that previous data indicate that small anions are quite mobile in similar nonbilayer films,[5,15] we are inclined to discount counterion effects for the present bilayer.

New Synthesis and Properties of 11,11,12,12-Tetracyano-9,10-anthraquinodimethane: An Electron Acceptor Displaying a Single-Wave, Two-Electron Reduction and a Coproportionation Pathway to the Radical Anion

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Abstract: The title compound (abbreviated as TCAQ) has been synthesized starting from 9,10-bis(cyanomethyl)anthracene with the intermediacy of dicyano and tricyano analogues of TCAQ. Electronic spectral data point to a distorted, nonplanar structure for TCAQ. Electrochemical studies reveal a single-wave, two-electron reduction to the dianion TCAQ²⁻ at a potential comparable to the second reduction of TCNQ and benzo-TCNQ. Two additional reduction waves of TCAQ, at substantially more negative potentials than the first one, indicate the formation of the trianion radical TCAQ³⁻· and the tetraanion TCAQ⁴⁻. Spectral monitoring in the near-IR region of the TCAQ reduction during coulometry exhibits an absorption peak at 1060 nm which is attributed to the anion radical TCAQ⁻·. This finding, along with the observation of intense ESR signals, points to a coproportionation reaction; TCAQ + TCAQ²⁻ ⇌ 2TCAQ⁻·. Full characterization of TCAQ⁻· has been achieved by a high-resolution ESR spectrum, with the assistance of the ENDOR technique.

The observation of electrical conductivity in certain anion radical salts of TCNQ by Du Pont chemists[1] paved the way for the development of a multidisciplinary research area—organic conductors. Charge-transfer salts of TCNQ exhibit a wide array of electrical properties ranging from pyrene–TCNQ, an insulator,[1c] to morpholinium–TCNQ, a semiconductor,[1c] to TTF–TCNQ, the first organic metal,[2] to HMTSF–TCNQ, the first organic compound to remain metallic as the temperature approaches zero.[3] Additionally, TCNQ and its derivatives form anion radical salts with copper and silver which display bistable switching phenomena when subjected to electrical[4] and optical fields.[5] The synthesis of the so-called "cyanocarbons" has been an actively pursued research effort over the past 2 decades and has resulted in several new TCNQ-type acceptors, both in terms of substitution[6] and π-system extension.[7] The latter was thought to be of great importance in reducing intramolecular Coulomb repulsion and thereby enhancing the conductivities of the anion radical salts.[8]

The nature of the switching behavior in the metal salts of TCNQ and its derivatives was found to be dependent on the nature of substituents and thereby on the electron affinities.[4c] While acceptors with relatively lower electron affinities, e.g., 2,5-TCNQ(Me)₂, 2,5-TCNQ(OMe)₂, tend to give metal salts exhibiting threshold switching, electron–withdrawing substituents, e.g., as in metal salts of TCNQF₄, favor memory switching behavior. Thus, in view of the electrical properties being strongly structure-dependent, we have been interested in examining the variation of switching properties with successive benzo substitution (Chart I). In this regard, we have sought to synthesize TCAQ—11,11,12,12-tetracyano-9,10-anthraquinodimethane (**1**).

Chart I
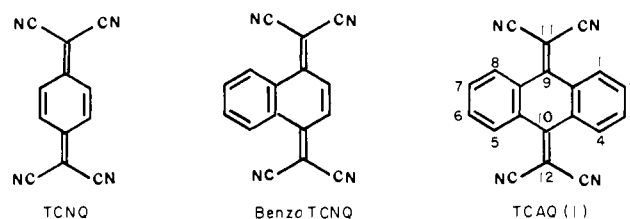
When we undertook our synthetic studies, there were two reports in literature of an unsuccessful attempt by Nogami, Mikawa, and

[†] The Johns Hopkins University.
[‡] Physikalisch–Chemisches Institut der Universität Basel.

(1) (a) Cairns, T. L.; McKusick, B. C. *Angew. Chem.* **1958**, *80*, 2778. (b) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370. (c) Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. *Ibid.* **1962**, *84*, 3374.

(2) (a) Ferraris, J. P.; Cowan, D. O.; Walatka, V., Jr.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. (b) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J. *Solid State Commun.* **1973**, *12*, 1125.

(3) Bloch, A. N.; Cowan, D. O.; Bechgaard, K.; Pyle, R. E.; Banks, R. H.; Poehler, T. O. *Phys. Rev. Lett.* **1975**, *34*, 1561.

(4) (a) Potember, R. S.; Poehler, T. O.; Cowan, D. O. *Appl. Phys. Lett.* **1979**, *34*, 405. (b) Potember, R. S.; Poehler, T. O.; Rappa, A.; Cowan, D. O.; Bloch, A. N. *J. Am. Chem. Soc.* **1980**, *102*, 3659. (c) Potember, R. S.; Poehler, T. O.; Cowan, D. O.; Bloch, A. N. "Proceedings of the NATO Conference on Chemistry and Physics of One-Dimensional Materials"; Alcacer, L., Ed.; Reidel: Boston, 1980; p 419.
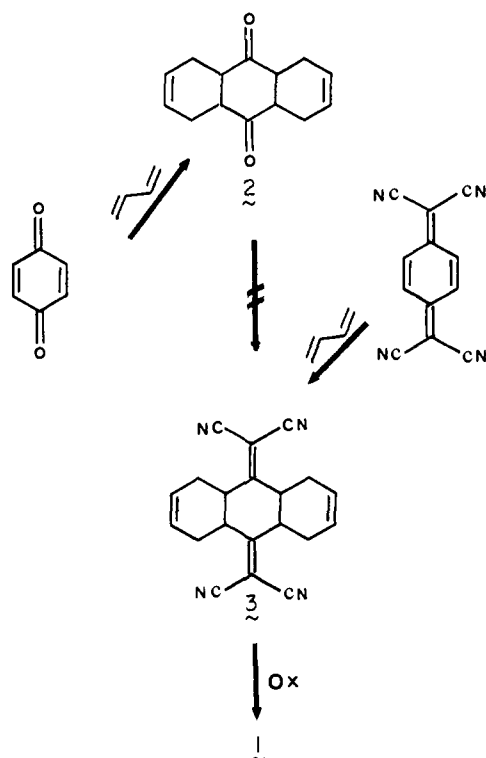
(5) (a) Potember, R. S.; Poehler, T. O.; Benson, R. C. *Appl. Phys. Lett.* **1982**, *41*, 548. (b) Benson, R. C.; Hoffman, R. C.; Potember, R. S.; Bourkoff, E.; Poehler, T. O. *Ibid.* **1983**, *42*, 855. (c) Kamitsos, E. I.; Tzinis, C. H.; Risen, W. M. *Solid State Commun.* **1982**, *42*, 561. (d) Kamitsos, E. I.; Risen, W. M. *Ibid.* **1983**, *45*, 165.

(6) Wheland, R. C.; Martin, E. L. *J. Org. Chem.* **1975**, *40*, 3101.

