Anal. Calcd. for $C_{16}H_{16}O_8Br_2$: Br, 32.2. Found: Br, 32.3.

B. From 7,7,8,8-Tetrakis-(methoxycarbonyl)-quinodimethan.—To a solution of 25 mg. (0.0744 mmole) of tetrakis-(methoxy-carbonyl)-quinodimethan in a small volume of benzene was added excess bromine dissolved in benzene. The resulting solution was warmed briefly on a steam-bath. Removal of solvent *in vacuo* gave 30 mg. (81%) of crystalline α,α'-dibromo-*p*-phenylenebis-(dimethyl malonate) which, after washing with hexane, had melting point 145–146° and mixed melting point with authentic α,α'-dibromo-*p*-phenylenebis-(dimethyl malonate), 142–145°.

α-Methoxy-*p*-phenylenebis-(dimethyl malonate) (XII).—A. From *p*-Phenylenebis-(dimethyl malonate).—A mixture of 300 mg. (0.954 mmole) of *p*-phenylenebis-(dimethyl malonate), 180 mg. of sodium methoxide and 75 ml. of methanol was refluxed under nitrogen for 1.25 hours. Iodine was then added until a permanent color remained. The solution was partially concentrated *in vacuo*, and the residue was treated with dilute sodium bisulfite solution and extracted with ether. Removal of the ether gave an oil which, after crystallization from benzene-hexane followed by two crystallizations from acetone-water, gave white microcrystals (20 mg.) of α-methoxy-*p*-phenylenebis-(dimethyl malonate), m.p. 143–144°. The infrared spectrum of the product shows absorption at 3030 cm.$^{-1}$ (Ar-H); 2980, 2860 cm.$^{-1}$ (C–H); 1745 cm.$^{-1}$ (ester carbonyl) and 1760 cm.$^{-1}$ (α-methoxy ester carbonyl).

Anal. Calcd. for $C_{16}H_{16}O_8$: C, 55.4; H, 5.47; methoxyl, 42.2. Found: C, 55.4; H, 5.49; methoxyl, 42.1.

B. From 7,7,8,8-Tetrakis-(methoxycarbonyl)-quinodimethan.—A solution of 30 mg. of tetrakis-(methoxycarbonyl)-quinodimethan in 3 ml. of boiling methanol was treated with a catalytic amount of sodium methoxide. The yellow color disappeared, and addition of water to the solution caused a white solid to precipitate, which on recrystallization from acetone–water gave 18 mg. of α-methoxy-*p*-phenylenebis-(dimethyl malonate), m.p. 146–146.5°; mixed melting point with the previously obtained α-methoxy-*p*-phenylenebis-(dimethyl malonate), 145.5–147°.

α-*n*-Butylamino-*p*-phenylenebis-(dimethyl malonate) (XIII).—A solution of 82 mg. of 7,7,8,8-tetrakis-(methoxycarbonyl)-quinodimethan in a few ml. of tetrahydrofuran was treated with two drops of *n*-butylamine. After standing for 0.5 hour at room temperature, the solution, which had turned from yellow to colorless, was filtered and evaporated under a nitrogen stream. The oily residue was crystallized from ether-hexane to give 80 mg. of white needles, m.p. 88–89°. The product was insoluble in water but soluble in dilute hydrochloric acid. Further recrystallization from ether-hexane gave white needles of α-*n*-butylamino-*p*-phenylene-bis-(dimethyl malonate), m.p. 92–93°.

Anal. Calcd. for $C_{20}H_{27}O_8N$: C, 58.7; H, 6.64; N, 3.42. Found: C, 58.6; H, 6.71; N, 3.28.

The infrared spectrum of the product shows absorption at 3030 cm.$^{-1}$ (aromatic CH), 2975 and 2860 cm.$^{-1}$ (aliphatic CH), 1740 cm.$^{-1}$ (normal ester carbonyl) and 1765 cm.$^{-1}$ (α-amino-ester carbonyl). The ultraviolet spectrum of the product in ether is typically aromatic with absorption at 226 mμ (ϵ 12,600), 261 mμ (ϵ 400) and 272 mμ (ϵ 278).

[CONTRIBUTION NO. 738 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., INC., WILMINGTON 98, DEL.]

Substituted Quinodimethans. II. Anion-radical Derivatives and Complexes of 7,7,8,8-Tetracyanoquinodimethan

BY L. R. MELBY, R. J. HARDER, W. R. HERTLER, W. MAHLER, R. E. BENSON AND W. E. MOCHEL

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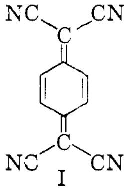
7,7,8,8-Tetracyanoquinodimethan (TCNQ) is a strong π-acid which forms stable, crystalline anion-radical salts of the type $M^+TCNQ^{\overline{\cdot}}$ and a new class of complex salts represented by $M^+(TCNQ^{\overline{\cdot}})(TCNQ)$ which contain formally neutral TCNQ. The complex anion-radical salts have the highest electrical conductivities known for organic compounds, exhibiting volume electrical resistivities as low as 0.01 ohm cm. at room temperature. These complex salts are paramagnetic, and both conductivity and electron paramagnetic resonance absorption are anisotropic as determined by measurements along major crystal axes.

7,7,8,8-Tetracyanoquinodimethan (TCNQ, I) and the physical properties of certain of its stable anion-radical derivatives have been the subjects of preliminary communications from this Laboratory,[1-3] and detailed accounts of the synthesis and chemistry of TCNQ are appearing concurrently.[4,5] The present report deals in detail with various TCNQ complexes and anion-radical derivatives whose magnetic properties and high electrical conductivity have been the subjects of primary interest.



I

The ability of quinones to form stable solid complexes with aromatic amines has been known for many decades,[6] and in modern terms such complex formation is ascribed to interaction of the electron-poor π-orbital system of the quinone (π-acid or acceptor) with the electron-rich π-orbitals of the amine (π-base or donor). Some of the solid complexes formed between aromatic diamines and relatively strong π-acids, such as polyhalo quinones, exhibit electron paramagnetic resonance (E.P.R.) absorption,[7,8] indicating unpairing of electron spins. Some complexes of this type are classed as semiconductors because of exponential variation of their electrical resistivities with temperature.[9]

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(1) 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**, 6408 (1960).

(2) R. G. Kepler, P. E. Bierstedt and R. E. Merrifield, *Phys. Rev. Letters*, **5**, 503 (1960).

(3) D. B. Chesnut, H. Foster and W. D. Phillips, *J. Chem. Phys.*, **34**, 684 (1961).

(4) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962).

(5) W. R. Hertler, H. D. Hartzler, D. S. Acker and R. E. Benson, *ibid.*, **84**, 3387 (1962).

(6) W. Schlenk, *Ann.*, **368**, 277 (1909).

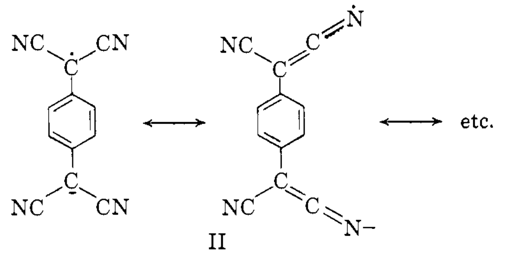
(7) H. Kainer and A. Uberle, *Chem. Ber.*, **88**, 1147 (1955).

(8) D. Bijl, H. Kainer and A. C. Rose-Innes, *J. Chem. Phys.*, **30**, 765 (1959).

(9) The conductivity of semiconductors is often referred to by the reciprocally related term resistivity, and the latter will be used throughout this paper. Resistivity, given the symbol ρ, is defined by the relationship $\rho = (R \times A)/L$ where R is the electrical resistance (ohms).

For example, there has been considerable recent interest in the semiconductor character of chloranil/*p*-phenylenediamine-type complexes, whose resistivities are of the order of 10^4 to 10^8 ohm cm. at room temperature.[8,10] We now report on a variety of new electrically conducting organic compounds which are based on TCNQ. The unique character of TCNQ as a π-acid derives partly from the high electron affinity of the polyene system conferred by the powerful electron-withdrawing effect of the four cyano groups and partly from the planarity and high symmetry of the TCNQ structure.

Tetracyanoquinodimethan forms three types of electrically conducting compounds. First, in keeping with its quinoid character, TCNQ forms crystalline π-complexes (charge-transfer complexes) with aromatic hydrocarbons, amines and polyhydric phenols. These complexes are characterized by intermediate to high resistivity (10^3 to 10^4 ohm cm.) and very weak E.P.R. absorption. In addition, TCNQ forms two series of stable, salt-like derivatives, each involving complete transfer of an electron to TCNQ with the formation of the anion-radical $\mathrm{TCNQ}^{\overline{\cdot}}$ represented by the resonance hybrid II. The first series is represented by the simple salt formula $\mathrm{M}^{+n}(\mathrm{TCNQ}^{\overline{\cdot}})_n$ in which M may be a metallic or organic cation. These salts are characterized by intermediate to high resistivity[2] (10^4 to 10^{12} ohm cm.) and weak E.P.R. absorption in the solid state.[3] Members of the second of the salt-like series, the complex salts represented by the formula $\mathrm{M}^{+n}(\mathrm{TCNQ}^{\overline{\cdot}})_n(\mathrm{TCNQ})$, contain a molecule of formally neutral TCNQ in addition to $\mathrm{TCNQ}^{\overline{\cdot}}$; this series is characterized by exceptionally low electrical resistivity[2] (10^{-2} to 10^3 ohm cm.) and variable e.p.r. absorption,[3] and both of these properties are anisotropic as determined by measurements on single crystals.[2,3] Details of the preparation and chemistry of these derivatives will be discussed in the order presented above, *i.e.*, π-complexes, simple anion-radical salts and complex anion-radical salts.



II

TCNQ π-Acidity.—TCNQ is a strong π-acid and forms charge-transfer or π-complexes with a variety of Lewis bases. Complexes with aromatic π-bases are believed to result from overlap of the respective acid and base π-orbital systems and the magnitude of this interaction is reflected in the association constant for complex formation, K, and the energy of the charge-transfer spectral absorption band. If the association equilibrium is written as

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{C}$$

then the association constant K is

$$K = \frac{(\mathrm{C})}{\{(\mathrm{A}) - (\mathrm{C})\}\{[\mathrm{B}] - [\mathrm{C}]\}}$$

where (A) and (C) are molar concentrations of π-acid and complex, respectively, and [B] and [C] are mole fractions of π-base and complex, respectively.[11] For example, previous work in these laboratories has shown that the complex between tetracyanoethylene (TCNE) and hexamethylbenzene exhibits $K = 263$, indicative of a strong interaction.[11a] Comparison of the π-complexing ability or π-acid strength of TCNQ with that of TCNE can be made by referring to the association constants in Table I.

TABLE I

ASSOCIATION CONSTANTS FOR π-COMPLEX FORMATION

π-Base	Association constant K^a TCNE	TCNQ
Durene	54.2	5.6
Hexamethylbenzene	263	14.5
Pyrene	29.5	78.4
Polarographic half-wave reduction potential, v.[b]	+0.152	+0.127

[a] These constants were determined spectrophotometrically in methylene chloride solvent at room temperature as described in ref. 11a. We are indebted to Dr. W. D. Phillips and Miss Ellen Wallace for providing these data. [b] The half-wave potentials cited are for reversible one-electron reduction in anhydrous acetonitrile, 0.1 *M* with respect to lithium perchlorate and *versus* an aqueous saturated calomel electrode.

Relative to the small π-base systems represented by durene and hexamethylbenzene, TCNE is the stronger acid, whereas relative to pyrene, which has an extended π-orbital system, TCNQ is the stronger acid. This apparent inconsistency suggests the inadequacy of attempting to establish relative π-acid or π-base strengths based on K-values unless reference is made to the size and geometry of the π-orbital systems involved. It is probable that a more reliable estimation of π-acid or π-base strength can be obtained through polarographic studies wherein the effects of molecular size and steric hindrance are minimized. The half-wave potentials for one-electron reductions of TCNE and TCNQ are appended to the above table of association constants and on this basis TCNE is the somewhat stronger π-acid.[12]

TCNQ π-Complexes (Table IV). Synthesis.—In most organic solvents the complexes of TCNQ with many donor compounds are much less soluble than either of the components so that a large variety

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A is the area (cm.^{2}), and *L* the length (cm.) of the sample being examined. Thus, ρ has the dimensions ohm cm. The typical inorganic semiconductor silicon has a room temperature resistivity of about 10^3 ohm cm. Most organic compounds are insulators and have resistivities of the order of 10^{10} to 10^{14} ohm cm. which show the exponential temperature dependence characteristic also of semiconductors. Metallic conductors exhibit resistivities of about 10^{-6} ohm cm. and their resistivities vary linearly with temperature.

