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# Preparation and Oxidation of the Bis(tetra-*n*-butylammonium) Salt of 2,2′-(2,7-Pyrenediyl)bis[propanedinitrile] Dianion

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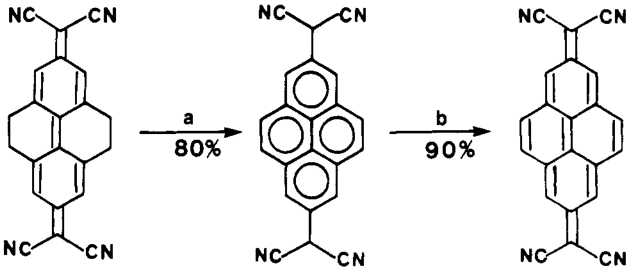
2,2′-(2,7-Pyrenediyl)bis[propanedinitrile] (**2**) is synthesized in 12 steps from 1,4,5,8-naphthalenetetracarboxylic dianhydride in 7% overall yield. Upon oxidation with a variety of reagents an insoluble purple solid is formed whose infrared spectrum and elemental analysis imply it not to be 11,11,12,12-tetracyanopyreno-2,7-quinodimethane (TCNP) and whose insolubility suggests it to be polymeric. Upon oxidation at a platinum or vitreous carbon electrode the bis(tetra-*n*-butylammonium) salt (**15**) of the conjugate base of **2** (in 0.1 M tetra-*n*-butylammonium perchlorate in acetonitrile) undergoes a reversible one-electron oxidation [$E_{pa1}$ = 0.075 V relative to Ag/AgCl(s)] and an irreversible second oxidation ($E_{pa2}$ = 0.340 V). At low temperatures (−20 °C, 0.9 mM) the product of the first oxidation, the radical anion of TCNP, dimerizes.

A number of organic salts consisting of segregated stacks of acceptor and donor molecules have recently been found to be conductors of electricity.[1] Those that are highly conductive are characterized by the transfer of charge from the donor to the acceptor being only partial.[1a,c] Other features of the donor and acceptor components are planar structures, high symmetry, delocalized π molecular orbitals, closed-shell configurations in the neutral donor and acceptor precursors, and charge distributions in their ions that diminish coulombic repulsions. Although a variety of donors have been prepared, the number of acceptors is few, most research having been done with tetracyanoquinodimethane (TCNQ). We attempted to synthesize the pyrene analogue of TCNQ, 11,11,12,12-tetracyanopyreno-2,7-quinodimethane (**1**, TCNP), because its larger size compared to TCNQ should diminish coulombic repulsion in its dianion[1b] and make it a more compatible acceptor for large donors.[1c] While this work was in progress Maxfield, Willi, Cowan, Bloch, and Poehler[2] reported a synthesis of TCNP (Scheme I) and of its anionic reduction products from TCNTP.[3] The work below includes an alternative and efficient synthesis of **2**. Base converts this acid into its conjugate dianion, but oxidation does not give **1** as an isolable material.

Scheme I



TCNTP **2** **1**

[a] (a) Pd/C, PhCl; (b) DDQ, $CH_3CN$, Δ.

Table I. IR and UV Spectral Data of **2**

| IR $\bar{\nu}_{max}$ (KBr pellet), $cm^{-1}$ this work | IR $\bar{\nu}_{max}$ (KBr pellet), $cm^{-1}$ reported[a] | UV $\lambda_{max}$, nm (log ε) this work | UV $\lambda_{max}$, nm (log ε) reported[a] |
|---|---|---|---|
| 3025 (w) | 3025 | 237 (4.53) | |
| 2944 (s) | | 246.5 (4.73) | |
| 2255 (w) | 2250 | 264 (4.33) | 260 (3.97) |
| 1608 (m) | 1605 | 275 (4.39) | 272 (4.05) |
| 1448 (w) | 1442 | 309 (4.26) | 305 (3.95) |
| 1408 (w) | 1403 | 323 (4.65) | 323 (4.00) |
| 1327 (m) | 1312 | 337 (4.60) | 338 (4.08) |
| 1002 (m) | | 372 (3.83) | |
| 900 (s) | | | |
| 875 (s) | | | |
| 712 (s) | | | |
| 694 (m) | | | |
| 382 (m) | | | |

[a] Reference 2.

## Synthesis

2,2′-(2,7-Pyrenediyl)bis[propanedinitrile] (**2**) was prepared from 1,4,5,8-naphthalenetetracarboxylic dianhydride in 7% overall yield as outlined in Scheme II, a synthesis that is easy to carry out on a large scale. (We used >80 g of dianhydride **3**.) It includes as key steps (1) the condensation of tetrabromide **6** with diethyl malonate, (2) the dehydrogenation to **13**, and (3) the introduction of further nitrile functions by following a procedure of Sandman and Garito.[4]

Dianhydride **3** was converted to tetramethyl ester **4** by hydrolysis with KOH and esterification with dimethyl sulfate.[5] Reduction with diisobutylaluminum hydride (DIBAL)[6] gave the tetraol **5**, which with $PBr_3$[7] gave bromide **6**, in preparation for the first key step. Condensation with diethyl malonate[8] gave **7**, which after saponification (KOH, MeOH) and decarboxylation[8] gave the diacid **8** (a material whose wide melting range suggests it to be a mixture of diastereomers). Esterification (MeOH, $H_2SO_4$) and DIBAL[6] reduction gave diol **10**, which with $SOCl_2$/pyridine[9] yielded dichloride **11**. Cyanation (NaCN, $Me_2SO$) completed the first part of the synthesis. Dehydrogenation with

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[1] For reviews, see: (a) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79. (b) Garito, A. F.; Heeger, A. J. *Ibid.* **1974**, *7*, 232. (c) 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; pp 25–45. (d) Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519 and reviews cited therein.

[2] Maxfield, M.; Wili, S. M.; Cowan, D. O.; Bloch, A. N.; Poehler, T. O. *J. Chem. Soc., Chem. Commun.* **1980**, 947. Cowan and Maxfield have informed us that they remeasured the spectrum of the material identified originally as TCNP and found a strong absorption at 2255 $cm^{-1}$ and a weak one (5 times smaller) at 2210 $cm^{-1}$.

[3] (a) Maxfield, M.; Cowan, D. O.; Bloch, A. N.; Poehler, T. O. *Nouv. J. Chim.* **1979**, *3*, 647. (b) See also: Aharon-Shalom, E.; Becker, J. Y.; Agranat, I. *Ibid.* **1979**, *3*, 643.

[4] The procedure was used for preparing 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP). Sandman, D. J.; Garito, A. F. *J. Org. Chem.* **1974**, *39*, 1165.

[5] Denisova, L. I.; Morozova, N. A.; Plakhov, V. A.; Tochilken, A. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1964**, *34*, 521.

[6] Burnham, J. W.; Eisenbraun, E. J.; Hamming, M. C.; Keen, G. W. *Org. Prep. Proced. Int.* **1972**, *4*, 35.

[7] Hunter, D. H.; Stothers, J. B. *Can. J. Chem.* **1973**, *51*, 2884.

