[CONTRIBUTION NO. 665 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., INC., WILMINGTON 98, DEL.]

Substituted Quinodimethans. I. Preparation and Chemistry of 7,7,8,8-Tetracyanoquinodimethan

BY DONALD S. ACKER AND WALTER R. HERTLER

RECEIVED MARCH 15, 1962

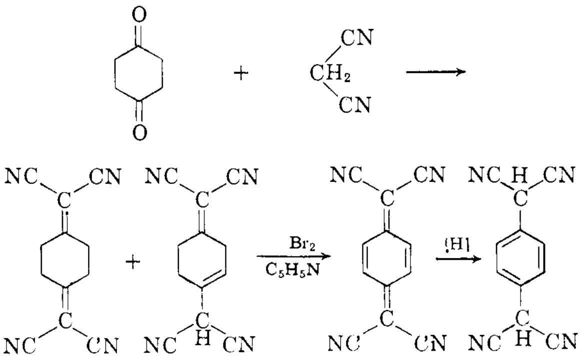
7,7,8,8-Tetracyanoquinodimethan has been synthesized from the condensation product of 1,4-cyclohexanedione and malononitrile. Tetracyanoquinodimethan is easily reduced to an anion-radical or to *p*-phenylenedimalononitrile. The latter has served as the intermediate in a synthesis of 7,7,8,8-tetrakis-(methoxycarbonyl)-quinodimethan. These quinodimethans readily undergo 1,6-addition reactions.

The recent discovery of tetracyanoethylene[1] and the demonstration of its versatile chemistry[2] prompted us to explore the chemistry of other structures containing the highly electronegative cyano group. Of particular interest are those structures in which the double bond of tetracyanoethylene is replaced by a conjugated system. The quinodimethan ring system was selected as one which should lend itself to investigation.

Although the literature on quinodimethans is quite extensive, only relatively few have been sufficiently stable to permit isolation and characterization. All of the quinodimethans which are stable in the monomeric form at room temperature have aromatic substituents on carbons 7 and 8, the best known example being tetraphenyl-*p*-quinodimethan. Quinodimethan itself polymerizes very readily and can be kept monomeric in the condensed phase only in dilute solution and at very low temperatures.[3] No stable quinodimethans with other functional groups on the α-carbon atoms have been reported.

In our investigations, 7,7,8,8-tetracyanoquinodimethan (I, TCNQ) has been prepared and found to exhibit several exceptional properties. Of particular interest is the ease with which this compound accepts one electron to form stable anion-radical derivatives.[4] The solid state properties of these derivatives are remarkable, many being characterized by exceptionally low electrical resistivities.[5] No quinodimethan anion-radicals have been previously reported, although several quinodimethans including tetraphenylquinodimethan have been converted to cation-radicals.[6] In no case have these cation radicals been isolated in the solid state. The novelty and unusual solid state properties of the TCNQ anion-radical have led us into a general investigation of negatively substituted quinodimethans. This first paper on the chemistry of these compounds reports the synthesis, characterization and 1,6-addition reactions of TCNQ and tetrakis-(methoxycarbonyl)-quinodimethan.

Synthesis of TCNQ.—Malononitrile readily condenses with 1,4-cyclohexanedione to give 1,4-bis-(dicyanomethylene)cyclohexane (IIa). Condensation in benzene solution apparently gives a mixture of IIa and IIb since even the most highly purified material melted over a 6° range (204–210°), and there is absorption in the infrared at 3030 cm.$^{-1}$ which is best attributed to the unsaturated CH stretching frequency. However, if the condensation is carried out in aqueous solution, a high yield of IIa, m.p. 216–217°, is obtained directly from the reaction mixture. Treatment with pyridine and either N-bromosuccinimide or bromine gives TCNQ in excellent yields. Other oxidizing agents such as selenium dioxide have been used to effect this conversion to TCNQ, but the yields have been poor.



IIa IIb I III

Properties of TCNQ.—Tetracyanoquinodimethan, m.p. 293.5–296°, is a rust-colored, crystalline solid which can be sublimed at temperatures above 250° at atmospheric pressure or at 200° under vacuum. When crystals are crushed between soft glass melting point cover glasses and heated, a beautiful blue film forms on the glass plates at about 200°. This film undoubtedly results from reaction of TCNQ with bases present in the glass to give the TCNQ anion-radical.

