(32.2 g. crude products) and recrystallized from absolute methanol, melting point, sublimes.

Anal. Calcd. for $C_{12}H_{34}Si_4O_3$: Si, 33.18; mol. wt., 338.8. Found: Si, 33.38; mol. wt. (cryoscopic), 334.

The analytical results suggest that this material is tris(dimethylmethoxysilyl)dimethylsilyl methane. However, this structure cannot be assigned to this product until careful fractional crystallization has been carried out, since it conceivably could have been a mixture of tetrakis(dimethylmethoxysilyl)methane and dimethylsilylmethanes of lower degrees of methoxylation.

This preparation was then repeated using a flask equipped with a reflux condenser and gas collection apparatus, 20 g. of tetrakis-(dimethylsilyl)methane, 100 ml. of absolute methanol, and 10 drops of chloroplatinic acid solution. During a 19-hr. reflux period 25 drops of additional catalyst solution was added and the theoretical volume of hydrogen was collected. The reaction mixture was then treated as before; the crude product was recrystallized from absolute methanol; 20.3 g. (68.3%) of tetrakis(dimethylmethoxysilyl)methane was obtained; melting point, sublimes.

Anal. Calcd. for $C_{13}H_{36}Si_4O_4$: C, 42.33; H, 9.84; Si, 30.47; mol. wt., 368.8. Found: C, 42.53; H, 9.86; Si, 30.33; mol. wt. (cryoscopic), 351.

B. Ethanolysis of Tetrakis(dimethylsilyl)methane. In the usual way, 13.3 g. (0.054 mole) of tetrakis(dimethylsilyl)methane, 56 ml. of absolute ethanol, and 3 drops of chloroplatinic acid solution were refluxed for 8 hr. During this time an additional 6 drops of the catalyst solution was added. The mixture was cooled in a Dry Ice-acetone bath and filtered; the precipitate recrystallized from absolute ethanol; 10 g. (44%) of tetrakis(dimethylethoxysilyl)methane, m.p. 114–115°, was obtained.

Anal. Calcd. for $C_{17}H_{44}Si_4O_4$: C, 48.06; H, 10.44; Si, 26.45. Found: C, 48.11; H, 10.37; Si, 26.37.

Acknowledgment.—The authors are grateful to P. C. Lauterbur and J. J. Burke for the H^1 n.m.r. spectra and their interpretation.

Substituted Quinodimethans. VII. Substituent and Structural Effects in Cyano-Substituted Quinodimethans

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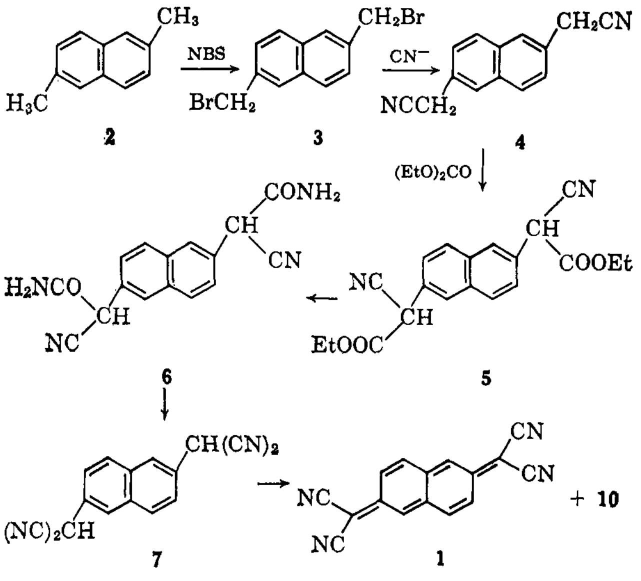
Received June 12, 1963

The stable quinodimethans 11,11,12,12-tetracyano-2,6-naphthoquinodimethan, methyl-7,7,8,8-tetracyano-*p*-quinodimethan, *n*-propyl-7,7,8,8-tetracyano-*p*-quinodimethan, and 2,5-dimethyl-7,7,8,8-tetracyano-*p*-quinodimethan undergo one-electron reduction to give stable anion-radicals. The properties of these quinodimethans and anion-radicals are compared with those of other stable quinodimethans.

The recent synthesis in this laboratory of 7,7,8,8-tetracyanoquinodimethan[1] (TCNQ) led to the discovery that TCNQ forms a variety of stable, crystalline, paramagnetic anion-radical salts, some of which exhibit unusually low electrical resistivities. A detailed description of these stable anion-radical salts is given in paper II of this series.[2] Because of the unusual stability and electrical properties of TCNQ anion-radical salts, it seemed desirable to investigate the steric and electromeric effects of ring substituents on TCNQ and its anion-radical and to search for new quinodimethan π-acid systems. The present paper reports the results of these studies.

A. 11,11,12,12-Tetracyanonaphtho-2,6-quinodimethan (TNAP) Synthesis.—To study the effect of a lengthened, conjugated system on the properties of negatively substituted quinodimethans and their anion-radicals, the synthesis of 11,11,12,12-tetracyano-2,6-naphthoquinodimethan (TNAP, 1) was undertaken. 2,6-Dimethylnaphthalene (2) was chosen as the starting material because of its ready availability. Bromination of 2 with two equivalents of N-bromosuccinimide (NBS) gave 2,6-bis(bromomethyl)naphthalene (3). The structure of 3 was confirmed by nuclear magnetic resonance which showed the presence of two methylene groups and the absence of a methyl group, which would result from the introduction of the two bromine atoms on the same carbon atom. Treatment of the dibromide 3 with cyanide ion gave 2,6-naphthalenediacetonitrile (4) which was treated with ethyl carbonate and base to give diethyl 2,6-naphthalenedicyanoacetate (5). Treatment of the cyano ester 5 with aqueous ammonia gave 2,6-naphthalenedicyanoacetamide (6) which was dehydrated with phosphorus oxychloride to give 2,6-naphthalenedimalononitrile (7). The final step in the synthesis was the oxidation of the dimalononitrile 7 with N-bromo-, N-chloro-, or N-iodosuccinimide to give TNAP (1) along with some highly insoluble substance (10).