[8] Bergson, G.; Pikas, A.-L. *Acta Chem. Scand.* **1965**, *19*, 755. See also: Kende, A. S.; Greenhouse, R.; Hill, J. A. *Tetrahedron Lett.* **1979**, 2867. Mitchell, D.; Eilert, J. H.; Bauld, N. L. *Ibid.* **1979**, 2865.

[9] Cornforth, J. W.; Robinson, R. *J. Chem. Soc.* **1942**, 684. Benzene was used as a solvent.

0022-3263/82/1947-1011$01.25/0

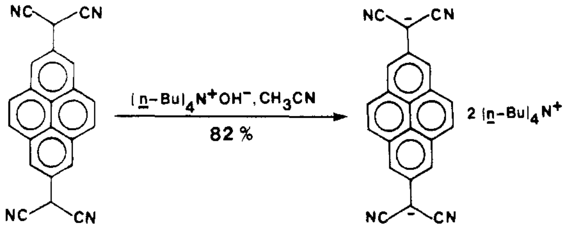
Table II. IR and UV Spectral Data of 15

| IR $\bar{\nu}_{max}$ (KBr pellet), $cm^{-1}$ | | UV $\lambda_{max}$, nm (log $\epsilon$) | |
|---|---|---|---|
| this work | reported[a] | this work | reported[a] |
| 2957 (s) | | 234 (4.43) | |
| 2870 (m) | | 295 (4.38) | 292 (3.91) |
| 2157 (s) | 2160 | 310 (4.75) | 312 (4.08) |
| 2120 (s) | 2120 | 323 (5.18) | 327 (4.52) |
| 1600 (s) | 1604 | 337 (4.83) | 341 (4.26) |
| 1578 (m) | | 365 (4.83) | 371 (4.36) |
| 1478 (m) | 1450 | | |
| 1377 (m) | | | |
| 1318 (s) | 1315 | | |
| 1208 (m) | | | |
| 1150 (m) | | | |
| 764 (m) | | | |

[a] Reference 2.

2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) aromatized **12** to the desired substituted pyrene, **13**, which was transformed to **2** by Sandman and Garito's procedure[4] (carbethoxylation and cyanation to give **14** and then saponification and concomitant decarboxylation).

The structure was assigned to the tetranitrile **2** on the basis of its method of synthesis, its elemental analysis for carbon, hydrogen, and nitrogen, its $^1H$ NMR spectrum [in $Me_2SO$-$d_6$; $\delta$ 8.38 and 8.28 (2 s, 7.75 H, aromatic), 6.68 (s, 2.26 H, $C(CN)_2$**H**)], its infrared (IR) spectrum, and its ultraviolet (UV) spectrum. The IR and UV spectra, as well as those of the bis(tetra-*n*-butylammonium) salt **15** prepared from **2** according to eq 1, are similar to analogous spectra reported by Cowan et al.[2] for materials made by a different synthesis. The spectral data are summarized in Tables I and II.



(1)

2

15

Solutions of both **2** and **15** are extremely sensitive to air. They turn a deep purple color ($\lambda_{max}$ = 530–540 nm) that persists for a few hours and then fades to colorless. (The absorbance at 530–540 nm also then disappears.) Attempts to elucidate the structure of the transient intermediate were unsuccessful, but TCNP or its radical anion could not be recognized. (A 6.15-mM acetone solution of **15**, deep purple after exposure to air for 5 h, showed nitrile stretches in its infrared spectrum at 2156 and 2122 $cm^{-1}$ and not at 2205 $cm^{-1}$[10,11] where $TCNP^2$ is expected to absorb. A similar 2.46-mM acetone solution of **15**, also deep purple after exposure to air for 4 h, gave no signal in the ESR spectrometer.)

## Results and Discussion

Table III. Elemental Analysis of the Purple Solid

| sample | anal., % C | H | N | O | total, % | preparative method |
|---|---|---|---|---|---|---|
| 1 | 77.57 | 3.32 | 15.45 | 3.74 | 99.68 | DDQ/ $CH_3CN$ |
| 2 | 76.63 | 2.52 | 16.17 | 4.78 | 100.10 | DDQ/ $CH_3CN$ |
| 3 | 74.07 | 2.98 | 15.23 | 7.83 | 100.11 | DDQ/ $CH_3CN$ |
| 4 | 74.49 | 2.55 | 14.99 | 7.97[a] | 100.0 | NaH/$Br_2$/ $CH_3CN$ |
| TCNP (1) | 80.48 | 2.46 | 17.06 | | | |

[a] Oxygen percentage determined by difference.

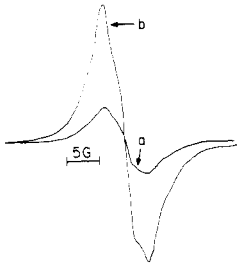


**Figure 1.** ESR spectrum of the purple solid obtained by reacting **2** with DDQ in $CH_3CN$: (a) at room temperature; (b) at liquid $N_2$ temperature.

**Attempts To Oxidize 2 Chemically.** The following oxidizing agents all convert **2** into purple solids: 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in either acetonitrile or dioxane; *N*-bromo-, *N*-chloro-, or *N*-iodosuccinimide combined with triethylamine (TEA) in $CH_3CN$ or *N,N*-dimethylformamide (DMF); pyridinium hydrobromide perbromide/TEA in $CH_3CN$; sodium hydride (NaH) and iodine in $CH_3CN$; NaH/bromine in either $CH_3CN$ or DMF. The products of each of these oxidations appear to be similar in as much as their infrared spectra are detailed and seemingly identical. These samples do not, however, appear to be TCNP, although similar experiments (using DDQ in $CH_3CN$) conducted elsewhere gave a purple solid (mp >360 °C) said to be this material.[12] The infrared spectra (KBr) of our samples exhibit absorptions at 2255 $cm^{-1}$, indicative of saturated nitriles,[10,11] while the reported material absorbed at 2205 $cm^{-1}$.[2] The elemental analyses in Table III do not correspond to those of TCNP, and they point to the presence of oxygen. An attempt to measure the electronic spectrum failed because of low solubility: a mixture of 8.7 mg of the material and 25 mL of $CH_3CN$ gave a solution without absorption.[13] Low solubility also accounts for why experiments to detect electrochemistry also failed (a 10-mg sample in 2 mL of HMPA/7 mL of $CH_3CN$ with 0.1 M TBAP[14] exhibited no current). Accordingly, we suppose that during their isolation the samples incorporated water or oxygen and polymerized.

These purple solids exhibit signals in electron spin resonance (ESR) spectra (Figure 1) at $g$ = 2.0011 but no fine structure. The $g$ value indicates the radical to be organic, presumably a $\pi$-type radical, not a metallic impurity.[15] Magnetic susceptibility measurements[16] show the concentration of the radical species to be small; for

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[10] Kitson, R. E.; Griffith, N. E. *Anal. Chem.* **1952**, *24*, 334.

[11] For comparison the reported nitrile stretches are as follows. (a) For TCNQ at 2220 $cm^{-1}$ (KBr): Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370. (b) For TNAP at 2210 $cm^{-1}$ (KBr): Diekmann, J.; Hertler, W. R.; Benson, R. E. *J. Org. Chem.* **1963**, *28*, 2719. (c) For TCNTP at 2210 $cm^{-1}$ (KBr): ref 3a.