Scheme I

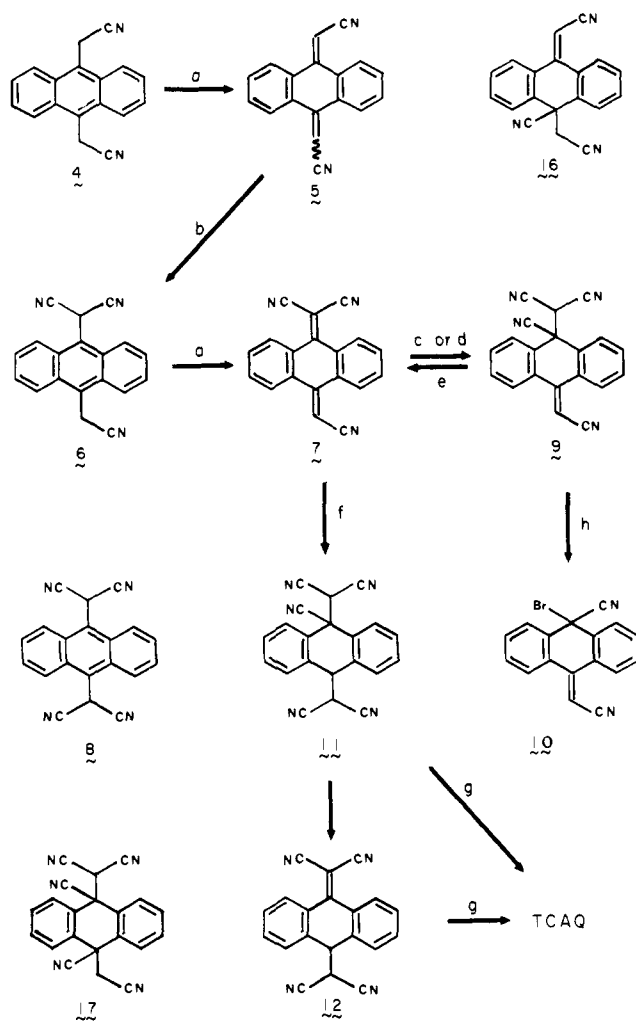**Scheme II**

Scheme III

co-workers,[9]   In the meantime, three different syntheses by workers at Matsushita Electric Industrial Co. in Japan have appeared in patent literature.[10a-c]   Also, Yamaguchi et al.[10d] have disclosed their successful, moderate-yield synthesis in 1983 and, more recently, Aumüller and Hünig[10e] have described a simple, one-step, high-yield procedure, Our methodology consists of arriving at TCAQ via its dicyano and tricyano analogues, which to our knowledge is unprecedented. In this paper, we describe (a) our synthesis of TCAQ, (b) some of its additional physical, chemical, and electrochemical properties, and (c) full characterization of the anion radical TCAQ⁻·, formed to a large measure by a coproportionation pathway.

Results and Discussion

Synthesis. Initially, we chose to follow a synthetic route similar to that employed by the Du Pont workers for the synthesis of TCNQ,[1b] wherein Knoevenagel condensation of an appropriate 1,4-diketone with malononitrile is the key step in the construction of the desired carbon framework. Subsequent oxidation would then provide the tetracyanoquinodimethane (Scheme I). However, under a variety of conditions, the task of converting diketone **2** to **3** was met with futility. High enolizability of the diketone **2** and steric interactions of perihydrogens appear to be the major obstacles. Although these observations are consistent with those of Tatemitsu,[10d] the Matsushita group[10b] claims to have obtained TCAQ by an identical scheme in >75% yield. In our hands, even
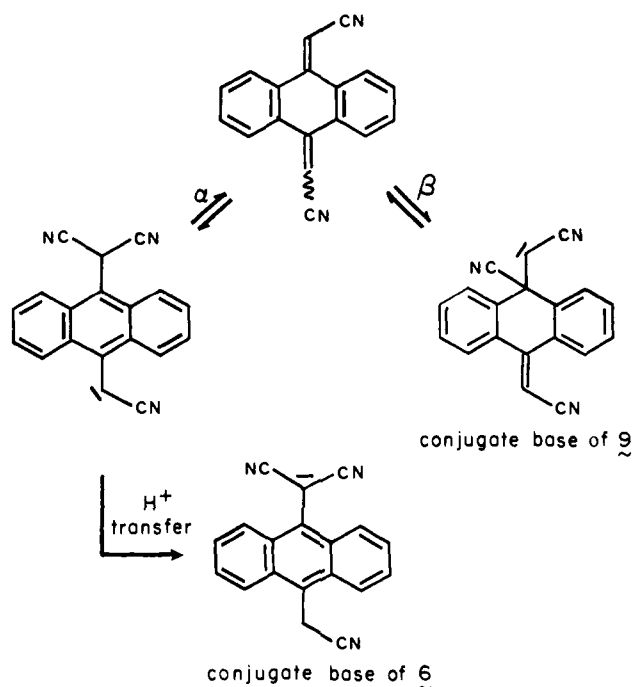
(7) For leading references, see: (a) Kaplan, M. L.; Haddon, R. C.; Bramwell, F. B.; Wudl, F.; Marshall, J. H.; Cowan, D. O.; Gronowitz, S. *J. Phys. Chem.* **1980**, *84*, 427. (b) Gerson, F.; Heckendorn, R.; Cowan, D. O.; Kini, A. M.; Maxfield, M. *J. Am. Chem. Soc.* **1983**, *105*, 7017.

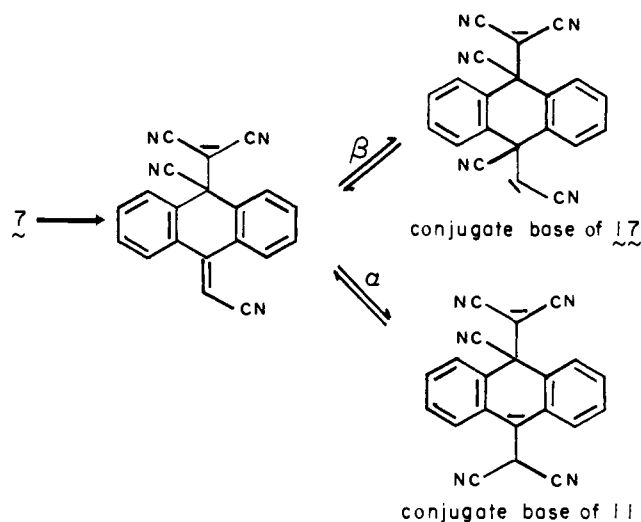(8) See, e.g.; Garito, A. F.; Heeger, A. J. *Acc. Chem. Res.* **1974**, *7*, 232.

(9) (a) Nogami, T.; Mikawa, H. *Mol. Cryst. Liq. Cryst.* **1982**, *86*, 315. (b) Nogami, T.; Kanda, Y.; Tanaka, H.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3601.

(10) (a) Hotta, S.; Tosaka, T.; Sonoda, N.; Shimotsuma, S. European Patent Applied EP 61 264, Sept 1982; *Chem. Abstr.* **1983**, *98*, 99701n. (b) Matsushita Electric Industrial Co., Ltd. Japanese Patent 58 10554, Jan 1983; *Chem. Abstr.* **1983**, *98*, 197809y. (c) Hotta, S.; Tosaka, T.; Sonoda, N.; Shimotsuma, S. European Patent Applied EP 76 639, Apr 1983; *Chem. Abstr.* **1983**, *99*, 105013d. (d) Yamaguchi, S.; Tatemitsu, G.; Sakata, Y.; Misumi, S. *Chem. Lett.* **1983**, 1229. (e) Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1984**, 618.

under conditions like those described by the Matsushita group, the Knoevenagel condensation was unsuccessful.

