75 g atom) of freshly cut sodium and 500 ml of anhydrous ethanol. When the solution of sodium was completed, 116 g (0.67 mole) of diethyl succinate was added and the mixture was refluxed for four hours. During the refluxing period, a white solid formed and the mixture became quite thick. The mixture was allowed to stand under nitrogen overnight.

The reaction mixture was acidified with dilute sulfuric acid and filtered. Recrystallization of the crude product from aqueous ethanol yielded 31.1 g (36% yield) of a light-yellow solid melting at 129-131°. The low yield undoubtedly was due to the fact that refluxing was not carried out for a sufficient length of time as described in Roberts' article.<sup>22</sup>

### Cyclohexanedione

This compound is available from Columbia Organic Chemical Co., Inc. It was also synthesized by a procedure described by Vincent et al.<sup>24</sup>

To 5.12 g (0.02 mole) of diethyl succinoylsuccinate, an equal weight of water and a few small pieces of soft glass rods were added. The entire mixture was placed in a stainless-steel bomb, and a partial vacuum was obtained by pulling on an aspirator. The bomb was heated in an oil bath at 195-200° for approximately 15 minutes. After cooling to room temperature, the contents of the bomb were washed out with ether. After evaporation of the volatile materials, the crude product was recrystallized from cyclohexane to yield 1.76 g of the product melting at 77-79°.

### Bis (Dicyanomethylene) Cyclohexane

To a cold solution of 1.12 g (0.01 mole) of 1,4-cyclohexanedione and 1.98 g (0.03 mole) of freshly distilled malononitrile dissolved in 25 ml of methanol was added 5 drops of pyridine. The solution turned brown upon addition of the amine. After 10 minutes, a white solid appeared in the reaction flask. The amount of the solid increased as the stirring was continued. The cold bath was removed after 15 minutes, and the mixture was stirred for an additional hour as it warmed to room temperature. The mixture, which had turned dark brown and almost black by this time, was filtered and the solid washed with fresh methanol. The washings yielded a white solid (1.86 g, 89% yield) which was recrystallized from glacial acetic acid, mp 227-229°.

### Bromine-Pyridine Dehydrogenation of 1,4-Bis(Dicyanomethylene)Cyclohexane

To 1.04 g (0.005 mole) of 1,4-bis(dicyanomethylene)Cyclohexane in 75 ml of methylene chloride were added 3 ml of pyridine and 1 ml of bromine. After a few minutes, the bright orange solution suddenly turned to blue black, then gradually to green and finally to yellow brown. The reaction mixture was refluxed for a total of nine hours. The orange-brown mixture was then filtered, the solid washed first with water then with 5% sodium bisulfite and again with

water to yield 1.00 g of yellowish-green solid. This solid melted at 245-255° turning black and was insoluble in common organic solvents such as benzene and chloroform. It dissolved in pyridine to form a green solution, but upon standing turned dark brown. Recrystallizations of the crude product from acetic acid still yielded material which did not melt sharply.

When the above product was placed in fresh methylene chloride with additional bromine and pyridine and refluxed for four hours, a brown colored solid melting at 290-293° was obtained.

#### Reaction of Thionyl Chloride with p-Benzoquinone

A solution of p-benzoquinone (2.16 g, 0.02 mole) in thionyl chloride (20 ml) was refluxed for 30 hours in a 100 ml round-bottom flask fitted with a reflux condenser and a calcium sulfate tube. The thionyl chloride was removed by heating under reduced pressure, and the residue was left to cool in vacuum. The product, yellow crystals (mp ~ 105°), rapidly turned dark upon exposure to air.

#### Condensation of 1,1,4,4-Tetrachloro-2,5-Cyclohexadiene with Malononitrile

To the above yellow crystalline product, malononitrile (3.3 g, 0.05 mole) was added as rapidly as possible. The mixture became a brown liquid after 15 minutes in a 100-115° bath, and after one and one-half hours, a vigorous reaction took place. The reaction mixture was left to cool under vacuum, and the dark bluish solid was washed with acetonitrile. The solid did not appear to be the desired product, TCNQ.