[12] The characteristics reported in ref 2 are as follows: mp >360 °C; $\bar{\nu}_{max}$ (KBr) 2205, 1595, 1401, 1372, 1312 $cm^{-1}$; $\lambda_{max}$ (butyronitrile) 243 nm (log $\epsilon$ 4.60), 340 (3.31), 557 (4.12).

[13] At this concentration (1.05 mM) TCNP is supposed to have absorbances of 41.8 at $\lambda_{max}$ 243 nm, 2.1 at $\lambda_{max}$ 340 nm, and 13.8 at $\lambda_{max}$ 557 nm. See ref 12.

[14] TBAP = tetra-*n*-butylammonium perchlorate; TBAF = tetra-*n*-butylammonium fluoride.

[15] Bersohn M.; Baird, J. C. "An Introduction to Electron Paramagnetic Resonance"; W. A. Benjamin: New York, 1966; Chapter 5.

[16] Magnetic susceptibilities were measured for samples no. 1–3 (Table III) at room temperature by using a Faraday balance. With an assumed molecular weight of 330, the measured $\chi_M$'s were, respectively, $-1.98 \times 10^{-4}$, $-1.09 \times 10^{-4}$, and $-1.48 \times 10^{-4}$. $\chi_{Dia}$ was estimated to be $-213 \times 10^{-6}$ ("The Handbook of Chemistry and Physics", 53rd ed.; CRC Press: Cleveland, OH, 1972; pp E-114–119). Since $\chi_M = \chi_P + \chi_{Dia}$, the values for $\chi_P$ are $1.57 \times 10^{-5}$, $1.04 \times 10^{-4}$, and $6.52 \times 10^{-5}$. If the radical species present is assumed to be organic, with $g$ = 2.00, their mole fractions are 0.012, 0.082, and 0.051.

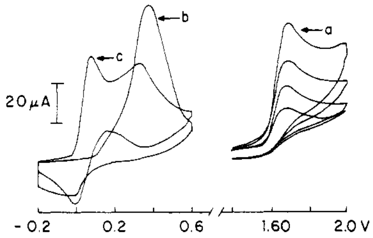
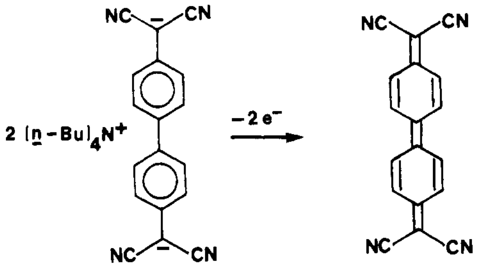


**Figure 2.** Cyclic voltammograms: (a) of 2 (0.88 mM) in 0.1 M TBAP/$CH_3CN$ at a Pt-bead electrode; (b) a with 7% (v/v) HMPA added; (c) b with $Ph_3CLi$ (2 equiv) added.

samples 1–3 in Table III the amounts are approximately 1, 8, and 5 mol %. The intensity[17] of the ESR signal varies inversely with temperature (in accord with Curie's law), implying that the reason that the radical concentration is low when measured by the magnetic susceptibility is not because spins on neighboring radicals couple weakly as they do in complexes of the TCNQ radical anion.[18] We do not know the structure of the paramagnetic species, but it does not appear to be the TCNP radical–anion because the one nitrile stretch at 2255 $cm^{-1}$ in the IR spectrum is also not in accord with this hypothesis.[19]

**Electrochemistry.** Chemicals having failed to oxidize tetranitrile 2 to TCNP, the alternative, that electrodes would oxidize its dianion [in the form of its bis(tetra-*n*-butylammonium) salt (15)] and give the desired material, was studied. Agranat et al.[3b] had used such an approach, i.e., controlled-potential electrolysis of the dianions, to prepare TCNDQ[20] (16, eq 2) and TCNTP (Scheme I).



16

Tetranitrile 2 is slightly soluble in a solution of 0.1 M TBAP/$CH_3CN$, and cyclic voltammetry (CV) shows that it undergoes an irreversible one-electron oxidation: $E_{pa}$[21] = +1.69 V, $E_{pa} - E_{pa/2} \approx 70$ mV (Figure 2a). (The reference electrode for this and all voltammograms listed below is Ag/AgCl(s).) Electron transfer is rapid ($i_{pa}/v^{1/2}$ is constant), but the oxidation is irreversible because electron transfer is followed by a rapid irreversible chemical transformation. Upon addition of HMPA (7% v/v compared to $CH_3CN$) the solution turns a dark brownish orange, and the CV exhibits a broad irreversible wave with $E_{pa}$ = +0.37 V and $E_{pa} - E_{pa/2}$ = 80–100 mV (Figure 2b). Although there is no conclusive evidence, we believe the peak is most likely associated with the oxidation of the monoanion conjugate base of 2.[22] A small broad cathodic wave can be seen on the reverse sweep at about $E_{pc}$ = −0.1 V. Adding $(Ph)_3CLi$ or *n*-BuLi to this solution turns it bright orange and makes its electrochemical behavior (Figure 2c) identical with that of the disalt 15.

Table IV. Peak Potentials $E_{pa_1}$, $E_{pa_2}$, and $E_{pc}$ (in Volts) in Cyclic Voltammograms of 15

| electrolyte | solvent | $E_{pa_1}$ | $E_{pa_2}$ | $E_{pa_2} - E_{pa_1}$ | $E_{pc}$ |
|---|---|---|---|---|---|
| $LiClO_4$ | $CH_3CN$ | 0.010 | 0.325 | 0.315 | −0.050 |
| $LiClO_4$ | THF/HMPA (5:2) | −0.010 | 0.350 | 0.360 | −0.080 |
| TBAP | $CH_3CN$ | 0.075 | 0.340 | 0.265 | −0.010 |
| TBAP | DMF | 0.040 | 0.340 | 0.300 | −0.050 |
| TBAP | DMF (−23 °C) | 0.160 | 0.530 | 0.370 | |

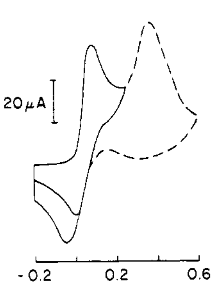


**Figure 3.** Cyclic voltammogram of 15 (0.88 mM) in 0.1 M TBAP/$CH_3CN$ at a Pt-bead electrode measured after several sweeps.

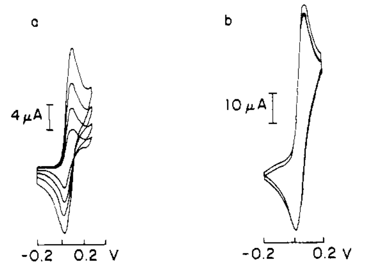


**Figure 4.** Cyclic voltammograms of 15 (0.88 mM) in 0.1 M TBAP/$CH_3CN$ at a Pt-bead electrode: (a) scan rate $v$ = 20, 50, 100, 200 mV/s; (b) repeated scans of the first wave.