Properties of TNAP.—TNAP was isolated as stable, high-melting, purple crystals having a metallic sheen Solutions of TNAP in organic solvents are red, and the ultraviolet spectrum of an acetonitrile solution of TNAP

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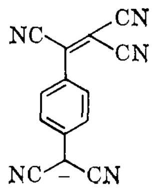
[1] D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962).

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

has absorption maxima at 472 (87,000), 258 (14,050), and 248 mμ (ε 18,000). For comparison, the nearest analog to TNAP is probably TCNQ which has λ_{max} 395 mμ (ε 63,600).[1] The bathochromic shift observed in going from TCNQ to TNAP is expected because of the more extensively conjugated system of TNAP. Interestingly, the shape of the 472-mμ peak of TNAP is virtually identical to that of the 395-mμ peak of TCNQ, both peaks having a pronounced shoulder on the short wave-length side. 11,11,12,12-Tetraphenyl-2,6-naphthoquinodimethan has been reported to give a red solution with $\lambda_{max} \sim 500$ mμ.[3] The infrared spectrum of TNAP shows absorption at 2210 (conjugated nitrile), 1590 (conjugated C=C), and 1520 cm.$^{-1}$ (conjugated cyanosubstituted C=C) in agreement with the assigned structure. As expected from its high degree of unsaturation, TNAP readily undergoes polarographic reduction. In acetonitrile solution,[4] TNAP shows two equal reduction waves with half-wave potentials of +0.21 v. and −0.17 v., corresponding to two one-electron reductions, the first step giving the negative ion-radical TNAP$^{\overline{\cdot}}$ and the second step giving the dianion of 2,6-naphthylenedimalononitrile, or an equivalent state of reduction. Using the first reduction potential as a measure of relative π-acid strength,[2] TNAP is seen to be a stronger π-acid than either TCNQ (+0.127 v.) or tetracyanoethylene (+0.152 v.).

Anion Radical of TNAP.—As expected from its high oxidation–reduction potential as determined by polarography, TNAP readily undergoes chemical reduction to give salts of TNAP$^{\overline{\cdot}}$ Iodide ion, for example, is a convenient reducing agent. Thus, TNAP reacts with potassium iodide in acetonitrile solution to give $K^+TNAP^{\overline{\cdot}}$ as a bright green solid and with sodium iodide in acetonitrile to give $Na^+TNAP^{\overline{\cdot}}$ as a dark blue solid. Both of these compounds give red solutions (acetonitrile) with principal absorption bands at 418 (25,500), 518 (12,600), 838 (5800), 938 (23,500), and 1105 mμ (ε 66,200). The infrared spectra of both compounds (KBr wafer) show a very broad, strong band centered near 2 μ with a nitrile band at 2175 cm.$^{-1}$. These compounds are paramagnetic in solution and in the solid state as determined by electron paramagnetic resonance spectroscopy (e.p.r.). The solid-state electrical properties of these anion-radical salts are reminiscent of those of the anion-radical salts of TCNQ[2] in that KTNAP and NaTNAP have volume electrical resistivities of 53 ohm-cm. and 2.7 × 10^4 ohm-cm., respectively. TNAP forms complex ion-radical salts containing formally neutral TNAP with certain cations, as has been observed previously with TCNQ.[2] For example $(Ph_3PMe)^+(TNAP)_2^{\overline{\cdot}}$ is a black crystalline solid having a volume electrical resistivity of 84 ohm-cm. (compaction).[5] The solution spectrum of this complex shows absorption characteristic of both TNAP and TNAP$^{\overline{\cdot}}$. Thus, the chemical and physical properties of TNAP$^{\overline{\cdot}}$ closely parallel those of TCNQ$^{\overline{\cdot}}$.

[6-(Tricyanovinyl)-2-naphthyl]dicyanomethanide.—TCNQ reacts with malononitrile to give the blue anion **8**.[6] TNAP reacts with malononitrile to give a green anion having λ_{max} 727 mμ, which is assigned the structure [6-(tricyanovinyl)-2-naphthyl]dicyanomethanide (**9**) on the basis of elemental analysis and analogy with **8**. A bathochromic shift of 102 mμ is observed in going from **8** to **9** in accord with the structural assignments.



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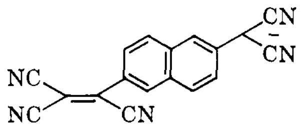

9

Oligomeric TNAP.—From the final step in the synthesis of TNAP (*vide supra*) there was obtained in addition to the desired product a highly insoluble lavender substance (**10**) with the same elemental analysis as TNAP. The extreme insolubility and high melting point of this substance suggested a polymeric structure, but at the same time precluded determination of molecular weight by solution methods. The X-ray powder pattern was indicative of a highly crystalline material. The infrared spectrum, determined as a Nujol mull, showed weak aromatic absorption near 1500 and 1600 cm.$^{-1}$ and absorption at 820 and 770 cm.$^{-1}$ characteristic of a 2,6-disubstituted naphthalene. The infrared spectrum (KBr wafer) differed markedly, showing strong absorption at 2150–2200 cm.$^{-1}$ characteristic of conjugated cyano groups. Apparently extensive decomposition occurred during preparation of the potassium bromide wafer. Treatment of **10** with potassium bromide in dimethylformamide caused a deep red color to form. Treatment of **10** with malononitrile in hot dimethylformamide gave the same green dye **9** obtained by treating TNAP with malononitrile. The yield of **9** as determined by the visible absorption spectrum was 44%. If **10** is assumed to be an oligomer of TNAP, then the reaction with malononitrile could be rationalized as a nucleophilic attack by malononitrile anion at a tetracyanoethane linkage in the oligomer. It is tempting to assign a paracyclophane structure to this oligomer and to the oligomer of 7,7,8,8-tetrakis(methoxycarbonyl)-quinodimethan reported earlier,[1] but there is at present insufficient evidence for such assignment. Irradiation of an acetonitrile solution of TNAP with a sunlamp failed to produce any **10**; only soluble decomposition products were formed.