(10) M. M. Labes, R. Sehr and M. Bose, *J. Chem. Phys.*, **32**, 1570 (1960); P. L. Kronick and M. M. Labes, *ibid.*, **35**, 2016 (1961).

(11) (a) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2278 (1958); (b) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

(12) M. E. Peover [*Nature*, **191**, 702 (1961)] discussed the polarography of several π-acids and the utility of the method for comparing acceptor strengths. This reference cites a value of +0.25 volt for the half-wave potential of TCNE in acetonitrile, but with tetraethylammonium perchlorate as the electrolyte. For other work on the polarography of π-acids the reader is referred to work to be published by E. A. Abrahamson and Lucille E. Williams of this Laboratory.

of such π-complexes can be readily isolated. With very few exceptions these are 1:1 complexes. The complexes are generally prepared by adding hot solutions of the donor to TCNQ in solvents such as tetrahydrofuran, chloroform or dichloromethane. When highly purified starting materials are used, complexes of analytical purity can be isolated directly. This procedure is generally necessary since most of the complexes cannot be recrystallized without some degradation, though in the solid state they are quite thermally stable. The aromatic diamine complexes especially are very difficultly soluble. In Table I are listed such complexes, with pertinent data. In general, melting point determinations are unsuitable for characterization since most of the complexes decompose over a wide temperature range which is markedly dependent on rate of heating. In Table I are also described several complexes with TCNQ which are unique in having metal chelates as donor components. These include 1:1 complexes with copper 8-quinolinolate and with nickel and copper 2-pyrrolealdehydeimine.

Electrical Properties.—Although donors of highest basicity (*i.e.*, the diamines) have given the most conductive complexes, no consistent correlation can be made between structure or basicity of the donor and electrical resistivity of the corresponding TCNQ complex.[13] For example, the 1:1 *p*-phenylenediamine/TCNQ complex has a resistivity of about 10^3 ohm cm. On the other hand, N,N,N′,N′-tetramethyl-*p*-phenylenediamine affords a complex with a resistivity of about 10^6 to 10^8 ohm cm. even though one would expect the methylated amine to have a higher π-base strength by virtue of hyperconjugative effects. This difference in resistivities may be related to molecular packing within crystals, the smaller NH_2 groups of the unmethylated amine allowing greater contiguity of the donor/acceptor pair with consequently increased π-orbital overlap. This would be expected to present a lower energy barrier to the electron transport required for conductivity. In addition, impurity effects may be important in conferring these differences.

Electron Paramagnetic Resonance Absorption.—Complexes of this type are considered by Mulliken[14] to involve bonding between the components by partial or complete transfer of a π-electron from the donor to the acceptor. If the π-acid (acceptor) is represented by A and π-base (donor) by B, then two electronic states may exist and these can be represented by the extreme forms

$$\underset{\text{i}}{AB} \qquad \underset{\text{ii}}{\overset{-}{A}\ \overset{+}{B}}$$

Form i corresponds to a diamagnetic, spin-paired state in which no electron transfer has occurred, while ii results from electron transfer. Depending, among other things, on the relative electron affinity of A and the ionization potential of B, it is theoretically possible that in the solid state there could exist complexes represented wholly by either i or ii or by a continuum of states intermediate between the two. Furthermore, the complete electron transfer form ii could exist in a diamagnetic singlet ground state with corresponding paramagnetic, triplet, excited state, or in a paramagnetic doublet state. The TCNQ π-complexes thus far obtained have been either totally diamagnetic in the solid state, or have exhibited only weak paramagnetism.[15] There is no apparent relationship between the magnitude of the resistivities and the degree of electron transfer as indicated by quantitative E.P.R. absorption measurements. For example, although the resistivities of the *p*-phenylenediamine and N,N-dimethyl-*p*-phenylenediamine derivatives (Table IV) are 10^3 and 10^9 ohm cm., respectively, the E.P.R. signal intensities corresponded, respectively, to about 4×10^{20} and 4×10^{21} unpaired electrons per mole of acceptor-donor pairs.[16] Thus, the less conductive complex appeared to contain the larger number of unpaired electrons. However, little-known impurity effects may be influencing both electrical resistivities and E.P.R. signal intensities, probably in non-parallel fashion. It should be borne in mind that the E.P.R. measurements do not necessarily reflect directly the degree of electron transfer, since even in the extreme state of complete electron transfer (ii above) the unpaired electrons may be extensively correlated pairwise giving a ground singlet state with a thermally accessible triplet state. Only triplet state entities would impart paramagnetism assuming no doublet state contributions.[17]

In solution dissociation into the corresponding ion-radical species may occur. For example, in acetonitrile the visible absorption spectrum of the N,N,N′,N′ - tetramethyl - *p* - phenylenediamine/TCNQ π-complex shows dissociation to the extent of about 80% into ion-radical species as indicated by comparison with the spectra of Wurster's blue perchlorate and the anion-radical salt $Li^+TCNQ^{\overline{\cdot}}$ (see below). Kainer and Uberle have reported similar observations on spectral characteristics of diamine complexes with chloranil.[7]

Simple Salts of the $TCNQ^{\overline{\cdot}}$. Anion-radical (Tables V and VI). Synthesis.—TCNQ undergoes facile one-electron reduction when treated with metal iodides or with certain metals. For example, TCNQ in acetonitrile will react at room temperature with metallic copper or silver to form metal salts of the anion-radical $TCNQ^{\overline{\cdot}}$. In the iodide reaction, the TCNQ oxidizes iodide ion to free iodine and takes up the electron to form $TCNQ^{\overline{\cdot}}$. With the free metal, direct oxidation–

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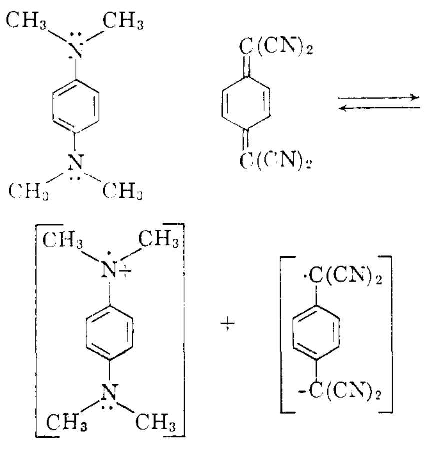
(13) The electrical resistivities of these π-complexes were determined on specimens prepared by mechanical compaction of microcrystalline products since single crystals of sufficient size were not obtainable. Single crystal resistivities are generally one to two orders of magnitude less than those of compactions, since measurements on the latter include the effects of electrical resistance associated with imperfect interparticle contact.

(14) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

(15) It should be noted that the paramagnetism referred to here is that revealed by E.P.R. absorption. The paramagnetic species involved are of sufficiently low concentration that macroscopic susceptibility measurements indicate an over-all diamagnetic susceptibility.

(16) These E.P.R. absorption measurements were carried out by Dr. W. D. Phillips. Absorption by weighed solid samples was compared with solid diphenylpicrylhydrazyl standard. The accuracy of the measurements was estimated to be ±25%.

(17) D. B. Chesnut and W. D. Phillips [*J. Chem. Phys.*, **35**, 1002 (1961)] discuss spin correlation in $TCNQ^{\overline{\cdot}}$ anion radical salts and also in the diaminodurene/chloranil π-complex.



reduction occurs and, in the case of copper, for example, the cuprous salt of $TCNQ^{-}$ is formed.

$$CuI + TCNQ \longrightarrow Cu^{+}TCNQ^{-} + {}^{1}/_{2}I_2 \quad (1)$$

$$Cu^0 + TCNQ \longrightarrow Cu^{+}TCNQ^{-} \quad (2)$$

The iodide reaction is the more convenient for direct preparation of simple metal $TCNQ^{-}$ salts and proceeds with facility when hot solutions of the iodide and TCNQ in acetonitrile or acetone are mixed. In this way the lithium, sodium and potassium salts of $TCNQ^{-}$ have been prepared. The $TCNQ^{-}$ salts precipitate as red or purple crystalline solids with a metallic sheen, the by-products remaining in solution. In practice, an excess of metal iodide is used so that the iodine by-product can be scavenged as I_3^-, *e.g.*

$$3LiI + 2TCNQ \xrightarrow{CH_3CN} 2Li^{+}TCNQ^{-} + Li^{-} + I_3^{-}$$

With this stoichiometry, higher yields are realized since the oxidative reverse reaction ${}^{1}/_{2}I_2 + TCNQ^{-} \rightarrow TCNQ + I^{-}$ is largely obviated. The occurrence of this oxidation has been established since free TCNQ can be isolated by oxidation of $TCNQ^{-}$ salts with a large excess of iodine.

It should be emphasized that the reaction of *metal* iodides with TCNQ generally affords *simple* salts represented by the formula $M^{+}TCNQ^{-}$ in contrast to *complex* salts usually obtained from organic iodide salts. These complex salts contain formally neutral TCNQ and are described in detail in the next section. An exception to the metal iodide generalization is cesium iodide which forms the complex salt III whose molecular unit comprises one molecule of neutral TCNQ bound with two of the simple salts (see Table V).

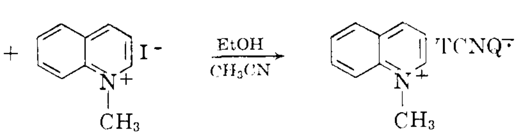
$$2CsI + 3TCNQ \longrightarrow \underset{\text{III}}{Cs^{+}_{2}(TCNQ^{-})_2(TCNQ)}$$

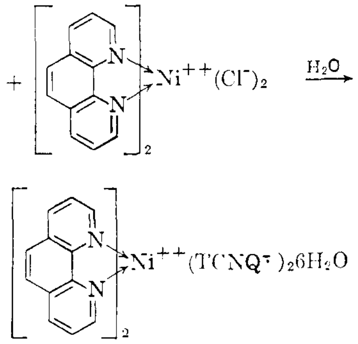
The solubility of $Li^{+}TCNQ^{-}$ in water or ethanol at room temperature is about 1% by weight in contrast to other metal-TCNQ salts which are virtually insoluble in water and organic solvents. This feature makes $Li^{+}TCNQ^{-}$ a convenient intermediate, since metatheses in these media provide a wide variety of $TCNQ^{-}$ derivatives containing metallic, organometallic and onium cations. Examples of such metathetical reactions are illustrated in the equations

$$Li^{+}TNCQ^{-} + FeSO_4 \xrightarrow{H_2O} Fe^{++}(TCNQ^{-})_2{\cdot}3H_2O$$

$$+ AgNO_3 \xrightarrow{H_2O} Ag^{+}TNCQ^{-}$$

$$+ Et_3NHCl \xrightarrow{H_2O} Et_3NH^{+}TCNQ^{-}$$





Detailed description of these and other simple salts are indicated in Tables V and VI.

Chemical and Physical Properties in Solution.—In organic solvents, such as acetone, acetonitrile or alcohol, simple $TCNQ^{-}$ salts form solutions whose green color is due to absorption by monomeric $TCNQ^{-}$ (see discussion of spectra below). However, concentrated solutions in water assume a vivid blue color that is ascribed to absorption by a dimeric species.[18] Dilution of the blue aqueous solutions results in dissociation of the dimer with consequent reversion to the green color of monomeric $TCNQ^{-}$.[19]

Green alcoholic solutions of $Li^{+}TCNQ^{-}$ are stable for many hours even in the presence of air, but aqueous solutions undergo quite rapid color loss to yellow-colored decomposition products. Aqueous solutions prepared from deaerated water are considerably more stable. When a dilute alcoholic solution of $Li^{+}TCNQ^{-}$ is ebulliated with air, color loss slowly occurs, presumably due to oxidation of $TCNQ^{-}$. Rapid oxidation of the anion is effected by treatment with ferric ion.