An attempted Diels–Alder reaction of TCNQ with excess butadiene resulted in the formation of compound **3** in ca. 3–5%

558 *J. Am. Chem. Soc., Vol. 107, No. 3, 1985*

Kini et al.

Scheme IV

Table I. UV–Visible Spectra of TCNQ, Benzo-TCNQ, and TCAQ

compound	solvent	λ_{max} (log ϵ)	log ϵ_l/ log ϵ_s^d
TCNQ	CH_3CN^a	395 (4.8388)	
	CH_3CN^c	393 (4.838), 376 sh (4.637), 227 (3.406)	1.42
benzo-	$CH_2Cl_2^b$	409 (4.52), 392 (4.54), 288 (4.84)	
TCNQ	$CH_2Cl_2^c$	404 (4.50), 388 (4.53), 290 (3.89)	1.16
TCAQ	CH_3CN^c	343 (4.38), 303 (4.21), 280 (4.43)	0.99
	$CH_2Cl_2^c$	347 (4.43), 305 (4.22), 283 (4.48)	
	DMF^c	346 (4.32), 305 (4.20), 281 (4.37)	
	CH_3CN^e	342 (4.39), 302 (4.20), 279 (4.45)	
	CH_3CN^f	342 (4.40), 302 (4.22), 279 (4.46)	

[a] Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370. *[b]* Chatterjee, S. *J. Chem. Soc. B* **1967**, 1170. *[c]* This work. *[d]* ϵ_l and ϵ_s: extinction coefficients of longest and shortest wavelength absorptions, respectively. *[e]* Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1984**, 618. *[f]* Yamaguchi, S.; et al. *Chem. Lett.* **1983**, 1229.

yield, the major product being a polymeric material. Because of the poor yield and high cost of TCNQ, this route was not further pursued.

We then turned to the method depicted in Scheme II. Refluxing a solution of 9,10-bis(cyanomethyl)anthracene (4)[11] in 1,2-dichloroethane with 2.5 equiv of bromine for 1 h resulted in ca, 75% yield of 11,12-dicyano-9,10-anthraquinodimethane (5), which is very stable at room temperature.[12] Upon reacting 5 with excess sodium cyanide in dioxane/95% ethanol mixture under reflux for 24 h, followed by acid workup, compound 6 was isolated in almost quantitative yield. The D_2O-exchange experiment by NMR clearly supported the structure 6 with an exchangeable proton and not the isomeric structure 16 arising out of normal Michael addition of cyanide ion. We rationalize this in terms of an initial α attack by the cyanide ion followed by an internal proton transfer, giving a more stable anion (conjugate base of 6). The product of the normal β attack, conjugate base of 16, is relatively unstable and can be converted to the more stable anion under equilibrium conditions (Scheme III). Analogous α attack of nucleophiles on another Michael acceptor, 9-fluorenylidenenitromethane, has recently been observed wherein the product is a resonance-stabilized dibenzocyclopentadienyl ion.[13]

Oxidation of 6 with bromine furnished 11,11,12-tricyano-9,10-anthraquinodimethane (7) in 75% yield. Thus, the stage was set for the final cyanide ion addition/oxidation sequence to complete the synthesis of TCAQ.

However, the reaction of 7 with cyanide ion in 95% ethanol or DMF *at room temperature* resulted in the isolation of adduct 9, instead of the expected adduct 8. This is undoubtedly due to the higher electrophilicity of the dicyanomethylene group relative to the cyanomethylene group in 7. An attempt to effect thermal rearrangement 9 → 8, nominally a 1,5-sigmatropic shift of the cyano group, by refluxing in benzene or toluene gave, however, the tricyano compound 7.[14] The adduct 9 when treated with bromine in methylene chloride was converted into the bromo compound 10. On the other hand, the reaction of 7 with cyanide ion in DMF *at 100 °C* gave a fairly labile adduct 11.[15] Although
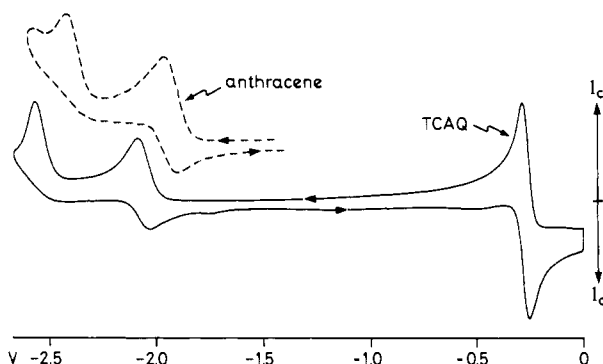
Figure 1. Cyclic voltammograms of TCAQ and anthracene: solvent, acetonitrile; supporting electrolyte, Et_4NBF_4; temperature, 298 K; reference electrode, $Ag/AgCl/KCl$ 3 M; working electrode, hanging mercury drop; sweep, 200 mV/s; I_c, cathodic current, I_a, anodic current.

its insolubility in relatively nonpolar chloroform or methylene chloride prevented NMR characterization, we base our structural assignment on its ready decomposition in polar solvents (acetonitrile, DMF, Me_2SO) to 12, a retro-Michael reaction.[14] Attempted recrystallization of compound 11 was also accompanied by its conversion to 12. The formation of the adduct 11, and not the isomeric adduct 17, can once again be readily rationalized in terms of an α attack of the cyanide ion on the conjugate base of 9, yielding a resonance-stabilized ion, conjugate base of 11 (Scheme IV). The structure of the adduct 12 was clearly established from ^{13}C NMR data (see Experimental Section). Finally, the reaction of either adducts 11 or 12 with bromine/triethylamine in acetonitrile at room temperature gave TCAQ in 90% yield.

TCAQ, a yellow crystalline solid, does not melt when heated up to 350 °C. Differential scanning calorimetry (DSC) shows an exothermic process at 367 °C instead of an endotherm characteristic of melting.[16] The dicyano and tricyano analogues 5 and 7, in contrast, exhibit endotherms (melting) at 290 and 239 °C, respectively. Infrared spectrum of the black residue obtained after DSC analysis of TCAQ shows virtually no absorption peaks, suggesting a decomposition to carbonaceous matter.

In the infrared spectrum of TCAQ, cyano stretch appears at 2227.5 cm^{-1}, consistent with the conjugated nitrile function. NMR, mass spectral, and combustion analysis data (see Experimental Section) are all in agreement with the structure and with the published data.[10d,e] The UV absorption spectrum of TCAQ

(11) Miller, M. W.; Amidon, R. W.; Tawney, P. O. *J. Am. Chem. Soc.* **1955**, *77*, 2845.

(12) For the pyrolytic preparation and low-temperature NMR characterization of the transient 9,10-anthraquinodimethane, see: Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1970**, *92*, 1436. It is thus clear that only two cyano substituents can drastically alter the high reactivity toward polymerization of the parent quinodimethane.

(13) Hoz, S.; Speizman, D. *J. Org. Chem.* **1983**, *48*, 2904.

(14) Retro-Michael reaction by the action of heat, base, or in ionizing solvents is well documented. See, e.g.; March, J. "Advanced Organic Chemistry"; McGraw-Hill: New York, 1968; p 767.