B. Alkyl - Substituted 7,7,8,8 - Tetracyanoquinodimethans Synthesis.—The presence of an alkyl group on the ring of TCNQ could be expected to lead to a derivative not appreciably different in its π-acid character from TCNQ itself. However, the solid-state properties of an anion-radical derived from an alkyl-substituted TCNQ might be expected to differ markedly from those of the parent because of steric effects. Accordingly, it was of interest to synthesize several alkyl derivatives of TCNQ for conversion to anion-radical salts.

1,4-Cyclohexanedione has been used effectively as an intermediate in the synthesis of TCNQ.[1] The requisite

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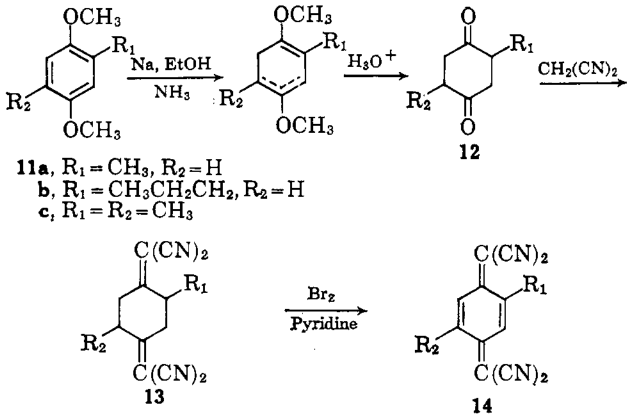
(3) G. Wittig and W. Wiemer, *Ann.*, **483**, 144 (1930).

(4) Polarographic reduction was carried out in acetonitrile solution 0.1 *M* in lithium perchlorate and was measured against an aqueous saturated calomel electrode. The potentials so obtained may, therefore, be compared directly with those reported in earlier papers of this series.

(5) The formulation $(TNAP^{\overline{\cdot}})_2$ is based on the formulation $(TCNQ^{\overline{\cdot}})_2$ proposed in ref. 2 to represent a supermolecular solid state species consisting of TCNQ and TCNQ$^{\overline{\cdot}}$.

(6) J. K. Williams, *J. Am. Chem. Soc.*, **84**, 3478 (1962).

substituted 1,4-cyclohexanediones were prepared by a Birch reduction of ring substituted *p*-dimethoxybenzenes. Thus, methyl-*p*-dimethoxybenzene **11a**, available from *p*-toluhydroquinone, was converted to methyl-1,4-cyclohexanedione (**12a**) by reduction with sodium and ethanol in liquid ammonia followed by hydrolysis of the intermediate vinyl ether with dilute mineral acid. Condensation of **12a** with two moles of malononitrile readily afforded methyl-1,4-bis(dicyanomethylene)cyclohexane (**13a**), which was oxidized to methyl-TCNQ (**14a**) by treatment with bromine and pyridine. In similar fashion, *n*-propyl-TCNQ (**14b**) and 2,5-dimethyl-TCNQ (**14c**) were prepared from the substituted *p*-dimethoxybenzenes **11b** and **11c**, respectively.



11a, $R_1 = CH_3, R_2 = H$
b, $R_1 = CH_3CH_2CH_2, R_2 = H$
c, $R_1 = R_2 = CH_3$

12

13

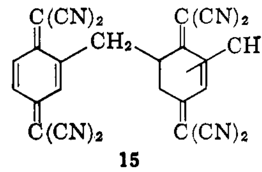
14

Oxidation of **13a** to methyl-TCNQ (**14a**) was accompanied by formation of a highly insoluble, yellow by-product **15**, which is believed to be a dimer of **14a** on the basis of its elemental analysis and absorption spectrum. Dimer **15** can be cracked at 175° to give methyl-TCNQ in good yield.

Properties.—Methyl-TCNQ, *n*-propyl-TCNQ, and 2,5-dimethyl-TCNQ all are yellow, sublimable solids similar to TCNQ. Introduction of a methyl group in TCNQ raises the visible absorption spectrum maximum from 395 mμ for TCNQ to 396 mμ for **14a**; *n*-propyl-TCNQ (**14b**) absorbs at 397 mμ, while 2,5-dimethyl-TCNQ has its maximum absorption at 403 mμ. The extinction coefficients were all found to be near 60,000.

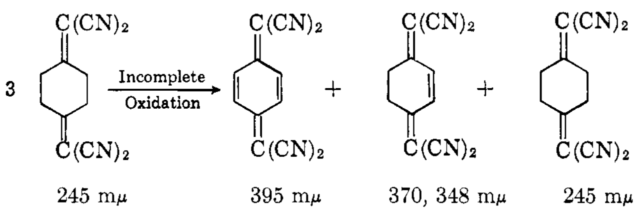
While TCNQ is only sparingly soluble in acetonitrile or tetrahydrofuran, the nonsymmetrical methyl-TCNQ and *n*-propyl-TCNQ dissolve very readily in these solvents. 2,5-Dimethyl-TCNQ, however, is only sparingly soluble.

Compound **15**, the by-product in the synthesis of methyl-TCNQ, shows absorption at 348 and 396 mμ with a shoulder near 370 mμ. The maximum at 396 mμ undoubtedly is due to a monosubstituted TCNQ moiety and, therefore, a dimeric structure **15** is proposed as a possibility.



15

Support for the structure of **15** is derived from the finding that oxidation of 1,4-bis(dicyanomethylene)-cyclohexane with an equimolar amount of oxidizing agent gave a mixture of products exhibiting absorption at 395, 370, and 346 mμ in addition to absorption at 245 mμ due to starting material. Since *p*-phenylenedimalononitrile is transparent above 320 mμ,[7] the absorption at 346 and 370 mμ is believed to be due to a 2,3-dihydro-TCNQ moiety. The correctness of this assignment would corroborate structure **15**. However, attempts to isolate 2,3-dihydro-TCNQ by chromatography and gradient sublimation failed.



Unfortunately, the insolubility of **15** precluded a molecular weight study. Treatment of **15** with a mild base, such as sodium acetate, or heating at 175° gave methyl-TCNQ. Formation of **15** from methyl-TCNQ by treatment with base failed to occur, however.

These alkyl-substituted TCNQ derivatives readily form anion-radicals when reduced at a dropping mercury electrode. The reduction potentials[4] are listed in Table I along with those of TCNQ for comparison.