#### Reaction of Thionyl Chloride with Chloranil

Thionyl chloride (10 ml) and chloranil (2.46 g, 0.01 mole) were refluxed for one-half hour, then 10 ml more of thionyl chloride was added and reflux continued. All the volatiles were removed under reduced pressure. To the remaining yellow crystalline solid was added malononitrile (2.0 g, 0.03 mole). The reaction mixture was heated for one and three-quarters hours, at

which time there remained in the flask some black material and also some shiny greenish-yellow crystals. Cold acetonitrile was used to extract the solid, 2.4 g insoluble material. The residue gave a green solution in hot acetonitrile and was soluble in glacial acetic acid. There also appeared to be some other products in addition to the starting material. This reaction is being studied further.

#### Attempted Preparation of Dicyanomethylenequinone Oxime

A procedure similar to that described for the condensation of phenylacetonitrile with nitrobenzene<sup>13</sup> was used.

To a yellow solution of 7.26 g of malononitrile and 40 g of potassium hydroxide (85% assay) dissolved in 160 ml of methanol was added 12.3 g of nitrobenzene. The solution turned orange and then red. The contents of the flask were heated at 50-55° for four hours. At the end of the heating period, a deep-red solid had precipitated; after it had cooled to room temperature, 400 ml of water was added with stirring to give a dark colored solution. The reaction mixture was acidified by adding a solution of 72 g of acetic acid in 80 ml of water. During the acidification a strong cyanide odor was detected. However, no solid was obtained.

The above reaction was repeated with the following modification. At the end of the four-hour heating period at 50-55°, the reaction mixture was filtered to isolate the deep-red solid. Upon acidification of this solid, assumed to be the potassium salt of dicyanomethylenequinone oxime, with either acetic acid or dilute mineral acid a considerable amount of gaseous product was liberated. The evolved gas was trapped and was shown to be hydrocyanic acid by conversion to the ferriferrocyanide.

#### Reaction of Terephthalaldehyde with Malononitrile

To a solution of 1.34 g (0.01 mole) of terephthalaldehyde dissolved in 50 ml of methanol was added 1.98 g (0.03 mole) of malononitrile. A pale

yellow solid formed immediately. Three drops of piperidine were added, and the mixture was stirred at room temperature for one hour. The mixture was filtered to yield 2.11 g melting at 271-274°. This solid was soluble in hot acetic acid and in tetrahydrofuran. After four recrystallizations from acetic acid, the product melted at 282-284°.

#### Dicarbomethoxyacetylene

Into a 2-liter three-necked flask equipped with a condenser, a drying tube, and a stirrer were added acetylene dicarboxylic acid (91.2 g, 0.8 mole), methanol (153.6 g, 4.8 mole), dichloroethane (480 ml) and concentrated sulfuric acid (4.8 ml). The reaction mixture was refluxed for 19 hours. The slightly yellow solution was transferred to a separatory funnel and washed twice with 200 ml of 5% sodium bicarbonate, then with water until the product layer was neutral to litmus. The product was dried over calcium sulfate, filtered, and the solvent and excess methanol were removed under reduced pressure. The residue was fractionally distilled to give 55.84 g (49.0%) of dicarbomethoxyacetylene, bp 94-97°/17.5-18.0 mm,  $n_D^{24.7}$  1.4457. There was 5.61 g of brown polymeric residue.

#### Dicarboethoxyacetylene

A procedure described in Organic Synthesis, Volume 32, Page 55, was followed.

To an ice cold 2-liter one-necked flask containing anhydrous ethanol (575.9 g, 735 ml, 12.5 mole) was slowly added concentrated sulfuric acid (111 ml, 2.04 mole). To the cooled solution was added acetylenedicarboxylic monopotassium salt and a drying tube, and stirring continued for 72 hours.

After standing, the clear liquid was decanted and the salt was washed with 500 ml of water. The liquid and the wash were combined and extracted with four 500 ml portions of methylene chloride. The combined extracts were washed with 200 ml of cold water, 150 ml of saturated sodium bicarbonate solution, and 200 ml of cold water and then dried over calcium sulfate.

The methylene chloride was distilled off and fractional distillation of the residue gave 67.73 g (60.4%) of dicarboethoxyacetylene, bp 100-106°/7.5-8.5 mm,  $n_D^{25}$  1.4403.

#### Hexamethyl Mellitate

The method described by Diels<sup>14</sup> was used. Several runs were made in order to obtain a substantial amount of the product.

To an ice-cold solution of dicarbomethoxyacetylene (10.0 g, 0.0705 mole) in glacial acetic acid (25 ml) was slowly added with stirring 15 ml of pyridine. A brown color developed after one-half hour, and the solution was allowed to stand for four days. At this time a small amount of crystals had appeared in the viscous oily mixture. The mixture was extracted with cyclohexane to yield 5.1 g of white crystals. Upon recrystallization from methanol, it melted at 192-194°.