(15) Adduct 11, insoluble in $CHCl_3$ and CH_2Cl_2 at room temperature, can be obtained in moderate purity by washing it with boiling $CHCl_3$ under Soxhlet conditions. IR (KBr) shows a C≡N stretch at 2260 cm^{-1}, in agreement with the structure 11 with nonconjugated nitrile functions. Melting point determination of 11 shows some darkening of the color at ca. 200 °C and melting at 230–232 °C (cf. mp of 7, 235–237 °C) indicative of thermal retro-Michael reaction 11 → 7.

(16) We thank Michael D. Mays for DSC measurements.

Table II. Cyclic Voltammetric Data of TCNQ, Benzo-TCNQ, and TCAQ[a]

compound	solvent	$E_{1/2}(1)$	$E_{1/2}(2)$
TCNQ	BuCN	−0.09 (1e)	−0.75 (1e)
benzo-TCNQ	BuCN	−0.26 (1e)	−0.745 (1e)
TCAQ	BuCN	−0.71 (2e)	
TCNQ	DMF	−0.125 (1e)	−0.72 (1e)
benzo-TCNQ	DMF	−0.30 (1e)	−0.735 (1e)
TCAQ	DMF	−0.705 (2e)	
TCAQ[b]	CH$_3$CN	−0.285 (2e)	

[a] vs. Ag/AgNO$_3$, electrolyte Bu$_4$NBF$_4$, except as otherwise noted. [b] vs. Ag/AgCl/KCl 3 M electrolyte Et$_4$NBF$_4$; $E_{1/2}(3) = -2.06$ (1e); $E_p(4) = -2.58$ (1e, irreversible).

in methylene chloride shows bands at 347 nm (log ϵ = 4.43), 305 nm (4.22), and 283 nm (4.48). Thus, the lowest energy electronic transition is blue-shifted by ca. 50 and 60 nm, compared to TCNQ and benzo-TCNQ, respectively. In addition, the ratio of intensities of long and short wavelength bands has changed dramatically in TCAQ (Table I). These data, which are in good agreement with those of Aumüller and Hünig[10e] as well as Yamaguchi et al.[10d] (see Table I), strongly suggest a highly distorted (nonpolar) structure for TCAQ. In fact, such a structure has been verified by X-ray crystallographic analysis which indicates that the central ring in TCAQ is bent into a boat form and the two benzene rings are noncoplanar.[17] In this way, the severe steric interactions between the cyano groups and the perihydrogens are avoided. The situation is analogous to 9-bis(cyanomethylene)anthrone[18a] and benzo-TCNQ,[18b] both with boat-shaped quinonoid moieties. The distortion of the quinodimethane portion of benzo-TCNQ is, however, not as severe as in TCAQ, as evidenced from the crystallographic[18b] and UV data.

Electrochemistry. Figure 1 shows the cyclic voltammogram of TCAQ in acetonitrile, taken at room temperature and with tetraethylammonium tetrafluoroborate as the supporting electrolyte (working electrode, hanging mercury drop electrode; counter electrode, glassy carbon electrode). The first and the second reversible redox waves appear at the potentials $E_{1/2}$ = −0.285 and −2.06 V vs. Ag/AgCl/KCl 3 M reference electrode. The peak intensities are twice as large for the former than for the latter wave; moreover, the separations of their cathodic and anodic peaks amount to 0.03 and 0.06 V, respectively. These findings are consistent with a two-electron transfer for the wave at $E_{1/2}$ = −0.285 V and with a one-electron transfer for that at $E_{1/2}$ = −2.06 V. In addition, there is an irreversible, presumably, one-electron reduction wave with a cathodic peak at −2.58 V. The first two-electron reduction was also observed by Aumüller and Hünig.[10e] The occurrence of all three reduction waves was confirmed by polarography under the same experimental conditions.[19a] In N,N-dimethylformamide (DMF) with tetra-n-butylammonium tetrafluoroborate as the supporting electrolyte (working electrode, platinum button; counter electrode, nickel), only one redox wave was observed at $E_{1/2}$ = −0.705 V vs. Ag/AgNO$_3$ reference electrode (Table II), corresponding to the first wave ($E_{1/2}$ = −0.285 V) in the cyclic voltammogram (Figure 1). Coulometric analysis of this redox wave was carried out to confirm the number of electrons involved in the process. Current vs. charge profiles of reduction (at −0.90 V vs. Ag/AgNO$_3$) and reoxidation (at −0.2
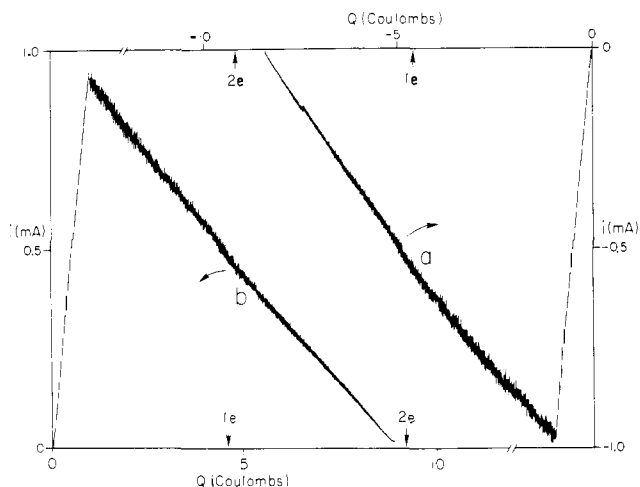

Figure 2. Current vs. charge plots of coulometric analysis of TCAQ (14.5 mg, 47.7 μmol) in 0.1 M Bu$_4$NBF$_4$ in DMF: working electrode, Pt basket; (a) reduction at −0.9 V vs. Ag/AgNO$_3$; (b) reoxidation at −0.2 V vs. Ag/AgNO$_3$.

V vs. Ag/AgNO$_3$) in 0.1 M tetra-n-butylammonium tetrafluoroborate/DMF employing a platinum basket working electrode indicate reversible, two-electron reactions (Figure 2). Therefore, the first reversible redox wave in the cyclic voltammogram of TCAQ is characterized by an *overall process* yielding the dianion TCAQ^{2-} and represented by eq 1.

$$TCAQ + 2e^- \rightleftharpoons TCAQ^{2-} \qquad (1)$$

However, since intense ESR signals of the anion radical TCAQ$^-\cdot$ were observed upon reduction of TCAQ under a variety of experimental conditions (vide infra), a coproportionation reaction, formulated in eq 2, must take place to a considerable extent. A

$$TCAQ + TCAQ^{2-} \rightleftharpoons 2TCAQ^-\cdot \qquad (2)$$
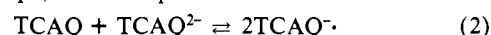
coproportionation constant (K_{SEM}) of ~1.0 was estimated according to an analysis described by Myers and Shain[19b] and it agrees well with the reported value (0.83).[10e]

UV–visible spectral analysis of aliquots, taken during the electrochemical reduction, revealed gradual disappearance of TCAQ absorption bands and concomitant emergence of new maxima at 292, 308, 400, and 540 nm; a well-defined isosbestic point at 395 nm was observed (Figure 3a). As indicated by a combined ESR and UV–visible spectral study, the species giving rise to the new absorption maxima are presumably both TCAQ$^-\cdot$ and TCAQ^{2-}. (It is known, owing mainly to the work of Hoijtink and co-workers,[20] that anion radicals and dianions of conjugated π systems absorb in the same long-wave range of the spectrum.) An analysis similar to that in the UV–visible was carried out in the near-IR region with ca. tenfold more concentrated solution. A weak transition at 1060 nm (Figure 3b), which attained its maximum intensity at ca. 1 equiv. of charge added, is very likely due to TCAQ$^-\cdot$. It also supports our notion that TCAQ$^-\cdot$ is formed, to a large extent, by the coproportionation pathway.