Table I

Compound	1st Half-wave potential, v.	2nd Half-wave potential, v.
TCNQ	+0.13	−0.28
Methyl-TCNQ	+ .12	− .26
Propyl-TCNQ	+ .10	− .31
2,5-Dimethyl-TCNQ	+ .02	− .28

It is seen that introduction of alkyl groups in the TCNQ molecule progressively lowers the reduction potential for anion-radical formation. This observation agrees with the expectation of decreased π-acid character for alkyl-substituted TCNQ derivatives.

Anion-Radical Salts of Alkyl-TCNQ Derivatives.—As indicated by their reduction potentials, the alkyl-TCNQ derivatives form anion-radicals on treatment with such mild reducing agents as iodide ion. The anion-radicals can be reoxidized to the corresponding quinodimethans with bromine or chlorine.

Methyl-TCNQ readily afforded solid purple-blue paramagnetic anion-radical salts having the composition M^+methyl-TCNQ$^{\overline{\cdot}}$ when treated with sodium or lithium iodide. Propyl-TCNQ and 2,5-dimethyl-TCNQ reacted similarly.

The reaction of methyl-TCNQ with substituted ammonium, phosphonium, and arsonium iodides gave a class of paramagnetic salts consisting of the cation, a paramagnetic anion-radical, and a formally neutral molecule of methyl-TCNQ. This behavior is similar to that of TCNQ.[2] Interestingly, the dimer of methyl-TCNQ **15** afforded the identical anion radical salts obtained from methyl-TCNQ itself when treated with the respective iodides. Apparently iodide ion is also sufficiently basic to effect cleavage of the dimer **15**. The identity of the anion-radical salts from methyl-TCNQ and **15** was established by X-ray diffraction.

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[7] A solution of *p*-phenylenedimalononitrile in acetonitrile has absorption maxima at 257 (350), 265 (392), 271 (320), and 320 mμ (ε 371).

The spectral properties of these anion-radical salts paralleled those of the corresponding salts of TCNQ. Again, a broad absorption near 1.5 μ for the simple salts and similar broad absorption near 3 μ for the complex salts was noteworthy. These bands have previously been assigned to electronic absorption.[2]

In general, it was found that with increased alkyl substitution it became more difficult to obtain very pure anion-radical salts. Since impurities have a very marked effect on the electrical conductivity of the anion-radical salts, a precise and meaningful study of changes in electrical conductivity and other physical parameters with substituent changes unfortunately becomes prohibitively difficult.

It was found possible, however, to prepare rather pure complex anion-radical salts in single crystal form having the composition $Ph_3AsCH_3^+$(TCNQ·methyl-TCNQ)$^{\overline{\cdot}}$ and $Ph_3PCH_3^+$(TCNQ·methyl-TCNQ)$^{\overline{\cdot}}$ by reaction of the respective arsonium and phosphonium iodides with equimolar amounts of TCNQ and methyl-TCNQ. The identity of the mixed complexes was established by elemental analyses and their decomposition points, which differed from those of the corresponding pure TCNQ, methyl-TCNQ complexes, and a physical mixture thereof. The electrical properties of these mixed complexes were not markedly different from those of the pure TCNQ and methyl-TCNQ complexes.

TABLE II

Anion-radical salt	Volume resistivity, ohm-cm.
Na^+ methyl-TCNQ$^{\overline{\cdot}}$	1.2×10^6
Li^+ methyl-TCNQ$^{\overline{\cdot}}$	3×10^6
Na^+ propyl-TCNQ$^{\overline{\cdot}}$	1.3×10^7
$Ph_3(CH_3)P^+$ (methyl-TCNQ)$_2^{\overline{\cdot}}$	3.4×10^1
$Ph_3(CH_3)As^+$ (methyl-TCNQ)$_2^{\overline{\cdot}}$	1.5×10^2
$Ph_3(CH_3)As^+$ (TCNQ methyl-TCNQ)$^{\overline{\cdot}}$	4.4×10^1

Conclusions

The most apparent difference in behavior between TCNQ and some of the quinodimethans described here is the ability of the latter to form dimers or polymers. In the case of TNAP, this may occur by way of a relatively low-lying triplet state. In the case of methyl TCNQ a new reactive site is available. The electronic effects of the alkyl substituents on the properties of the quinodimethans may be assigned to a normal inductive effect which produces a systematic decrease in the oxidation–reduction potentials relative to TCNQ. The alkyl substituents examined do not seem to alter markedly the solid-state properties of the parent TCNQ anion-radical.

Experimental

2,6-Bis(bromomethyl)naphthalene (3).—A mixture of 50 g. (0.32 mole) of 2,6-dimethylnaphthalene, 120 g. (0.675 mole) of N-bromosuccinimide, 800 ml. of carbon tetrachloride, and 200 mg. of benzoyl peroxide was stirred at reflux under nitrogen for 4 hr. Then 500 mg. of azobisisobutyronitrile was added, and this mixture was stirred at reflux for 24 hr. The resulting mixture was cooled and filtered. The filter cake was washed well with water and then recrystallized from acetone to give 61.6 g. (62%) of 2,6-bis(bromomethyl)naphthalene as white crystals, m.p. 162–178°. Repeated crystallization from acetone raised the m.p. to 182.5–184°.

Anal. Calcd. for $C_{12}H_{10}Br_2$: C, 45.9; H, 3.21; Br, 50.9. Found: C, 45.8; H, 3.16; Br, 50.9.

The p.m.r. spectrum of the product confirmed the absence of a methyl group.

2,6-Naphthalenediacetonitrile (4).—To a stirred slurry of 134 g. (2.74 moles) of sodium cyanide and 1.3 l. of anhydrous dimethyl sulfoxide was added 168 g. (0.54 mole) of 2,6-bis(bromomethyl)naphthalene with cooling and at such a rate that the temperature remained at 25–28°. After stirring for 2 hr. the solution was poured into a large volume of ice–water, and the precipitate collected. The crude solid was extracted with 400 ml. of boiling acetonitrile, and the extract was evaporated to a residue which was suspended in ether–methanol and filtered to give 49.5 g. of brown solid, m.p. 146–160°. Recrystallization from ethyl acetate and then from acetone–ethanol gave 8.7 g. (8%) of 2,6-naphthalenediacetonitrile, melting point 162–165°. Further recrystallizations raised the melting point to 163.5–165.5°.