#### Preparation of Hexaethyl Mellitate

To an ice-cold solution of dicarboethoxyacetylene (3.4 g, 0.02 mole) in 5 ml of glacial acetic acid, 3 ml of pyridine was added dropwise. The reaction mixture upon warming to room temperature became a viscous, dark brown liquid. After the reaction mixture stood for about two weeks in an open container, some crystals appeared. This solid melted at 74-75°. The yield was extremely poor.

#### Preparation of Dimesitylnickel and Trimerization of Dimethylacetylene Dicarboxylate

Anhydrous nickel bromide (4.4 g) was placed in 100 ml of tetrahydrofuran (THF) which was freshly distilled from ethyl Grignard reagent. To this mixture was added dropwise mesityl Grignard reagent (prepared from 8 g of mesityl bromide in 200 ml of dry THF) under a nitrogen atmosphere and at -20° or less. The mixture became dark green and was stirred

at  $-10^{\circ}$  to  $-20^{\circ}$  or less. At  $-20^{\circ}$ , 27 g of dicarbomethoxyacetylene was added. The mixture was kept at  $-10^{\circ}$  for four hours and  $0^{\circ}$  for two hours. The mixture was stirred an additional two days at room temperature. The THF was removed at reduced pressure, and 400 ml of water was added. The mixture was extracted three times with 500 ml portions of ether. The extracts were dried over calcium sulfate and treated with decolorizing carbon. The ether was removed at reduced pressure, and the oily residue was triturated with cyclohexane. The crystals were collected and recrystallized repeatedly from a benzene-cyclohexane mixture yielding 7.0 g (26%) of hexamethylmellitate, mp  $185-187^{\circ}$ , reported  $187^{\circ}$ .

#### Attempted Reaction of Hexamethyl Mellitate with Ammonia

Ammonia (15 ml) was added to hexamethyl mellitate (1.70 g, 0.004 mole); after stirring for 48 hours the solution became clear. The reaction mixture was heated to dryness. The white solid recovered did not melt below  $300^{\circ}$ ; it was further heated at  $230^{\circ}$  overnight. The greyish solid (0.43 g) was slurried and stirred in ammonia for six hours, filtered, washed with water, and dried. Then thionyl chloride (5 ml) was added in order to dehydrate, assuming the solid to be the amide. The reaction mixture was stirred for one hour, then poured into ice, filtered, dried, and redissolved in acetic acid. Nothing was recovered from the filtrate, and the insoluble portion does not appear to be the imide (insoluble in DMF).

#### Dicarbonamidoacetylene

To 8.0 ml of concentrated ammonia cooled to  $-10^{\circ}$  was added with stirring 2.0 g of dicarbomethoxyacetylene. After a few minutes, a white solid appeared. The reaction mixture was stirred for one hour and then filtered. The solid was washed with small amounts of ethanol and then dried. The product (1.1 g) melted at  $210-218^{\circ}$ .

### Preparation of Dicyanoacetylene

According to the directions of Blomquist et al.<sup>16</sup>, dicarbonamidoacetylene (6.0 g) was dehydrated by heating to 215° with phosphorus pentoxide (50 g) and 100 g of sand. The system was evacuated, and the mixture was heated in four separate tubes. The product was collected continuously in a tube cooled to -78°. The dehydration was more successful when a small quantity of glass wool was placed over the contents of each tube. Yields of 0.5 to 1.1 g of dicyanoacetylene, mp 17-19°, reported 21°, were obtained per run.

### Attempted Preparation of Dicyanoacetylene

Into a flask equipped with a stirrer, 6 g of dicarbonamidoacetylene was added to 25 ml of thionyl chloride. The mixture was heated with an oil bath, and at approximately 50° a reaction evolving gases occurred. The mixture was heated further to 75° with no apparent change. The mixture was cooled in an ice bath, and 200 ml of water was slowly added. The mixture was filtered, and 0.4 g of impure starting material was collected. The filtrate was extracted with methylene chloride and dried over calcium sulfate. The solvent was removed leaving a trace of oil which would not crystallize. The aqueous layer previously extracted was made alkaline with sodium hydroxide solution and extracted with methylene chloride. The methylene chloride extract was treated as before, again leaving only a trace of oil. No product was isolated.