The coalescence of first- and second-electron reduction potentials to a single wave ($E_{1/2}$ = −0.285 V), on going from TCNQ to benzo-TCNQ to TCAQ (Table II), is clearly the effect of successive benzo substitution. It is tempting to implicate increased conjugative effects for such a trend, as found by Chen and co-workers[21] for successively more conjugated bis(4H-thiapyrans) and related donors. But we suggest that the molecular distortion in TCAQ causes the first potential, $E_{1/2}(1)$, to shift to a more negative range while not affecting the second potential, $E_{1/2}(2)$, since the steric interactions are already relieved in TCAQ^{2-} (vide infra). Alternatively, TCAQ may be viewed to consist of two

(17) Subsequent to our completion of the synthesis, we were informed by Prof. Siegfried Hünig of an independent synthesis of TCAQ in his laboratory.[10e] At that stage, based on the UV spectrum and a molecular weight determination (Galbraith Laboratories), we were considering a dimeric structure for TCAQ. However, an X-ray structure determination by Prof. Hünig has since demonstrated a monomeric and highly distorted structure with the central ring in TCAQ existing in a boat form. We thank Prof. Hünig for the preprint and results of the X-ray work. Galbraith Laboratories has also informed us of the inherent inaccuracy in molecular weight determinations of samples of low solubility, such as TCAQ.

(18) (a) Silverman, J.; Yannoni, N. F. *J. Chem. Soc. B* **1967**, 194. (b) Iwasaki, F. *Acta Crystallogr., Sect. B* **1971**, B27, 1360.

(19) (a) We thank J. Knöbel, Basel, for his assistance in the cyclic voltammetry and polarography studies. (b) Myers, R. L.; Shain, J. *Anal. Chem.* **1969**, 41, 980.

(20) See, e.g.; Balk, P.; Hoijtink, G. J.; Schreurs, J. W. H. *Recl. Trav. Chim. Pays-Bas* **1957**, 76, 813. Hoijtink, G. J.; Zandstra, P. J. *Mol. Phys.* **1960**, 3, 371. Hoijtink, G. J.; Buschow, K. H. J. *J. Chem. Phys.* **1964**, 40, 2501.

(21) Chen, C. H.; Doney, J. J.; Reynolds, G. A.; Saeva, F. D. *J. Org. Chem.* **1983**, 48, 2757.
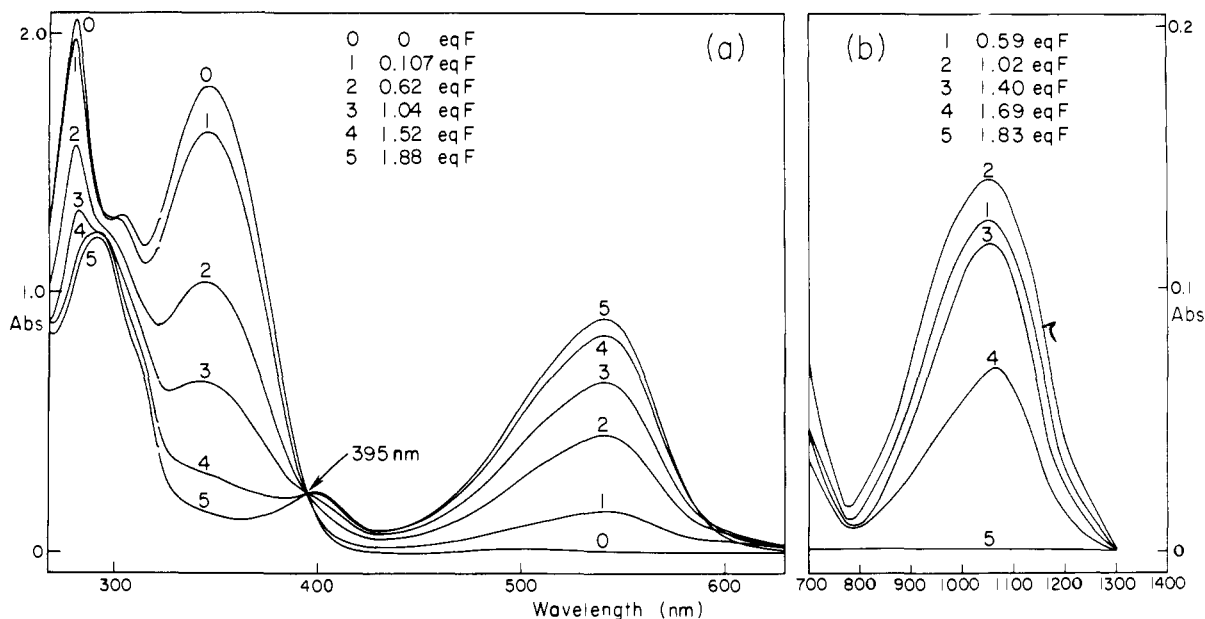
Figure 3. (a) UV–visible spectra during electrochemical reduction of 1.085×10^{-5} M TCAQ in 0.1 M Bu$_4$NBF$_4$ in DMF; (b) near-IR spectra during electrochemical reduction of 1.198×10^{-4} M TCAQ in 0.1 M Bu$_4$NBF$_4$ in DMF.
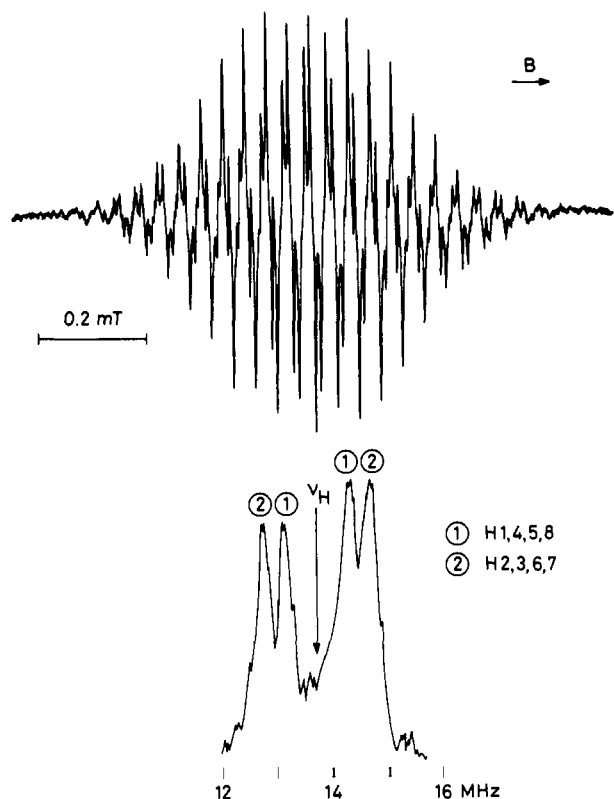

Figure 4. ESR (top) and proton ENDOR (bottom) spectra of TCAQ$^-$·: solvent, DME–THF (1:1); counterion, K$^+$; temperature, 213 K; ν_H = frequency of the free proton.

independent electron sinks (two distorted diphenyldicyanoethylene units). A two-electron single-wave reduction has quite recently been observed by Wellman and West[22] for a novel polyquinone structurally related to TCAQ.