Treatment of solutions of $TCNQ^{-}$ with strong mineral acids brings about conversion to TCNQ accompanied by the reduction product *p*-phenylenedimalononitrile (H_2TCNQ, IV). This transformation probably occurs by disproportionation of an intermediate protonated radical as formulated in the equation

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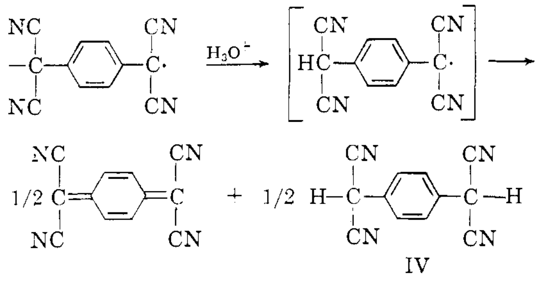
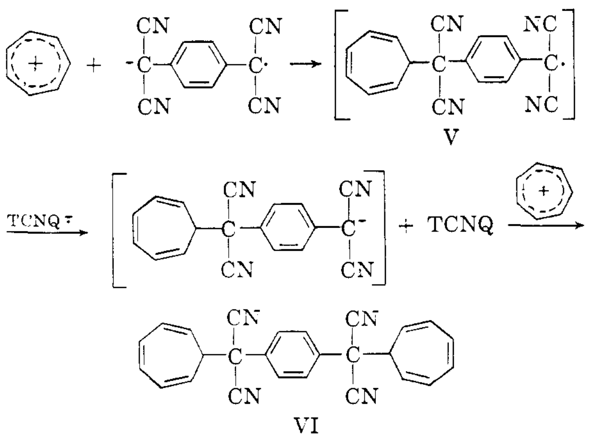
[18] Private communication from Dr. R. H. Boyd. Conductance measurements indicated the dimeric nature of the blue species.

[19] These observations are reminiscent of the behavior of the diaminodurene cation radical (DAD^{+}) described by L. Michaelis and S. Granick [*J. Am. Chem. Soc.*, **65**, 1747 (1943)]. They found that in alcohol DAD^{+} gave an amber-colored solution imputed to the paramagnetic monomeric ion, while in water a green color was formed due to association of the ions. These observations have been confirmed in E.P.R. absorption experiments by Dr. W. D. Phillips. The green aqueous solution of DAD^{+} exhibited no E.P.R. absorption, while the amber alcoholic solution at room temperature gave a many-lined spectrum that could be accounted for by electron-nucleus hyperfine interaction.



Acid-decomposition reactions of this type with simple TCNQ$^{\overline{\cdot}}$ salts have afforded TCNQ and H_2TCNQ in nearly quantitative yields based on the above stoichiometry.

Whereas most salts react in a strightforward metathetical fashion with Li^+TCNQ^-, the reaction with tropylium iodide afforded a high yield of a mixture of TCNQ and α,α'-ditropyl-$\alpha,\alpha,\alpha',\alpha'$-tetracyano-*p*-xylene (VI). The high yield of these products and the absence of ditropyl suggests that covalent bond formation occurred between the ionic species to form a radical (V). Subsequent reduction of the radical and further reaction with tropylium ion could afford the observed products.



Spectral Properties.—The electronic absorption spectrum of the TCNQ$^{\overline{\cdot}}$ ion in acetonitrile exhibits major maxima at 420 and 842 mμ, with molar extinctions of 24,300 and 43,300, respectively, and minor bands at 744, 760, 680 and 665 mμ. The intensity ratio of the 420 and 842 mμ bands is about 0.5 for simple salts, and determination of this ratio serves as a useful criterion in characterization of TCNQ$^{\overline{\cdot}}$ derivatives. The extent of dissociation of the tetramethyl-*p*-phenylenediamine/TCNQ π-complex described above was established in this manner. The spectrum of the simple salt $Et_3NH^+TCNQ^-$ is reproduced in Fig. 1.

The infrared absorption spectra of TCNQ$^{\overline{\cdot}}$ simple salts exhibit a small bathochromic shift of the —C≡N absorption compared to that observed in neutral TCNQ. Thus, TCNQ has a very sharp, intense —C≡N band at 4.50 μ, while the corresponding band in $Et_3NH^+TCNQ^{\overline{\cdot}}$ is at 4.55–4.60 μ and is considerably broadened. However, the most noteworthy characteristic of simple anion-radical salt spectra is the very strong near-infrared absorption; a broad band with a maximum at about 1 to 1.5 μ appears and is ascribed to electronic rather than vibrational absorption. This is illustrated in the infrared spectrum of $Et_3NH^+TCNQ^{\overline{\cdot}}$ reproduced in Fig. 2.

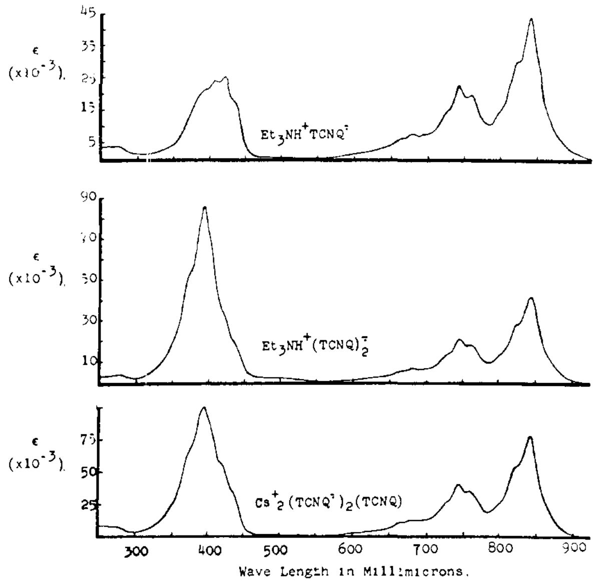


Fig. 1.—Electronic absorption spectra in acetonitrile.

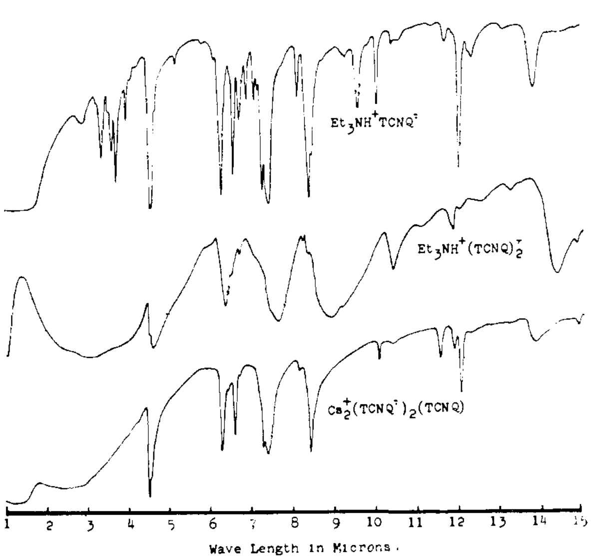


Fig. 2.—Infrared absorption spectra (KBr wafers).

Polarography.—Polarographic studies of solutions of $Li^+TCNQ^{\overline{\cdot}}$ reveal two waves; the first is anodic and characteristic of the reversible, one-electron oxidation as in eq. 1, and the second wave is cathodic and characteristic of the thermodynamically irreversible, one-electron reduction of TCNQ$^{\overline{\cdot}}$ according to eq. 2, Table II.

TABLE II

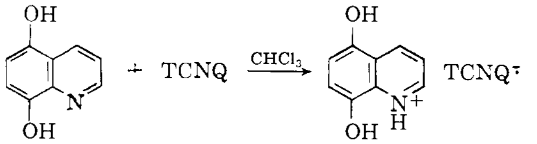
POLAROGRAPHY OF TCNQ$^{\overline{\cdot}}$ SIMPLE SALTS

		$E_{1/2}$, volt
(1)	$TCNQ^{\overline{\cdot}} \underset{+e}{\overset{-e}{\rightleftharpoons}} TCNQ$	+0.127
(2)	$TCNQ^{\overline{\cdot}} \xrightarrow{+e} TCNQ^{=}$	−0.291

The polarogram of $\text{Li}^+\text{TCNQ}^{\cdot-}$ is, therefore, similar to that previously reported for TCNQ,[4] except that the first wave is anodic and the second is cathodic, whereas with TCNQ both waves are cathodic.[20]

Electron Paramagnetic Resonance Absorption.—In the solid state, most simple $\text{TCNQ}^{\cdot-}$ salts exhibit weak E.P.R. absorption as a result of extensive spin correlation.[3] The resultant spin pairing is reflected in the diamagnetism of such salts as determined by static magnetic susceptibility measurements.[2] On the other hand, the E.P.R. spectrum of a dilute solution of $\text{Li}^+\text{TCNQ}^{\cdot-}$ in tetrahydrofuran[21] exhibits over forty lines, compared with forty-five lines expected on the basis of isotropic hyperfine contact interaction between the unpaired electron and H^1 and N^{14} nuclei of the TCNQ molecule. Broadening of this spin resonance by added neutral TCNQ has allowed determination of the rate of electron exchange in solution between charged and uncharged species. This exchange rate was determined to be about 10^9 liter mole^{-1} sec.$^{-1}$ in acetonitrile at 23° indicative of an extremely rapid electron exchange process.[21] It should be noted that strong E.P.R. absorption is exhibited only by green solutions containing monomeric $\text{TCNQ}^{\cdot-}$, while aqueous blue solutions containing the dimeric species show only a very weak E.P.R. signal. The paramagnetism of the blue solution can be increased by heat,[21] indicating dissociation of the diamagnetic dimer to paramagnetic monomer. This behavior is similar to that of the $\text{DAD}^{\cdot+}$ cation radical referred to above.[19]

Electrical Properties.—Solid $\text{Li}^+\text{TCNQ}^{\cdot-}$ has an electrical resistivity of about 10^5 ohm cm. (powder compaction), which is intermediate between values for typical insulators and metallic conductors.[9] Resistivity values in the intermediate range 10^4–10^9 ohm cm. are typical of most of the simple $\text{TCNQ}^{\cdot-}$ salts (see Table V). With few exceptions, the simple salts are obtained in micro-crystalline form so that single crystal resistivity measurements are not usually attainable. However, in those instances where sufficiently large single crystals were obtained, the resistivities along three major crystal axes were essentially equivalent (isotropic), in contrast to the marked *anisotropy* of resistivity observed in single crystals of complex salts (see Tables VII and IX). Although most simple salts have relatively high resistivities, several exceptions have been encountered. For example, the product derived from 5,8-dihydroxyquinoline and TCNQ in chloroform was identified as the simple salt VII. Its resistivity is of the order of 15 ohm cm. which closely approximates the very low values generally observed for complex salts.



VII

The source of the proton required to form the cation is not known but it is probably derived from the base; the question of such adventitious protonation will be discussed in the next section on complex salts.

Another particularly interesting exception to the general behavior of $\text{TCNQ}^{\cdot-}$ simple salts is found in the product from metathesis of cupric sulfate with $\text{Li}^+\text{TCNQ}^{\cdot-}$. As stated previously, metallic copper or cuprous iodide reacts with TCNQ to form $\text{Cu}^+\text{TCNQ}^{\cdot-}$. On the other hand, the product of the metathetical reaction with cupric sulfate in water had a composition corresponding to the expected $\text{Cu}^{++}(\text{TCNQ}^{\cdot-})_2$. However, static magnetic susceptibility studies showed that this composition was diamagnetic, indicating the absence of important contributions by either $\text{TCNQ}^{\cdot-}$ or Cu^{++}. Furthermore, the infrared spectrum of the solid product shows bands at 6.65 and 9.85 μ attributable to $(\text{TCNQ}^{\cdot-})$. These data and the appreciable electron mobility implied by its relatively low resistivity (200 ohm cm.) suggest a solid state equilibrium depicted by structure VIII.

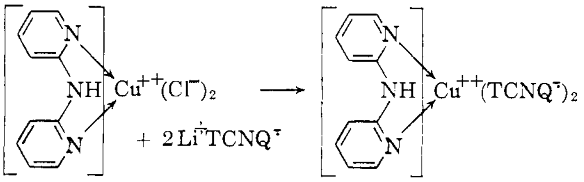
$$2[\text{Cu}^{++}(\text{TCNQ}^{\cdot-})_2] \rightleftharpoons \text{Cu}^{+}_2(\text{TCNQ}^{\cdot-})_2(\text{TCNQ})_2 \rightleftharpoons \text{Cu}^{+}_2(\text{TCNQ}^{=})(\text{TCNQ})_3$$

VIII

This compound is stable only in the solid state. In benzene it releases neutral TCNQ and forms Cu^+-$\text{TCNQ}^{\cdot-}$, a transformation which is analogous to that which occurs spontaneously with cupric iodide.

$$\text{Cu}^{++}(\text{TCNQ}^{\cdot-})_2 \longrightarrow \text{Cu}^+\text{TCNQ}^{\cdot-} + \text{TCNQ}$$
$$2\text{Cu}^{++}\text{I}_2^- \longrightarrow 2\text{Cu}^+\text{I}^- + \text{I}_2$$

It is of some interest that the simple cuprous salt $\text{Cu}^+\text{TCNQ}^{\cdot-}$ has an electrical resistivity of the same order of magnitude as that of the "cupric" compound. An exceptionally low resistivity value is also observed in the copper chelate derivative IX (ρ = 40 ohm cm.) obtained by metathesis of Li^+-$\text{TCNQ}^{\cdot-}$ with the chelate chloride.