### Attempted Preparation of Dicyanoacetylene

The general directions of Newman et al.,<sup>25</sup> in which they reduced certain amides to nitriles with lithium aluminum hydride, were followed.

Lithium aluminum hydride (2.25 g) was added to dicarbonamidoacetylene (6.0 g) suspended in 200 ml of THF. The mixture was stirred an additional 48 hours at room temperature. About 50 ml of liquid was distilled from the reaction mixture and its infrared spectrum taken. This distillate had no absorption at 2400 cm<sup>-1</sup>, characteristic of dicyanoacetylene. Any excess lithium aluminum hydride was destroyed by the addition of ethyl acetate. Water,

followed by 20% sodium hydroxide, was added to the reaction mixture. The mixture was extracted with methylene chloride and dried over calcium sulfate.

Part of the extract was distilled and its infrared spectrum taken. Again no absorption occurred at  $2400\text{ cm}^{-1}$ .

#### Bromination of Fumaronitrile

To a solution of 4.0 g of fumaronitrile in 50 ml of acetic acid, 8.0 g of bromine was slowly added. The brown color disappeared rapidly when the mixture was heated to  $65-70^\circ$ . The bulk of the acetic acid was removed under vacuum at room temperature. During the removal of the acetic acid, the mixture became very dark. No product was isolated.

#### Attempted Preparation of Dicyanoacetylene

To a stirred solution of 40 g of N,N-dimethylaniline and 4.0 g of fumaronitrile, 8.0 g (1 eqv) of bromine were slowly added. The solution immediately became greenish. The mixture was heated, and the volatile product was removed under reduced pressure. About 5 ml of liquid with a strong odor of N,N-dimethylaniline was collected at  $60-70^\circ/25\text{ mm}$ . The infrared spectrum of the distillate had an absorption of  $2200\text{ cm}^{-1}$ , but none at  $2400\text{ cm}^{-1}$ , characteristic of dicyanoacetylene. The mixture was dissolved in methylene chloride and extracted with 10% hydrochloric acid. The methylene chloride extract was dried over calcium sulfate and the solvent removed under reduced pressure leaving 0.5 g of fumaronitrile. No other product was isolated.

#### Preparation of Dibromodurene

A procedure similar to that described by Smith and Guss<sup>26</sup> was used.

Bromine (67.2 g, 0.42 mole) was added slowly to a solution of durene (26.8 g, 0.20 mole) in chloroform (150 ml) containing a crystal of iodine. The reaction mixture was stirred at room temperature in the absence of any strong light (shielded with a cloth). After about an hour, a copious amount of precipitate appeared and the mixture thickened. An additional 250 ml of chloroform was added. The solution was stirred three more hours, then washed successively with 200 ml of water, 250 ml of 5% sodium bisulfite, and twice more with 250 ml each of water. After chloroform solution was dried overnight, the solvent was removed to yield 58.9 g of crude white product melting at

170-180°. The product was recrystallized from chloroform-alcohol solution to yield 52.1 g (89% yield) of white needles melting at 200-202°.

#### Oxidation of Dibromodurene

Dibromodurene (5.84 g) was heated in a mixture of pyridine (200 ml) and water to give a clear solution. To this hot solution was added 12.64 g of potassium permanganate in small portions. Efficient stirring was maintained throughout the reaction. After completion of addition, the mixture was refluxed for four hours. The deep maroon-colored contents of the flask turned brown during this heating period, and some white solid appeared on the condenser wall. The hot brown reaction mixture was filtered, and the brown solid (No. 1) was washed with fresh pyridine. The brown cake of manganese dioxide was saved. The filtrate was placed back in the flask, heated, and treated with potassium permanganate exactly as before. After the mixture was refluxed for two hours, it was again filtered (solid No. 2). Following concentrating the filtrate by heating under reduced pressure, only a small amount of white solid (No. 3) was obtained. The two cakes (solid Nos. 1 and 2) of manganese dioxide obtained in the previous filtration were heated in a solution of sodium hydroxide (9 g in 125 ml of water) and filtered while hot. The filtrate was combined with the white solid (No. 3) obtained from the concentration of the original filtrate. The combined solution was now heated and treated with potassium permanganate (19 g) added in small portions. After refluxing for two hours, the hot mixture was filtered. Upon acidification of the filtrate to pH 2 with sulfuric acid, considerable evolution of gas was observed. It appeared that carbon dioxide was being liberated. Although the solution became cloudy, no solid appeared. Upon addition of ether in an attempt to extract the product, a white solid (8.0 g) precipitated. This material turned orange at about 180°, bright red with bubbling at 195°, and appeared to melt with bubbling at 202°. This product has not been further characterized.

