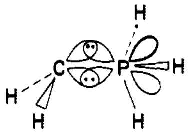
suggest that there is significant back-bonding from the carbon to the heteroatom for P and S leading to partial double-bond character. For the phosphonium ylide a reasonable amount of double-bond character is expected, with less double-bond character expected for the sulfonium ylide. This is consistent with the decrease in bond lengths over normal C–P and C–S single bonds observed for the ylides.[2] The bonding in the phosphonium ylide



is surprising in light of the low rotation barrier. However, the significant contribution of the d orbitals on P to the bonding leading to a hypervalent P causes this to occur. The CH_2 can approximately freely rotate about the P and as it rotates, builds in character from a different d orbital. It is the general angular form of the d orbitals that are oriented toward the two lobes of the CH_2 group that lead to the low rotation barrier. The results of Mitchell et al.[7b] suggest that $CH_2^-SH_2^+$ is best described as a $CH_2(^1A_1)$ solvated by H_2S. However, our results for the optimum form of $CH_2^-SH_2^+$ show the presence of a partial double bond, and even for the unstable rotamer there is still an S–C σ bond. The bonding in $CH_2^-SH_2^+$ is thus significantly different from that on $CH_2^-OH_2^+$.

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Registry No. Methylamine, 74-89-5; methanol, 67-56-1; methylphosphine, 593-54-4; methanethiol, 74-93-1.

Radical Anions and Radical Trianions of Tetracyanoarenoquinodimethanes. An ESR and ENDOR Study

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Abstract: The ESR spectra of the radical anions of 7,7,8,8-tetracyano-2,3,5,6-tetrafluorobenzo-1,4-quinodimethane (**2**), 9,9,10,10-tetracyanonaphtho-1,4-quinodimethane (**3**), 9,9,10,10-tetracyanonaphtho-2,6-quinodimethane (**4**), 7,7,7′,7′-tetracyanodipheno-4,4′-quinodimethane (**5**), 11,11,12,12-tetracyano-4,5,9,10-tetrahydropyreno-2,7-quinodimethane (**6**), and 11,11,12,12-tetracyanopyreno-2,7-quinodimethane (**7**) have been reexamined under higher resolution. Their analysis has been assisted by the ENDOR technique. Reliable hyperfine data, thus far missing in the literature, have been obtained. The radical trianions of **3**, **4**, and **7**, prepared by both chemical and electrolytic methods, have also been characterized by ESR spectroscopy. The π spin and/or π charge distribution in the radical anions, the dianions, and the radical trianions are discussed in terms of simple MO models. The electronic structure and the ease of formation of the radical trianions are related to those of the radical anions of the corresponding dialkyl-substituted aromatic hydrocarbons.

The recent search for organic metals and superconductors[2] has provided the impetus for the syntheses of numerous organic electron donors and acceptors. This research was initiated by the Du Pont group's observations of electrical conductivity in organic salts of 7,7,8,8-tetracyanobenzo-1,4-quinodimethane (tetracyanoquinodimethane = TCNQ).[3] Donor–acceptor complexes, such as tetrathiofulvalene–tetracyanoquinodimethane (TTF–TCNQ), display metal-like conductivity ($\sim 10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$);[2] on the other hand, some metal salts of TCNQ, e.g., Cu and Ag, exhibit electrical or optical field induced switching phenomena on a nanosecond time scale.[4]

One particular aspect of the syntheses of tetracyanoarenoquinodimethanes other than TCNQ was to extend the π-system of the acceptor. Such an increase, which reduces the intramolecular Coulomb interactions in the radical anion of the acceptor, was thought to be of great importance for attaining high electrical conductivity. In addition to TCNQ (**1**),[3] the following tetracyanoarenoquinodimethanes have been synthesized in the last two decades: 7,7,8,8-tetracyano-2,3,5,6-tetrafluorobenzo-1,4-quinodimethane ($TCNQF_4$) (**2**),[5] 9,9,10,10-tetracyanonaphtho-1,4-quinodimethane (benzo-TCNQ) (**3**),[6] 9,9,10,10-tetracyanonaphtho-2,6-quinodimethane (TNAP) (**4**),[7] 7,7,7′,7′-tetracyanodipheno-4,4′-quinodimethane (TCNDQ) (**5**),[8,9] 11,11,12,12-

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[1] (a) Universität Basel. (b) The Johns Hopkins University.

[2] See, e.g.: Garito, A. F.; Heeger, A. J. *Acc. Chem. Res.* **1974**, *7*, 232. Perlstein, J. H. *Angew. Chem.* **1977**, *89*, 534; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519. Cowan, D.; Shu, P.; Hu, C.; Krug, W.; Carruthers, T.; Poehler, T.; Bloch, A. In "Chemistry and Physics of One-Dimensional Metals"; Keller, H. J., Ed.; Plenum Press: New York, 1977; Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79. Cowan, D. O.; Kini, A.; Chiang, L. Y.; Lerstrup, K.; Talham, D. R.; Poehler, T. O.; Bloch, A. N. *Mol. Cryst. Liq. Cryst.* **1982**, *86*, 1.

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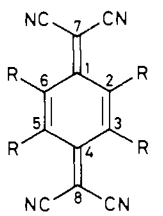
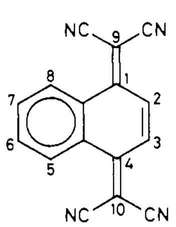


1, R=H
2, R=F



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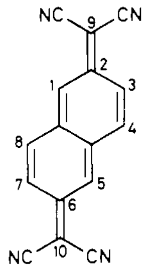

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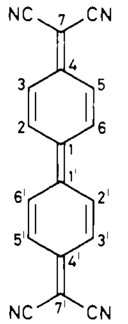

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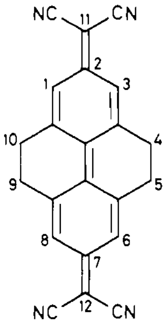

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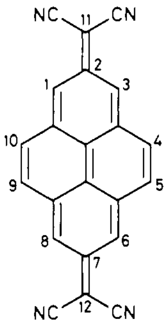

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tetracyano-4,5,9,10-tetrahydropyreno-2,7-quinodimethane (TCNTP or TCNTHP) (**6**),[9,10] and 11,11,12,12-tetracyanopyreno-2,7-quinodimethane (TCNP) (**7**).[11]

ESR spectra were reported for all radical anions $\mathbf{1}^{-}\cdot$,[12] $\mathbf{2}^{-}\cdot$,[13] $\mathbf{3}^{-}\cdot$,[14] $\mathbf{4}^{-}\cdot$,[14] $\mathbf{5}^{-}\cdot$,[8,9] $\mathbf{6}^{-}\cdot$,[9] and $\mathbf{7}^{-}\cdot$,[11b] but except the simplest one, due to $\mathbf{1}^{-}\cdot$, these spectra were either not analyzed[9,11b] or yielded, at least partially, incorrect hyperfine data.[8,13,14] One of the reasons for this unsatisfactory state of affairs is the large density of hyperfine lines that arises from several relatively small coupling constants of comparable magnitude. Consequently, as can be concluded from the spectra reproduced in the literature for $\mathbf{5}^{-}\cdot$,[8] $\mathbf{6}^{-}\cdot$,[9] and $\mathbf{7}^{-}\cdot$,[11b] the resolution was low[8,9] or completely absent.[11b]

In the present paper, we describe a reinvestigation of the ESR spectra of $\mathbf{2}^{-}\cdot$ to $\mathbf{7}^{-}\cdot$ under improved conditions. Owing to greatly increased resolution and use of the ENDOR technique, our hyperfine data stand on a firmer ground than those reported previously. Apart from the radical anions, the radical trianions $\mathbf{3}^{3-}\cdot$, $\mathbf{4}^{3-}\cdot$, and $\mathbf{7}^{3-}\cdot$ have been prepared and characterized by ESR spectroscopy.