The infrared spectrum of TCNQ is consistent with the proposed structure. The C≡N stretching frequency is found at 2220 cm.$^{-1}$, as would be expected for a conjugated nitrile. The C═C stretching frequency at 1540 cm.$^{-1}$ is in the range

---

(1) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

(2) (a) W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *ibid.*, **80**, 2783 (1958); (b) W. J. Middleton and V. A. Engelhardt, *ibid.*, **80**, 2788 (1958); (c) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *ibid.*, **80**, 2806 (1958); (d) G. N. Sausen, V. A. Engelhardt and W. J. Middleton, *ibid.*, **80**, 2815 (1958); (e) W. J. Middleton, V. A. Engelhardt and B. S. Fisher, *ibid.*, **80**, 2822 (1958); (f) O. W. Webster, W. Mahler and R. E. Benson, *J. Org. Chem.*, **25**, 1470 (1960).

(3) L. A. Errede and B. F. Landrum, *J. Am. Chem. Soc.*, **79**, 4952 (1957).

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

(5) R. G. Kepler, P. E. Bierstedt and R. E. Merrifield, *Phys. Rev. Letters*, **5**, 503 (1960); D. B. Chesnut, H. Foster and W. D. Phillips, *J. Chem. Phys.*, **34**, 684 (1961).

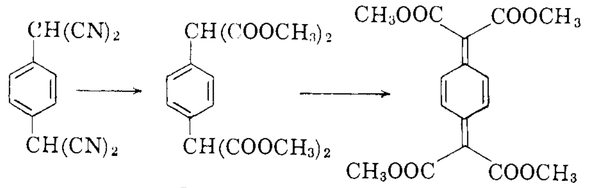
(6) E. Weitz and F. Schmidt, *Ber.*, **75**, 1921 (1942).

expected for a conjugated cyanoölefin.[7] The ultraviolet absorption of TCNQ in ethanol is complicated by the presence of absorption from the TCNQ anion-radical and other unidentified reaction products. The absorption due to TCNQ (λ_{max} 395 mμ, ε 63,600) can be determined by use of a KBr wafer or in acetonitrile solution.

Polarographic Reduction of TCNQ.—Polarographic studies show that the reduction of TCNQ to *p*-phenylenedimalononitrile ($TCNQH_2$) is a reversible reaction. The reversible couple in 90% acetic acid containing 0.2 molar sodium acetate is +0.15 to +0.16 v. (dropping mercury electrode *vs.* saturated calomel electrode). In acetonitrile solution containing 0.1 molar lithium perchlorate, TCNQ gives two reduction waves with half-wave potentials of +0.127 and −0.291 v. (with the same electrode system) whose diffusion currents are nearly equal. These are attributed to stepwise reduction to the semiquinodimethan (*i.e.*, TCNQ anion-radical) and to *p*-phenylenedimalonitrile or an equivalent state of reduction. Under similar conditions, TCNE undergoes reduction at +0.152 and −0.568 v.[8]

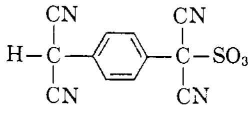
Tetracyanoquinodimethan has also been reduced by use of thiophenol, mercaptoacetic acid or hydrogen iodide to give *p*-phenylenedimalononitrile (III) as the major product. Lesser amounts of other possible isomers may also be formed during the reduction but these have not yet been isolated or characterized. *p*-Phenylenedimalononitrile can be oxidized to TCNQ by treatment with N-chlorosuccinimide.

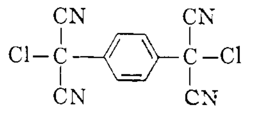
Tetrakis-(methoxycarbonyl)-quinodimethan.—*p*-Phenylenedimalononitrile has also served as an intermediate to a quinodimethan stabilized by alkoxy-carbonyl groups. *p*-Phenylenedimalononitrile was converted to *p*-phenylenebis-(dimethyl malonate) (IV) by refluxing with aqueous methanolic hydrogen chloride. The disodium salt of this tetraester on treatment with iodine gave 7,7,8,8-tetrakis-(methoxycarbonyl)-quinodimethan (V), albeit in poor yield. Tetrakis-(methoxycarbonyl)-quinodimethan is a yellow crystalline solid, the ultraviolet spectrum of which shows a λ_{max} at 363 mμ (ε 38,000).