IX

We are continuing investigation of these and related copper compounds.

Complex Salts of $\text{TCNQ}^{\cdot-}$ and TCNQ (Tables VII, VIII and IX). Introduction.—In addition to the simple anion-radical salts described above, TCNQ forms a second series of anion-radical derivatives which contain molar proportions of neutral TCNQ associated with $\text{TCNQ}^{\cdot-}$ and a cation. These complex salts have molecular units represented by the formulas $\text{M}^+(\text{TCNQ}^{\cdot-})(\text{TCNQ})$ and $\text{M}^+_2(\text{TCNQ}^{\cdot-})_2(\text{TCNQ})$. Of these two types of complexes the latter is quite rare, and so most of the discussion will be devoted to the $\text{M}^+(\text{TCNQ}^{\cdot-})$-(TCNQ) type. In solution, spectral, polarographic and conductivity data indicate dissociation into the three species formulated in the molecular unit $\text{M}^+(\text{TCNQ}^{\cdot-})(\text{TCNQ})$, but in the solid state

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[20] The half-wave potentials were determined in anhydrous acetonitrile, 0.1 *M* with respect to lithium perchlorate and *versus* an aqueous saturated calomel electrode.

[21] W. D. Phillips, J. C. Rowell, H. Foster and D. B. Chesnut, to be published.

there is probably complete electron delocalization between $\text{TCNQ}^{\overline{\cdot}}$ and TCNQ as implied by the formulation $(\text{TCNQ})^{\overline{\cdot}}_2$.

These complexes are probably the most interesting of the TCNQ derivatives because of their remarkable physical properties and especially because of their very high electrical conductivities in the solid state. They exhibit electrical resistivities in the range of 0.01 to about 100 ohm cm., the lower limit representing the lowest value yet observed for an organic compound.[22] These resistivities show the exponential temperature dependence characteristic of intrinsic semiconductors.[23] In addition, resistivity values on single crystals have been shown to be markedly anisotropic, differing by several orders of magnitude when measured along three major crystal axes; this phenomenon is in marked contrast to the isotropic resistivity behavior of the simple salts.

Synthesis.—Complex salts have been prepared in which the cation M^+ is represented by alkyl- or aryl-substituted ammonium (including N-heterocycles), phosphonium, arsonium, stibonium, sulfonium and oxonium ions. It should be noted that neutral TCNQ is usually not incorporated into products containing inorganic cations even when neutral TCNQ is present during synthesis. On the other hand, organic cations generally afforded complex salts under analogous synthesis conditions. There are four major synthetic routes to these complexes. Though some methods are more general than others, all can be applied to the preparation of the triethylammonium derivative X (see Table VII), and so the methods will be discussed mainly with respect to that derivative. The four routes are formulated in the equations

$$\text{Et}_3\text{NH}^+\text{TCNQ}^{\overline{\cdot}} + \text{TCNQ} \xrightarrow{\text{CH}_3\text{CN}} \text{X Et}_3\text{NH}^+(\text{TCNQ})_2^{\overline{\cdot}}\ (50\%) \quad (1)$$

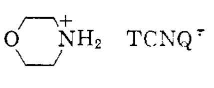
$$3\text{Et}_3\text{NH}^+\text{I}^- + 2\text{TCNQ} \xrightarrow{\text{CH}_3\text{CN}} \text{X}\ (50\%) \quad (2)$$

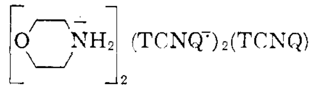
$$2\text{Et}_3\text{N} + \text{H}_2\text{TCNQ} + 3\text{TCNQ} \xrightarrow{\text{CH}_3\text{CN}} \text{X}\ (90\%) \quad (3)$$

$$\text{Et}_3\text{N} + 2\text{TCNQ} \xrightarrow{\text{CH}_3\text{CN}} \text{X}\ (77\%) \quad (4)$$

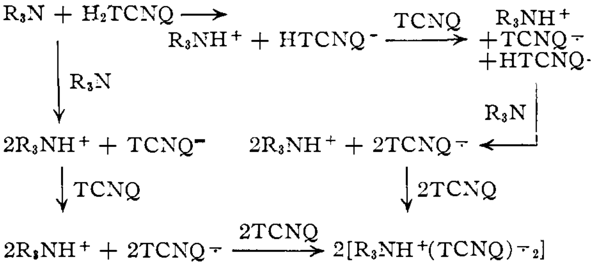
In method 1, solutions of the simple salt (prepared by metathesis of $\text{Et}_3\text{NH}^+\text{Cl}^-$ with $\text{Li}^+\text{TCNQ}^{\overline{\cdot}}$) and neutral TCNQ are mixed and characteristic black needles of the complex crystallize from the solution. It should be noted that the neutral component cannot be separated by recrystallization of the complex; it is recovered unchanged. This first method probably represents the most general route to the complex anion-radical salts and is dependent only on the availability of the simple salts and on their having a reasonable degree of solubility in acetonitrile.

In method 2, the iodide ion serves as the electron source for the formation of $\text{TCNQ}^{\overline{\cdot}}$, the iodide being oxidized to free iodine. In practice, the stoichiometry of reactants charged is such that the liberated iodine is scavenged as triiodide. The method is suitable for virtually all onium iodides including substituted -ammonium, -phosphonium, -arsonium, -stibonium and -sulfonium salts (see especially Tables VIII and IX). It should be noted that a few exceptions have been encountered in which the iodide route affords the simple salt rather than the complex salt. For example, morpholinium iodide can form either the simple salt XI or the complex salt XII depending on the ratio of reactants used (see Tables VI and VII).

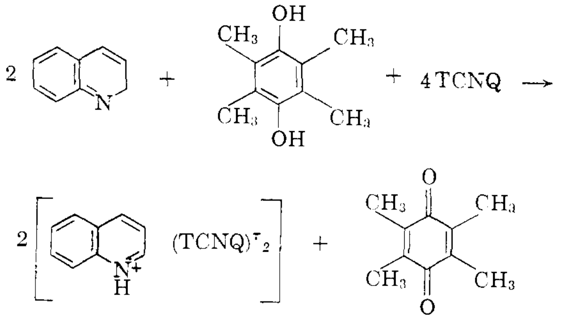

XI


XII

Method 3, in which the H_2TCNQ acts as both proton and electron donor, is particularly suitable for the preparation of trisubstituted ammonium complex salts starting from free amines (including basic N-heterocycles). The path in this transformation is not certain but two possibilities are included in the sequence



A variant of this procedure consists in replacing the H_2TCNQ by another proton-electron source, such as durohydroquinone.



Method 4 is applicable to tertiary aliphatic amines and is of special interest since the reaction occurs at room temperature in acetonitrile in the absence of added catalyst or proton-electon donor. The source of the ammonium proton is unknown but it is probably derived from the amine[24] as

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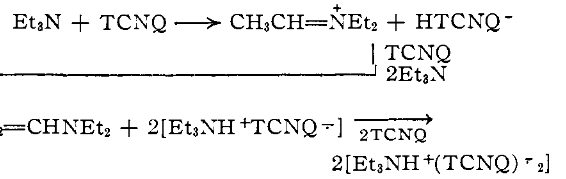
[22] Note that J. Kommandeur and F. R. Hall [*Bull. Am. Phys. Soc., Series II*, **4**, 421 (1959)] have reported a resistivity of 8 ohm cm. for the metastable iodine/perylene complex; and H. Akamatu, H. Inokuchi and Y. Matsunaga [*Bull. Chem. Soc. Japan*, **29**, 213 (1956)] reported resistivities as low as 1 ohm cm. for the unstable bromine/perylene complexes.

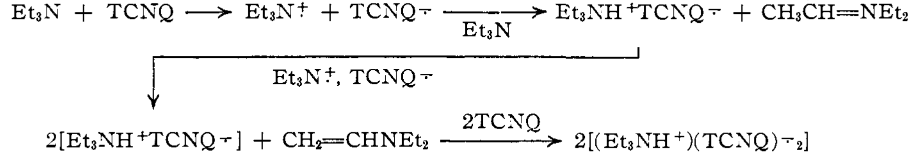
[23] The expressions $\rho = \rho_0 \exp(E/kT)$ or $\rho = \rho_0 \exp(E_g/2kT)$ define the relation between resistivity (ρ) and temperature in intrinsic semiconductors; E is referred to as the activation energy, and E_g as the energy gap. The activation energy, E, will be used throughout this paper. For comparison purposes, the energy gap in silicon is approximately 1 electron volt (e.v.), corresponding to an activation energy of 0.5 e.v.

[24] D. Buckley, S. Dunstan and H. B. Henbest [*J. Chem. Soc.*, 4880 (1957)] reported that amines, including triethylamine, were dehydrogenated by chloranil at room temperature to give vinylamine derivatives together with the reduction product tetrachlorohydroquinone.

is the electron required for the formation of $TCNQ^{\overline{\cdot}}$. The following alternative possibilities would afford the required components; the first involves hydride ion transfer and the second an electron transfer which gives rise to an aminium radical.

(1)


$$Et_3N + TCNQ \longrightarrow CH_3CH{=}\overset{+}{N}Et_2 + HTCNQ^- \xrightarrow[2Et_3N]{TCNQ} CH_2{=}CHNEt_2 + 2[Et_3NH^+TCNQ^{\overline{\cdot}}] \xrightarrow[2TCNQ]{} 2[Et_3NH^+(TCNQ)^{\overline{\cdot}}_2]$$

(2)


$$Et_3N + TCNQ \longrightarrow Et_3N^{\dot{+}} + TCNQ^{\overline{\cdot}} \xrightarrow[Et_3N]{} Et_3NH^+TCNQ^{\overline{\cdot}} + CH_3\dot{C}H{=}NEt_2 \xrightarrow{Et_3N^{\dot{+}},\ TCNQ^{\overline{\cdot}}} 2[Et_3NH^+TCNQ^{\overline{\cdot}}] + CH_2{=}CHNEt_2 \xrightarrow{2TCNQ} 2[(Et_3NH^+)(TCNQ)^{\overline{\cdot}}_2]$$

Both schemes would require the ultimate formation of a vinylamine, but our attempts to isolate a vinylamine derivative have so far been unsuccessful. An obvious alternative source of proton and electron would be the solvent, but when the reaction was carried out in acetonitrile, we failed to isolate the expected coupling product, succinonitrile. It should be noted that this reaction with highly purified starting materials affords the complex salt in good yield (77%) and the product is identical with that obtained *via* the other three routes cited.[25]

The synthesis of the ferricinium $(TCNQ)^{\overline{\cdot}}_2$ complex salt (see Table VIII) from ferrocene and neutral TCNQ illustrates an interesting example of oxidation–reduction. Synthesis conditions were essentially those used for π-complex formation wherein the neutral donor and acceptor combine. However, in this case, the ferrocene is oxidized to ferricinium ion with concomitant formation of $TCNQ^{\overline{\cdot}}$. The latter then combines with neutral TCNQ and the ferricinium complex salt is formed. Isolation of the product fails unless a large excess of ferrocene is used, but despite the excess of reducing component the amount of $TCNQ^{\overline{\cdot}}$ generated is limited to that which can be stabilized in the form of the complex anion-radical $(TCNQ)^{\overline{\cdot}}_2$. Dissolution in benzene decomposed the complex salt into the original neutral components.

General Properties.—The complex salt $Et_3NH^+(TCNQ)^{\overline{\cdot}}_2$ exhibits various properties which are found in general among the class of complex salts. The compound exhibits a decomposition point around 195° depending upon the rate of heating.[26] It can be recrystallized from acetonitrile without change in composition (*i.e.*, the crystallized product retains the formally neutral TCNQ component). In the solid state, it is quite stable to air, samples having been retained for many months without detectable change in composition. Conductivity and molecular weight determinations in acetonitrile show the compound to be dissociated into three particles as required by the complex salt formulation.