Results

Scheme I summarizes the reactions by which tetracyanoarenoquinodimethane derivatives, dealt with in the present work, are interconverted. Herein X stands for compounds **1**–**7** and X-H_2 denotes their dihydro precursors, the arenodimalononitriles, in which each of the two exocyclic, cyano-substituted carbon atoms bears a hydrogen.

Radical Anions. According to Scheme I, the radical anions $X^{-}\cdot$ could be prepared either by one-electron reduction of the respective neutral tetracyanoarenoquinodimethanes X or by deprotonation of the dihydro precursors X-H_2 and a subsequent one-electron oxidation of the resulting dianions X^{2-}. The choice between the two alternative reaction paths was dictated by availability of the starting material, which was X for **1**, **2**, **3**, and **6** and X-H_2 for **4**, **5**, and **7**.

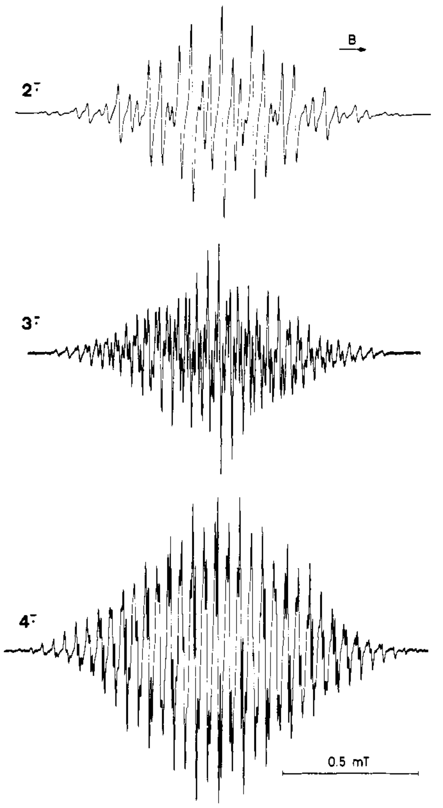
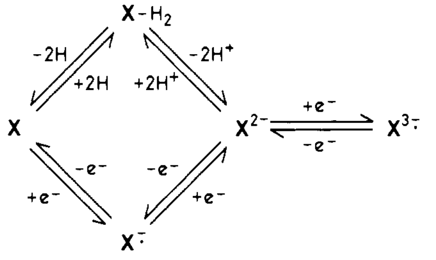


Figure 1. ESR spectra of the radical anions of 7,7,8,8-tetracyano-2,3,5,6-tetrafluorobenzo-1,4- (**2**), 9,9,10,10-tetracyanonaphtho-1,4- (**3**), and 9,9,10,10-tetracyanonaphtho-2,6-quinodimethane (**4**). Solvent, DME; counterion, Hg_2^{2+} or Hg^{2+} for $\mathbf{2}^{-}\cdot$ and K^+ for $\mathbf{3}^{-}\cdot$ and $\mathbf{4}^{-}\cdot$; temperature, 273 K.

Scheme I



Under the preparative conditions described in the Experimental Section, the radical anions $\mathbf{1}^{-}\cdot$ to $\mathbf{7}^{-}\cdot$ were persistent and could be studied by ESR spectroscopy in the temperature range 178–298 K. The spectra extend over a rather narrow field region of ca. 1.4 mT. High resolution was generally achieved, in particular at temperatures about 273 K (line widths ΔB_{pp} of 0.005–0.008 mT, except for $\mathbf{2}^{-}\cdot$ with ΔB_{pp} of 0.015 mT). Since well-resolved ESR spectra of $\mathbf{2}^{-}\cdot$ to $\mathbf{7}^{-}\cdot$ have so far been missing in the literature (cf. introduction), those obtained in the present work are reproduced for all six radical anions (Figures 1 and 2).

Analysis of the ESR hyperfine patterns was both facilitated and secured by ^{19}F ($\mathbf{2}^{-}\cdot$) and proton ENDOR spectra ($\mathbf{3}^{-}\cdot$ to $\mathbf{7}^{-}\cdot$) observed in the frequency range of 9–18 MHz (Figure 3). The correctness of the analysis was in all cases confirmed by a computer simulation of the ESR derivative curve.

Table I lists the hyperfine data for the radical anions $\mathbf{2}^{-}\cdot$ to $\mathbf{7}^{-}\cdot$; those for $\mathbf{1}^{-}\cdot$ have been included for the sake of completeness. These values, which refer to 1,2-dimethoxyethane (DME) as the solvent, are not very sensitive to changes in environment. Also, with the notable exception of $\mathbf{6}^{-}\cdot$ (see below), they depend only

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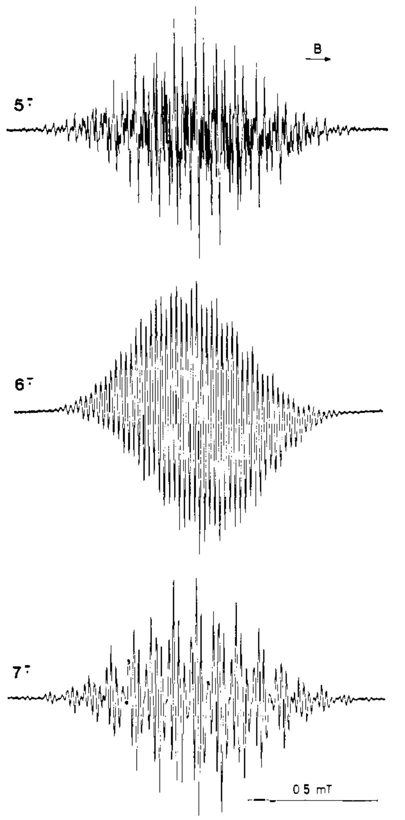

Figure 2. ESR spectra of the radical anions of 7,7,7′,7′-tetracyanodipheno-4,4′- (**5**), 11,11,12,12-tetracyano-4,5,9,10-tetrahydropyren-2,7- (**6**), and 11,11,12,12-tetracyanopyreno-2,7-quinodimethane (**7**). Solvent, DME; counterion, K^+; temperature, 273 K.

Table I. Coupling Constants (mT) for the Radical Anions of 7,7,8,8-Tetracyanobenzo-1,4- (**1**), 7,7,8,8-Tetracyano-2,3,5,6-tetrafluorobenzo-1,4- (**2**), 9,9,10,10-Tetracyanonaphtho-1,4- (**3**), 9,9,10,10-Tetracyanonaphtho-2,6- (**4**), 7,7,7′,7′-Tetracyanodipheno-4,4′- (**5**), 11,11,12,12-Tetracyano-4,5,9,10-tetrahydropyreno-2,7- (**6**), and 11,11,12,12-Tetracyanopyreno-2,7-quinodimethane (**7**)[a]

position	$1^{-\cdot}$	$2^{-\cdot}$
2, 3, 5, 6	0.142 (4 H)	0.153 (4 F)
CN	0.099 (4 N)	0.111 (4 N)

position	$3^{-\cdot}$	position	$4^{-\cdot}$
2, 3	0.182 (2 H)	1, 5	0.259 (2 H)
5, 8	0.040 (2 H)	3, 7	0.041 (2 H)
6, 7	0.040 (2 H)	4, 8	0.085 (2 H)
CN (exo)	0.111 (2 N)	CN (exo)	0.093 (2 N)
CN (endo)	0.078 (2 N)	CN (endo)	0.082 (2 N)

position	$5^{-\cdot}$
3, 5, 3′, 5′	0.152 (4 H)
2, 6, 2′, 6′	0.033 (4 H)
CN	0.082 (4 N)

position	$6^{-\cdot}$	$7^{-\cdot}$
1, 3, 6, 8	0.137 (4 H)	0.154 (4 H)
4, 5, 9, 10	0.021 (8 H)[b]	0.018 (4 H)
CN	0.077 (4 N)	0.088 (4 N)

[a] Experimental error: ±0.001 mT. [b] At low temperatures, this set of eight methylene protons separates into two sets of four (cf. text).

slightly on temperature. Their assignments to sets of equivalent nuclei are straightforward for $\mathbf{1}^{-\cdot}$, $\mathbf{2}^{-\cdot}$, and $\mathbf{6}^{-\cdot}$. Furthermore, it is reasonable to assign the proton coupling constants for $\mathbf{5}^{-\cdot}$ by analogy with those for $\mathbf{6}^{-\cdot}$, since the latter radical anion is a bis-ethano-bridged derivative of the former. Some ambiguities exist only in the assignments of the hyperfine data for $\mathbf{3}^{-\cdot}$, $\mathbf{4}^{-\cdot}$, and $\mathbf{7}^{-\cdot}$. They could, in general, be removed by recurring to Hückel-type calculations refined by the McLachlan[15] procedure (see Discussion).