Anal. Calcd. for $C_{14}H_{10}N_2$: C, 81.5; H, 4.89; N, 13.6. Found: C, 81.4; H, 5.09; N, 13.2.

The infrared spectrum of the product showed absorption at 2280 cm.$^{-1}$ characteristic of a nonconjugated cyano group.

An alternative procedure which generally gives an improved yield is as follows.

A mixture of 170 g. (0.55 mole) of 2,6-bis(bromoethyl)naphthalene, 113 g. (2.3 mmoles) of dried sodium cyanide, and 3 l. of methanol was stirred at reflux overnight. Approximately two-thirds of the solvent was removed under reduced pressure, and water was added. Recrystallization of the filter cake from acetone–ethanol gave 27.7 g. (25%) of nearly white crystals of 2,6-naphthalenediacetonitrile, m.p. 163–165°. The infrared spectrum of the product was identical with that of the 2,6-naphthalenediacetonitrile prepared in the previous section.

Diethyl 2,6-naphthalenedicyanoacetate (5).—To the dried sodium ethoxide prepared by the reaction of 2.02 g. (0.088 g.-atom) of sodium with ethanol was added 8.7 g. (0.0425 mole) of 2,6-naphthalenediacetonitrile, 15 ml. of toluene, and 50 ml. of diethyl carbonate. The resulting mixture was stirred while solvent was distilled from the flask. Additional toluene was added from a dropping funnel at approximately the same rate that distillate was collected. When the distillation temperature reached 115°, the mixture was cooled and poured into a mixture of ice and 10% hydrochloric acid. The mixture was extracted with methylene chloride and the extract was boiled with decolorizing charcoal and evaporated to dryness. The residue was suspended in ether-pentane and filtered to give 16 g. of tan solid. Recrystallization from ether gave 10 g. (68%) of diethyl 2,6-naphthalenedicyanoacetate, m.p. 118–120.5°, presumably as a mixture of *meso* and *dl* isomers.

Anal. Calcd. for $C_{20}H_{18}N_2O_4$: C, 68.6; H, 5.18; N, 8.00. Found: C, 68.5; H, 5.08; N, 8.14.

The infrared spectrum of the product showed absorption at 2250 (nonconjugated C≡N), 1750 (ester C=O), 1605, 1505 (aromatic), and 1210–1285 cm.$^{-1}$ (C—O str.).

2,6-Naphthalenedicyanoacetamide (6).—A solution of 10 g. (0.0286 mole) of diethyl 2,6-naphthalenedicyanoacetate in 125 ml. of concentrated ammonium hydroxide was warmed on a steam bath for 1.5 hr. The resulting mixture was cooled, diluted with water, and filtered. The filter cake was washed with water, cold acetonitrile, and ether to give 6.8 g. (90%) of white 2,6-naphthalenedicyanoacetamide, m.p. 215–238° dec. Recrystallization from acetonitrile gave white crystals, m.p. 253–258° dec.

Anal. Calcd. for $C_{16}H_{12}N_4O_2$: C, 65.8; H, 4.14; N, 19.2. Found: C, 65.7; H, 4.12; N, 18.9.

The infrared spectrum of the product showed absorption at 3400, 3200 (N—H str.), 2260 nonconjugated C≡N), 1695 (amide C=O), and 1625 cm.$^{-1}$ (NH_2 def.).

2,6-Naphthalenedimalononitrile (7).—A mixture of 5.5 g. (0.0188 mole) of 2,6-naphthalenedicyanoacetamide, 4.4 g. of sodium chloride, 500 ml. of acetonitrile, 2 drops of pyridine, and 9.7 ml. of phosphorus oxychloride was stirred at reflux under nitrogen for 20 hr. The resulting mixture was cooled, diluted with a large volume of water, and filtered to give 4.45 g. of tan solid, m.p. 222–232° dec. Recrystallization from acetonitrile gave 2.5 g. (52%) of 2,6-naphthalenedimalononitrile as white crystals, m.p. 238–241° dec. Further recrystallization raised the melting point to 241–243° dec.

Anal. Calcd. for $C_{16}H_8N_4$: C, 75.0; H, 3.15; N, 21.9. Found: C, 75.0; H, 3.23; N, 21.6.

The ultraviolet spectrum of the product in acetonitrile solution had λ_{max} 227 mμ (ϵ 128,000) characteristic of a naphthalene derivative. The infrared spectrum of the product shows absorption at 3050 (Ar—H), 2940 (tertiary C—H), and 2260 cm.$^{-1}$ (nonconjugated $C\equiv N$). Solutions of 2,6-naphthalenedimalononitrile are somewhat unstable to air as evidenced by development of a red color.

11,11,12,12-Tetracyano-2,6-naphthoquinodimethan (TNAP, 1).—To a warm solution of 500 mg. (1.96 moles) of 2,6-naphthalenedimalononitrile in 25 ml. of acetonitrile was added 900 mg. of N-iodosuccinimide. A dark color formed at once. The solvent was removed under reduced pressure, and the residue was washed well with cyclohexane and water to give 500 mg. of purple solid. The crude product was dissolved in about 2.1 l. of acetonitrile and filtered to remove some light-colored insoluble material. The filtrate was passed through a column of 350 g. of "Florex" and eluted with an additional 5 l. of acetonitrile. Removal of solvent and recrystallization of the residue from acetonitrile (sparingly soluble) gave 190 mg. (40%) of metallic purple plates of 11,11,12,12-tetracyano-2,6-naphthoquinodimethan, m.p. >420°.

Anal. Calcd. for $C_{16}H_6N_4$: C, 75.6; H, 2.38; N, 22.0. Found: C, 75.5; H, 2.45; N, 22.1.