Decomposition of a complex salt with mineral acid affords a mixture of TCNQ and H_2TCNQ in quantitative yield, in accordance with the equation $M^+(TCNQ^{\overline{\cdot}})(TCNQ) \xrightarrow{H_3O^+} M^+ + {}^1/_2H_2TCNQ + {}^3/_2TCNQ$. The stoichiometry based on $TCNQ^{\overline{\cdot}}$ is equivalent to that described previously for the acid decomposition of simple salts, but in this case the product contains additional TCNQ corresponding to that contained in the original complex.

Spectral Properties.—Electronic absorption spectra of the complexes in solution show absorption which is essentially a summation of the bands characteristic of neutral TCNQ and the anion-radical. For example, in acetonitrile the spectrum of $Et_3NH^+(TCNQ^{\overline{\cdot}})(TCNQ)$ (ϵ_{395} 85,800 and ϵ_{842} 43,400) is essentially a composite of that of Et_3NH^+-$TCNQ^{\overline{\cdot}}$ (ϵ_{394} 21,500, ϵ_{842} 43,500) and TCNQ (ϵ_{395} 63,600). These anion-radical spectra are reproduced in Fig. 1. For complex salts of this type the intensity ratio of the 395 and 842 mμ bands is approximately two when it is not complicated by cation absorption. On the other hand, a few complexes of the type $(M)^{++}(TCNQ^{\overline{\cdot}})_2$-$(TCNQ)$ have been encountered (see Table VII) and these exhibit a 394/842 band intensity ratio of about 1.2 to 1.5. Determination of these ratios provides a convenient means for preliminary assignment of complex salt compositions. The spectrum of $Cs^+_2(TCNQ^{\overline{\cdot}})_2(TCNQ)$ is reproduced in Fig. 1.

Infrared spectra of the complex salts are characterized by strong general absorption which masks much of the cation absorption found in the corresponding simple salts. The most characteristic general feature is a very broad, strong electronic absorption band at 3 μ (see Fig. 2).

Polarography.—Polarograms of complex salts consist of two waves which are additive curves of neutral TCNQ and $TCNQ^{\overline{\cdot}}$.[20] The first wave is a composite wave with an anodic component arising from oxidation of $TCNQ^{\overline{\cdot}}$ to TCNQ and a cathodic component resulting from reduction of TCNQ to $TCNQ^{\overline{\cdot}}$. The second wave represents reduction of both the $TCNQ^{\overline{\cdot}}$ originally present in the complex and the $TCNQ^{\overline{\cdot}}$ formed from reduction of TCNQ. If the complex is completely dissociated in acetonitrile, the wave heights of the anodic and cathodic components are directly proportional to the ratio of $TCNQ^{\overline{\cdot}}$ to TCNQ in the complex. For example, the wave heights of the anodic and cathodic components of the first

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[25] In our previous communication (ref. 1), we reported the formation of the complex quinolinium $(TCNQ)^{\overline{\cdot}}_2$ salt from quinoline and TCNQ in acetonitrile. This particular reaction occurred in very low yield. We have since determined that the quinoline originally used contained a contaminant which acted as a proton and electron source, and the reaction failed when highly pure synthetic quinoline was used.

[26] We previously stated (ref. 1) that the triethylammonium complex salt could be sublimed at 200° (0.1 mm.) with only slight decomposition. This is erroneous and, in fact, under these conditions extensive decomposition occurs. For this observation we are indebted to Dr. G. J. Sloan.

wave of Et_3NH^+ ($TCNQ^{\overline{\cdot}}$) (TCNQ) in acetonitrile are in a 1:1 ratio.

Paramagnetism.—Salts of the type $M^+TCNQ^{\overline{\cdot}}$ were previously indicated to exhibit weak E.P.R. absorption whereas the complex salts may exhibit strong or weak E.P.R. absorption. In certain cases, the E.P.R. absorption characteristics may be analyzed in terms of pairwise spin correlation giving ground singlet and thermally accessible triplet states[3,17] rather than the doublet state implied by the simplified general formula. Similarly, static magnetic suceptibilities of, for example, $Et_3NH^+(TCNQ)^{\overline{\cdot}}_2$ and $(C_6H_5)_3CH_3P^+(TCNQ)^{\overline{\cdot}}_2$ show singlet–triplet behavior. On the other hand, many of the N-heterocyclic onium $(TCNQ)^{\overline{\cdot}}_2$ complexes appear to exhibit temperature independent paramagnetism.[2] Details of these magnetic measurements and their interpretation are given in the references cited.

Electrical Properties.—The electrical properties of the TCNQ complex salts are of special interest in that they are the most electrically conductive organic compounds known.[2,27] Many of the complexes were obtained only in micro-crystalline form which precluded single crystal measurements and required measurement on compacted material. However, in many cases single crystals of sufficient size were obtained so that measurements along three major crystal axes could be carried out.[2] These include, among others, the triethylammonium, methyltriphenylphosphonium, methyltriphenylarsonium and N-(*n*-propyl)-quinolinium $(TCNQ)^{\overline{\cdot}}_2$ complexes. The phosphonium and arsonium compounds were obtained as single crystals as large as 10 mm. × 10 mm. × 2 mm. (see Table IX). Electrical measurements on single crystals of the complex salts have demonstrated the marked anisotropy of resistivity relative to crystal axis. The data in Table III illustrate this property; the letters *a*, *b* and *c* refer to three major crystal axes, the *a*-axis being arbitrarily designated as that of lowest resistivity. In other cases the complexes were obtained in the form of small needles, allowing measurement in one crystal direction only. For example, quinolinium $(TCNQ)^{\overline{\cdot}}_2$ exhibited a single crystal resistivity of 0.01 ohm cm. and a very low activation energy for conduction (less than 0.01 e.v.), suggestive of metallic conduction behavior.[2] Compaction resistivities for the quinolinium $(TCNQ)^{\overline{\cdot}}_2$ complex were about 0.15 to 0.5 ohm cm. (see footnote 13). It should be further noted that the quinolinium complex exhibited small, but real, differences in resistivity depending upon the method of preparation. Thus, preparations from quinolinium hydroiodide and TCNQ or from the free base with H_2TCNQ and TCNQ had compaction resistivities of about 0.5 ohm cm. (see Table VIII), whereas analytically identical preparations from the free base with durohydroquinone and TCNQ had resistivities of about 0.15 to 0.2 ohm cm. These resistivity differences may be related to variations in physically important impurity levels.

TABLE III

COMPOUND AND RESISTIVITY (OHM-CM.)

Axis	Triethyl-ammonium $(TCNQ)^{\overline{\cdot}}_2$	Methyltriphenyl-phosphonium $(TCNQ)^{\overline{\cdot}}_2$	N-(*n*-Propyl)-quinolinium $(TCNQ)^{\overline{\cdot}}_2$
a	0.25	60	0.5
b	20	600	6
c	1000	10^5	450

Complex Salts with Mixed Cations.—The marked similarity in macroscopic crystal form of the methyltriphenylphosphonium and -arsonium complex salts suggested that it might be possible to prepare a complex salt containing both cations. It was in fact found that large crystals containing the two cations could be obtained by allowing TCNQ to react with a mixture of the respective onium iodides (see Experimental). Furthermore, the ratios of the cations in the crystals were directly dependent upon the relative concentrations of the two iodides in the reaction mixture.

The pure phosphonium complex shows a transition at 45° which results in an abrupt change in the energy difference between the singlet and triplet states. No such transition was observed in the pure arsonium compound up to a temperature of 200°. Complexes containing both cations exhibited an increase in the transition temperature above that for the pure phosphonium compound and the increase was proportional to the amount of arsonium cation contained in the mixed complex.[28]

Effect of Cation on Complex Salt Properties.—In a gross sense the physical properties of $TCNQ^{\overline{\cdot}}$ salts and complexes seem to be dominated by interactions among TCNQ moieties although differences due to cation structure are evident. For example, there is a marked difference in the electrical resistivity and the magnetic character of the quinolinium *versus* the methyltriphenylphosphonium complex salt. These differences may be related, on the one hand, to steric effect of the cation on molecular packing within crystals and, on the other hand, to electronic involvement of the cation. The relative importance and consequences of such effects and of impurity effects are as yet unexplained. We are continuing investigation of these and related problems.

Acknowledgments.—The authors wish to thank Misses Naomi E. Schlichter and Ellen Wallace for determining the spectra and assisting in their interpretation. The polarographic data were kindly provided by Miss Lucille E. Williams and Dr. T. Berzins. Helpful discussions with Drs. W. D. Phillips, R. G. Kepler, E. A. Abrahamson, P. E. Bierstedt, D. S. Acker and D. C. Blomstrom are gratefully acknowledged.

Experimental

The examples given below include only a few of the compounds tabulated. With minor variations, they illustrate all of the various preparative procedures and include, in particular, details for those complexes which can be obtained in macrocrystalline form. Characterization data are included in the tables.

Copper 8-Quinolinolate/TCNQ π-Complex (Table IV).—To a boiling solution of 0.10 g. (0.5 mmole) of copper 8-quinolinolate (previously recrystallized from acetonitrile) in 50 ml. of chloroform was added all at once a boiling solution of 0.18 g. (0.5 mmole) of TCNQ in 50 ml. of chloroform.

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[27] Details of these electrical properties will be published elsewhere; manuscript in preparation by Dr. R. G. Kepler.

[28] Private communication from Dr. R. G. Kepler; details of this magnetic susceptibility behavior will be published elsewhere.

TABLE IV

π-COMPLEXES OF TCNQ

Donor[a]	Solvent	Yield, %	Decomp. range, °C.	Analyses, % Calculated C	Calculated H	Calculated N	Found C	Found H	Found N	Resistivity, ohm-cm.[b]	Remarks
p-Phenylenediamine	$CHCl_3$	83	162->300	69.2	3.9		69.4	3.9		3×10^{3c}	Purple-black microplat.
2-Methyl-*p*-phenylenediamine	$CHCl_3$	44	150–155	69.9	4.3	25.8	69.3	4.5	25.2	3×10^5	Black microcrystals
N,N-Dimethyl-*p*-phenylenediamine	$CHCl_3$	38	112–117	70.6	4.7	24.7	70.6	4.8	24.7	2×10^{9d}	Black leaflets
N,N′-Dimethyl-*p*-phenylenediamine	CH_2Cl_2	50	111–114	70.6	4.7	24.7	70.4	4.9	24.0	2×10^4	Black needles
N,N,N′,N′-Tetramethyl-*p*-phenylenediamine	$CHCl_3$	71	128–129	71.7	5.5	22.8	71.7	5.6	23.2	10^6	Blue-black platelets
Diaminodurene	THF	86	190->300	71.7	5.5	22.8	71.7	5.8	22.4	10^9	Purple microplatelets
2,3-Diaminonaphthalene	$CHCl_3$	27	165->300	72.9	3.9	23.2	72.7	3.8	23.4	10^{10}	Black microcrystals
1,5-Diaminonaphthalene	$CHCl_3$	59	197	72.9	3.9	23.2	72.4	3.8	23.8	10^{9e}	Black needles
2-Aminofluorene	CH_3CN	80	207–242	78.0	3.9	18.2	78.1	4.0	17.7	10^9	Brown-black needles
2-Aminochrysene	CH_2Cl_2	51	211–217	80.5	3.8	15.6	80.4	3.9	15.9	10^{10}	Brown needles
Hydroquinone[f]	THF	Low	180–185	69.5	2.7	21.6	69.1	2.8	21.6		Black microcrystals
Pyrogallol[g]	CH_2Cl_2	Low	105	63.2	3.5	12.3	63.5	4.0	12.4		
Anthracene	THF	42	282–283	81.7	3.7	14.7	81.9	3.8	14.9	10^{11}	Black needles
Pyrene	THF	52	260	82.7	3.5	13.8	82.4	3.7	14.4	10^{12}	Purple needles
4,6,8-Trimethylazulene	THF	85	160–167	80.2	4.8	15.0	80.4	5.0	15.0	10^9	Black crystals
Copper 8-quinolinolate	$CHCl_3$	48	195	64.7	2.9	11.4[h]	64.7	2.9	11.5[h]	3×10^7	Black plates
Copper chelate of pyrrole-2-aldehydeimine	$CHCl_3$	69	170->300	58.2	3.1	14.0[h]	58.2	3.1	13.9[h]	5×10^{10}	Purple needles
Nickel chelate of pyrrole-2-aldehydeimine	CH_2Cl_2		210–220	58.9	3.1	25.0	58.7	3.2	25.2	10^{11}	Blue-black needles

[a] Unless otherwise noted the mole ratio of donor to TCNQ is 1:1 in the isolated complex. All of the complexes were prepared by addition of a solution of the donor to a hot solution of TCNQ. THF is tetrahydrofuran. [b] Determined on compactions at room temperature. [c] Activation energy for conduction, 0.28 e.v. Quantitative E.P.R.[4] $\times 10^{20}$ (±25%) unpaired electrons per mole; see ref. 16. [d] 4×10^{21} (±25%) unpaired electrons per mole. [e] 2×10^{19} (±25%) unpaired electrons per mole. [f] Donor to TCNQ mole ratio 1:2. [g] Donor to TCNQ mole ratio 2:1. [h] Copper analyses.