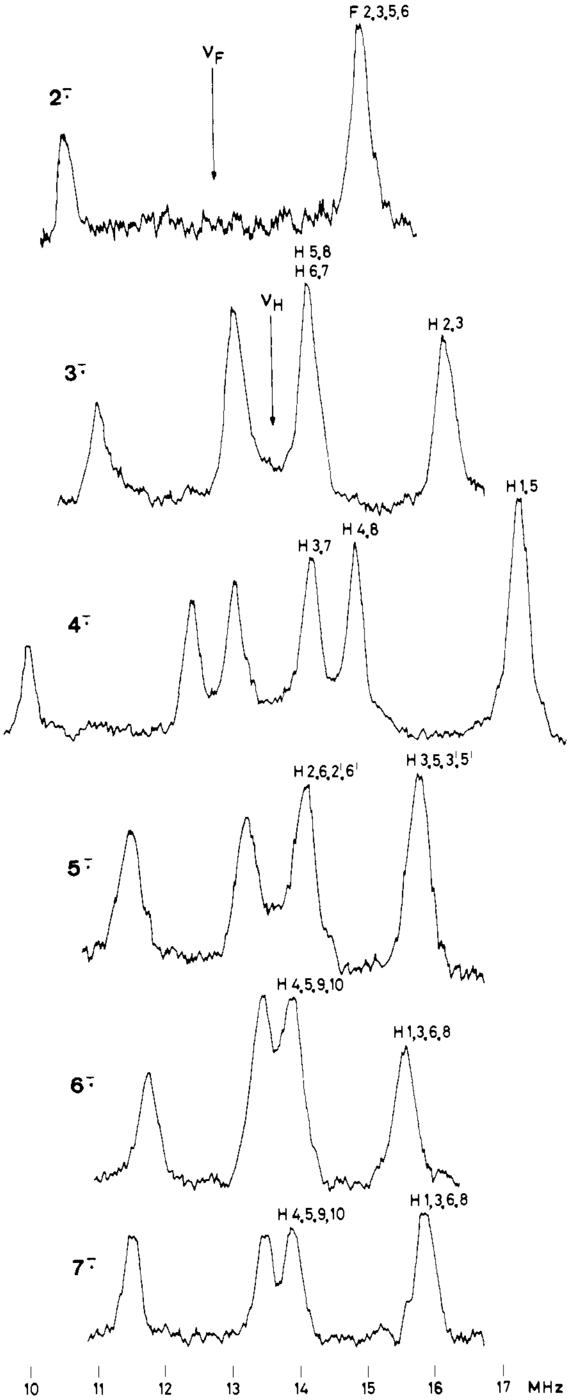

Figure 3. ^{19}F ENDOR spectrum of the radical anion of 7,7,8,8-tetracyano-2,3,5,6-tetrafluorobenzo-1,4-quinodimethane (**2**) and proton ENDOR spectra of the radical anions of 9,9,10,10-tetracyanonaphtho-1,4-(**3**), 9,9,10,10-tetracyanonaphtho-2,6- (**4**), 7,7,7′,7′-tetracyanodipheno-4,4′- (**5**), 11,11,12,12-tetracyano-4,5,9,10-tetrahydropyreno-2,7-(**6**), and 11,11,12,12-tetracyanopyreno-2,7-quinodimethane (**7**). Solvent and counterion as for the ESR spectra in Figures 1 and 2; temperature, 253 K for $\mathbf{2}^{-\cdot}$, 208 K for $\mathbf{3}^{-\cdot}$ and $\mathbf{4}^{-\cdot}$, and 273 K for $\mathbf{5}^{-\cdot}$, $\mathbf{6}^{-\cdot}$, and $\mathbf{7}^{-\cdot}$. ν_F and ν_H are the frequencies of the free ^{19}F nucleus and the proton, respectively.

The g factors of radical anions $\mathbf{1}^{-\cdot}$ and $\mathbf{3}^{-\cdot}$ to $\mathbf{7}^{-\cdot}$ are all 2.0027 ± 0.0001, while that of $\mathbf{2}^{-\cdot}$ is 2.0029 ± 0.0001.

The temperature dependence of the ESR spectrum of $\mathbf{6}^{-\cdot}$ is clearly due to the inversion of the 4,5- and 9,10-ethano chains.

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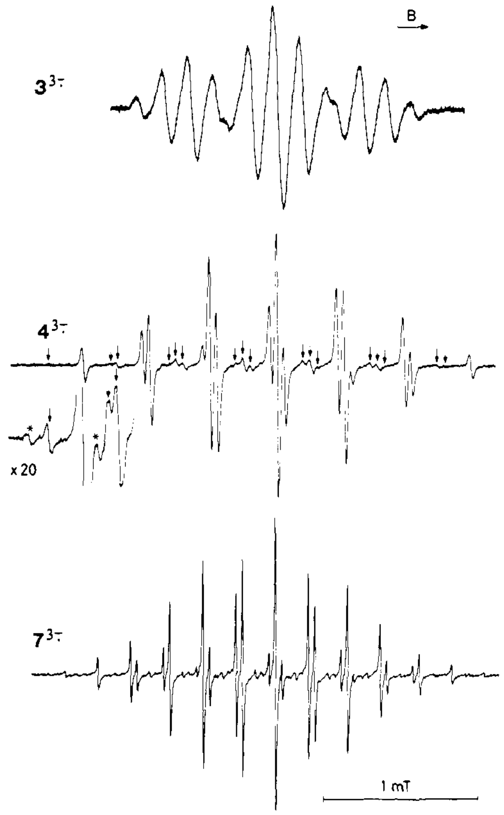

Figure 4. ESR spectra of the radical trianions of 9,9,10,10-tetracyanonaphtho-1,4- (**3**), 9,9,10,10-tetracyanonaphtho-2,6- (**4**), and 11,11,12,12-tetracyanopyreno-2,7-quinodimethane (**7**). Solvent, DME; counterion, K^+ for $\mathbf{3}^{3-\cdot}$ and $\mathbf{4}^{3-\cdot}$ and n-Bu_4N^+ for $\mathbf{7}^{3-\cdot}$; temperature, 213 K for $\mathbf{3}^{3-\cdot}$, 253 K for $\mathbf{4}^{3-\cdot}$, and 233 K for $\mathbf{7}^{3-\cdot}$. In the spectrum of $\mathbf{4}^{3-\cdot}$, the low-field part is reproduced under amplification, which renders the ^{13}C satellite lines (marked by arrows or asterisks) more evident.