IV V

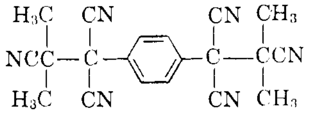
The poorer electron-withdrawing ability of the ester group as compared to the nitrile group would be expected to render tetrakis-(methoxycarbonyl)-quinodimethan less stable than TCNQ. Indeed, such appears to be the case. When tetrakis-(methoxycarbonyl)-quinodimethan is heated above 175° or stored in the presence of light, an insoluble product is formed. This insoluble product analyzes well for a polymer of the quinodimethan, and the highly crystalline x-ray powder pattern and the rather sharp decomposition point are suggestive of a dimeric or trimeric structure. Since the infrared spectrum of the product shows the presence of 1,4-disubstituted benzene rings, the dimer or trimer is probably cyclic. This instability of tetrakis-(methoxycarbonyl)-quinodimethan is reminiscent of quinodimethan itself which rapidly forms polymer and cyclic dimer.[9]

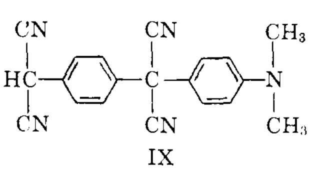
Addition Reactions of Substituted Quinodimethans.—These new quinodimethans enter into addition reactions in a 1,6-manner, and enough examples are available to demonstrate the generality of this type of reaction. Thus, when an aqueous acetonitrile suspension of TCNQ is saturated with sulfur dioxide, the 1,6-adduct VI with sulfurous acid is formed. This was isolated as its tetramethylammonium salt in 92% yield. Although halogens do not appear to add to TCNQ under normal conditions, trace amounts of triethylamine or tetramethylammonium chloride catalyze the rapid addition of chlorine to give the 1,6-adduct VII. This reaction apparently proceeds by the initial attack of the negative Cl^- as proposed by Dickinson[10] in his investigation of the action of chlorine on tricyanoethylene.

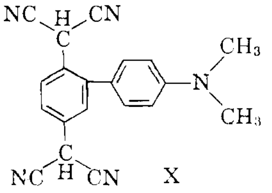

VI


VII

The thermal decomposition of excess α,α′-azobis-(isobutyronitrile) in the presence of TCNQ leads to the adduct VIII. Reaction of TCNQ with N,N-dimethylaniline leads to a stable, colorless adduct to which the structure IX has been assigned on the basis of elemental and spectroscopic analyses. The structure X, which is possible if TCNQ entered into a 1,4-addition reaction, is ruled out since no color is developed upon treatment with oxidizing agents.


VIII


IX


X

The tetrakis-(methoxycarbonyl)-quinodimethan readily takes on bromine to give α,α′-dibromo-*p*-phenylenebis-(dimethyl malonate) (XI). The same dibromo derivative XI was obtained by treating the disodium salt of *p*-phenylenebis-(dimethyl malonate) with bromine.

---

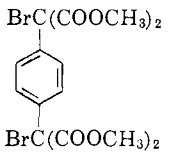
(7) C. E. Looney and J. R. Downing, *J. Am. Chem. Soc.*, **80**, 2840 (1958).

(8) T. Berzins, unpublished results.

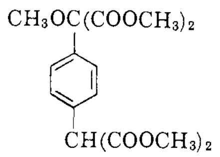
(9) H. E. Winberg, F. S. Fawcett, W. E. Mochel and C. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960).

(10) C. L. Dickinson, D. W. Wiley and B. C. McKusick, *ibid.*, **82**, 6132 (1960).

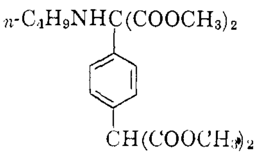
Methanolic sodium methoxide reacts with tetrakis-(methoxycarbonyl)-quinodimethan to give the α-methoxy-*p*-phenylene-bis-(dimethyl malonate) (XII), which was also formed when the disodium salt of *p*-phenylenebis-(dimethyl malonate) was treated with iodine in methanolic solution. A further example of the susceptibility of tetrakis-(methoxycarbonyl)-quinodimethan to nucleophilic attack was found in its reaction with *n*-butylamine to give α-*n*-butylamino-*p*-phenylenebis-(dimethyl malonate) (XIII). That XIII correctly represents the structure of the product is deduced from the infrared spectrum, which displays a normal ester C=O stretching band at 1740 cm.$^{-1}$ and an ester stretching band at 1765 cm.$^{-1}$ characteristic of an α-amino ester. Similarly, the infrared spectrum of XII showed two ester C=O peaks at 1745 cm.$^{-1}$ and at 1760 cm.$^{-1}$.