The dark solution was concentrated to a volume of 50 ml. and was allowed to stand at room temperature overnight. Black, shiny prisms of the complex separated. The product was collected and washed on the filter with a large volume of chloroform.

$Li^+TCNQ^{\overline{\cdot}}$. (Table V).—To a boiling solution of 20.4 g. (0.1 mole) of TCNQ in 2000 ml. of acetonitrile[29] was added a boiling solution of 40 g. (0.3 mole) of lithium iodide in 100 ml. of acetonitrile. Purple crystals separated from the dark brown solution. The mixture stood for 4 hours at room temperature and while still warm the purple solid was collected and washed on the filter with acetonitrile until the washings were bright green. The solid was then washed with a large volume of ether.

$Cu^{++}(TCNQ^{\overline{\cdot}})_2$ (Table V).—To a filtered solution of 2.2 g. (11 mmmoles) of $Li^+TCNQ^{\overline{\cdot}}$ in 200 ml. of water was added a solution of 12 g. (large excess) of cupric sulfate pentahydrate in 70 ml. of water. The finely divided green solid was collected on a filter and dried in a vacuum desiccator. The yield was 2.2 g.

$Cs^+_2(TCNQ^{\overline{\cdot}})_2(TCNQ)$ (Table V).—To a solution of 2.0 g. (10 mmoles) of TCNQ in 200 ml. of boiling acetonitrile contained in a 500-ml. erlenmeyer flask was added, all at once, a filtered solution of 2.9 g. (11 mmoles) of cesium iodide in 50 ml. of boiling methanol. The flask was covered and allowed to stand overnight at room temperature. The brown solution was decanted from the long purple crystals which were then carefully washed by decantation with several 50-ml. portions of acetonitrile until the brown color was removed. The crystals, up to 10 mm. long and 1 mm. on a side, were then collected on a funnel and washed with dichloromethane; yield 1.64 g. Although the above procedure affords quite large crystals, the results are difficultly reproducible in that the solution has a tendency to deposit some free TCNQ. In some runs, the TCNQ could be mechanically separated from the crystals of complex while in others microscopic examination showed that the surfaces of some of the crystals were plated with a yellow layer (presumably free TCNQ). When the mole ratio of cesium iodide to TCNQ was increased to 1.5, the complex was obtained in consistently purer form although the crystals were considerably smaller.

N-Methylquinolinium $TCNQ^{\overline{\cdot}}$ (Table VI).—To a filtered solution of 0.84 g. (4 mmoles) of $Li^+TCNQ^{\overline{\cdot}}$ in 200 ml. of boiling absolute ethanol was added a boiling solution of 1.1 g. (4 mmoles) of N-methylquinolinium iodide in 10 ml. of ethanol, and the mixture was allowed to stand at room temperature for 2 hours. The shiny, deep-purple needles were collected on a funnel and washed with ice-cold ethanol, then with ether. The product was recrystallized from acetonitrile.

Morpholinium $TCNQ^{\overline{\cdot}}$ (Table VI).—Seed crystals of this salt were obtained by mixing almost boiling solutions of 0.4 g. (2 mmoles) of TCNQ in 30 ml. of acetonitrile and 1.1 g. (5 mmoles) of morpholine hydroiodide in 30 ml. of acetonitrile in a 125-ml. erlenmeyer flask. The mixture was allowed to stand overnight at room temperature; the glistening reddish-purple prisms were collected on a filter and washed successively with acetonitrile and chloroform. The yield was 0.15 g.

To obtain the salt in quantity, the above reaction was carried out on a 10-fold scale. The solutions, at a temperature of 65°, were mixed in a 1-liter erlenmeyer flask, and a seed crystal was immediately added. The mixture was allowed to stand overnight and afforded 2.05 g. of product.

$(Morpholinium)_2(TCNQ^{\overline{\cdot}})_2(TCNQ)$ (Table VII).—When the reaction described above was carried out with 0.4 g. of TCNQ in 25 ml. of acetonitrile and 0.54 g. (2.5 mmoles) of the hydroiodide in 20 ml. of acetonitrile, there was obtained exclusively the complex salt in the form of black plates.

$Et_3NH^+(TCNQ)^{\overline{\cdot}}_2$ (Table VII). **a. From Triethylamine and TCNQ.**—To an almost boiling solution of 2.8 g. (9.8 mmoles) of TCNQ in 250 ml. of tetrahydrofuran was added a solution of 0.75 ml. (5.35 mmoles) of triethylamine. The solution turned intensely green, and after several hours shiny crystals of the complex salt had separated. After standing for a total of 21 hours, the solid was collected on a filter and washed with tetrahydrofuran to give 1.18 g. of fine black needles. The product upon recrystallization from acetonitrile separated as black rods.

b. From Triethylamine, H_2TCNQ, and TCNQ in Acetonitrile.—To a gently boiling solution of 3.0 g. (15 mmoles) of TCNQ in 350 ml. of acetonitrile was added a hot solution of 1.0 g. (5 mmoles) of H_2TCNQ^4 in 50 ml. of acetonitrile. Then a solution of 1.5 ml. of triethylamine in 15 ml. of acetonitrile was added and the dark green solution was allowed to stand at room temperature overnight. The black needles were collected and washed on the funnel with ice-cold acetonitrile and then with dichloromethane; yield 3.16 g.

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(29) It is imperative that highly purified acetonitrile be used in all manipulations involving TCNQ. Commercially available spectroscopic grade acetonitrile is satisfactory, but material of lesser purity should be distilled from phosphorus pentoxide. Absence of a green color on boiling with TCNQ is indicative of adequate solvent purity.

TABLE V

TCNQ$^{\overline{\cdot}}$ SALTS CONTAINING METAL AND COMPLEXED METAL CATIONS

Product[a]	Cation source	Yield, %	Decompn. range, °C.	Analyses, %								Resistivity, ohm cm.[b]	Remarks
				Calculated				Found					
				C	H	N	Metal	C	H	N	Metal		
$Li^+TCNQ^{\overline{\cdot}}$[c]	LiI	98	>300	68.3	1.9	26.5	3.3	68.8	2.3	26.4	2.9	2×10^5	Purple microcrystals
$Na^+TCNQ^{\overline{\cdot}}$[c]	NaI	59	>300	63.4	1.8	24.4	10.4	63.4	1.9	24.4	10.0	3×10^4	Purple microcrystals
$K^+TCNQ^{\overline{\cdot}}$[c]	KI	70	>300	59.2	1.7	23.0	16.1	59.5	2.1	22.8	15.7	5×10^3	Red needles
$Cs^+TCNQ^{\overline{\cdot}}$	CsCl	67		42.7	1.2	16.6	39.5	43.0	1.2	16.8	37.3	3×10^4[d]	Purple crystals
$(Cs^+)_2(TCNQ^{\overline{\cdot}})_2(TCNQ)$[c]	CsI	58–82		49.4	1.4	19.1	30.1	49.5	1.6	19.1	28.5	9×10^4[e]	Purple prisms
$Ba^{++}(TCNQ^{\overline{\cdot}})_2$[c]	BaI_2	70		52.8	1.5	20.5	25.2	53.3	1.9	19.4	24.8	8×10^5	Purple crystals
$Mn^{++}(TCNQ^{\overline{\cdot}})_2 \cdot 3H_2O$	$MnCl_2$	98	~170	55.7	2.7	21.7	10.6	56.8	2.6	21.1	10.7	9×10^4	Blue powder
$Fe^{++}(TCNQ^{\overline{\cdot}})_2 \cdot 3H_2O$	$FeSO_4$	95	~170	55.6	2.7	21.6	10.8	56.4	2.4	20.7	10.9	5×10^4	Blue powder
$Co^{++}(TNCQ^{\overline{\cdot}})_2 \cdot 3H_2O$	$CoSO_4$	91	~170	55.3	2.7	21.5	11.3	56.1	2.5	21.5	11.2	9×10^4	Blue powder
$Ni^{++}(TCNQ^{\overline{\cdot}})_2 \cdot 3H_2O$	$NiCl_2$	95	~170	55.3	2.7	21.5	11.3	56.7	2.6	21.6	11.1	9×10^4	Blue powder
$Cu^+TCNQ^{\overline{\cdot}}$	CuI	54		53.9	1.5	20.9	23.7	53.9	1.7	21.2	23.7	2×10^2[f]	Blue-black needles
$Cu^{++}(TCNQ^{\overline{\cdot}})_2$	$CuSO_4$	80		61.1	1.7	23.8	13.5	60.3	1.9	23.6	13.3	2×10^2[g]	Green powder
$Ag^+TCNQ^{\overline{\cdot}}$[h]	$AgNO_3$	98		46.2	1.3	18.0	34.6	45.6	1.6	16.5	33.6	8×10^5	Blue powder
$Ce^{+3}(TCNQ^{\overline{\cdot}})_3 \cdot 6H_2O$[h]	$Ce(NO_3)_3$	98		50.2	3.5	19.5	16.3	50.2	3.2	19.7	16.1		Blue powder
$Sm^{+3}(TCNQ^{\overline{\cdot}})_3 \cdot 6H_2O$	$Sm(NO_3)_3$	92		49.6	2.8	19.3		51.1	2.8	19.3		2×10^4	Blue powder
$Pb^{++}(TCNQ^{\overline{\cdot}})_2 \cdot 1.5H_2O$	$Pb(NO_3)_2$	99		44.9	1.7	17.4	32.3	44.7	1.7	16.3	32.6	2×10^5	Blue powder
$Cu(NH_3)_2{}^{++}(TCNQ^{\overline{\cdot}})_2$	$Cu(NH_3)_4{}^{++}SO_4{}^{=}$	94		57.0	2.8	27.7	12.6	56.1	3.4	27.7	11.9	7×10^2	Green powder
$Cu(H_2NCH_2CH_2NH_2)_2{}^{++}(TCNQ^{\overline{\cdot}})_2$	$Cu(H_2NCH_2CH_2NH_2)^{++}SO_4{}^{=}$	97		56.8	4.1	28.4	10.7	56.9	3.9	26.9	10.8	4×10^4	Blue powder
Cu(2,2′-dipyridylamine)$^{++}(TCNQ^{\overline{\cdot}})_2$	$CuCl_2$ + 2,2′-dipyridylamine	80		63.5	2.7	24.0	9.9	61.7	2.8	23.7	9.8	40[i]	
$Fe(phen)_3{}^{++}(TCNQ^{\overline{\cdot}})_2{}^{i}6H_2O$[j]	$FeSO_4$ + 3 phen.	95	260	64.8	4.0	17.6	5.0	64.0	3.8	17.8	5.1	10^6	
$Ni(phen)_3{}^{++}(TCNQ^{\overline{\cdot}})_2 \cdot 6H_2O$	$NiCl_2$ + 3 phen.	98		64.6	4.0	17.6	5.3	66.0	3.8	17.8	4.6	10^8	Green powder
$Ni(phen)_2{}^{++}(TCNQ^{\overline{\cdot}})_2 \cdot 6H_2O$	$Ni(phen)_2Cl_2$[k]	96		61.6	3.9	18.0	6.3	61.7	3.9	18.0	5.7	2×10^8	Green powder
$(Cr^{+3})_2(AcO^-)_4(OH^-)(TCNQ^{\overline{\cdot}}) \cdot 6H_2O$	$Cr(OAc)_3$	30		35.9	4.3	8.4	15.5	35.9	4.3	8.7	15.6	10^9	Blue powder

[a] Unless otherwise noted the preparations were carried out by metathesis of the cation source with $Li^+TCNQ^{\overline{\cdot}}$ in water. [b] Determined on compactions at room temperature unless otherwise noted. [c] Reaction of cation source with TCNQ in boiling CH_3CN. [d] Activation energy 0.15 e.v. [e] Activation energy 0.36 e.v.; single crystal measurement gave the values 500, 6 × 10^4 and 6 × 10^4 along three principle axes. [f] Activation energy 0.13 e.v. [g] Activation energy 0.12 e.v. [h] Forms free TCNQ in light. [i] Activation energy 0.06 e.v. [j] phen represents 1,10-phenanthroline. [k] Pfeiffer and Tapperman, *Z. anorg. allgem. Chem.*, 215, 273 (1933).