#### Preparation of Tribromomesitylene

Bromine (96.0 g) was slowly added to a solution of mesitylene (24.0 g, 0.20 mole) in 200 ml of chloroform containing a crystal of iodine. The contents

of the flask were shielded from strong light. The dark brown reaction mixture was stirred overnight at room temperature. Some white solid had precipitated out; 200 ml of chloroform was added and stirring continued for nine additional hours. The solution was then concentrated down, and the resulting solid which precipitated was separated and washed, first with 5% sodium bisulfite solution and then with water to yield 45.4 g of white solid. Recrystallization of the product from chloroform-alcohol gave white needles melting at 229-232°.

#### 1, 2, 4, 5-Tetracarboxamidobenzene

In a 2-liter three-necked flask equipped with a tru-bore stirrer and a dropping funnel was added pyromellitic dianhydride (109 g, 0.5 mole) in 1 liter of distilled water and 500 ml of concentrated ammonia. The reaction mixture was stirred and gradually heated until only a beige solid remained. The solid was dried and heated to 200-210° for 24 hours to convert the ammonium salt to the diimide. The crude diimide was slurried in concentrated ammonia (750 ml) and stirred at room temperature for 16 hours. The mixture was filtered, and the solid was reslurried with concentrated ammonia and refiltered. The filter cake was washed with concentrated ammonia and, finally, water. The product was dried over calcium sulfate. The yield was 118.5 g (94.8%) of tetracarboxamidobenzene.

#### 1, 2, 4, 5-Tetracyanobenzene

To tetracarboxamidobenzene (112.5 g, 0.45 mole) in 900 ml of dimethylformamide was added a total of 400 g of thionyl chloride, keeping the temperature at 50-60°. The reaction mixture was stirred a total of nine hours at 60°, then it was poured into crushed ice and filtered. The filter cake was washed with water until neutral and dried under vacuum.

The tetracyanobenzene was recrystallized from glacial acetic acid and then further purified by recrystallizing from ethanol. White needles at mp 269-270° turned dark green; infrared spectrum agrees with previous synthesized product.

#### Attempted Bromination of 1, 2, 4, 5-Tetracyanobenzene

Tetracyanobenzene (1.78 g, 0.01 mole) in 50 ml of carbon tetrachloride was added a mixture of anhydrous aluminum chloride (10.65 g, 0.08 mole) and bromine (12.78 g, 0.08 mole) in carbon tetrachloride (200 ml). The clear dark-red mixture containing some undissolved tetracyanobenzene was stirred for 12 hours and heated at 70-75° for an additional eight hours. The reaction mixture was filtered, washed with carbon tetrachloride, and air dried. Solid material recovered, 7.63 g, containing some starting tetracyanobenzene, was washed with water, dried, and washed with acetonitrile. Recovered 1.50 g did not melt below 300°; product was not identified.

#### Attempted Preparation of $\alpha$ -Ketosuccinonitrile

To a mixture of 5 g of cyanoacetic acid and 30 ml of benzene, 7 g (1 eqv) of thionyl chloride was added. The mixture was stirred at room temperature for 24 hours. During this time, a large quantity of precipitate appeared and the solution became pink. The solid was filtered off and the crystals put in THF and stirred with cuprous cyanide for two days. The cuprous cyanide was then filtered off, and the THF was removed at reduced pressure. The solid was leached out with hot benzene, from which 0.5 g of cyanoacetic acid was isolated. No other products were isolated.

#### Preparation of 4, 4'-Dihydroxy-3, 5, 3', 5'-Tetra-t-Butyldiphenylmethane

This compound is commercially available from Ethyl Corporation. However, due to the long delay in obtaining this compound, preparation in the laboratory was carried out using a procedure similar to that described by Kharasch & Joshi.<sup>21</sup>

To a solution of 20.6 g (0.1 mole) of 2,6-di-t-butylphenol and 15 ml of 36% formaldehyde dissolved in 50 ml of ethanol, was slowly added a solution of sodium hydroxide (8.0 g in 15 ml of water). A nitrogen atmosphere was maintained throughout the entire course of the reaction. The green solution was

heated at 50-55° for 15 minutes. During this heating period, a vigorous reaction took place with separation of a yellow-brown solid from the mixture. The mixture was filtered, and the solid turned purple. The solid was dissolved in ethanol and acidified with acetic acid to yield 10 g of yellow solid melting at 155-156°.