XI



XII



XIII

Other Reactions of Substituted Quinodimethans.—These quinodimethans have not given characterizable adducts with dienes. With cyclopentadiene or 2,3-dimethylbutadiene and TCNQ, polymeric products were formed. No Diels–Alder addition product could be isolated with anthracene. However, TCNQ did react with anthracene to give a black crystalline π-complex.

As a strong Lewis acid, TCNQ forms charge-transfer complexes with many electron-rich substances. It also reacts smoothly with primary and secondary amines to give products in which one or two cyano groups are replaced. Malononitrile reacts with TCNQ in the presence of base to give a deeply colored anion.[11] Subsequent papers from this Laboratory will describe in detail these displacement reactions and the formation and properties of the charge-transfer complexes of TCNQ.

Acknowledgments.—We wish to give recognition to the valuable suggestions of Dr. D. C. Blomstrom.

Experimental

1,4-Bis-(dicyanomethylene)-cyclohexane (II).—A mixture of 14 g. of malononitrile, 11.2 g. of 1,4-cyclohexanedione,[12] 6 ml. of acetic acid and 2 g. of ammonium acetate in 200 ml. of benzene was stirred under reflux using a water separator until the theoretical amount of water had been removed (2 hours). The reaction mixture was cooled, and the solid product was collected and washed well with water. Recrystallization from ethyl acetate gave 15.9 g. (76.5%) of product, m.p. 197–212°, which was pure enough for further reaction. An analytical sample, m.p. 204–210°, was prepared by several recrystallizations from ethyl acetate. The infrared spectrum of this product (KBr wafer) showed absorption at 3030 cm.$^{-1}$ (unsaturated CH), 2940 cm.$^{-1}$ (saturated CH), 2250 cm.$^{-1}$ (nitrile) and 1612 cm.$^{-1}$ (conjugated —C=C—).

Anal. Calcd. for $C_{12}H_8N_4$: C, 69.2; H, 3.87; N, 26.9. Found: C, 69.4; H, 4.09; N, 26.3.

An alternative procedure was found to be more convenient.[13] A mixture of 100 g. of 1,4-cyclohexanedione and 119 g. of malononitrile was melted by warming on a steam-bath. To the melt was added a solution of 1 g. of β-alanine in 200 ml. of water. The resulting mixture was warmed on a steam-bath with swirling until crystals began to form and then was allowed to stand until it cooled to room temperature. The product was collected and washed with water and ether to give 180 g. (97%) of white crystals of 1,4-bis-(dicyanomethylene)-cyclohexane, m.p. 216–217°.

Tetracyanoquinodimethan (I). Method A.—A suspension of 7.65 g. (0.037 mole) of 1,4-bis-(dicyanomethylene)-cyclohexane and 16 g. (0.09 mole) of N-bromosuccinimide in 150 ml. of acetonitrile was stirred at −20° under nitrogen in a solid carbon dioxide–acetone-bath while a solution of 7.2 g. of pyridine in 100 ml. of ether was added. After stirring at −15° to −20° for an additional 15 minutes, the reaction mixture was allowed to warm to room temperature. The addition of cold water precipitated the tetracyanoquinodimethan which was recrystallized from ethyl acetate to give 6.41 g. (84%) of rust-colored crystals, m.p. 289–291°. Acetonitrile or tetrahydrofuran are also good recrystallization solvents for TCNQ.

Anal. Calcd. for $C_{12}H_4N_4$: C, 70.6; H, 1.97; N, 27.4. Found: C, 71.0; H, 1.94; N, 27.4.

The ultraviolet absorption spectrum of TCNQ in a KBr wafer or in acetonitrile solutions shows λ_{max} 395 mμ, ϵ 63,600. The infrared spectrum (KBr wafer) shows bands at 3080 cm.$^{-1}$ (unsaturated CH), 2220 cm.$^{-1}$ (conjugated nitrile) and 1540 cm.$^{-1}$ (conjugated —C=C—).