The second reversible redox wave ($E_{1/2} = -2.06$ V) in the cyclic voltammogram of TCAQ (Figure 1) can reasonably be attributed to the formation of trianion radical TCAQ^{3-}·, as expressed by eq 3.

$$TCAQ^{2-} + e^- \rightleftarrows TCAQ^{3-}\cdot \tag{3}$$

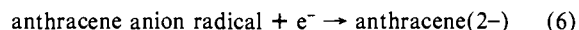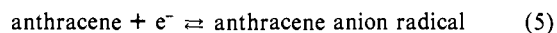(22) Wellman, D. E.; West, R. *J. Am. Chem. Soc.* **1984**, *106*, 355.

Occurrence of the trianion radical in solutions of exhaustively reduced tetracyanoarenoquinodimethanes has been demonstrated by ESR spectroscopy in a previous work.[7b]

The third irreversible reduction wave with a cathodic peak at -2.58 V is indicative of the formation of tetraanion TCAQ^{4-}, as depicted in eq 4.

$$TCAQ^{3-}\cdot + e^- \rightarrow TCAQ^{4-} \tag{4}$$

Our interpretation of the second and the third waves in the reduction of TCAQ in terms of eq 3 and 4, respectively, is strongly supported by the cyclic voltammogram of anthracene (Figure 1). In this voltammogram, taken under the same conditions as that of TCAQ, two waves very similar to the third and fourth waves of TCAQ are observed. The two waves of anthracene are attributed to the reactions formulated in the eq 5 and 6[23] which correspond to eq 3 and 4, respectively.

$$anthracene + e^- \rightleftarrows anthracene\ anion\ radical \tag{5}$$

$$anthracene\ anion\ radical + e^- \rightarrow anthracene(2-) \tag{6}$$

Surprisingly, the shifts of the second and third waves of TCAQ relative to those of anthracene are only -0.13 and -0.16 V, respectively. This finding can be rationalized as follows. It has been concluded from the studies of tetracyanoarenoquinodimethanes[7b] that the negative charges in the dianions tend to localize on the two C(CN)$_2$ groups. For steric reasons, this tendency is expected to be enhanced in TCAQ^{2-}. Since the C9-C11 and C10-C12
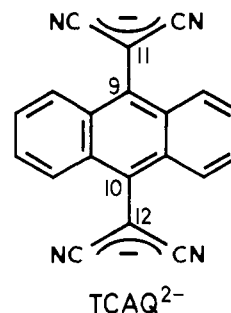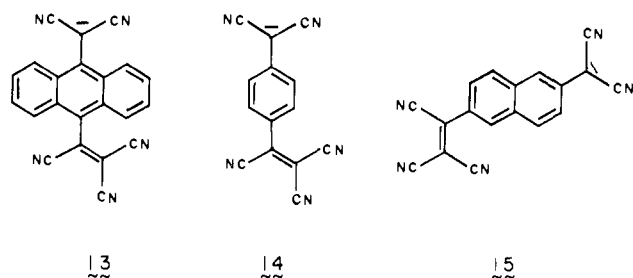

TCAQ^{2-}

bonds become essentially single in the dianions, the steric interferences between the cyano substituents and the perihydrogen atoms in TCAQ^{2-} should be more readily alleviated by twisting

(23) See, e.g.: House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003. House, H. O.; Koepsell, D. G.; Jaeger, W. *Ibid.* **1973**, *38*, 1167.

11,11,12,12-Tetracyano-9,10-anthraquinodimethane

J. Am. Chem. Soc., Vol. 107, No. 3, 1985 561

Chart II

the negatively charged $C(CN)_2$ groups out of the aromatic plane rather than by bending the central ring in the anthradiyl moiety. The π systems of these groups are thus expected to be largely isolated and their interactions with the anthracene π system in $TCAQ^{2-}$ are accordingly very weak.

ESR Spectroscopy. Intense ESR signals of a persistent anion radical (g = 2.00265 ± 0.00010) were obtained from TCAQ during electrolytic reduction in 1,2-dimethoxyethane (DME), containing tetra-n-butylammonium perchlorate as the supporting salt, as well as upon reaction with potassium metal in DME or tetrahydrofuran (THF). A highly resolved ESR spectrum (line width ΔB_{pp} of 0.005 mT), taken at 213 K in a 1:1 v/v mixture of DME and THF, is displayed in Figure 4, along with the corresponding proton ENDOR signals. The hyperfine data derived from these spectra, undoubtedly due to $TCAQ^{-}\cdot$, are 0.070 and 0.042 mT, each for four equivalent protons, and 0.081 mT for four equivalent ^{14}N nuclei (experimental error: ±0.001 mT). Calculation of the Hückel–McLachlan[24] type with the use of the well-tried heteroatom parameters[7b] suggests that the larger proton coupling constant (0.070 mT) should be assigned to the hydrogen atoms in the positions 2,3,6,7, thus leaving the smaller one (0.042 mT) for those in 1,4,5,8. The narrow field range (ca. 1.1 mT) over which the ESR spectrum of $TCAQ^{-}\cdot$ extends is characteristic of the anion radicals of tetracyanoarenoquinodimethanes.[7b] It is in accord with the MO model which locates the largest π-spin populations at the cyano-substituted, exocyclic carbon centers.

When solutions exhibiting the ESR spectrum of $TCAQ^{-}\cdot$ were brought into prolonged contact with the potassium metal, this spectrum gradually disappeared, as expected for a complete reduction to the dianion $TCAQ^{2-}$. Upon further exposure of the solutions to the metal mirror, ESR signals of various species, differing from one experiment to another, were observed. The only identified species was the anion radical of anthracene,[25] and none of the spectra could unequivocally be attributed to the trianion radical $TCAQ^{3-}\cdot$. It must be assumed that $TCAQ^{3-}\cdot$ is rather unstable, despite its relative ease of formation and the reversibility of the pertaining wave ($E_{1/2}$ = -2.06 V) on the time scale of the cyclic voltammetry experiment (sweep 200 mV/s).

Chemical Properties. TCAQ, when reacted with malononitrile anion in DMF, gives a deep blue-colored product, anthracene-9-tricyanovinyl-10-dicyanomethide anion (**13**) (Chart II), isolated as tetrabutylammonium salt. Analogous products derived from TCNQ and TNAP, **14** and **15**, respectively, have been reported and studied.[26,27] Decreased conjugative interactions due to the perihydrogens in **13** are again evident from the UV–visible spectral data for compounds **13–15** (Table III). Compounds of this type, wherein the electron-rich and the electron-deficient moieties are connected through a conjugated carbon framework, show unusual properties such as electrochromism[28] and a nonlinear second harmonic coefficient[29] as well as potential applications in pho-

Table III. UV–Visible Spectra and Infrared C≡N Stretching Frequencies

compound	solvent	λ_{max} (log ϵ)	ν_{CN}, cm^{-1}
14[a]	EtOH	625 (4.72)	2217
		350 (3.75)	2198
		292 (3.89)	2164
15[b]	CH$_3$CN	727 (4.60)	2200
		405 (3.83)	2175
		354 (4.006)	2140
		328 (4.004)	
		266 (4.26)	
13	CH$_2$Cl$_2$	615 (4.18)	2212
		421 (3.95)	2178
		327 (4.14)	2145
		272 (4.32)	
		263 (4.33)	
		253 (4.39)	
		233 (4.31)	

[a] See ref 26a. [b] See ref 27.

tographic and optical information storage technologies.[30]

An attempted chemical reduction of TCAQ to $TCAQ^{2-}$ by sodium or potassium in DMF followed by the addition of aqueous Bu_4NBr to isolate $(Bu_4N)_2TCAQ$ resulted in the isolation of anthraquinone. Electrolytically generated $TCAQ^{2-}$ in DMF, upon exposure to oxygen, was not converted to anthraquinone as evidenced by the cyclic voltammogram of the oxygenated (and then deoxygenated) $TCAQ^{2-}$ solutions.