The infrared spectrum of the product shows absorption at 2210 (conjugated $C\equiv N$), 1590 (conjugated $C=C$), and 1520 cm.$^{-1}$ (conjugated cyano olefin). The electronic spectrum in acetonitrile solution shows absorption at 472 (87,000), 258 (14,050), and 248 mμ (ε 18,000). The volume electrical resistivity of TNAP (compaction) was found to be 4.6 × 10^6 ohm-cm.

Potassium TNAP$^{\overline{\cdot}}$.—A mixture of 50 mg. (0.198 mmole) of TNAP (1) and 50 mg. of potassium iodide in 15 ml. of acetonitrile was warmed for 10 min. and then filtered. The resulting green solid was washed with water and acetonitrile and finally boiled with 25 ml. of acetonitrile and filtered to give 58 mg. (100%) of bright green potassium TNAP$^{\overline{\cdot}}$.

Anal. Calcd. for $C_{16}H_6N_4K$: C, 65.5; H, 2.06; N, 19.1. Found: C, 65.9; H, 2.20; N, 19.1.

The infrared spectrum of the product showed a very strong broad band centered at 5000 cm.$^{-1}$ which is probably electronic in origin. In addition there was absorption at 2175 cm.$^{-1}$ ($-C\equiv N$). The electronic spectrum of the product in acetonitrile solution shows principal absorption bands at 1105 (66,200), 938 (23,500), 838 (5800), 518 (12,600 broad), and 418 mμ (ε 25,500). The solution is red.

Sodium TNAP$^{\overline{\cdot}}$.—To a warm mixture of 100 mg. (0.395 mole) of TNAP (1) and 35 ml. of acetonitrile was added 200 mg. of sodium iodide. After standing for 30 min., filtration gave 105 mg. (96%) of dark blue sodium TNAP$^{\overline{\cdot}}$.

Anal. Calcd. for $C_{16}H_6N_4Na$: C, 69.3; H, 2.18; N, 20.2; Na, 8.3. Found: C, 69.5; H, 2.71; N, 20.9; Na, 7.2.

Methyltriphenylphosphonium (TNAP$^{\overline{\cdot}}$)$_2$.—To a warm mixture of 50 mg. (0.198 mole) of TNAP and 50 ml. of acetonitrile was added 70 mg. of methyltriphenylphosphonium iodide. After five minutes' additional warming, the mixture was filtered, and the filtrate concentrated at reduced pressure to about one-fourth volume. The black crystals which separated were collected and washed with ethanol to give 46 mg. of $(C_6H_5)_3PCH_3$ (TNAP$^{\overline{\cdot}}$)$_2$ as fine black needles.

Anal. Calcd. for $C_{19}H_{18}P(C_{16}H_6N_4)_2$: C, 78.0; H, 3.85; N, 14.3. Found: C, 78.1; H, 3.94; N, 14.0.

The product could not be recrystallized without undergoing a change in composition. A compaction of this compound displayed a volume electrical resistivity of 84 ohm-cm. The electronic spectrum of the product in acetonitrile had absorption maxima at 472 (100,000) and 1105 mμ (ε 63,000), indicating a ratio of TNAP to TNAP$^{\overline{\cdot}}$ somewhat greater than one.

Tetraethylammonium Salt of [6-(Tricyanovinyl)-2-naphthyl]dicyanomethanide (9).—A mixture of 200 mg. (0.79 mmole) of TNAP, 2 g. of malononitrile, and 10 ml. of dimethylformamide was warmed on a steam bath for 5 min. and then filtered into an aqueous solution of tetraethylammonium chloride. The resulting precipitate was collected and recrystallized twice from ethanol to give 50 mg. of the tetraethylammonium salt of [6-(tricyanovinyl)-2-naphthyl]dicyanomethanide (9) as metallic green crystals, m.p. 183–183.5° dec.

Anal. Calcd. for $C_{26}H_{26}N_6$: C, 73.9; H, 6.20; N, 19.9. Found: C, 73.3; H, 6.26; N, 19.8.

The electronic spectrum of the product in acetonitrile solution showed absorption at 727 (39,700), 405 (6750), 354 (10,150), 328 (10,100), and 266 mμ (ε 18,200). The infrared spectrum of the product showed absorption at 2100, 2175, 2140 ($C\equiv N$), and 1610 cm.$^{-1}$ ($C=C$).

Oligomer of TNAP (10).—From a typical oxidation of 2,6-naphthalenedimalononitrile in which 300 mg. of crude product was obtained, there was isolated after extraction of TNAP by boiling acetonitrile (140 mg. of pure TNAP isolated) 62 mg. of lavender solid which was purified by extraction with acetonitrile in a Soxhlet apparatus for 3 days. There was thus obtained 42 mg. of unextracted lavender solid **10** which decomposed gradually above 340° without melting.

Anal. Calcd. for $(C_{16}H_6N_4)_n$: C, 75.6; H, 2.58; N, 22.0. Found: C, 75.0; H, 2.59; N, 22.1.

Treatment of a suspension of **10** in 1:5 dimethylformamide–acetonitrile with a large excess of malononitrile followed by warming on a steam both gave a deep green solution with ϵ_{690} 18,800 (calculated for $n = 1$). A solution of **9** in dimethylformamide had λ_{max} 690 mμ (ε 42,700).

Methyl-1,4-bis(dicyanomethylene)cyclohexane.—To 43 g. (0.34 mole) of methyl-1,4-cyclohexanedione was added 46.2 g. (0.70 mole) of malononitrile and a catalytic amount of β-alanine in a small amount of water. The mixture was heated under reflux for 2 hr. The product was isolated by filtration and recrystallized from acetonitrile. The yield of crude methyl-1,4-bis(dicyanomethylene)cyclohexane was 54 g. (72%). A recrystallized sample melted at 186–194°.

Anal. Calcd. for $C_{13}H_{10}N_4$: C, 70.2; H, 4.5; N, 25.2. Found: C, 70.1; H, 4.8; N, 25.0.