The CV's of 15 in a wide variety of solvents and at two electrodes[23] are similar. A typical example is shown in Figure 3, and various $E_{pa}$'s are listed in Table IV. As can be seen in Figure 4, the first oxidation appears to be reversible. In particular, the voltammograms exhibit the following properties characteristic of reversible (points 1–3) one-electron (points 4 and 5) processes:[24] (1) $E_{pa}$ and $E_{pc}$ are independent of scan rate in the range $v$ = 20–200 mV/s (Figure 4a); (2) repeated scans show no deterioration of reversibility (Figure 4b); (3) $i_{pa}/i_{pc}$ as calculated by the semiempirical equation of Nicholson[25] is essentially unity

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[17] For the purple solid, the intensity $I$ of the ESR signal was $I_{77K}/I_{298K}$ = 3.85 (Curie-law-type behavior, $I \propto 1/T$, requires $I_{77K}/I_{298K}$ = 3.87). The intensities were estimated by following the procedure described in: Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance: Elementary Theory and Practical Applications"; McGraw-Hill: New York, 1972; pp 32–36.

[18] The intensity of the ESR signal for various TCNQ salts increases with increasing temperature, and this has been ascribed to spin correlation. For example, for triethylammonium [TCNQ(TCNQ$^-$·)] $J$ = 0.041 eV. See: Chesnut, D. B.; Foster, H.; Phillips, W. D. *J. Chem. Phys.* **1961**, *34*, 684.

[19] RbTCNQ (Nujol mull) exhibits nitrile stretches at 2160, 2187, and 2219 $cm^{-1}$. See: Bozio, R.; Girlando, A.; Pecile, C. *J. Chem. Soc., Faraday Trans. 2* **1975**, 1237. Note that the stretches due to the two nitriles $\alpha$ to the anion are the most intense absorptions in this spectrum and also in the spectrum of dianion 15. Thus, amounts of such materials as small as 8.2 and 5.1 mol % should have been seen.

[20] Previous attempts to synthesize TCNDQ by chemical oxidation gave polymers. See: Sandman, D. J.; Garito, A. F. *J. Org. Chem.* **1974**, *39*, 1165. Hartzler, H. D. *J. Am. Chem. Soc.* **1964**, *86*, 2174. Hertler, W. R. U.S. Patent 3 153 658, 1964; *Chem. Abstr.* **1965**, *62*, 4145a.

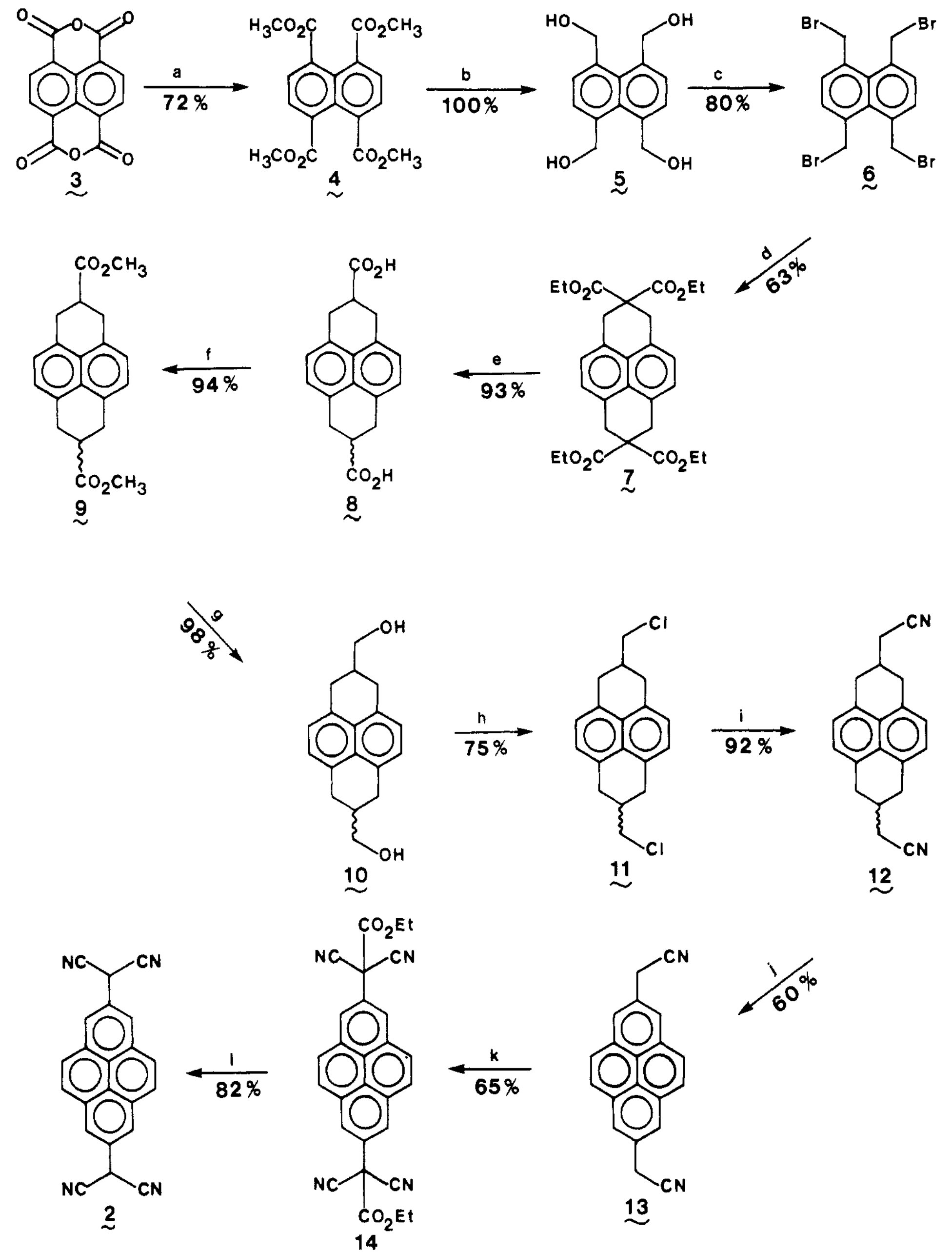
[21] $E_{pa}$ = anodic peak potential; $i_{pa}$ = current at anodic peak potential; $E_{pa/2}$ = the potential at $i_{pa/2}$; $E_{pc}$ = cathodic peak potential; $i_{pc}$ = current at cathodic peak potential; $v$ = sweep velocity (mV/s).

[22] It is reasonable to assume that the highly acidic methine proton ($\alpha$ to two nitriles and one aryl group) ionizes in the polar medium, for its $pK_a$ should be ca. 11. See: Pearson, R. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439.

[23] CV's of 15 were studied in 0.1 M TBAP/$CH_3CN$, 0.1 M $LiClO_4$/$CH_3CN$, 0.1 M TBAP-$LiClO_4$/$CH_3CN$-HMPA (14:1), 0.1 M $LiClO_4$/THF-HMPA (5:2), and 0.1 M TBAP/DMF by using both platinum and vitreous carbon working electrodes.

[24] Bard, A.; Marz, A. *J. Am. Chem. Soc.* **1979**, *101*, 2959.