Method B.—A mixture of 12 g. of 1,4-bis-(dicyanomethylene)-cyclohexane, 200 ml. of acetonitrile and 19.2 g. of bromine was cooled to 10° with stirring under nitrogen. Cooling was continued and a solution of 19.2 ml. of pyridine in 30 ml. of acetonitrile was added at such a rate that the temperature remained between 0–10° during the addition, which required 15 minutes. After completion of the addition, the mixture was stirred at 0° for 30 minutes and then allowed to warm to 20° over a period of 1 hour. Cold water (300 ml.) was added and the mixture filtered. The filter cake was washed with water to give a quantitative yield of TCNQ, m.p. 293–295° dec. Recrystallization from acetonitrile gave 9.33 g. (80%) of rust-colored crystals of TCNQ, m.p. 293.5–296°.

Method C.—A mixture of 2.84 g. of 1,4-bis-(dicyanomethylene)-cyclohexane and 2.22 g. of selenium dioxide in 50 ml. of acetonitrile was heated under reflux for 6 hours and filtered hot. The solvent was removed on a steam-bath under reduced pressure and the residue recrystallized from ethyl acetate to give 0.45 g. of TCNQ, m.p. 290–292°.

Method D.—A mixture of 206 mg. (1 mmole) of *p*-phenylenedimalononitrile, 266 mg. of N-chlorosuccinimide and 10 ml. of acetonitrile was swirled in an ice-bath. Yellow crystals began to form. One drop of triethylamine was added, and after 2 minutes the mixture was diluted with 10 ml. of water and filtered to give 190 mg. (93%) of slightly impure TCNQ, m.p. 289–312° dec. This product was identified by comparison of its infrared spectrum with that of an authentic sample.

***p*-Phenylenedimalononitrile (III). Method A.**—A solution of TCNQ in glacial acetic acid was treated with excess thiophenol and allowed to evaporate to dryness. The residue was extracted with ether and the remaining solid recrystallized from methanol to give *p*-phenylene-dimalononitrile, m.p. 244–245°. The infrared spectrum of the product shows absorption at 2900 cm.$^{-1}$ (C-H), 2270 cm.$^{-1}$ (nitrile) and 855 cm.$^{-1}$ (1,4-di-substituted benzene).

Anal. Calcd. for $C_{12}H_6N_4$: C, 69.9; H, 2.93; N, 27.2. Found: C, 70.1; H, 2.97; N, 27.5.

Method B.[14]—A mixture of 4.1 g. of tetracyanoquinodimethan, 8.0 g. of mercaptoacetic acid and 100 ml. of

---

[11] J. K. Williams, *J. Am. Chem. Soc.*, **84**, Sept. 20 (1962).

[12] J. R. Vincent, A. F. Thompson, Jr., and L. I. Smith, *J. Org. Chem.*, **3**, 603 (1939).

[13] We wish to thank Dr. W. W. Prichard who first carried out this reaction under these conditions.

[14] We wish to thank Dr. J. K. Williams, who conducted this experiment.

glacial acetic acid was heated at reflux under a nitrogen atmosphere for 15 minutes. When the hot reaction mixture was diluted with 100 ml. of water and then cooled in ice, *p*-phenylenedimalononitrile crystallized as white needles. After the product had been washed with water and dried, it weighed 3.6 g. (80%) and melted at 241–243°.

Method C.—To a suspension of 4.0 g. of TCNQ in 200 ml. of acetone was added 8 ml. of 55% aqueous HI, and the mixture was warmed gently on a steam-bath with occasional stirring for 30 minutes. The hot brown solution was filtered into a 1-l. flask and 600 ml. of methylene chloride was added. The mixture stood covered at room temperature overnight, and the product was collected and washed on the filter with dichloromethane to give 2.7 g. (67.5%) of *p*-phenylenedimalononitrile as pure white platelets, m.p. 246–248°.

TCNQ-Anthracene π-Complex.—To a hot solution of 104 mg. of TCNQ in 15 ml. of tetrahydrofuran was added 100 mg. of anthracene. When the green solution had become homogeneous a stream of nitrogen was blown across the surface of the still warm solution until fine black needles were observed on the side of the flask. The flask was then immersed in a mixture of solid carbon dioxide and isopropyl alcohol. Filtration gave 80 mg. (39%) of the complex as black needles, m.p. 282–283° with sublimation occurring above 220°.

Anal. Calcd for $C_{12}H_4N_4 . C_{14}H_{10}$: C, 81.7; H, 3.69; N, 14.7. Found: C, 81.9; H, 3.80; N, 14.9.