Methyl-7,7,8,8-tetracyanoquinodimethan and Its Insoluble Derivative.—To a solution of 20 g. (0.09 mole) of methyl-1,4-bis(dicyanomethylene)cyclohexane and 28.8 g. (0.10 mole) of bromine in 370 ml. of acetonitrile was added 28.8 ml. (0.36 mole) of pyridine slowly over a period of about 20 min. Cooling was provided by an ice–salt bath. After the addition was complete, the reaction mixture was stirred for an additional 0.5 hr. with cooling and then for 2 more hr. at room temperature. Cold water (55 ml.) was then added to the reaction mixture. The resultant solid product was removed by filtration and washed with 230 ml. of cold water. The crude product was recrystallized from 900 ml. of acetonitrile. A substantial amount of greenish yellow material (6.9 g.) failed to dissolve and was collected by filtration. This greenish yellow product melted at 190–195°.

The filtrate was heated with decolorizing charcoal and then filtered and cooled. On concentration under nitrogen to a volume of approximately 50 ml., 3.6 g. (20%) of methyl-TCNQ was obtained and collected by filtration.

Anal. Calcd. for $C_{13}H_6N_4$: C, 71.5; H, 2.8; N, 25.7. Found: C, 71.3; H, 3.4; N, 25.8.

A sublimed sample of methyl-TCNQ melted at 200–201°. The insoluble greenish yellow derivative could be cracked in refluxing *o*-dichlorobenzene to give pure monomeric methyl-TCNQ.

***n*-Propyl-1,4-cyclohexanedione.**—To 600 ml. of liquid ammonia was added a solution of 29 g. (0.16 mole) of *n*-propyl-*p*-dimethoxybenzene[8] and 48 g. (1.04 moles) of absolute ethanol in 80 ml. of ether. Twenty-three grams (1.0 mole) of sodium was then added in portions. After 5 hr. the reaction mixture turned white, and at this point 70 g. of ammonium chloride was added. The ammonia was allowed to evaporate under a stream of nitrogen. The residual organic layer was washed with water and heated with dilute hydrochloric acid for 1 hr. The organic product was distilled to yield 9 g. (37%) of a fraction which boiled at 75–77° (0.3 mm.). The infrared spectrum and elemental analysis are in accord for *n*-propyl-1,4-cyclohexanedione.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.1; H, 9.1. Found: C, 69.8; H, 9.0.

***n*-Propyl-1,4-bis(dicyanomethylene)cyclohexane.**—A mixture of 5.2 g. (0.034 mole) of *n*-propyl-1,4-cyclohexanedione and 4.55 g. (0.068 mole) of malononitrile was stirred for 3 days in the presence of a catalytic amount of β-alanine in a small amount of water. The semisolid product solidified upon rubbing with ether. It was washed with water and ether until 7.07 g. (83%) *n*-propyl-1,4-bis(dicyanomethylene)cyclohexane remained. From the filtrate was isolated another 0.9 g. of product. The total yield was 8 g. (95%). After recrystallization from ethyl acetate the product melted at 114–117°.

Anal. Calcd. for $C_{15}H_{14}N_4$: C, 72.0; H, 5.6; N, 22.4. Found: C, 71.9; H, 5.6; N, 22.5.

***n*-Propyl-TCNQ.**—To a solution of 3 g. (12 mmoles) of *n*-propyl-1,4-bis(dicyanomethylene)cyclohexane dissolved in 150 ml. of acetonitrile was added a solution of 6.4 g. (36 mmoles) of N-bromosuccinimide in 60 ml. of acetonitrile. Pyridine (2.95 ml.) was

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[8] T. B. Johnson and W. W. Hodge, *J. Am. Chem. Soc.*, **35**, 1014 (1913).

then added dropwise and the reaction mixture was stirred for 3 hr. At the end of this period, 600 ml. of cold water was added to the mixture, and a brown-red oil separated. This oil slowly solidified on prolonged stirring. The solid was collected by filtration and washed with water and ether; the yield was 2.5 g. (80%). Purification of the crude product was achieved by chromatography on a silicic acid column with methylene chloride as solvent and eluent. The *n*-propyl-TCNQ was only slightly adsorbed on the column, but some dark material remained at the top. Purified *n*-propyl-TCNQ could thus be isolated in 70% yield. Sublimation of a 1-g. sample of purified *n*-propyl-TCNQ at 110° (0.2 mm.) gave 0.33 g. of a very pure product, m.p. 125–127°.

Anal. Calcd. for $C_{15}H_{10}N_4$: C, 73.2; H, 4.1; N, 22.8. Found: C, 73.4; H, 4.3; N, 23.1.

2,5-Dimethyl-1,4-bis(dicyanomethylene)cyclohexane.—A mixture of 11 g. (0.078 mole) of 2,5-dimethyl-1,4-cyclohexanedione[9] and 10.4 g. (0.15 mole) of malononitrile was warmed on a steam bath for 2 hr. with a catalytic amount of β-alanine in a small amount of water. The mixture was then stirred for 3 days at room temperature. The semisolid product was washed with ether, water, and again with ether. This procedure afforded 14.5 g. (79%) of analytically pure 2,5-dimethyl-1,4-bis(dicyanomethylene)cyclohexane, m.p. 180–235°. The melting point range presumably is due to the presence of the *cis* and *trans* isomers; preliminary evidence indicates that the two isomers may be separable by fractional crystallization from ethyl acetate.

Anal. Calcd. for $C_{14}H_{12}N_4$: C, 71.2; H, 5.1; N, 23.7. Found: C, 71.2; H, 5.2; N, 23.3.

2,5-Dimethyl-TCNQ.—To a mixture of 10 g. (0.042 mole) of 2,5-dimethyl-1,4-bis(dicyanomethylene)cyclohexane and 4.3 ml. (13.4 g., 0.084 mole) of bromine in 250 ml. of acetonitrile was added dropwise 13.2 ml. (13.2 g., 0.16 mole) of pyridine with cooling. After stirring for 3 hr., 750 ml. of water was added, and the resulting solid collected by filtration and washed with water. The product was recrystallized from 650 ml. of acetonitrile to give 5.5 g. of tan, crystalline 2,5-dimethyl-TCNQ, m.p. 265–267°. On concentration of the mother liquor another 1.9 g. portion of product was obtained. The combined yield was 7.4 g. (75%).

Anal. Calcd. for $C_{14}H_8N_4$: C, 72.4; H, 3.5; N, 24.1. Found: C, 72.5; H, 3.7; N, 23.9.