Initial experiments to form copper–TCAQ films on copper metal by the reaction of copper with $TCAQ/CH_3CN$ solutions have not been successful, perhaps not a surprising observation considering the electrochemical results. However, such films can also be formed thermally, and we are currently investigating these possibilities.

Experimental Section

1, 11,12-Dicyano-9,10-anthraquinodimethane (5). Bromine (2.56 mL, 7.99 g, 50 mmol) was added to a suspension of 9,10-bis(cyanomethyl)-anthracene (5.21 g, 20 mmol) in 1,2-dichloroethane (300 mL). The mixture was gently refluxed for 1 h under a blanket of argon when a red, homogeneous solution resulted. It was then chilled in the freezer. A white solid that crystallized was collected and washed with cold 1,2-dichloroethane until the washings were colorless. The filtrate was reduced to half the volume and chilled to obtain another batch of the product: total yield 3.68 g (72%); mp 290–292 °C dec. Analytical sample was obtained as a white fluffy solid by recrystallization from benzene (Norit): mp 293–293.5 °C dec; NMR (CDCl$_3$) δ 6.01 and 5.99 (2 s, 2 H), 7.5–7.8 (m, 6 H), 8.3–8.5 (m, 2 H); IR (KBr pellet) 3040, 2200, 1580, 1560, 1475, 1450, 1370, 1310, 1290, 1268, 1170, 960, 880, 825, 770, 750, 740, 640 cm^{-1}; mass spectrum, m/e (rel intensity) 254 (100, M$^+$). Anal.

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Calcd for $C_{18}H_{10}N_2$: C, 85.02; H, 3.96; N, 11.01. Found: C, 85.10; H, 4.05; N, 11.01.

2. 9-(Dicyanomethyl)-10-cyanomethylanthracene (6). A mixture of compound **5** (2 g, 7.87 mmol), sodium cyanide (6 g, 0.12 mol), dioxane (140 mL), and 95% ethanol (60 mL) was kept under reflux in an argon atmosphere for 24 h. The dark red mixture was then cooled and poured onto 200 g of ice containing 26 mL of concentrated HCl (caution: HCN evolution), and the resulting mixture was stirred for 1 h. It was then extracted with methylene chloride (3 × 100 mL) and the organic extract was washed with water, dried (MgSO₄), and concentrated to dryness in vacuo to obtain a 2.22 g of crude **6** (100%). Recrystallization from 1:1 v/v methylene chloride–hexanes mixture with Norit treatment gave pure **6**: 1.127 g (51%); mp 187–188 °C; NMR (CDCl₃) δ 4.69 (s, 2 H), 6.43 (s, 1 H, D₂O exchangeable), 7.7–7.9 (m, 4 H), 8.25–8.5 (m, 4 H); IR (KBr pellet) 3420, 2938, 2256, 2240, 1535, 1455, 1435, 1360, 1010, 930, 894, 840, 772, 760, 707, 670, 625, 600 cm⁻¹; mass spectrum, *m/e* (rel intensity) 281 (13, M⁺), 241 (100, M⁺ − C₂H₂N). Anal. Calcd for $C_{19}H_{11}N_3$: C, 81.12; H, 3.94; N, 14.94. Found: C, 80.32; H, 4.07; N, 14.47.

3. 11,11,12-Tricyano-9,10-anthraquinodimethane (7). Bromine (0.113 mL, 0.352 g, 2.2 mmol) was added to a partly homogeneous solution of compound **6** (0.562 g, 2 mmol) in 1,2-dichloroethane (125 mL), and the mixture was kept under gentle reflux in an atmosphere of argon for 1 h. The red homogeneous solution was cooled, and the solvent was removed in vacuo. The residue was recrystallized from 1:2 v/v methylene chloride–hexanes mixture with Norit treatment to obtain a yellow solid: 0.44 g (79%); mp 235–237 °C dec; NMR (CDCl₃) δ 6.06 (s, 1 H), 7.4–7.8 (m, 5 H), 8.0–8.5 (m, 3 H); IR (KBr pellet) 3060, 2225, 2217, 1570, 1545, 1530, 1470, 1445, 1360, 1335, 1270, 1190, 1170, 1110, 830, 780, 760, 750, 690, 670 cm⁻¹; mass spectrum, *m/e* (rel intensity) 279 (100, M⁺), 252 (13, M⁺ − HCN).

4. Adduct 9. A mixture of the tricyanoquinodimethane **7** (0.2 g, 0.717 mmol) and sodium cyanide (0.5 g, 10 mmol) in 95% ethanol (30 mL) was stirred at room temperature for 1 h. The resultant orange solution was poured onto 50 g of ice and 50 mL of 3% HCl (caution: HCN evolution). The resulting mixture was stirred for 1 h, and the precipitated solid was collected, washed with water, and vacuum dried: 0.22 g (100%); mp (1:1 benzene/hexanes) 198–199 °C dec; NMR (CDCl₃) δ 3.84 (s, 1 H, D₂O exchangeable), 6.02 (s, 1 H), 7.6–7.8 (m, 5 H), 8.0–8.2 (m, 2 H), 8.3–8.45 (m, 1 H); IR (KBr pellet) 3450, 3100, 3080, 3045, 2900, 2220, 1620, 1595, 1570, 1475, 1450, 1360, 1310, 1290, 1255, 1170, 1150, 1125, 1100, 1050, 1035, 965, 955, 920, 905, 890, 875, 860, 830, 775, 760, 750, 737, 725, 700, 680, 650, 630, 585, 565, 520, 500 cm⁻¹; electron impact mass spectrum, *m/e* (rel intensity) 279 (100, M⁺−HCN), 241 (38, M⁺−C₃HN₂); chemical ionization (CH₄) mass spectrum, *m/e* (rel intensity) 307 (17, M⁺ + 1), 280 (21.5), 279 (99), 278 (11). Anal. Calcd for $C_{20}H_{10}N_4$: C, 78.42; H, 3.29; N, 18.29. Found: C, 77.77; H, 3.75; N, 17.90. The above reaction with DMF as the solvent (room temperature, 24 h) also gave the same product in 64% yield (after re-crystallization).

5. Adducts 11 and 12. A mixture of the tricyanoquinodimethane **7** (2 g, 7.17 mmol) and sodium cyanide (4 g, 80 mmol) in dry DMF (75 mL) was stirred under argon at 100 °C for 5 h. The resultant deep pink mixture was poured onto 300 g of ice and 40 mL of 37% HCl (caution: HCN evolution). This was stirred for 1 h, and the precipitated solid was collected, washed with water, and vacuum dried. IR (KBr) of this crude product shows two bands at 2260 and 2225 cm⁻¹ in the cyanide stretch region, suggesting it to be a mixture of **11** and **12**. Fairly pure **11** and pure **12** can be obtained as follows. The crude product was Soxhlet extracted with CHCl₃ in an argon atmosphere for 2 days. The fraction that remains in the thimble was fairly pure **11**. The CHCl₃ extract consisted of mainly **12** and was purified by two recrystallizations from 1:1 v/v CHCl₃–hexanes.