Above 273 K, the inversion was fast on the hyperfine time scale ($k > 10^7\ s^{-1}$) so that the two protons of each methylene group were equivalent (eight-proton coupling constant of 0.021 mT; cf. Table I). Below 193 K, the inversion became sufficiently slow to render the two protons nonequivalent (two four-proton coupling constants of 0.027 and 0.016 mT). At intermediate temperatures, alternating line widths[16,17a] were apparent, this effect being most pronounced in the range 213–233 K. The Arrhenius activation energy for the inversion was estimated as 28 ± 5 kJ/mol, somewhat lower than the value (36.4 ± 2.5 kJ/mol) reported for the analogous inversion in the radical anion of 4,5,9,10-tetrahydropyrene.[18]

Table II. Coupling Constants (mT) for the Radical Trianions of 9,9,10,10-Tetracyanonaphtho-1,4- (3), 9,9,10,10-Tetracyanonaphtho-2,6- (4), and 11,11,12,12-Tetracyanopyreno-2,7-quinodimethane (7),[a] Along with the Corresponding Values for the Radical Anions of 1,4- (3A) and 2,6-Dimethylnaphthalene (4A) and 2,7-Dimethylpyrene (7A)

position	$\mathbf{3}^{3-\cdot\,b}$	$\mathbf{3}^{3-\cdot\,c}$	$\mathbf{3A}^{-\cdot}$
2, 3	0.163 (2 H)	0.162 (2 H)	0.163 (2 H)
5, 8	0.555 (2 H)	0.512 (2 H)	0.517 (2 H)
6, 7	0.163 (2 H)	0.162 (2 H)	0.179 (2 H)
CN (endo)	<0.030 (2 N)	<0.030 (2 N)	
CN (exo)	<0.030 (2 N)	<0.030 (2 N)	

position	$\mathbf{4}^{3-\cdot\,b}$	$\mathbf{4}^{3-\cdot\,c}$	$\mathbf{4A}^{-\cdot}$
1, 5	0.432 (2 H)	0.424 (2 H)	0.465 (2 H)
3, 7	0.390 (2 H)	0.388 (2 H)	0.268 (2 H)
4, 8	0.432 (2 H)	0.424 (2 H)	0.479 (2 H)
CN (endo)	<0.015 (2 N)	<0.015 (2 N)	
CN (exo)	<0.015 (2 N)	<0.015 (2 N)	

position	$\mathbf{7}^{3-\cdot\,b}$	$\mathbf{7}^{3-\cdot\,c}$	$\mathbf{7A}^{-\cdot}$
1, 3, 6, 8	0.487 (4 H)	0.466 (4 H)	0.471 (4 H)
4, 5, 9, 10	0.221 (4 H)	0.212 (4 H)	0.210 (4 H)
CN	<0.010 (4 N)	<0.010 (4 N)	

[a] Experimental error: ±0.008 ($\mathbf{3}^{3-\cdot}$), ±0.004 ($\mathbf{4}^{3-\cdot}$), or ±0.002 mT ($\mathbf{7}^{3-\cdot}$). [b] Counterion, K^+. [c] Counterion, n-Bu_4N^+.

Radical Trianions. The obvious way to prepare the radical trianions $X^{3-\cdot}$ of the tetracyanoarenoquinodimethanes (Scheme I) was a one-electron reduction of the corresponding dianions X^{2-}, obtained either by a two-electron reduction of the neutral compounds X (X = **1**–**3**, **6**) or by deprotonation of the dihydro precursors X-H_2 (X = **4**, **5**, and **7**). The reactions leading to $X^{3-\cdot}$, which are described in the Experimental Section, were monitored by ESR spectroscopy. No signals attributable to $\mathbf{1}^{3-\cdot}$, $\mathbf{2}^{3-\cdot}$, $\mathbf{5}^{3-\cdot}$, and $\mathbf{6}^{3-\cdot}$ could be detected, but well-defined spectra of novel paramagnetic species were observed upon exhaustive chemical and electrolytic reduction of the dianions $\mathbf{3}^{2-}$, $\mathbf{4}^{2-}$, and $\mathbf{7}^{2-}$. With electrolysis, appearance voltages V_a, which can be related to the third half-wave reduction potentials, $E_{1/2}^{(3)}$, of **3**, **4**, and **7**[19] (see Discussion), were determined. The formation was reversible, as proved by experiments, in which the new species were reconverted to the respective dianions and radical anions (cf. Experimental Section). This reversibility and the excellent accord between the MO models presented in the Discussion and the experimental findings, such as the ease of formation and hyperfine data, leave no doubt that the paramagnetic species in question are indeed the radical trianions $\mathbf{3}^{3-\cdot}$, $\mathbf{4}^{3-\cdot}$, and $\mathbf{7}^{3-\cdot}$.

The persistence of $\mathbf{3}^{3-\cdot}$, $\mathbf{4}^{3-\cdot}$, and $\mathbf{7}^{3-\cdot}$ was poorer than that of the corresponding radical anions, and their ESR spectra were taken in a lower temperature range of 178–253 K. These spectra (Figure 4) extend over a field region of 1.8–2.8 mT, which is comparable to that found for the radical anions of aromatic hydrocarbons. The observed hyperfine patterns arise exclusively from protons and in no case were splittings from ^{14}N nuclei resolved. A striking feature in the spectrum of $\mathbf{3}^{3-\cdot}$ is the large width of the hyperfine components ($\Delta B_{pp} \sim 0.06$ mT), whereas the line widths exhibited by the spectra of $\mathbf{4}^{3-\cdot}$ ($\sim$0.025 mT) and $\mathbf{7}^{3-\cdot}$ ($\sim$0.015 mT) do not unduly exceed those usually encountered with aromatic radical anions. The line broadening is presumably both homogeneous and inhomogeneous in origin. Homogeneous broadening, which must be particularly effective for $\mathbf{3}^{3-\cdot}$, arises most likely from an electron exchange between the radical trianions and the respective dianions still present in the solutions, while inhomogeneous broadening is caused by the unresolved ^{14}N hyperfine splittings. (These are predicted by MO models to increase in the same order, $\mathbf{7}^{3-\cdot} < \mathbf{4}^{3-\cdot} \ll \mathbf{3}^{3-\cdot}$, as the line widths.)

Attempts to observe the ENDOR spectra of $\mathbf{3}^{3-\cdot}$, $\mathbf{4}^{3-\cdot}$, and $\mathbf{7}^{3-\cdot}$ were unsuccessful. This failure is presumably due to relatively small concentrations of these radical trianions in solution as well as to the above-mentioned electron exchange with the respective dianions.[20] The lack of ENDOR data presents, however, no handicap in the analysis of the ESR spectra in view of the apparent simplicity of their hyperfine patterns (Figure 4). The pertinent coupling constants do not strongly depend on temperature but are rather sensitive to the nature of the three counterions. Consequently, Table II gives these values for the radical trianions $\mathbf{3}^{3-\cdot}$, $\mathbf{4}^{3-\cdot}$, and $\mathbf{7}^{3-\cdot}$ with two different counterions (K^+ and n-Bu_4N^+; solvent DME). The assignments of the coupling constants to sets of equivalent protons is based on MO models and on analogy with hyperfine data for reference species, such as the radical anions

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(16) Fraenkel, G. K. *J. Phys. Chem.* **1967**, *71*, 139. Hudson, A.; Luckhurst, G. R. *Chem. Rev.* **1969**, *69*, 191.

(17) See also: Gerson, F. "High Resolution ESR Spectroscopy"; Verlag Chemie and Wiley: Weinheim and New York, 1970; (a) Appendix A.2.3; (b) Appendix A.1.3.

(18) Iwaizumi, M.; Isobe, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1547. The cited value for the Arrhenius activation energy is a revised one, reported in: Iwaizumi, M.; Matsuzaki, T.; Isobe, T. *Ibid.* **1972**, *45*, 1030.

(19) Gerson, F.; Ohya-Nishiguchi, H.; Wydler, C. *Angew. Chem.* **1976**, *88*, 617; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 552.

(20) Such an exchange can decrease the ENDOR enhancement. See, e.g.: Freed, J. H. *J. Phys. Chem.* **1967**, *71*, 38.

of 1,4-dimethylnaphthalene (**3A**),[21] 2,6-dimethylnaphthalene (**4A**),[21] and 2,7-dimethylpyrene (**7A**)[22] (see Discussion). The proton coupling constants for $\mathbf{3A}^{-\cdot}$, $\mathbf{4A}^{-\cdot}$, and $\mathbf{7A}^{-\cdot}$ have also been included in Table II.