Scheme II[a]



[a] (a) $SO_2(OMe)_2$, KOH, MeOH; (b) DIBAL-H, toluene; (c) $PBr_3$, $Br^-N^+(n\text{-}Bu)_4$, $CH_2Cl_2$; (d) NaOEt/EtOH, $(EtO_2C)_2CH_2$; (e) (1) KOH, MeOH, (2) 230 °C (0.15 mm); (f) MeOH, $H_2SO_4$; (g) DIBAL-H, toluene; (h) $SOCl_2$, py, PhH; (i) NaCN, $Me_2SO$; (j) DDQ, dioxane; (κ) (1) NaOEt, $(EtO)_2CO$, (2) CNCl; (l) (1) KOH, (2) HCl.

in the scan range $v$ = 20–200 mV/s; (4) $E_{pa} - E_{pc}$ = 60 mV (after full IR compensation); (5) after controlled-potential electrolysis in 0.1 M TBAP/DMF at 0.2 V (after the first wave), continued until 0.95 F/mol had passed, the solution exhibited an ESR signal which disappeared when the solution was reelectrolyzed (−0.2 V); after this second electrolysis, the solution exhibited a CV identical with that prior to the first electrolysis, although the peak currents were usually only 70–80% as large.

Analysis of the irreversible second wave in Figure 3 is less obvious. The anodic current increases when the voltage is swept from 0.10 to 0.5 V and then drops sharply after $E_{pa2}$. Also, the current flow rapidly diminishes when scans through the second wave are repeated, the decrease being greater when the electrode is composed of vitreous carbon than when it is platinum. These effects indicate that the electrode is being fouled by the adsorption of electrochemically inactive material, a possibility that finds precedent in work by Peover,[26] by Pysh and Yang,[27] and by Peover and White,[28] who found that polycyclic hydrocarbons, in particular pyrene derivatives, act as foulants.

Another anomaly in Figure 3 is that on the back sweep the cathodic wave is very large, and its peak potential and current are sensitive to the state of the electrode. With a freshly polished electrode in $CH_3CN$ solution, the first cyclic sweep through both anodic waves usually displays an $E_{pc}$ 40–60 mV cathodic of the $E_{pc}$ displayed when the sweep is reversed after only the first anodic wave. The peak cathodic current in the first scan (not displayed in

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[25] Nicholson, R. *Anal. Chem.* **1966**, *38*, 1406.

[26] Peover, M. *Trans. Faraday Soc.* **1964**, *60*, 417.

[27] Pysh, S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124.

[28] Peover, M.; White, B. *J. Electroanal. Chim.* **1967**, *13*, 93.

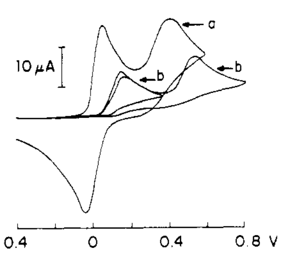


**Figure 5.** Cyclic voltammograms of 15 (9.49 mM) in 0.1 M TBAP/DMF at a Pt-bead electrode: (a) at room temperature; (b) at -20 °C.

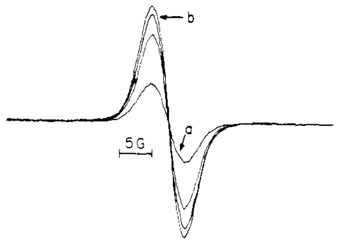


**Figure 6.** ESR spectrum of radical-anion 17 prepared from 15 (9.49 mM, in 0.1 M TBAP/DMF) by controlled potential electrolysis: (a) at ca. -20 °C; (b) at room temperature.

Figure 3) is very large (with a vitreous carbon electrode $i_{pc}$ is greater than 5 times $i_{pa}$; with a Pt electrode $i_{pc} \geq 2i_{pa}$), but in subsequent cycles both $i_{pa}$ and $i_{pc}$ drop considerably. One possible explanation is that the adsorbable film formed on the electrode after the second oxidation is desorbed sharply in the region of $E_{pc}$.

The electrochemistry of 15 in DMF presented another interesting phenomenon. The first couple, which at room temperature is reversible, becomes irreversible when the temperature is lowered to -20 °C (Figure 5, ca. 1 mM solution). Raising the temperature to room temperature again restores the reversible couple. We believe that in DMF at low temperature the product of the first one-electron oxidation, the radical-anion 17, dimerizes to a dianion species. Support for this hypothesis is provided by two observations. (1) Increasing the concentration of 15 in the solution raises the temperature at which the cathodic backwave is lost (a ca. tenfold concentration increase raises the temperature to about 0 °C). (2) The intensity of the ESR spectrum of solutions of radical-anion 17 (ca. 1 mmol, 0.1 M TBAP in DMF) decreases when the temperature is decreased (Figure 6).[29] The dimerization proposed here for TCNP$^{-}\cdot$ was proposed previously to account for changes observed in the electronic absorption spectra of TCNQ$^{-}\cdot$[30] and TCNDQ$^{-}\cdot$:[31] the absorbtions (in $H_2O$ for the former and in DMF for the latter) do not obey Beer's law; they attenuate at increased concentration. The spectrum of TCNQ$^{-}\cdot$ also shows a temperature dependence, the absorbance due to the dimer increasing with decreasing temperature. The near-IR absorbances of radical-anion 17 in DMF (at 1110, 1285, and 1342 nm),[32] follow Beer's law at room temperature, but this is not surprising since at room temperature TCNQ$^{-}\cdot$ does not dimerize in DMF, $CH_3CN$, or $CH_3OH$ although it does in water.[30]

No fine structure is seen in the ESR spectrum ($g$ = 1.9978) of TCNP$^{-}\cdot$ (Figure 7), which probably is attributable to the expected 225 lines overlapping. Broadening by electron-electron exchange appears to be insignificant for the lines are the same width (17-G total width) when the TCNP$^{-}\cdot$ concentration is varied between $10^{-2}$ and $10^{-5}$ M in 0.1 M TBAP in DMF (see Figures 6 and 7). (TCNQ$^{-}\cdot$ displays a 45-line spectrum with ca. a 13-G total width at $10^{-4}$ M in THF.[33])

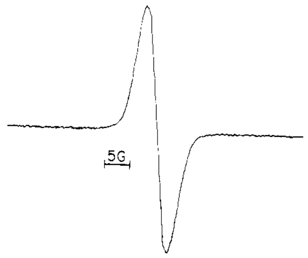
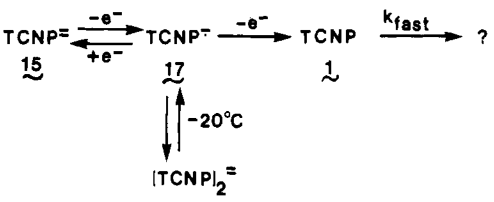


**Figure 7.** ESR spectrum of radical-anion 17 (ca. $10^{-4}$ M) in 0.1 M TBAP/DMF at room temperature.

Scheme III



Several attempts were made to prepare TCNP by electrolysis. In $CH_3CN$, electrolysis at a controlled potential of 0.6 V turned the solution a magenta-purple, and a copious precipitate formed, but attempts to isolate TCNP failed. (Water was added to the electrolysis mixture, and the precipitate was collected and dried. The IR spectra did not indicate TCNP to be present as nitrile stretches were observed at 2250 cm$^{-1}$ but not at 2205 cm$^{-1}$.) In DMF as the solvent, the amount of precipitate formed was less, and the color of the solution was brown. Again, no TCNP could be isolated. (The IR spectrum of the isolated precipitate was similar to that of the product isolated from the experiment using $CH_3CN$, with nitrile stretches at 2252 cm$^{-1}$.) Attempts were also made to reduce the oxidized solutions electrochemically, but no radical-anion 17 was detected in the CV. We conclude that TCNP, presumably the product of the oxidative electrolysis, is unstable under the conditions of the reaction.