The ultraviolet spectrum of a tetrahydrofuran solution of this complex shows absorption at 480–490 mμ. This same black complex was formed when a mixture of anthracene and TCNQ in acetonitrile was heated under reflux for an extended period in an attempt to isolate the Diels–Alder adduct. When refluxing xylene was used as the solvent, the TCNQ was recovered unchanged.

***p*-Phenylenebis-(dimethyl malonate) (IV).**—*p*-Phenylene dimalononitrile (500 mg., 2.4 mmoles) was refluxed for 3.5 hours with 30 ml. of methanol containing 173 mg. of water while a rapid stream of dry hydrogen chloride was passed through the solution. Dilution of the mixture with water gave a granular crystalline precipitate of *p*-phenylenebis-(dimethyl malonate), which was filtered and washed with water. The product weighed 783 mg. (97%) and had a melting point of 149–151°. Repeated crystallization from benzene–pentane raised the melting point to 151.5–152°. The infrared spectrum of this compound has an ester C═O stretching band at 1740 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{18}O_8$: C, 56.8; H, 5.36: Found: C, 56.8; H, 5.40.

7,7,8,8-Tetrakis-(methoxycarbonyl)-quinodimethan (V).—*p*-Phenylenebis-(dimethyl malonate) (960 mg., 2.84 mmoles), 350 mg. (6.5 mmoles) of sodium methoxide and 100 ml. of methanol were refluxed under nitrogen for 1.25 hours. The solution was then evaporated to dryness *in vacuo*. The residue was covered with benzene, and iodine was added with swirling until a permanent color remained in the benzene solution. The mixture was filtered, and the filter cake was slurried with potassium iodide–sodium bisulfite solution. The mixture was filtered, and the filter cake was washed with water and hexane. The yellow-green solid (245 mg., 26%) on crystallization from benzene–hexane gave bright yellow, prismatic needles of tetrakis-(methoxycarbonyl)-quinodimethan. This compound began to melt at 147° but gradually resolidified to a white substance, which began to turn orange at 259° and gradually decomposed.

Anal. Calcd. for $C_{16}H_{16}O_8$: C, 57.1; H, 4.80. Found: C, 57.5; H, 4.89.

The ultraviolet spectrum of tetrakis-(methoxycarbonyl)-quinodimethan in acetonitrile has λ_{max} 363mμ, ε 38,000. The infrared spectrum shows absorption at 1710 (conjugated ester) and 1578 cm.$^{-1}$ (conjugated carbonyl-substituted C═C). A sample of tetrakis-(methoxycarbonyl)-quinomethan on storing in a clear glass vial for several weeks turned pale pink in color. This product was purified by extraction with toluene in a Soxhlet apparatus. The residual insoluble pale pink solid had m.p. 310–315.5° dec.

Anal. Calcd. for $(C_{16}H_{16}O_8)_n$: C, 57.1; H, 4.80. Found: C, 57.1; H, 4.84.

The infrared spectrum of the product shows absorption at 810 and 820 cm.$^{-1}$ suggestive of a 1,4-disubstituted benzene. The X-ray powder pattern of the product is more characteristic of a crystalline compound than a polymer. These data suggest that the product may be a cyclic oligomer.

Tetramethylammonium α-(*p*-Phenylenedimalononitrile) Sulfonate.—A suspension of 2.04 g. (0.01 mole) of powdered TCNQ in 200 ml. of 50% aqueous acetonitrile was saturated with sulfur dioxide and allowed to stand overnight. Tetramethylammonium chloride was added and the acetonitrile was removed at reduced pressure on a rotary evaporator. The precipitate was collected and washed with water to give 3.3 g. (92%) of product, which did not show a definite melting or decomposition point. An analytical sample was prepared by recrystallization from methanol.

Anal. Calcd. for $C_{16}H_{17}N_5SO_3$: N, 19.5; S, 8.92. Found: N, 19.2; S, 9.04.

The infrared spectrum shows the expected absorptions at 2250 cm.$^{-1}$ (nitrile); 1255, 1045 cm.$^{-1}$ (SO_2O–); and 950, 1491 cm.$^{-1}$ (Me_4N^+).