The g factors of all three radical trianions, $\mathbf{3}^{3-\cdot}$, $\mathbf{4}^{3-\cdot}$, and $\mathbf{7}^{3-\cdot}$, are 2.0027 ± 0.0001.

Two additional findings in the ESR spectra of the radical trianions are noteworthy:

(1) The eminent satellite lines in the spectrum of $\mathbf{4}^{3-\cdot}$ (marked by arrows in Figure 4) stem from ^{13}C isotopes in natural abundance. Their relatively high intensity is accounted for by an accidental degeneracy of several ^{13}C and proton coupling constants, all having the value of 0.43 ± 0.01 mT. According to MO calculations, combined with the Karplus–Fraenkel[23] relationship, this value is tentatively assigned to the ^{13}C nuclei in three pairs of equivalent carbon sites: 3, 7; 4, 8; and 4a, 8a. Weaker satellite lines (marked by asterisks in Figure 4) were also detected at the peripheries of the same spectrum. The value of 0.68 ± 0.01 mT for the associated ^{13}C coupling constant suggests an assignment to nuclei in two equivalent carbon sites, 1 and 5.

(2) Careful examination of the ESR spectra of $\mathbf{3}^{3-\cdot}$, $\mathbf{4}^{3-\cdot}$, and $\mathbf{7}^{3-\cdot}$ reveals that the lines are broader on the high-field than on the low-field side; the effect is more pronounced, the lower the temperature and the higher the viscosity of the solution. Specific broadening of this kind, which depends on the inner product of g and hyperfine anisotropy tensors,[16,17b] has been frequently observed for lines associated with the coupling constants of nuclei such as ^{13}C,[24,25] ^{14}N,[17b,26,27] ^{31}P,[28] and ^{33}S,[25,29] but is difficult to detect for lines involving interaction with protons. The ESR spectra of $\mathbf{3}^{3-\cdot}$, $\mathbf{4}^{3-\cdot}$, and $\mathbf{7}^{3-\cdot}$, in which the resolved hyperfine patterns arise exclusively from protons, thus provide an example of this rare finding. A complete averaging of the hyperfine anisotropies in solution must be impeded by the low tumbling (long rotational correlation times) of the large dissolved species, which consist of the huge radical trianions more or less tightly paired with three positively charged counterions.

Discussion

MO Models. The energies and the LCAO coefficients of the lowest unoccupied (LUMO) and the next lowest unoccupied π orbital (NLUMO) have been computed in the frame of the Hückel model for the 7,7,8,8-tetracyanobenzo-1,4- (**1**), 9,9,10,10-tetracyanonaphtho-1,4- (**3**), 9,9,10,10-tetracyanonaphtho-2,6- (**4**), 7,7,7′,7′-tetracyanodipheno-4,4′- (**5**), and 11,11,12,12-tetracyanopyreno-2,7-quinodimethane (**7**). The π systems of the two remaining members in the series 7,7,8,8-tetracyano-2,3,5,6-tetrafluorobenzo-1,4- (**2**) and 11,11,12,12-tetracyano-4,5,9,10-tetrahydropyreno-2,7-quinodimethane (**6**), are here approximated by those of **1** and **5**, respectively. For the C(CN)$_2$ groups, the parameters $h_{\mathrm{N}} = 1.0$, $k_{\mathrm{C{\equiv}N}} = 2.0$, and $k_{\mathrm{C-CN}} = 0.9$ were used, as proposed previously.[30] Moderate variations of these parameters affect only slightly the LCAO coefficients of the two orbitals.

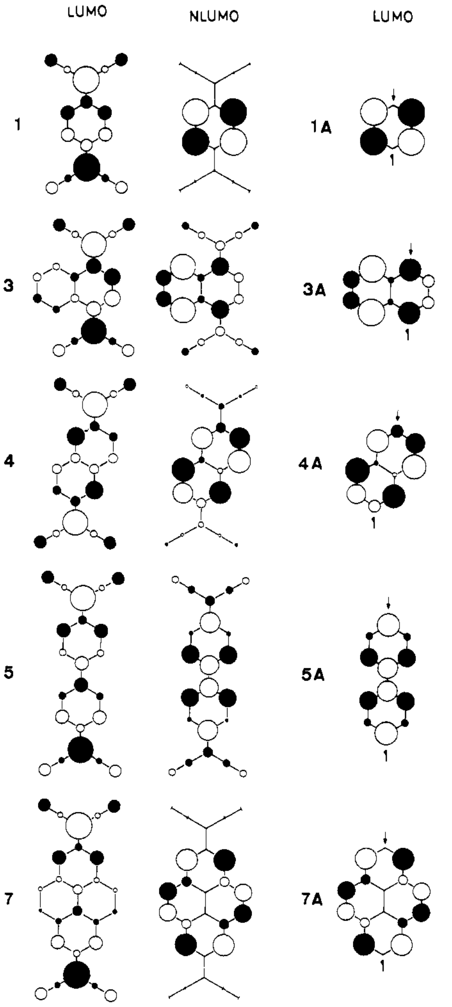

Figure 5. Left: Lowest unoccupied (LUMO) and the next lowest unoccupied orbitals (NLUMO) of 7,7,8,8-tetracyanobenzo-1,4- (**1**), 9,9,10,10-tetracyanonaphtho-1,4- (**3**), 9,9,10,10-tetracyanonaphtho-2,6- (**4**), 7,7,7′,7′-tetracyanodipheno-4,4′-(**5**), and 11,11,12,12-tetracyanopyreno-2,7-quinodimethane (**7**). Right: Lowest unoccupied orbitals (LUMO) of p-xylene (**1A**), 1,4- and 2,6-dimethylnaphthalene (**3A** and **4A**), 4,4′-bitolyl (**5A**), and 2,7-dimethylpyrene (**7A**). The areas of the circles are proportional to the squares of the LCAO coefficients. Blank and filled circles symbolize different signs of these coefficients which were calculated with the use of parameters $h_{\mathrm{N}} = 1.0$, $k_{\mathrm{C{\equiv}N}} = 2.0$, and $k_{\mathrm{C-CN}} = 0.9$ for the C(CN)$_2$ groups in **1**, **3**, **4**, **5**, and **7** (cf. text) and $h_{\mathrm{C(Me)}} = -0.3$ for the methyl-substituted centers (marked by arrows) in **1A**, **3A**, **4A**, **5A**, and **7A**.

The shapes of the LUMO's and the NLUMO's of **1**, **3**, **4**, **5**, and **7** (Figure 5), which are the singly occupied orbitals in the radical anions and the radical trianions, respectively, are faithfully reflected by the π spin distributions found experimentally for these paramagnetic species. Accordingly, the π spin populations, calculated by the McLachlan[15] procedure for single occupancies of the orbitals in question, correlate well with the observed proton coupling constants. This correlation substantiates the assignments made for these data in Tables I and II.

The MO models presented above do not account for the nonequivalence of the two vicinal cyano substituents in **3** and **4**. In fact, two different coupling constants, each for a pair of ^{14}N nuclei, were observed for $\mathbf{3}^{-\cdot}$ and $\mathbf{4}^{-\cdot}$ (Figure 1), the difference being much larger for the former (0.033 mT) than for the latter radical anion (0.011 mT). The assignments of these values (Table I) are justified below.

The nonequivalence of the two vicinal cyano substituents in **3** can be introduced in the frame of the Hückel approximation by

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(21) Gerson, F.; Weidmann, B.; Heilbronner, E. *Helv. Chim. Acta* **1964**, *47*, 1951.