These results are consistent with Scheme III, describing the electrochemistry of 15. Similar conclusions regarding 15, 17, and TCNP were independently reached by Cowan et al.,[2] who suppose the rapid reaction of TCNP to be its precipitation.

Some attempts were made to prepare charge-transfer salts of TCNP, but since neutral TCNP could not be prepared, the experiments involved combining 15 with appropriate cation complexes. $(TTF)_3(BF_4)_2$,[34] however, gave no precipitate ($CH_3CN$ was used as the solvent), while $(TTF^{2+})(2Br^{-})$[35] (in $CH_3CN$) gave a gray-purple solid whose infrared spectrum seemed similar to that of the purple solid obtained before, with nitrile stretches at 2250 cm$^{-1}$.[36]

**One Final Point.** Insofar as the difference between the first and second oxidation potentials in Table IV measure

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[29] That the decrease in the observed ESR signal is not caused by changes in the spectrometer's $Q$ factor is implied by the observation that a solution of diphenylpicrylhydrazyl (1 mmol, 0.1 M TBAP in DMF) shows no change in signal intensity over the same temperature range.

[30] Boyd, R. H.; Phillips, W. D. *J. Chem. Phys.* **1965**, *43*, 2927.

[31] Addison, A. W.; Dalal, N. S.; Hoyano, Y.; Huizenga, S.; Weiler, L. *Can. J. Chem.* **1977**, *55*, 4191.

[32] Cowan et al. report that TCNP$^{-}\cdot$ has absorbances at $\lambda_{max}$ = 910, 1124, and 1350 nm (see ref 2).

[33] Jones, M. T.; Hertler, W. R. *J. Am. Chem. Soc.* **1964**, *86*, 1881. See also: Fischer, P. H. H.; McDowell, C. A. *Ibid.* **1963**, *85*, 2694.

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[36] Perhaps larger donor cations would be more effective for the larger anion.

intramolecular coulomb repulsion,[1a] it is reasonable that in the larger molecule, **15**, it is only ca. 265–300 mV (in good agreement with the independent measurement by Cowan et al.[2]), whereas in the smaller TCNQ the value is ca. 600 mV.[37]

## Conclusions

The dianion **15** was observed to display two electrochemical waves, the first one reversible. The radical–anion **17** dimerizes at low temperatures. Attempts to prepare TCNP either chemically or electrolytically indicate that it is not a stable, easily isolable compound but that it undergoes further reactions at room temperature.

## Experimental Section

$^1$H NMR spectra were determined by using either a Varian A-60 or a Bruker WP-80 Fourier transform spectrometer [$(CH_3)_4Si$ was used as an internal standard]. IR spectra were measured by using a Perkin-Elmer 621 spectrophotometer (calibrated by using polystyrene film) and UV, visible, and near-IR spectra by using a Cary Model 17 spectrophotometer. ESR spectra were measured with a Varian E-line X-band spectrometer equipped with a Varian E-101 microwave bridge and a Varian temperature controller (MnO impurity in SrO was used as the standard[38]). Cyclic voltammograms (CV) were measured by using a Princeton Applied Research 173/176 potentiostat driven by a Princeton Applied Research 175 universal programmer, and the data were collected by using a Houston Instrument 2000 recorder for sweep rates up to 200 mV/s and a storage oscilloscope for sweep rates that were higher. Melting points, determined on a Thomas-Hoover capillary melting point apparatus, are uncorrected. Elemental analyses were performed by Galbraith Laboratories.

The materials for the electrochemical experiments were purified as follows.[39] $CH_3CN$ (Gold Label, Aldrich) was distilled from $P_2O_5$ through a 45-cm bubble-bell column (reflux ratio 5:1), the first 10% being discarded. DMF (Gold Label, Aldrich) was stored over preactivated (260 °C, 2 days) 4-Å (Davison) molecular sieves for 12 h and then distilled (15 mm) through the bubble-bell column, the first 10% being discarded. THF (Gold Label, Aldrich) was distilled twice from benzophenone ketyl through the bubble-bell column, the first 10% being discarded each time. HMPA (99+%, Aldrich) was distilled (0.5 mm) through a 1.2-m vacuum-jacketed column filled with glass helices (reflux ratio 10:1), and the first 30% was discarded. It was then refluxed (0.5 mm) over $CaH_2$ for 2 days and distilled (0.5 mm), the first 30% being discarded. Tetra-*n*-butylammonium perchlorate (polarographic grade, Eastman) was weighed into an electrolyte storage flask and dried under vacuum (0.15 mm) for 24 h. Solvent was then added through a cannula to give a 0.1 M solution. Lithium perchlorate (anhydrous, Alfa) was weighed into the electrolyte storage flask and dried for 36–48 h at 130 °C under vacuum (0.15 mm), and solvent was then added through a cannula to give a 0.2 M solution. Triphenylmethyllithium was prepared from triphenylmethane (0.5 M solution in dry THF) and 0.95 equiv of *n*-BuLi (0.43 mL, 2.2 M/hexanes, Alfa) at −30 °C or less, the solution turning a deep red. All transfers were made by using dried, argon-flushed, gas-tight syringes.

Electroanalytical measurements were performed by using a three-electrode cell with two compartments separated by a fine fritted-glass disk. Each compartment was equipped with an inlet stoppered with a serum cap and a connection to either argon or a vacuum manifold. A pressure equalizer connected the two compartments. The working electrode compartment also contained a magnetic stirring bar. The platinum working electrode consisted of a small Pt bead of ca. 1-mm diameter sealed vacuum tight into a glass tube and connected by way of a tungsten wire that was not exposed to the air to a copper wire. The counterelectrode was a Pt coil. A silver wire was coated with silver chloride by anodic oxidation in 0.1 M HCl and used as a quasi-reference electrode. It was isolated from the solution by a glass tube ending in a capillary 0.5 mm from the surface of the working electrode. Before use, the cell was cleaned with Chromerge, $NaHCO_3$ solution, deionized water, and MeOH, dried (110 °C), assembled hot, evacuated (2 h), and finally flushed with argon. For the cyclic voltammograms the solutions were 0.8–8.8 mM and for the controlled-potential electrolyses up to 16.6 mM. (For the latter, the current passed was measured by using a PAR Model 379 digital coulometer, and the background was compensated for.)

The ESR spectra were measured for the "purple solid" by using a standard 4-mm cylindrical tube and for the oxidation products of disalt **15** formed by electrolysis (or by exposure to air) by using a flat cell. The temperature dependence of the radical–anion's ESR intensity was measured by transferring electrolyzed solutions to the flat cell (sealed with a rubber septum), cooling it to −20 °C with a dry ice/acetone bath, quickly placing the cell in the ESR cavity, and recording the spectra repeatedly as the cell warmed up. The cylindrical cell, unlike the flat one, could be cooled and its temperature measured while it was in the ESR cavity.