It is interesting to note that the procedure described in the literature does not require the acidification step.

#### 4, 4'-Dihydroxy-3, 5, 3'5'-Tetrabutyl-diphenylbromomethane

A solution of bromine (0.2 ml) in 2 ml of acetic acid was added to the diphenylmethane derivative, obtained above, in acetic acid (25 ml). An inert atmosphere was maintained in the reaction mixture. After one hour a clear white solid appeared. At the end of two hours, the mixture was quite thick with the white crystals. The solid was then removed from the flask while a nitrogen atmosphere was maintained and transferred quickly into a vacuum desiccator. This product was dried under vacuum and used without further purification.

#### 2, 6, 3', 5'-Tetrabutyl-4'-Hydroxyphenyl-4-Methylene-2, 5-Cyclohexadiene-1-One

To a solution of bromo compound (60 mg), obtained above, in ethanol (5 ml) was added 5% sodium hydroxide (0.2 ml). A slow current of nitrogen was passed over the solution. The addition of the base caused the solution to turn deep purple. The reaction mixture was poured into crushed ice after 20 minutes, neutralized with acetic acid, and then extracted with ether. The removal of the ether yielded 56 mg of a yellow solid which melted at 149-151°. Recrystallization of the solid from aqueous ethanol gave yellow needles melting at 158°.

#### Reaction of p-Hydroxybenzaldehyde With p-Aminophenol

To a solution of 4.88 g (0.04 mole) of p-hydroxybenzaldehyde and 4.36 g (0.04 mole) of p-aminophenol dissolved in 30 ml of ethanol was added 10 ml of pyridine. After a few minutes a copious quantity of greenish-yellow solid appeared. The reaction mixture was stirred at room temperature for two

hours and then filtered. The resulting solid was washed with a small amount of ethanol and dried under reduced pressure to give 6.7 g of the product, mp 215-216°. Recrystallization from aqueous ethanol gave yellow crystals melting at 217-219° to an orange liquid. The yellow crystals turned orange in color upon standing.

#### An Attempted Oxidation of p-Hydroxybenzal-p-Hydroxyaniline

A procedure similar to that described by Kharasch and Joshi<sup>21</sup> was followed.

To 1 g of the Schiff base product of p-hydroxybenzaldehyde and p-aminophenol in 50 ml of benzene were added a mixture of 6 g of potassium ferricyanide and 1 g of potassium hydroxide, in 50 ml of benzene and 25 ml of water. This reaction was carried out under oxygen-free atmosphere by passing a stream of nitrogen through the flask. The dark-red benzene layer turned yellow-brown after 15 minutes. Stirring was continued at room temperature for two hours, and the benzene layer was separated and dried. The removal of volatiles from the benzene layer left only a trace amount of solid melting at 110° (p-hydroxybenzaldehyde, mp 116°).

From the emulsified aqueous phase was obtained a large amount of yellow crystals which did not melt below 300°. This solid was not soluble in common organic solvents but formed a blue-green mixture in acetic acid. Upon extraction of the solid with acetic acid, a greenish-beige, extremely hygroscopic solid was obtained. This solid melted at about 235° to a honey-colored material.

#### Condensation of Phthalonitrile and 1, 2, 4, 5-Tetracyanobenzene with Copper Powder (Run One)

Phthalonitrile (1.892 g, 0.0148 mole), 1, 2, 4, 5-tetracyanobenzene (1.32 g, 0.0074 mole), and copper powder (0.477 g, .0075 g. a.) were finely ground together. The mixture was heated in an oil bath at 260° for three hours. The melt became dark green and then turned into a blue viscous mass that gradually solidified. The sides of the test tube had to be frequently scraped of sublimed phthalonitrile. The blue-black solid was washed with hot ethanol, dried, then

dissolved and stirred in concentrated sulfuric acid for 16 hours. A coarse fritted glass funnel was used to filter the greenish-black solution. Insoluble dark powder weighed 0.50 g. The filtrate was added to 2 liters of distilled water, and a dark blue polymer precipitated; amount recovered was 0.46 g.