Adduct 11:[32] mp 230–232 °C dec with darkening at ca. 200 °C; IR (KBr pellet) 3100, 3060, 2955, 2260, 1960, 1530, 1452, 1265, 1355,

1332, 1290, 1268, 1210, 1190, 1170, 1050, 1030, 1025, 1015, 988, 940, 915, 888, 880, 842, 760, 740, 662, 650, 605, 465, 452, 402, 362 cm⁻¹.

Adduct 12: mp 222–223 °C; ¹H NMR (CDCl₃) δ 8.22–8.17 (m, 2 H), 7.68–7.61 (m, 6 H), 4.58 (d, 1 H, *J* = 6.9 Hz, reduces to singlet upon D₂O exchange), 3.90 (d, 1 H, *J* = 7.0 Hz, D₂O exchangeable); ¹³C NMR (CDCl₃) δ 161.234 (d, C-9, *J* = 2.4 Hz), 132.57, 131.739, 129.694, 129.560, 127.988 (aromatic), 113.532 (s, NC-C-11), 110.534 (d × d, NC-C-12, *J* = 11.6, 4.9 Hz), 82.627 (s, C-11), 46.787 (d × m, C-10, *J* = 141 Hz), 32.027 (d × d, C-12, *J* = 145, 5.5 Hz); IR (KBr pellet) 3064, 2890, 2225, 1590, 1550, 1480, 1460, 1450, 1335, 1285, 1270, 1205, 1190, 1180, 1170, 788, 768, 742, 710, 698, 640, 635, 475 cm⁻¹; UV (CH₂Cl₂) 317 nm (ε 21 378), 246 (6750), 241 (7312), 234 (6609). Electron impact mass spectrum, *m/e* (rel intensity) 242 (37, M⁺ − C₃N₂), 241 (16, M⁺ − C₃HN₂), 240 (1, M⁺ − C₃H₂N₂), 120 (100, M²⁺ − C₃H₂N₂), 215 (17, M⁺ − C₃N₂ − HCN), 214 (60, M⁺ − C₃HN₂ − HCN), 213 (20, M⁺ − C₃H₂N₂ − HCN), 188 (34, M⁺ − C₃N₂ − 2HCN), 187 (41, M⁺ − C₃H₂N₂ − 2HCN), 186 (14, M⁺ − C₃H₂N₂ − 2HCN). Anal. Calcd for $C_{20}H_{10}N_4$: C, 78.42; H, 3.29; N, 18.29. Found: C, 78.24; H, 3.17; N, 18.26.

6. TCAQ (1). This compound can be obtained starting from either adduct **11** or **12** by an identical procedure. Bromine (1 mL) was added to a mixture of adduct **11** (0.22 g, 0.6 mmol) and triethylamine (0.5 mL) in dry acetonitrile (25 mL) under argon at room temperature. Deep pink color rapidly changed to orange, and the mixture was stirred for 30 min at room temperature. Acetonitrile was then removed on a rotavapor and the residue was passed through a column of silica gel with CH₂Cl₂ as the eluant to obtain 0.168 (92%) of TCAQ as yellow, crystalline solid; melting point data for DSC show no melting behavior (endotherm) but an exotherm at 367 °C (lit.[10e] mp >350 °C). ¹H NMR (CDCl₃) δ 8.32–8.20 (m, 4 H), 7.79–7.68 (m, 4 H); ¹³C NMR (CDCl₃) δ 159.997 (s, C-9, 10), 132.383 (d × d, C-1,4,5,8, *J* = 165, 7.4 Hz), 130.077 (s, C-4a,8a,9a,10a), 127.516 (br d, C-2,3,6,7, *J* = 165 Hz), 112.901 (s, CN), 83.127 (s, C-11,12); IR (KBr pellet) 2227.5, 1585, 1550, 1540, 1520, 1508, 1332, 1280, 1202, 1182, 782, 770, 740, 710, 692, 672, 630, 585, 475 cm⁻¹; electron impact mass spectrum, *m/e* (rel intensity) 304 (100, M⁺), 277 (25, M⁺ − HCN), 250 (17, M⁺ − 2HCN), 223 (10, M⁺ − 3HCN); chemical ionization (CH₄) mass spectrum, *m/e* (rel intensity) 333 (19, M⁺ + C₂H₅), 305 (100, M⁺ + 1), 280 (15, M⁺ + 1 − HCN). Anal. Calcd for $C_{20}H_8N_4$: C, 78.94; H, 2.65; N, 18.41. Found: C, 78.74; H, 2.64; N, 18.15.

7. Compound 13. To a solution of TCAQ (0.5 g, 1.65 mmol) and malononitrile (2.10 g, 31.8 mmol) in DMF (20 mL) was added NaH (60% in oil, 1 g, 25 mmol). Immediate dark blue coloration was seen, and the mixture was stirred at room temperature for 1 h. It was then poured onto 200 mL of water containing 3 g of tetrabutylammonium bromide. The dark blue precipitate was collected and washed with hexanes. It was recrystallized from ethanol–water to obtain 0.12 g (13%) of dark blue crystals of **13**: mp 170–171 °C; NMR (CDCl₃) δ 8.4–7.2 (several m, 8 H) 3.22–2.98 (t, 8 H), 1.69–1.15 (m, 16 H), 0.97 (t, 12 H); IR (KBr pellet) 2860, 2840, 2775, 2212, 2178, 2145, 1590, 1568, 1500, 1460, 1350, 1330, 1300, 1290, 1190, 1162, 785, 700, 690, 625 cm⁻¹; UV (CH₂Cl₂) 615 nm (ε 15 230), 421 (8833), 327 (13 707), 300 (10 965), 272 (21 017), 263 (21 321), 253 (24 824), 233 (20 408). Anal. Calcd for $C_{38}H_{44}N_6$: C, 78.05; H, 7.58; N, 14.27. Found: C, 78.38; H, 7.51; N, 13.55, 13.47.

Registry No. 1, 70359-39-6; 1²⁻, 93645-44-4; 1⁻·, 93645-45-5; 1³⁻·, 93683-30-8; 1⁴⁻, 93645-55-7; **2**, 33982-93-3; **3**, 84685-36-9; **4**, 62806-30-8; **5**, 93645-46-6; **6**, 93645-47-7; **7**, 93645-48-8; **8**, 85561-85-9; **9**, 93645-49-9; **10**, 93645-50-2; **11**, 93645-51-3; **12**, 93645-52-4; **13**, 93645-54-6; TCNQ, 1518-16-7; NCCH₂CN, 109-77-3; CH₂=CHC-H=CH₂, 106-99-0; benzoquinone, 106-51-4.

(32) Adduct **11** is insoluble in solvents like CDCl₃ and CD₂Cl₂, and therefore its NMR spectrum could not be obtained. In relatively polar CD₃CN or Me₂SO-*d₆*, it slowly decomposes to adduct **12** as evidenced by NMR. Electron impact and chemical ionization mass spectra do not show M⁺ but fragments 306 (5.6, M⁺ − HCN) and 241 (100, M⁺ − HCN − C₃HN₂).