**Tetramethyl 1,4,5,8-Naphthalenetetracarboxylate (4).** Dianhydride **3** (84.5 g, 0.315 mol), 186 mL of dimethyl sulfate (248 g, 2.0 mol), and 280 mL of MeOH were added to a 3-L, three-necked, round-bottomed flask equipped with a mechanical stirrer, addition funnel, and thermometer. A solution of KOH (121 g, 2.16 mol) in 1 L of MeOH was added over a 1-h period, and by cooling the mixture the temperature was kept below 40 °C. The solution was stirred at room temperature for 30 min and cooled to 0 °C, and the white precipitate was collected and washed with MeOH. The crude product was then suspended in 1 L of cold $H_2O$, swirled, collected, dried, and sublimed [205 °C (0.2 mm)], giving a white solid: 87 g (77%); mp 200–203 °C; $^1$H NMR ($CDCl_3$) $\delta$ 8.04 (s, 3.94 H, aromatic), 3.92 (s, 12.06 H, $OCH_3$); IR (KBr) 2998 (w), 2950 (m), 2920 (w), 2850 (w), 1778 (m), 1720 (vs, $CO_2CH_3$), 1600 (w), 1518 (m), 1442 (s), 1400 (w), 1392 (w), 1382 (w), 1284 (s), 1198 (s), 1160 (s), 1120 (w), 1110 (m), 1042 (w), 981 (m), 940 (w), 875 (w), 852 (m), 844 (w), 802 (w), 784 (w), 756 (m), 750 (m), 720 (m), 692 (w), 660 cm$^{-1}$ (w).

**1,4,5,8-Tetrakis(hydroxymethyl)naphthalene (5).** Diisobutylaluminum hydride (137 g, 0.96 mol) in 100 mL of dry toluene was added to an oven-dried, argon-flushed, 1-L, three-necked, round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and an argon inlet and connected via Gooch tubing to a 250-mL Erlenmeyer flask containing the tetraester **4** (35.0 g, 0.097 mol). Dry toluene (200 mL) was added to the ester and the slurry added in portions, additional toluene (50 mL) being used to complete the transfer. The mixture was refluxed for 10 h and stirred at room temperature for 6 h, and then ethyl acetate (35 mL) was carefully added. After the mixture had cooled, it was poured into 1800 mL of ice–water, and 300 mL of concentrated HCl was gradually added. After the mixture was stirred for 1 h, the white precipitate was collected, washed with $H_2O$, and dried: 24.4 g (101%); mp 218.5–219.5 °C; $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 7.57 (s, 4.04 H, aromatic), 5.07 (br s, 11.96 H, $\mathbf{CH_2OH}$, degenerate); IR (KBr) 3326 (s, br, OH), 3227 (s, br, OH), 2940 (vw), 1595 (w), 1423 (m), 1366 (m), 1411 (m), 1400 (m), 1054 (s), 1012 (s), 1001 (s), 990 (s), 960 (m), 844 (s), 809 (m), 771 (m), 740 (m), 696 (m), 680 cm$^{-1}$ (m). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50; O, 25.78. Found: C, 67.24; H, 6.72; O, 26.04 (by difference).

**1,4,5,8-Tetrakis(bromomethyl)naphthalene (6).** Tetraol **5** (35.9 g, 0.145 mol), tetra-*n*-butylammonium bromide (53.7 g, 0.166 mol), and 1 L of $CH_2Cl_2$ were added to a 2-L, three-necked, round-bottomed flask equipped with a mechanical stirrer, a drying tube, and an addition funnel. The flask was cooled in ice–$H_2O$, and phosphorus tribromide (184 g, 0.68 mol) was rapidly added in drops to the stirring suspension. The ice bath was removed and the mixture was stirred at room temperature for 24 h and then poured into ice. The layers were separated, and the organic layer was evaporated. The resulting solid was washed with $H_2O$, stirred with 500 mL of 5% $NaHCO_3$ solution for 30 min, collected, washed with $H_2O$, and dried in a vacuum desiccator (at 0.1 torr), affording the tetrabromide **6**: 57.0 g (79%); mp 255 °C dec; $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 7.84 (s, 4.05 H, aromatic), 5.39 (s, 7.95 H, $CH_2Br$); IR (KBr) 3058 (w), 3037 (vw), 1538 (m), 1486 (m), 1448

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(s), 1378 (m), 1321 (m), 1308 (s), 1303 (s), 1118 (m), 872 (s), 836 (m), 823 (vs), 702 (vs), 683 (m), 618 (m), 545 cm$^{-1}$ (vs, CBr). Anal. Calcd for $C_{14}H_{12}Br_4$: C, 33.64; H, 2.42; Br, 63.94. Found: C, 33.84; H, 2.45; Br, 63.63.

**Tetraethyl 1,3,6,8-Tetrahydropyrene-2,2,7,7-tetracarboxylate (7).** Sodium ethoxide solution, prepared from sodium metal (14.0 g, 0.609 mol) and 280 mL of absolute EtOH, was transferred to a 500-mL constant-addition funnel attached to an oven-dried, argon-flushed, 500-mL, three-necked, round-bottomed flask. The flask, equipped with a magnetic stirrer, a reflux condenser, and an argon gas inlet, contained the tetrabromide 6 (55.5 g, 0.111 mol), diethyl malonate (36.3 g, 0.226 mol), and 140 mL of absolute EtOH. While the solution in the flask was refluxed, the sodium ethoxide solution was added during 6 h. Reflux was then continued for another 2 h. After the mixture cooled, the crystallized product was dissolved in 200 mL ether, poured onto ice, extracted with ether (3 × 200 mL), washed with $H_2O$ (3 × 100 mL), dried ($MgSO_4$), and stripped. Recrystallization (95% EtOH, Norit) afforded the pure product: 34.6 g (63%); mp 106–108.5 °C; $^1H$ NMR ($CDCl_3$) δ 7.21 (s, 3.99 H, aromatic), 4.09 (q, 8.09 H, $J$ = 7.08 Hz, $OCH_2CH_3$), 3.56 (s, 7.97 H, $CH_2$), 1.10 (t, 11.96 H, $J$ = 7.08 Hz, $OCH_2CH_3$); IR (KBr) 2980 (w), 2972 (w), 1740 (vs, $CO_2Et$), 1600 (w), 1302 (m), 1258 (s), 1240 (s), 1224 (m), 1211 (m), 1193 (m), 1048 cm$^{-1}$ (m).