(22) The hyperfine data for the radical anion of 2,7-dimethylpyrene (**7A**) have not yet been reported in the literature. Those given in Table II were determined from ESR spectra of $\mathbf{7A}^{-\cdot}$ taken in the present work. Compound **7A** was synthesized according to the procedures described in: Allinger, N. L.; Gordon, B. J.; Hu, Shin-En; Ford, R. A. *J. Org. Chem.* **1967**, *32*, 2272. Umemoto, T.; Kawashima, T.; Sakata, Yh.; Misumi, S. *Tetrahedron Lett.* **1975**, 1005. The radical anion was prepared by reduction of **7A** with potassium metal in DME. Analysis of its ESR spectrum yields the following coupling constants: 0.471 and 0.210 mT for the two sets of four equivalent ring protons in the positions 1,3,6,8 and 4,5,9,10 respectively, and 0.105 mT for the six equivalent protons of the two methyl substituents.

(23) Karplus, M.; Fraenkel, G. K. *J. Chem. Phys.* **1961**, *35*, 1312.

(24) See, e.g.: De Boer, E.; Mackor, E. L. *J. Chem. Phys.* **1963**, *38*, 1450.

(25) See also: Gerson, F.; Wydler, C.; Kluge, F. *J. Magn. Reson.* **1977**, *26*, 271.

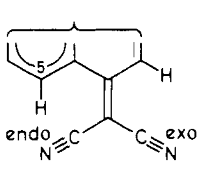
(26) See, e.g.: Freed, J. H.; Fraenkel, G. K. *J. Chem. Phys.* **1964**, *40*, 1815.

(27) See also: Gerson, F.; Plattner, G.; Yoshida, Z. *Mol. Phys.* **1971**, *21*, 1027.

(28) See, e.g.: Gerson, F.; Plattner, G.; Ashe, A. J., III; Maerkl, G. *Mol. Phys.* **1974**, *28*, 601.

(29) See, e.g.: Sullivan, P. D. *J. Am. Chem. Soc.* **1968**, *90*, 3618.

(30) Rieger, P. H.; Fraenkel, G. K. *J. Chem. Phys.* **1962**, *37*, 2795.



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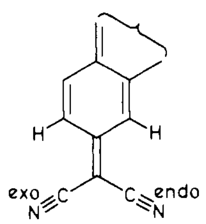

4

adopting a small auxiliary parameter ($h' \sim -0.1$) for the carbon centers of those substituents that are congested by the proximity of the hydrogen atoms in the peri positions (5 and 8) (endo substituents). This procedure is analogous to that previously applied to the sterically hindered carbon centers in the radical anions of *trans*-stilbene[31] and diphenylcyclopropenone.[32] In the case of **3**$^{-}\cdot$, the result suggests that the larger ^{14}N coupling constant should be assigned to the nuclei of the exo substituent. Although, in view of the essentially equal steric hindrance of the endo and exo cyano substituents, the same treatment is not appropriate for **4**, an analogous assignment was tentatively made for the slightly larger ^{14}N coupling constant for **4**$^{-}\cdot$.

Electronic Structure of the Reduced Tetracyanoarenoquinodimethanes. The simple MO models are not only useful in assigning the coupling constants but they also complement the experimental data in providing structural information on the reduced species.

The single occupancy of the LUMO in the radical anions **1**$^{-}\cdot$ to **7**$^{-}\cdot$ implies that the bulk of the π spin population is located on the cyano-substituted exocyclic carbon centers (Figure 5). (The rather narrow field region over which the spectra of **1**$^{-}\cdot$ to **7**$^{-}\cdot$ extend is a consequence of the absence of protons at these centers.) Such a spin distribution is not substantially altered by the enlargement of the π system along the series. Taking into account the partial π charge delocalization onto the cyano substituents, one may adequately describe the radical anions of the tetracyanoarenoquinodimethanes by a structural formula ($X^{-}\cdot$) in which each of the $C(CN)_2$ groups bears a half-electron spin or negative charge (Figure 6, top).

On going from the radical anions to the respective dianions, **1**$^{2-}$–**7**$^{2-}$, the LUMO becomes doubly occupied, so that the concomitant enhancement of the negative charge again affects mainly the two exocyclic carbon centers. Consequently, the relevant structural formula is that (X^{2-}) in which each of the $C(CN)_2$ groups accommodates one electron (Figure 6, middle).

The presence of the two highly charged $C(CN)_2$ groups in the dianions suggests that another additional electron should be preferentially taken up by the less charged residual arenediyl fragments. This naive argumentation is in perfect agreement with the shape of the NLUMO's (Figure 5), the singly occupied orbitals in the radical trianions. The triply charged tetracyanoarenoquinodimethanes can thus be represented by a structural formula ($X^{3-}\cdot$) that is tantamount to the radical anion of the respective aromatic hydrocarbon substituted by two negatively charged $C(CN)_2$ groups (Figure 6, bottom). Accordingly, one would expect that the LCAO coefficients of the NLUMO's of **1**, **3**, **4**, **5**, and **7** should be comparable to those of the LUMO's of dialkyl-substituted hydrocarbons such as *p*-xylene (**1A**), 1,4- and 2,6-dimethylnaphthalene (**3A** and **4A**), 4,4′-bitolyl (**5A**), and 2,7-dimethylpyrene (**7A**). Actually, the corresponding orbitals in the two series not only are similar in their shapes (Figure 5) but also, as is evident from Table III, are either equal or not greatly different in their energies (calculated in the Hückel approximation). Experimental verification of these MO predictions is provided by a comparison of the proton coupling constants for **3**$^{3-}\cdot$, **4**$^{3-}\cdot$, and **7**$^{3-}\cdot$ with the analogous values for **3A**$^{-}\cdot$, **4A**$^{-}\cdot$, and **7A**$^{-}\cdot$ (Table II), as well by a relationship between the ease of formation of the corresponding reduced species in the two series. While the similarity in the pertinent hyperfine data speaks for itself, an insight into the reduction potentials of the species in question demands a more careful consideration of the experimental findings. This will be aimed at in the next section.

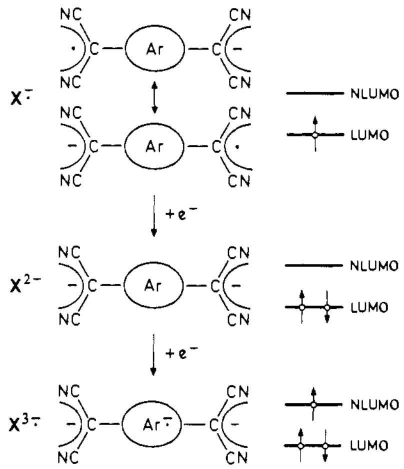

Figure 6. Left: Structural formulas for the radical anions ($X^{-}\cdot$), dianions (X^{2-}) and radical trianions ($X^{3-}\cdot$) of the tetracyanoarenoquinodimethanes **1**–**7**. Right: orbital occupancy in $X^{-}\cdot$, X^{2-}, and $X^{3-}\cdot$. Ar = arenediyl.

Table III. Energy Values (x), in β Units ($E = \alpha + x\beta$), of the Next Lowest Unoccupied Orbitals (NLUMO) and the Third Half-Wave Reduction Potentials $E_{1/2}^{(3)}$, in V vs. SCE, of 7,7,8,8-Tetracyanobenzo-1,4- (1), 9,9,10,10-Tetracyanonaphtho-1,4- (3), 9,9,10,10-Tetracyanonaphtho-2,6- (4), 7,7,7′,7′-Tetracyanodipheno-4,4- (5), and 11,11,12,12-Tetracyanopyreno-2,7-quinodimethane (7), and Corresponding Energy Values, x, of the Lowest Unoccupied Orbitals (LUMO) and the First Half-Wave Reduction Potentials, $E_{1/2}^{(1)}$, of *p*-Xylene (1A), 1,4- (**3A**) and 2,6-Dimethylnaphthalene (4A), 4,4′-Bitolyl (**5A**), and 2,7-Dimethylpyrene (**7A**)

	1	3	4	5	7
NLUMO[a]	−1.000	−0.772	−0.673	−0.854	−0.445
$E_{1/2}^{(3)}$ [b]	<−3.5	−3.23	−3.23	<−3.3	−2.60
	1A	3A	4A	5A	7A
LUMO[c]	−1.000	−0.714	−0.651	−0.799	−0.445
$E_{1/2}^{(1)}$ [d]	−3.34[e]	−2.47	−2.47	−2.72	−2.06