TABLE VI

SIMPLE $TCNQ^{\overline{\cdot}}$ SALTS CONTAINING ONIUM CATIONS

Cation	Method[a] and solvent	Yield, %	Decompn. range, °C.	Analyses, % Calculated C	H	N	Found C	H	N	Resistivity,[b] ohm-cm.	Remarks
NH_4^+	A, THF–MeOH	60	210–215	64.9	3.6	31.5	64.8	3.4	31.6	6 × 10^4	Maroon needles
$(C_2H_5)_3NH^+$	B, H_2O[c]	81	~180	70.6	6.5	22.9	70.7	6.9	23.1	10^8	Blue powder
$(n\text{-}C_4H_9)_4N^+$	B, H_2O		135	75.3	9.0	15.7	75.9	9.2	15.7	10^{12}	Blue powder
Morpholinium	A, CH_3CN	35	~220	65.8	4.8	24.0	66.1	5.1	24.0	10^9[d]	Red prisms
$(C_2H_5)_2(CH_3)(NCCH_2)N^+$	B, H_2O		~193	68.9	5.7	25.4	68.3	5.4	25.4	10^9	Blue powder
$(CH_3)_3(NCCH_2CH_2)N^+$	A, CH_3CN			68.2	5.4	26.5	68.2	5.5	25.5	10^6	Blue-black cryst.
$(C_6H_5)_3(CH_3)P^+$	B, H_2O	99	~170	77.3	4.6	11.6	77.1	4.7	11.4	4 × 10^{10}	Purple crystals
$[(CH_3)_2N]_3S^+$	B, H_2O[e]	88	~155		8.7[f]	26.7		8.5[f]	26.5	2 × 10^{10}	Purple solid
4-Hydroxy-2,3,5,6-tetramethylanilinium	C, CH_2Cl_2	60	168–174	71.4	5.5	18.9	71.2	5.4	19.2	160[g]	Black microcryst.
Pyridinium	D, CH_3CN	59	158–195	71.9	3.5	24.6	71.5	3.7	24.6	10^6	Purple prisms
N-Methylpyridinium	B, CH_3CN–EtOH	Trace	~235	72.5	4.0		72.6	4.1		10^5	Purple needles
4-Cyano-N-methylpyridinium	B, CH_3CN–EtOH	52	224–226	70.6	3.4	26.0	70.8	3.4	25.8	10^6	Purple needles
N-Methylquinolinium	B, CH_3CN–EtOH	76	240–244	75.9	4.1	20.1	75.8	3.9	19.9	10^7	Purple microcrystals
4-Cyano-N-methylquinolinium	B, CH_3CN–EtOH	51	196–198	74.0	3.5	22.6	74.3	3.7	21.9	10^5	Purple needles
5,8-Dihydroxyquinolinium	C, $CHCl_3$	72	168–169	68.9	3.3	19.1	69.0	3.4	19.0	15[h]	Black microcrystals
2-(4-Dimethylaminophenylazo)pyridinium	D, CH_3CN	88	230–245	69.5	4.5	26.0	69.0	4.8	25.8	10^6	Metallic green plate.
N-Methyl-2-(4-dimethylaminophenylazo)pyridinium	B, CH_3CN–EtOH	77	237–277	70.0	5.0		70.4	4.9		10^4	Metallic green plate

[a] Method A designates reaction of onium iodide with TCNQ; B, metathesis of iodide with $Li^+TCNQ^{\overline{\cdot}}$; C, reaction of free base with TCNQ; D, reaction of free base with H_2TCNQ and TCNQ. [b] Determined on compactions at room temperature unless otherwise noted. [c] Cation as chloride or bromide. [d] Single crystal resistivity 6 × 10^8 ohm cm. along each of three major axes. [e] Cation as bromide. [f] Sulfur analyses. [g] Activation energy 0.10 e.v. [h] Activation energy 0.07 e.v.

TABLE VII

COMPLEX SALTS CONTAINING ALKYLAMMONIUM CATIONS

Cation	Method[a] and solvent	Yield, %	Decompn. range, °C.	Analyses, % Calculated C	H	N	Found C	H	N	Resistivity, ohm-cm.[b]	Remarks
$(C_2H_5)_3NH^{+c}$	C, THF	77	>195	70.6	4.7	24.7	70.8	4.9	24.7	20[d]	Black needles
	A, CH_3CN	32					71.1	4.9	24.9		
	D, CH_3CN	62					70.8	4.6	25.0		
	CH_3CN[e]	22					70.9	4.9	25.0		
$(CH_3)_3NH^{+c}$	C, THF	90	>215	69.2	3.9	26.9	69.3	3.6	26.9	5 × 10^6	Black crystals
$(C_2H_5)_2(CH_3)N^{+c}$	A, CH_3CN	65	265–274	71.0	5.0	24.0	71.0	4.9	24.0	6 × 10^3	Black rods
$(C_2H_5)_4N^{+c}$	A, CH_3CN	79	255–268	71.4	5.2	23.4	71.4	5.2	23.4	2 × 10^4	Black crystals
$(CH_3)_2(t\text{-}C_4H_9)NH^{+c}$	D, CH_3CN	82	214	70.7	4.6	24.7	70.4	5.2	25.2	9	Black crystals
Triethylenediamine H^{+f}	C, THF	26	270	68.7	4.6	26.7	69.1	4.7	26.5	10	Black microcrystals
Morpholinium[f]	A, CH_3CN	40	210	67.0	4.1	24.9	66.9	4.1	24.8	10^5[g]	Black plates

[a] See footnote *a*, Table VI, for method descriptions. [b] Determined on compactions at room temperature unless otherwise noted. [c] These complexes have the compositions, cation $(TCNQ^{\overline{\cdot}})(TCNQ)$. [d] Activation energy 0.13 e.v.; single crystal resistivities in three crystal directions, 0.5, 40 and 1000 ohm-cm. [e] Prepared by addition of a solution neutral TCNQ to a solution of the simple salt $Et_3NH^+TCNQ^{\overline{\cdot}}$. [f] These complexes have the composition, $(cation)_2(TCNQ^{\overline{\cdot}})_2(TCNQ)$. [g] Single crystal resistivity, 5 × 10^8 ohm-cm.

c. **From Triethylammonium Iodide and TCNQ in Acetonitrile.**—A boiling solution of 1.0 g. (4.9 mmoles) of TCNQ in 100 ml. of tetrahydrofuran was treated with a boiling solution of 0.57 g. (2.5 mmoles) of triethylammonium iodide in 7 ml. of acetonitrile, and the mixture was allowed to stand at 0° for about 30 minutes. The black needles were collected, washed, and purified as described above. The yield was 0.42 g.

d. **From $Et_3NH^+TCNQ^{\overline{\cdot}}$ and TCNQ.**—A boiling, filtered solution of 0.61 g. (2.0 mmoles) of the simple salt Et_3NH^+ $TCNQ^{\overline{\cdot}}$ (Table VI) in 25 ml. of acetonitrile was treated with a boiling solution of 0.50 g. (2.5 mmoles) of TCNQ in 30 ml. of acetonitrile. The solution stood at room temperature for 20 minutes and afforded a first crop of the complex salt weighing 0.24 g. Additional product could be obtained by concentrating and cooling the filtrate.

Quinolinium $(TCNQ)^{\overline{\cdot}}_2$ (Table VIII). a. From Quinoline, Durohydroquinone and TCNQ in Acetonitrile.—To a boiling solution of 1.6 g. (6 mmoles) of TCNQ in 125 ml. of acetonitrile was added an almost boiling, freshly prepared solution of 0.4 g. (3.1 mmoles) of quinoline and 0.26 g. (1.5 mmoles) of durohydroquinone[30] in 30 ml. of acetonitrile. Blue-black needles separated almost immediately, and after 2 hours at room temperature the product was collected and washed on the filter with acetonitrile and ether; yield 1.1 g.

b. **From Quinoline Hydroiodide and TCNQ.**—To a boiling solution of 3.0 g. (15 mmoles) of TCNQ in 1300 ml. of dichloromethane (or 300 ml. of acetonitrile) was added a boiling solution of 1.9 g. (7.5 mmoles) of quinoline hydroiodide in 200 ml. of dichloromethane (or if acetonitrile was the solvent, a solution of 10 mmoles of the hydroiodide in 15 ml.). The product was isolated as described above.

Methyltriphenylphosphonium $(TCNQ)^{\overline{\cdot}}_2$ (Table IX).—To a hot (60°) filtered solution of 2.04 g. (10 mmoles) of TCNQ in 230 ml. of acetonitrile contained in a 500-ml. erlenmeyer flask was added rapidly a filtered, room-temperature solution of 4.0 g. (10 mmoles (of methyltriphenylphosphonium iodide in 60 ml. of acetonitrile. The mixture was allowed to stand at room temperature overnight to afford a crop of seed crystals which were collected and washed rapidly with acetonitrile.

To obtain large crystals, the above procedure was repeated, but immediately upon mixing the solutions, the reaction flask was placed in a one-gallon Dewar flask. After 2 or 3 minutes, the mixture was seeded with a well-formed seed crystal, and the Dewar flask was covered and allowed to stand undisturbed overnight. The large, black prisms were carefully filtered off and washed rapidly with two 15-ml. portions of acetonitrile.

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(30) The preparation of duroquinone is described in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 254, and reduction to the hydroquinone was carried out as described by T. H. James and A. Weissberger, *J. Am. Chem. Soc.*, **60**, 98 (1938).

TABLE VIII

COMPLEX SALTS CONTAINING AROMATIC AND HETEROCYCLIC CATIONS[a]

Cation	Method[b] and solvent	Yield, %	Decompn. range, °C.	Analyses, % Calculated C	H	N	Found C	H	N	Resistivity,[c] ohm-cm.	Remarks
4-Hydroxy-N-benzylanilinium	C, CH_2Cl_2	36	175->300	73.1	3.5	20.8	72.8	3.8	20.8	55[d]	Black microcrystals
4-Amino-N,N-diethylanilinium	C, $CHCl_3$	55	144->300	71.2	4.2	24.4	71.1	4.4	24.3	175[e]	Black rods
4-Amino-2,3,5,6-tetramethylanilinium	A, $CHCl_3$–EtOH	75	180–220	71.2	4.4	24.4	71.1	4.4	24.0	8[f]	Blue-black needles
Pyridinium	D, CH_3CN	42	168-185	71.4	2.9	25.8	71.5	3.3	25.6	37	Blue-black needles
4-Cyano-N-methylpyridinium	A, CH_3CN	26	258–260	70.5	2.9	26.6	71.0	3.4	26.8	48	Blue-black needles
Quinolinium	B, CH_3CN	91	~250	73.6	3.0	23.4	73.7	3.3	23.3	0.5[g]	Blue-black needles
	CH_2Cl_2	44					73.7	3.1	23.6		
	D, CH_3CN	87					73.7	3.0	23.1		
	CH_3CN[h]	71					73.6	3.1	23.2		
N-Methylquinolinium	A, CH_3CN	22	245–250	73.9	3.3	22.8	73.4	3.9	22.8	3	Blue-black needles
4-Cyano-N-methylquinolinium	A, CH_3CN	39	223-239	72.7	2.9	24.2	72.2	3.5	25.0	58	Blue-black needles
N-Ethylquinolinium	A, CH_3CN	57	237–239	74.2	3.6	22.3	74.1	3.8	22.2	8	Blue-black needles
N-(*n*-Propyl)-quinolinium	A, CH_3CN	92	226–228	74.5	3.8	21.7	74.8	4.1	21.9	2[i]	Black rods
N-(2-Phenethyl)-quinolinium	A, CH_3CN	78	248–250	76.7	3.8	19.6	76.7	4.0	19.6	3	Black needles
2,2′-Bipyridinium	D, CH_3CN	100	235–268	72.2	3.0	24.8	71.9	3.2	24.8	0.5	
N-Methyl-2-(4-dimethylaminophenylazo)-pyridinium	A, CH_3CN	74	248–249	70.0	4.0	25.8	69.9	4.1	25.5	12	Purple-black microcrystals
Ferricinium	C, CH_3CN[j]	Low		68.7	3.0	18.9	68.9	3.1	18.6	0.24[k]	Black needles
Dimethylferricinium	C, CH_3CN	60	170	69.4	3.5	18.0	69.8	3.5	17.1[l]	31	Black needles
Cobalticinium	B, H_2O[m]	20		68.4	3.0	18.7	68.6	3.4	18.6	6.5[n]	Black scales

[a] All of these complexes have the composition cation ($TCNQ^{\overline{\cdot}}$)(TCNQ). [b] See footnote *a*, Table VI, for method descriptions. [c] Determined on compactions at room temperature unless otherwise noted. [d] Activation energy 0.075 e.v. [e] Activation energy 0.09 e.v. [f] Activation energy 0.08 e.v. [g] Activation energy 0.013 e.v.; single crystal resistivity 0.01 ohm-cm. along long needle axis; see text for discussion of variation in resistivity with preparation method. [h] This preparation involved the use of the free base quinoline and TCNQ with durohydroquinone as the proton–electron donor. [i] Single crystal resistivities in three principal directions, 0.5, 6 and 450 ohm-cm. [j] Ten moles ferrocene per mole of TCNQ used. [k] Determined on single crystal. [l] Calcd. Fe, 9.0. Found. Fe, 8.8. [m] Cobalticinium chloride cation source. [n] Activation energy 0.034 e.v.