Condensation of Phthalonitrile 1, 2, 4, 5-Tetracyanobenzene with Copper Powder (Run Two)

The procedure was the same as previously described; the quantities of reactants were as follows: phthalonitrile (2.715 g, 0.0212 mole), 1, 2, 4, 5-tetracyanobenzene (1.32 g, 0.0074 mole), and copper powder (0.6354 g, 0.01 g atom). The crude material recovered was 3.45 g, of which all but 0.06 g was soluble in concentrated sulfuric acid.

Condensation of Phthalonitrile and 1, 2, 4, 5-Tetracyanobenzene

A finely ground mixture of phthalonitrile (2.0 g, 0.015 mole) and 1, 2, 4, 5-tetracyanobenzene (2.22g, 0.0127 mole) was heated at 260° for three hours. It was frequently necessary to scrape the sides of the flask to push the sublimed phthalonitrile back into the reaction mixture. The dark melt gradually thickened during the heating period and became a solid. This solid was washed with hot ethanol. The dark blue mixture was filtered, dried, and dissolved in concentrated sulfuric acid. The dark green solution was poured into 1 liter of distilled water, and the blue-green flocculent polymeric phthalocyanine (0.56 g) precipitated.

## REFERENCES

1. A. Pocchettino. Acad. Lincei Rendiconti, 15, No. 1 (1906), 355.
2. A. Szent-Györgyi. Science, 93 (1941), 609.
3. R. G. Kepler, P. E. Bierstedt, and R. E. Merifield. Phys. Rev. Letters, 5 (1960), 503.
4. D. S. Acker, R. J. Harder, W. R. Hertler, W. Mahler, L. R. Melby, R. E. Benson, and W. E. Mochel. J. Am. Chem. Soc., 82 (1960), 6408.
5. H. Mette and H. Pick. Z. Physik, 134 (1953), 566.
6. H. Inokuchi. Bull. Chem. Soc. Japan, 29 (1956), 131.
7. N. V. Riehl. Zhur. Fiz. Khim., 6 (1955), 959.
8. L. B. Valdes. Proc. Inst. Radio Engrs., 40 (1952), 1420.
9. R. G. Kepler. Proceedings of Conference on Electronic Conductivity in Organic Solids, Duke University, April 1960.
10. C. G. B. Garret. "Organic Semiconductor." Semiconductors. Ed. N. B. Hannay. New York: Reinhold Publishing Corp., 1959, ch. 15.
11. M. M. Hafez, N. Latif, and I. F. Zeid. J. Org. Chem., 26 (1961), 3988.
12. J. H. Wood, C. S. Colburn, L. Cox, and H. C. Garland. J. Am. Chem. Soc., 66 (1944), 1540.
13. R. B. Davis, L. C. Pizzini, and E. J. Bara. J. Org. Chem., 26 (1961), 4270.
14. O. Diels. Ber., 75 (1942), 1452.
15. M. Tsutsui and H. Zeiss. J. Am. Chem. Soc., 82 (1960), 6255.
16. A. T. Blomquist and E. C. Winslow. J. Org. Chem., 10 (1945), 156.
17. C. S. Marvel and M. M. Martin. J. Am. Chem. Soc., 80 (1958), 6600.
18. D. E. Pearson, W. W. Hargrove, J. K. T. Chow, and B. R. Suthers. J. Org. Chem., 26 (1961), 789.

REFERENCES (continued)

19. D. E. Pearson, H. W. Pope, W. W. Hargrove, and W. E. Stamper. J. Org. Chem., 23 (1958), 1412.
20. N. C. Yang and A. J. Castro. J. Am. Chem. Soc., 82 (1960), 6208.
21. M. S. Kharasch and B. S. Joshi. J. Org. Chem., 22 (1957), 1435.
22. E. A. Lawton and D. D. McRitchie. "Research on Thermostable Molecules and Polymers." Battelle Memorial Institute, WADC TR 57-642, ASTIA Doc. No. AD 142199, November 1957.
23. J. D. Roberts, W. T. Moreland, and W. Frazer. J. Am. Chem. Soc., 75 (1953), 637.
24. J. R. Vincent, A. F. Thompson, and L. I. Smith. J. Org. Chem., 3 (1939), 603.
25. M. S. Newman and T. Fukunaga. J. Am. Chem. Soc., 82 (1960), 693.
26. L. I. Smith and C. L. Moyle. J. Am. Chem. Soc., 55 (1933), 1676.

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