[a] Parameters: $h_N = 1.0$, $k_{C\equiv N} = 2.0$, $k_{C-CN} = 0.9$. [b] Cf. text. [c] Parameter: $h_{C(Me)} = -0.3$. [d] Except for 1A, all values were measured in the present work with 75% aqueous dioxane as the solvent. [e] Estimated by the relationship between the $E_{1/2}^{(1)}$ values and the appearance potentials, V_a.[19]

Formation of the Radical Trianions. The result of the MO calculations that the energies of the NLUMO's of **1**, **3**, **4**, **5**, and **7** are equal or comparable to those of the LUMO's of **1A**, **3A**, **4A**, **5A**, and **7A**, respectively (Table III), does not, of course, imply that the third half-wave reduction potentials, $E_{1/2}^{(3)}$, of the former should be close to the first half-wave reduction potentials, $E_{1/2}^{(1)}$, of the latter compounds. Since the reaction of the dianions **1**$^{2-}$, **3**$^{2-}$, **4**$^{2-}$, **5**$^{2-}$, and **7**$^{2-}$, yielding the corresponding radical trianions, involves the uptake of a third negative charge, it must require a considerably more negative potential than the conversion of the neutral hydrocarbons **1A**, **2A**, **4A**, **5A**, and **7A** to their radical anions. What can be expected, however, is that the half-wave potentials $E_{1/2}^{(3)}$ of the tetracyanoarenoquinodimethanes will become increasingly less negative in the same order (**1**, **5**, **3** $\sim$ **4**, **7**) as the $E_{1/2}^{(1)}$ values of the respective hydrocarbons. This expectation has been borne out by the experimentally observed ease of formation of the radical trianions. Whereas **3**$^{3-}\cdot$, **4**$^{3-}\cdot$, and **7**$^{3-}\cdot$ could be prepared, **1**$^{3-}\cdot$ and **5**$^{3-}\cdot$ (as well as the structurally related **2**$^{3-}\cdot$ and **6**$^{3-}\cdot$) could not. Furthermore, the relative appearance voltages V_a, −6.2, −6.2, and −5.0 V, determined for **3**$^{3-}\cdot$, **4**$^{3-}\cdot$, and **7**$^{3-}\cdot$, respectively, are consistent with the expected order. The conditions under which these data were acquired were the same as those used in a previous work[19] for electrolytic reduction of a series of aromatic hydrocarbons to their radical anions. A

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(31) Atherton, N. M.; Gerson, F.; Ockwell, J. N. *J. Chem. Soc. A*, **1966**, 109.

(32) Fürderer, P.; Gerson, F.; Krebs, A. *Helv. Chim. Acta* **1977**, *60*, 1226.

close correlation by a regression equation, $V_a = (1.92 \pm 0.06)E_{1/2}^{(1)}$, was found in that work between the appearance voltages, V_a, for the radical anions and the first half-wave reduction potentials, $E_{1/2}^{(1)}$, of the hydrocarbons. When this relationship is applied to the V_a values for $\mathbf{3}^{3-}\cdot$, $\mathbf{4}^{3-}\cdot$, and $\mathbf{7}^{3-}\cdot$, the third half-wave potentials, $E_{1/2}^{(3)}$, given in Table III for **3**, **4**, and **7** are estimated. It is evident that these $E_{1/2}^{(3)}$ values are shifted by −0.5 to −0.8 V relative to the half-wave potentials $E_{1/2}^{(1)}$ of the corresponding hydrocarbons, **3A**, **4A**, and **7A**. Those of **3** and **4** (−3.23 ± 0.10 V) lie close to the half-wave potentials $E_{1/2}^{(1)}$ of benzene (−3.31 V),[19] which is a range usually inaccessible for studies by polarography and cyclic voltammetry. It can be anticipated that the $E_{1/2}^{(3)}$ values of **1**, **2**, **5**, and **6** are even more negative than −3.3 V, and this is presumably the main reason for the failure to prepare the respective radical trianions in the present work. On the other hand, the $E_{1/2}^{(3)}$ value of **7** (−2.60 ± 0.10 V) gives evidence of the relatively great ease of formation of $\mathbf{7}^{3-}\cdot$. Although this value, in contrast to those of **3** and **4**, still lies within the range readily accessible for electrochemical studies, it is by far more negative than the third half-wave reduction potential of the 1,3,6,8-tetraaza derivative of **7** (−0.99 V),[14] which, to our knowledge, is the only such potential reported in the literature for a tetracyanoarenoquinodimethane.

Experimental Section

With the exception of **1**, a commercial product of FLUKA (Buchs, Switzerland), all starting materials used in the present work were synthesized in the Baltimore laboratory. The procedures serving for these syntheses have been reported in the literature: **2**,[5] **3**,[6] **4**-H_2,[7b] **5**-H_2,[8] **6**,[10] and **7**-H_2.[11a] The chemical, electrolytic, and photolytic reactions leading to the radical anions, dianions, and (for **3**, **4**, and **7**) the radical trianions are specified below. They were all carried out with the solvent DME and at 193 K, except the chemical oxidation of the dianions which required higher temperatures (273–293 K). The supporting salt in the electrolyses was tetra-*n*-butylammonium perchlorate. The electrolytic cell was constructed in the Basel laboratory several years ago and has been described elsewhere.[33] It has proved advantageous for generation of organic radical ions, especially those exhibiting low electron affinity[19] and/or poor persistence.[32,34] The design of the photolytic apparatus follows a description given in the literature.[35] Irradiation leading to the photooxidation of the dianions was performed on a Pyrex cell with a Philips SP 1000-W high-pressure mercury lamp. ESR spectra were taken on a Varian-E9 ESR spectrometer for chemically and electrolytically prepared radical anions and radical trianions and on a Varian-E3 ESR spectrometer for photooxidatively generated radical anions. ENDOR spectra could be observed only for chemically produced radical anions; the instrument was a Varian-ENDOR-1700 system attached to the E9 spectrometer.

7,7,8,8-Tetracyanobenzo-1,4-quinodimethane (1). The radical anion $\mathbf{1}^{-}\cdot$ was prepared by reduction of **1** with potassium metal. The extremely intense ESR spectrum of $\mathbf{1}^{-}\cdot$ did not disappear upon prolonged contact with the metallic mirror. It also persisted upon electrolytic reduction of **1**, even if a highly negative voltage was applied. Conversion of $\mathbf{1}^{-}\cdot$ to the dianion $\mathbf{1}^{2-}$ must thus be incomplete under these experimental conditions.

7,7,8,8-Tetracyano-2,3,5,6-tetrafluorobenzo-1,4-quinodimethane (2). Compound **2** was reduced to its radical anion, $\mathbf{2}^{-}\cdot$, by mercury metal. Use of potassium as the reducing agent led to decomposition caused by the well-known reactivity of halogen substituents toward alkali metals. Upon electrolysis of **2**, the ESR spectrum of $\mathbf{2}^{-}\cdot$ also persisted up to a highly negative voltage.

9,9,10,10-Tetracyanonaphtho-1,4-quinodimethane (3). Reduction of **3** by potassium metal yielded first the radical anion $\mathbf{3}^{-}\cdot$. Renewed contact of the solution with the metallic mirror for about 1 h led to the formation of the dianion $\mathbf{3}^{2-}$, manifested by the disappearance of the ESR spectrum of $\mathbf{3}^{-}\cdot$. Upon further reaction with potassium metal for a comparable period of time, a new ESR spectrum arising from the radical trianion $\mathbf{3}^{3-}\cdot$ was observed. When the experiment was conducted in such a way that only one-third of the solution of **3** was exhaustively reduced and, subsequently, this part (exhibiting the ESR spectrum of $\mathbf{3}^{3-}\cdot$) was mixed with the remaining unreacted solution of **3**, the spectrum of $\mathbf{3}^{3-}\cdot$ was reconverted into that of $\mathbf{3}^{-}\cdot$. Obviously, comproportionation represented by $\mathbf{3}^{3-}\cdot + 2 \times \mathbf{3} \rightarrow 3 \times \mathbf{3}^{-}\cdot$ occurred. The three reduction steps $\mathbf{3} \rightarrow \mathbf{3}^{-}\cdot \rightarrow \mathbf{3}^{2-} \rightarrow \mathbf{3}^{3-}\cdot$ were also performed electrolytically, whereby an appearance potential, V_a, of −6.2 ± 0.1 V was measured for $\mathbf{3}^{3-}\cdot$.