α,α′-Dichloro-*p*-phenylenedimalononitrile (VII).—A suspension of 2.04 g. (0.01 mole) of TCNQ in 100 ml. of acetonitrile containing 0.05 g. of tetramethylammonium chloride was treated with a 100% excess of chlorine. After 15 minutes the reaction appeared to be over, but the reaction mixture was not worked up until 3 hours had elapsed. It was then evaporated to dryness under reduced pressure, and the residue dissolved in boiling cyclohexane. Upon cooling, the solution deposited 2.14 g. (78%) of light-yellow crystals, m.p. 151–153.5°. Further recrystallization from cyclohexane gave an analytical sample, m.p. 150–151.5°, which still had a faint yellow color due to slight (0.4% as estimated by its ultraviolet absorption) contamination with TCNQ. The infrared spectrum is consistent with the proposed structure showing absorption at 807 (shoulder), 786 cm.$^{-1}$ (C–Cl and/or *p*-disubstituted aromatic) and 2250 cm.$^{-1}$ (nitrile).

Anal. Calcd. for $C_{12}H_4Cl_2N_4$: Cl, 25.8; N, 20.4. Found: Cl, 25.1; N, 20.6.

α,α,α′α′,β,β′-Hexacyano-β,β′-dimethyl-*p*-di-(*n*-propyl)-benzene (VIII).—A mixture of 4.92 g. (0.03 mole) of α,α′-azobis-(isobutyronitrile) and 2.04 g. (0.01 mole) of TCNQ in 500 ml. of benzene was heated overnight under reflux. Concentration of the resulting solution gave 2.97 g. (87%) of light-yellow product, m.p. 275–280°. An analytical sample, m.p. 284–287°, was prepared by recrystallization from acetonitrile. The infrared spectrum of the product shows weak absorption at 2250 cm.$^{-1}$ (nitrile) and at 833 cm.$^{-1}$ (1,4-disubstituted benzene).

Anal. Calcd. for $C_{20}H_{16}N_6$: C, 70.6; H, 4.74; N, 24.7. Found: C, 70.3; H, 4.63; N, 24.9.

α-(*p*-Dimethylaminophenyl)-*p*-phenylenedimalononitrile (IX).—A mixture of 0.41 g. of tetracyanoquinodimethan and 0.5 g. of N,N-dimethylaniline in 100 ml. of methyl Cellosolve was warmed on a steam-bath for 1 hour. The blue solution was diluted with a large volume of water and the precipitate (0.46 g.) of light-blue powder mixed with some very deep-blue crystals was collected. Recrystallization from cyclohexane with decolorizing charcoal gave a white product, m.p. 130–132°, which was assigned the structure IX on the basis of stability to oxidizing agents, infrared and ultraviolet spectra, and elemental analysis. The infrared spectrum of the product shows absorption at 3080 cm.$^{-1}$ (aromatic CH); 2900 and 2820 cm.$^{-1}$ (saturated CH); 2250 cm.$^{-1}$ (nitrile); 1614, 1562 and 1528 cm.$^{-1}$ (aromatic —C═C—); and 810 cm.$^{-1}$ (1,4-disubstituted benzene).

Anal. Calcd. for $C_{20}H_{15}N_5$: C, 73.8; H, 4.65; N, 21.5; mol. wt., 325. Found: C, 73.1; H, 5.22; N, 21.5; mol. wt., 330.

α,α′-Dibromo-*p*-phenylenebis-(dimethyl malonate) (XI).—**A. From *p*-Phenylenebis-(dimethyl malonate).**—*p*-Phenylenebis-(dimethyl-malonate) (1.32 g., 3.9 mmoles), 660 mg. of sodium methoxide and 100 ml. of methanol were allowed to reflux for 30 minutes, cooled, and treated with bromine until a permanent red color remained. The solution was then concentrated to about one-fourth of its original volume, and diluted with methylene chloride. The solution was then washed with dilute sodium bisulfite solution and water. Removal of the solvent *in vacuo* gave a yellow solid residue, which on crystallization from benzene–hexane yielded 930 g. (48%) of white crystalline α,α′-dibromo-*p*-phenylenebis-(dimethyl malonate), m.p. 133–137°. Further recrystallizations from benzene–hexane raised the melting point to 141–143°.

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).

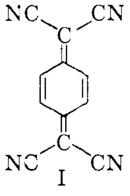
[CONTRIBUTION NO. 738 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., INC., WILMINGTON 98, DEL.]

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

RECEIVED MARCH 15, 1962

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.



I

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.

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]

---

(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).