TABLE IX

COMPLEX SALTS CONTAINING GROUP V AND GROUP VI ONIUM CATIONS

Cation[a]	Yield, %	Decompn. range, °C.	Analyses, % Calculated C	H	N	Other	Found C	H	N	Other	Resistivity, ohm cm.[b]	Typical crystal dimensions, mm.[c]
Methyltriphenylphosphonium	60	231–233	75.3	3.8	16.3	P, 4.5	75.4	3.9	16.3	P, 4.7	60; 600; 10^5[d]	10; 10; 1[e]
Ethyltriphenylphosphonium	41	223-225	75.5	4.0	16.0	P, 4.4	75.8	4.2	15.9	P, 4.5	<10; 10; 4000	5; 3; 0.2[e]
Tetraphenylphosphonium	33	228–237	77.1	3.8	15.0	P, 4.2	76.7	3.9	15.3	P, 4.3	10^3; 10^5; 2 × 10^6	0.5; 0.6; 2[e]
Methyltriphenylarsonium	56	224-227	70.8	3.6	15.4	As, 10.3	70.9	3.6	15.4	As, 10.3	57; 900; 10^5[f]	12; 12; 2[e]
Ethyltriphenylarsonium	44	212–219	71.1	3.8	15.1	As, 10.1	71.1	4.0	14.5	As, 10.3	2; 6600; —	0.6; 0.7; 3.0[e]
Tetraphenylstibonium	42	219–220	68.8	3.4	13.4	Sb, 14.5	69.1	3.7	14.6	Sb, 14.4	13; 1.5 × 10^4; —	0.2; 0.4; 1.1
2,4,6-Triphenylpyrylium[g]	21	270	78.6	3.5	15.6		78.2	3.6	15.2		(16)[h]	
Triphenylsulfonium	65	235–240	75.1	3.4	16.7	S, 4.8	75.2	3.6	16.6	S, 4.6	1.0[i]	
Tris-(dimethylamino)-sulfonium[j]	89	229			27.0	S, 5.6			26.6	S, 5.8	(30)[k]	
Triphenylselenonium	71	240-245	70.2	3.2	15.6	Se, 11.0	70.5	3.2	14.8	Se, 10.7	(400)	

[a] All of these complexes have the composition cation ($TCNQ^{\overline{\cdot}}$)(TCNQ) and were prepared by method A unless otherwise noted; see footnote *a*, Table VI, for method description. [b] Values in parentheses were determined on compactions at room temperature, others on single crystals; three values cited refer to measurements perpendicular to principal crystal faces. [c] Dimensions perpendicular to principal crystal faces, directions corresponding respectively to directions of resistivity determinations cited in previous column. [d] Activation energy 0.25 e.v. [e] Triclinic crystal system. [f] Activation energy 0.22–0.33 e.v. [g] Complex prepared by addition of neutral TCNQ in boiling acetonitrile to a solution of the simple salt previously prepared by metathesis of the cation fluoborate with $Li^+TCNQ^{\overline{\cdot}}$ in ethanol. [h] Activation energy 0.04 e.v. [i] Measured along long needle axis. [j] Prepared by addition of neutral TCNQ in acetonitrile to a solution of the simple salt for which see Table VI. [k] Activation energy 0.11 e.v.

$(C_6H_5)_3CH_3P^+(C_6H_5)_3CH_3As^+(TCNQ^{\overline{\cdot}})_2(TCNQ)_2$.—The preparation of the complex salt was carried out in the same manner as that of $(C_6H_5)_3CH_3P^+(TCNQ^{\overline{\cdot}})$(TCNQ) except that the TCNQ solution was treated with a solution of 2.02 g. (5 mmoles) of methyltriphenylphosphonium iodide and 2.24 g. (5 mmoles) of methyltriphenylarsonium iodide in 60 ml. of acetonitrile. Again, large well-formed crystals could be obtained by adding a seed crystal a few minutes after mixing the reactants. Elemental analyses were obtained on a large single crystal to eliminate the possibility that equal amounts of $(C_6H_5)_3CH_3P^+(TCNQ^{\overline{\cdot}})$(TCNQ) and $(C_6H_5)_3CH_3As^+(TCNQ^{\overline{\cdot}})$(TCNQ) had been formed.

Anal. Calcd. for $C_{86}H_{52}N_{16}AsP$: As, 5.3; N, 15.9; P, 2.2. Found: As 5.2; N, 15.9; P, 2.7.

Crystals containing the phosphonium and arsonium ions in ratios different from 1:1 could also be prepared by employing an appropriately different ratio of phosphonium and arsonium iodides.

Reaction of $Li^+TCNQ^{\overline{\cdot}}$ with Tropylium Iodide.—A solution of 1.00 g. (4.6 mmoles) of tropylium iodide in 15 ml. of water was placed in a filter flask, and 1.20 g. (5.7 mmoles) of $Li^+TCNQ^{\overline{\cdot}}$ was placed in a sintered glass funnel. Water (120 ml.) was added to the lithium salt, and the resulting deep blue solution was sucked through the filter, dropwise, into the tropylium iodide solution. The blue color of the anion radical was immediately discharged on contact and addition was stopped when the blue color persisted. The yellow precipitate was collected on a filter, washed with water, and dried to give 1.33 g. of organic product (98% of theory for TCNQ + α,α'-ditropyl-$\alpha,\alpha,\alpha',\alpha'$-tetracyano-*p*-xylene). No material was extracted from this product by boiling pentane (20 ml.), indicating the absence of ditropyl, which would be an expected product if tropyl radicals had been formed in the reaction.[31]

Treatment of the aqueous filtrate with 1.5 g. of silver nitrate in 10 ml. of water gave 1.07 g. (99% yield) of silver iodide.

The organic product was dissolved in methylene chloride, and the solution was concentrated until 0.39 g. of TCNQ had precipitated. Further removal of solvent gave an intermediate fraction weighing 0.09 g., which was not examined further. Complete removal of solvent then gave 0.80 g. of pale yellow prisms corresponding to 90% of theory for α,α'-ditropyl-$\alpha,\alpha,\alpha',\alpha'$-tetracyano-*p*-xylene, m.p. 200–206°. Recrystallization from benzene gave 0.96 g. of bright yellow leaflets which lost occluded solvent at about 100° and melted at 201-202°. The crystals were dried at 110° (1 hour) for analysis; the resulting buff-colored solid had m.p. 201-202°. The infrared spectrum had nitrile absorption at the same wave length (4.43 μ) as H_2TCNQ, and the aromatic ring absorption bands were also similar to those of H_2TCNQ.

Anal. Calcd. for $C_{26}H_{18}N_4$: C, 80.8; H, 4.7; N, 14.5. Found: C, 80.9; H, 4.8; N, 14.8.

Decomposition of $Et_3NH^+(TCNQ)^{\overline{\cdot}}_2$ with Hydrochloric Acid.—To 30 ml. of 2.4 *N* hydrochloric acid was added 2.10 g. (4.1 mmoles) of powdered $Et_3NH^+(TCNQ)_2$. The dark suspension became yellow-green on stirring at room temperature. After 16 hours, the solid was collected on a filter and washed with 2 ml. of 2.4 *N* hydrochloric acid in two portions. The combined filtrate and acid washings were retained for the isolation of triethylamine (see below). The solid was then washed with water and dried to give 1.66 g. of yellow-green crystals corresponding to 99% of theory for the TCNQ-H_2TCNQ mixture. The infrared spectrum of the crystals was very similar to that of an authentic 3:1 mixture of TCNQ and H_2TCNQ and was distinctly different from that of a 1:1 mixture. Treatment of an aqueous suspension of the product with dilute aqueous potassium hydroxide gave the purple color characteristics of mixtures of TCNQ and H_2TCNQ.

To the retained filtrate and acid washings was added 35 ml. of 10% aqueous sodium hydroxide, and the clear solution was extracted with 75 ml. of ether in three portions. Removal of solvent from the combined, dried ether extracts gave 0.27 g. (65%) of triethylamine, identified by infrared analysis and by mixed m.p. of its picrate with an authentic sample.

Oxidation of TCNQ$^{\overline{\cdot}}$ with Iodine—To 0.2 g. (0.37 mmole) of $Et_4N^+(TCNQ)^{\overline{\cdot}}_2$ and 10 ml. of acetonitrile was added 1.0 g. (4 mmoles) of iodine, and the mixture was warmed on a steam-bath whereupon the green solution turned red and deposited yellow crystals. Water (5 ml.) was added, and the mixture was filtered to obtain 0.12 mg. (79%) of TCNQ, m.p. 287-298° dec. Recrystallization from acetonitrile raised the m.p. to 293-294° dec. When one or two equivalents of iodine was used in similar experiments, no apparent change occurred.

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[31] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

[CONTRIBUTION NO. 739, FROM THE CENTRAL RESEARCH DEPARTMENT EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., INC., WILMINGTON 98, DEL.]

Substituted Quinodimethans. III. Displacement Reactions of 7,7,8,8-Tetracyanoquinodimethan

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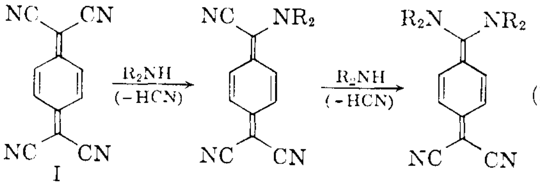
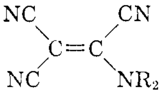
7,7,8,8-Tetracyanoquinodimethan (TCNQ) reacts with primary and secondary amines to give 7-amino-7,8,8-tricyanoquinodimethans or 7,7-diamino-8,8-dicyanoquinodimethans. Addition-elimination products also result from the reaction of TCNQ with nitrite ion or nitrogen dioxide.

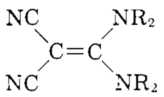
7,7,8,8-Tetracyanoquinodimethan (TCNQ, I) has recently been synthesized[1] and shown to undergo facile reduction to an anion-radical[2] with a variety of reagents including aliphatic amines. It has now been found that certain primary and secondary amines react with TCNQ to give products in which one or two cyano groups are replaced by the amine according to eq. 1. This behavior is reminiscent of the reaction of tetracyanoethylene with amines to give tricyanovinylamines (II) or 1,1-diamino-2,2-dicyanoethylenes (III).[3] TCNQ reacts with one equivalent of pyrrolidine to give an intensely purple, crystalline, diamagnetic compound which is assigned the structure 7-pyrrolidino-7,8,8-tricyanoquinodimethan (IV) on the basis of infrared and ultraviolet spectra and elemental analysis. The dramatic bathochromic shift observed in going from TCNQ (λ_{max} 395 mμ) to IV (λ_{max} 567 mμ) has a precedent in the bathochromic shift observed in passing from tetracyanoethylene to a tricyanovinylamine.[3]



I (1)



II



III

Reaction of either TCNQ or IV with an excess of pyrrolidine gives the same product, 7,7-dipyrrolidino-8,8-dicyanoquinodimethan (V), a pale yellow, high-melting mono-acidic base. In a similar fashion, TCNQ reacts with an excess of ammonia to give 7,7-diamino-8,8-dicyanoquinodimethan (VI).

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[1] (a) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962); (b) D. S. Acker, R. J. Harder, W. R. Hertler, W. Mahler, L. R. Melby, R. E. Benson and W. E. Mochel, *ibid.*, **82**, 6408 (1960).

[2] L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *ibid.*, **84**, 3374 (1962).

[3] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *ibid.*, **80**, 2806 (1958).