9,9,10,10-Tetracyanonaphtho-2,6-quinodimethane (4). Naphthalene-2,6-dimalononitrile (**4**-H_2) was deprotonated to the dianion $\mathbf{4}^{2-}$ with potassium *tert*-butoxide. The solutions of $\mathbf{4}^{2-}$ thus obtained were subjected to chemical, electrolytic, and photolytic oxidation; the chemical treatment consisted of the reaction of $\mathbf{4}^{2-}$ with tris(4-bromophenyl)ammoniumyl hexachloroantimonate.[36] Each of the three methods afforded the radical anion $\mathbf{4}^{-}\cdot$. The solutions of $\mathbf{4}^{2-}$ prepared by deprotonation of **4**-H_2 also served for the generation of the radical trianion $\mathbf{4}^{3-}\cdot$ by electrolytic reduction. For this purpose, however, more straightforward chemical and electrolytic procedures were those that started directly from the dihydro precursor **4**-H_2. Chemically, $\mathbf{4}^{3-}\cdot$ was obtained by contacting **4**-H_2 with potassium metal, the intermediate being the dianion $\mathbf{4}^{2-}$ formed by the reaction $\mathbf{4}\text{-H}_2 + 2\text{K} \rightarrow \mathbf{4}^{2-} + 2\text{K}^+ + \text{H}_2\uparrow$. It is noteworthy that when the solution of $\mathbf{4}^{3-}\cdot$ was left standing at 193 K without contacting the metallic mirror, $\mathbf{4}^{3-}\cdot$ reverted to $\mathbf{4}^{2-}$. This reaction manifested itself by the disappearance of the ESR spectrum of $\mathbf{4}^{3-}\cdot$ and a concomitant emergence of a green-yellowish fluorescence characteristic of the solutions of $\mathbf{4}^{2-}$. The presence of $\mathbf{4}^{2-}$ was also proved by its photooxidation to $\mathbf{4}^{-}\cdot$. Electrolytically, an appearance voltage, V_a, of −6.2 ± 0.1 V was required for $\mathbf{4}^{3-}\cdot$ when this radical trianion was generated from **4**-H_2 as the starting material. The individual steps leading from **4**-H_2 to $\mathbf{4}^{3-}\cdot$ are not readily identifiable in this case.

7,7,7′,7′-Tetracyanodipheno-4,4′-quinodimethane (5). Deprotonation of biphenyl-4,4′-dimalononitrile (**5**-H_2) was preferentially carried out with potassium metal, since reaction of **5**-H_2 with potassium *tert*-butoxide gave less satisfactory results. Photooxidation of the dianion $\mathbf{5}^{2-}$, obtained in this way by reaction of **5**-H_2 with the metallic mirror, was the simplest method for the generation of the radical anion $\mathbf{5}^{-}\cdot$. An alternative procedure, in which $\mathbf{5}^{2-}$ was oxidized to $\mathbf{5}^{-}\cdot$ with tris(4-bromophenyl)ammoniumyl hexachloroantimonate,[36] required the separation of the solution from the unreacted potassium metal prior to such a treatment. The radical trianion $\mathbf{5}^{3-}\cdot$ could not be prepared. Prolonged contact of **5**-H_2 with potassium metal failed to produce a new paramagnetic species, in contrast to the behavior of **4**-H_2 under analogous conditions. Neither was replacement of potassium by cesium as the reducing agent more successful in this reaction, which apparently did not proceed beyond the dianion $\mathbf{5}^{2-}$.

11,11,12,12-Tetracyano-4,5,9,10-tetrahydropyreno-2,7-quinodimethane (6). Reaction of **6** with potassium metal yielded the radical anion $\mathbf{6}^{-}\cdot$, which upon further contact with the metallic mirror was converted into the dianion $\mathbf{6}^{2-}$. Reduction of $\mathbf{6}^{2-}$ to the radical trianion $\mathbf{6}^{3-}\cdot$ could not be observed, despite prolonged exposure of the solution to the potassium metal.

11,11,12,12-Tetracyanopyreno-2,7-quinodimethane (7). Starting from pyrene-2,7-dimalonitrile (**7**-H_2), all reactions leading to the dianion $\mathbf{7}^{2-}$, the radical anion $\mathbf{7}^{-}\cdot$, and the radical trianion $\mathbf{7}^{3-}\cdot$ were closely analogous to those yielding $\mathbf{4}^{2-}$, $\mathbf{4}^{-}\cdot$, and $\mathbf{4}^{3-}\cdot$ from **4**-H_2 as the original material. A notable difference in the two series is the considerably greater ease of formation of $\mathbf{7}^{3-}\cdot$ relative to $\mathbf{4}^{3-}\cdot$, as demonstrated by the appearance voltage, V_a, of −5.0 ± 0.1 V, observed for $\mathbf{7}^{3-}\cdot$ upon electrolysis of **7**-H_2.

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Registry No. 1, 1518-16-7; $\mathbf{1}^{-}$, 34507-61-4; $\mathbf{1}^{2-}$, 87533-86-6; **2**, 29261-33-4; $\mathbf{2}^{-}$, 47043-66-3; $\mathbf{2}^{-}\cdot\text{Hg}^{2+}$, 87533-87-7; $\mathbf{2}^{-}\cdot\text{Hg}_2^{2+}$, 87533-88-8; $\mathbf{2}^{2-}$, 87583-93-5; **3**, 18389-97-4; $\mathbf{3}^{-}$, 87533-89-9; $\mathbf{3}^{-}\cdot\text{K}^+$, 87533-90-2; $\mathbf{3}^{2-}$, 87583-94-6; $\mathbf{3}^{3-}$, 87583-95-7; $\mathbf{3}^{3-}\cdot 3\text{K}^+$, 87583-96-8; **4**, 6251-01-0; $\mathbf{4}^{-}$, 47080-48-8; $\mathbf{4}^{-}\cdot\text{K}^+$, 4948-94-1; $\mathbf{4}^{2-}$, 87585-14-6; $\mathbf{4}^{3-}$, 87583-97-9; $\mathbf{4}^{3-}\cdot 3\text{K}^+$, 87583-98-0; **4**-$H_2$, 4948-93-0; **5**, 5722-42-9; $\mathbf{5}^{-}$, 68271-99-8; $\mathbf{5}^{-}\cdot\text{K}^+$, 87533-91-3; $\mathbf{5}^{2-}$, 54548-61-7; **5**-H_2, 3049-49-8; **6**, 73120-72-6; $\mathbf{6}^{-}$, 73120-77-1; $\mathbf{6}^{-}\cdot\text{K}^+$, 87533-92-4; $\mathbf{6}^{2-}$, 87583-99-1; **7**, 64535-30-4; $\mathbf{7}^{-}$, 87584-00-7; $\mathbf{7}^{-}\cdot\text{K}^+$, 87584-01-8; $\mathbf{7}^{2-}$, 76357-79-4; $\mathbf{7}^{3-}$, 87584-02-9; $\mathbf{7}^{3-}\cdot 3(n\text{-Bu}_4\text{N}^+)$, 87584-03-0; **7**-$H_2$, 76357-78-3; tris(4-bromophenyl)ammoniumyl hexachloroantimonate, 40927-19-3.

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