Ion-Radical Salts. Lithium Methyl-TCNQ$^{\cdot-}$.—A solution of 7 g. (0.052 mole) of lithium iodide in 31 ml. of boiling acetonitrile was added to a solution of 3.92 g. (0.018 mole) of methyl-TCNQ in 75 ml. of boiling acetonitrile, and the mixture was allowed to cool to room temperature. The resultant purple-black solid was removed by filtration and dried to give 2.1 g. (51%) of lithium methyl-TCNQ$^{\cdot-}$. It was further purified by dissolving in hot acetone and precipitating it with diethyl ether as a light blue powder.

Anal. Calcd. for $C_{13}H_6N_4Li$: C, 69.4; H, 2.7; N, 24.9. Found: C, 69.2; H, 3.1; N, 25.0.

Methyltriphenylphosphonium (Methyl-TCNQ$^{\cdot-}$)$_2$—To a hot solution of 2.2 g. (0.01 mole) of methyl-TCNQ in 55 ml. of acetonitrile was added a solution of 4.1 g. (0.01 mole) of methyltriphenylphosphonium iodide in 40 ml. of acetonitrile. The reaction mixture immediately turned dark blue-green; it was heated briefly and then reduced to a volume of approximately 50 ml. under a stream of nitrogen. Upon filtration, 2.5 g. (71%) of methyltriphenylphosphonium (methyl-TCNQ$^{\cdot-}$)$_2$ was collected as small blue-black rods, decomposition point 180–182°.

Anal. Calcd. for $C_{45}H_{30}N_8P$: C, 75.7; H, 4.2; P, 4.3. Found: C, 75.5; H, 4.1; P, 4.4.

In a similar manner, triethylammonium (methyl-TCNQ$^{\cdot-}$)$_2$ was prepared as a dark blue solid, decomposition point 173–176°.

Anal. Calcd. for $C_{35}H_{28}N_9$: C, 71.4; H, 5.2. Found: C, 70.8; H, 5.3.

From sodium iodide and methyl-TCNQ blue-purple microcrystals of sodium methyl-TCNQ$^{\cdot-}$ were obtained, decomposition point above 400°.

Anal. Calcd. for $C_{13}H_6N_4Na$: C, 64.8; H, 2.5. Found: C, 64.5; H, 2.7.

Similarly, *methyltriphenylarsonium* (*methyl-TCNQ$^{\cdot-}$*)$_2$ was obtained as small blue-black rods, decomposition point 171–173°.

Anal. Calcd. for $C_{45}H_{30}N_8As$: As, 9.9. Found: As, 10.3.

Sodium *n*-propyl-TCNQ$^{\cdot-}$ was obtained in a similar fashion as a purple-blue solid, decomposition point above 400°.

Anal. Calcd. for $C_{15}H_{10}N_4Na$: Na, 8.5. Found: Na, 7.9.

Methyltriphenylarsonium (TCNQ Methyl-TCNQ$^{\cdot-}$).[10]—A solution of 1 g. (0.005 mole) of TCNQ and 1.08 g. (0.005 mole) of methyl-TCNQ in approximately 120 ml. of pure acetonitrile was reduced in volume under nitrogen to approximately 80 ml., and a solution of 4.48 g. (0.01 mole) of methyltriphenylarsonium iodide in 30 ml. of acetonitrile was added. The resultant hot mixture was stored in a dewar flask for 25 hours, and the product removed by filtration and dried. There was obtained 2.05 g. (55%) of methyltriphenylarsonium (TCNQ methyl-TCNQ$^{\cdot-}$) as black rosettes, decomposition point 198–200°.

Anal. Calcd. for $C_{44}H_{28}N_8As$: C, 71.1; H, 3.8; N, 15.1; As, 10.1. Found: C, 71.1; H, 4.0; N, 15.0; As, 10.4.

A physical mixture of methyltriphenylarsonium (methyl-TCNQ)$_2^{\cdot-}$ with methyltriphenylarsonium (TCNQ$^{\cdot-}$)$_2$ melts at 181 with decomposition. Pure methyltriphenylarsonium (TCNQ$^{\cdot-}$)$_2$ melts at 224–227° with decomposition.

Methyltriphenylphosphonium (TCNQ Methyl-TCNQ$^{\cdot-}$).[10]—To a hot solution of 1.02 g. (0.005 mole) of TCNQ and 1.08 g. (0.005 mole) of methyl-TCNQ in 85 ml. of acetonitrile was added 4.04 g. (0.01 mole) of methyltriphenylphosphonium iodide in 30 ml. of acetonitrile. The resultant hot mixture was placed in a dewar flask and allowed to stand under nitrogen at room temperature for 48 hr. The solid product was removed by filtration and dried, thereby affording 1.4 g. (40%) of methyltriphenylphosphonium (TCNQ methyl-TCNQ$^{\cdot-}$) as small black crystals, decomposition point 204–208°. The melting point of this mixed complex anion-radical salt is intermediate between that of (A) the pure methyltriphenylphosphonium (TCNQ)$_2^{\cdot-}$ (224–227° dec.) and that of (B) methyltriphenylphosphonium (methyl-TCNQ$^{\cdot-}$)$_2$ (182° dec.), and differs from that of a physical mixture of A and B (m.p. 185° dec.).

Anal. Calcd. for $C_{44}H_{28}N_8P$: C, 75.5; H, 4.0; N, 16.0; P, 4.4. Found: C, 75.7; H, 4.0; N, 15.7; P, 4.3.

Acknowledgment.—The authors wish to thank Miss Naomi Schlichter and Miss Ellen Wallace for determining the spectra. The polarographic data were provided by Miss Lucille E. Williams, and the electrical resistivity data by Dr. R. G. Kepler. We wish to acknowledge helpful discussions with Drs. L. R. Melby, W. D. Phillips, D. S. Acker, and D. C. Blomstrom.

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(9) J. Fishman, E. R. H. Jones, G. Lowe, and M. C. Whiting, *J. Chem. Soc.*, 3948 (1960).

(10) We are indebted to Dr. R. J. Harder for this experiment.