**1,3,6,8-Tetrahydropyrene-2,7-dicarboxylic Acid (8).** Tetraester 7 (29.2 g, 0.059 mol) and 200 mL of MeOH were added to a 500-mL round-bottomed flask containing a stirring bar and attached to a reflux condenser. KOH (63 g, 1.12 mol) in 175 mL of $H_2O$ was added and the mixture refluxed for 19 h. A salt crystallized as the mixture cooled, and the mixture was concentrated until everything dissolved, diluted with some $H_2O$, washed with 50 mL of ether, and then acidified with dilute HCl. The solid was collected, washed with $H_2O$, and air-dried, giving the crude tetraacid (22.0 g, 97%). This was decarboxylated in a Bryn Mawr sublimer[40] by heating at 230 °C until the pressure decreased to 0.3 mm. The diacid was then sublimed [280 °C (0.1–0.3 mm)], yielding pure 8: 15.8 g (93%); mp >310 °C; $^1H$ NMR ($Me_2SO$-$d_6$) δ 7.21 (s, 3.92 H, aromatic), 3.4–2.95 (br m, 10.10 H, $CH(CH_2)_2$); no $CO_2H$ was observed; IR (KBr) 3020 (m, br), 2946 (m, br), 2890 (m, br), 2840 (m, br), 2620 (m, br), 1700 (vs, $CO_2H$), 1598 (m), 1448 (m), 1428 (m), 1420 (m), 1408 (m), 1298 (m), 1275 (m), 1245 (m), 1212 (m), 956 (m), 940 (m), 829 cm$^{-1}$ (m).

**Dimethyl 1,3,6,8-Tetrahydropyrene-2,7-dicarboxylate (9).** The diacid 8 (11.1 g, 0.038 mol), 550 mL of MeOH, and 40 drops of concentrated $H_2SO_4$ were added to a 1-L round-bottomed flask containing a magnetic stirring bar and attached to a reflux condenser. The solution was refluxed for 24 h and cooled, and most of the MeOH was stripped. The residue, dissolved in 200 mL of $CH_2Cl_2$, was washed with 100 mL of 10% $Na_2CO_3$ solution and 100 mL of $H_2O$, dried ($MgSO_4$), and stripped. Recrystallization (PhH/MeOH) afforded the pure diester 9: 11.4 g (94%); mp 202–220 °C; a mixture of cis and trans isomers; $^1H$ NMR ($CDCl_3$) δ 7.15 (s, 4.09 H, aromatic), 3.77 (s, 5.87 H, $OCH_3$), 3.45–2.95 (br m, 10.02 H); IR (KBr) 3025 (w), 2946 (m), 2935 (m), 1732 (vs, $CO_2CH_3$), 1598 (w), 1437 (m), 1382 (m), 1308 (m), 1258 (m), 1242 (m), 1194 (m), 1167 (s), 1008 (m), 858 (m), 841 cm$^{-1}$ (m).

**2,7-Bis(hydroxymethyl)-1,3,6,8-tetrahydropyrene (10).** Diisobutylaluminum hydride (125 mL, 0.363 mol, 2.9 M in toluene) was added to an oven-dried, argon-flushed, 500-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer and reflux condenser with an argon gas inlet and connected via Gooch tubing to a 125-mL Erlenmeyer flask containing the diester 9 (15.8 g, 0.049 mol). The diester was added in small portions, and dry toluene (50 mL) was used to complete the transfer. After refluxing for 1 h, the solution was cooled, 10 mL of ethyl acetate was added, and the mixture was poured onto ice and acidified. The precipitated solid, after toluene had been pressed out, was stirred with 5% HCl (400 mL) for 30 min, collected, washed, and dried in a vacuum desiccator (0.1 mm), giving the product: 12.8 g (98%); mp 231–244 °C; a mixture of cis and trans isomers; $^1H$ NMR ($Me_2SO$-$d_6$) δ 7.13 (s, 4.20 H, aromatic), 4.67 (br s, 2.02 H, OH), 3.6–2.65 (m, br, 13.77 H); IR (KBr) 3385 (s, br, OH), 3310 (s, br, OH), 2938 (m), 2919 (s), 2878 (m), 2830 (m), 1596 (m), 1472 (m), 1438 (m), 1428 (m), 1404 (m), 1372 (m), 1360 (s), 1282 (m), 1189 (m), 1173 (s), 1090 (m), 1061 (m), 1017 (s), 965 (m), 952 (m), 935 (m), 872 (m), 827 (s), 784 cm$^{-1}$ (m).

**2,7-Bis(chloromethyl)-1,3,6,8-tetrahydropyrene (11).** The diol 10 (12.7 g, 0.047 mol) and 500 mL of dry benzene were added to an oven-dried, argon-flushed, 1-L, three-necked, round-bottomed flask containing a magnetic stirring bar and connected to a reflux condenser with an argon gas inlet. Pyridine (16 mL, 0.20 mol) was added followed by $SOCl_2$ (14.2 g, 0.119 mol), and the mixture was refluxed for 12 h. After the mixture cooled, the solvents were stripped, and the residue, taken up in 700 mL of $CHCl_3$, was filtered, washed with $H_2O$ (3 × 100 mL), and dried ($MgSO_4$), and the solvent was stripped, yielding the dichloride 11 as an off-white solid: 10.9 g (75%); mp 135–150 °C (vacuum); mixture of cis and trans isomers; $^1H$ NMR ($CDCl_3$) δ 7.16 (s, 3.80 H, aromatic), 3.60 (d, 3.80 H, $J$ = 5.5 Hz, $CH_2Cl$), 3.4–2.7 (m, br, 8.40 H), 2.7–2.1 (br m, 2.00 H); IR (KBr) 3028 (w), 2935 (m), 2916 (m), 2901 (m), 1596 (m), 1443 (m), 1437 (m), 1428 (m), 1412 (m), 1290 (m), 1278 (m), 1268 (m), 822 (s), 788 (m), 746 (m), 738 (m), 718 cm$^{-1}$ (m).

**2,7-Bis(cyanomethyl)-1,3,6,8-tetrahydropyrene (12).** The dichloride 11 (10.8 g, 0.035 mol), NaCN (7.25 g, 0.147 mol), and 210 mL of dry $Me_2SO$ were added to an oven-dried, $N_2$-flushed, 500-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer and reflux condenser with $N_2$ gas inlet. After the mixture was stirred at 85–90 °C for 165 h, the solution was cooled and poured into ice–$H_2O$, and the precipitate was collected and washed with $H_2O$. Sublimation [225 °C (0.05 mm)] afforded the product: 9.3 g (92%); mp 212–243 °C; a mixture of cis and trans isomers; $^1H$ NMR ($CDCl_3$) δ 7.14 (s, 3.85 H, aromatic), 3.46–2.70 (br m, 8.19 H), 2.70–2.35 (br s, 5.96 H); IR (KBr) 3026 (w), 2914 (s), 2825 (m), 2243 (m, saturated CN), 1596 (m), 1444 (m), 1428 (m), 1408 (s), 829 cm$^{-1}$ (s).

**2,7-Bis(cyanomethyl)pyrene (13).** The dinitrile 12 (5.6 g, 0.020 mol), DDQ (15.0 g, 0.066 mol), and 500 mL of dry dioxane were added to an oven-dried, argon-flushed, 1-L, round-bottomed flask equipped with a magnetic stirrer and a reflux condenser with an argon gas inlet. The mixture was refluxed for 17 h, cooled, and concentrated, and the residue was taken up in 200 mL of 10% $NaHCO_3$ solution and filtered. The crude product was washed with $H_2O$, dried in air, and sublimed [260 °C (0.05 mm)], yielding the pure dinitrile 13: 3.27 g (60%); mp 285–287 °C dec; $^1H$ NMR ($Me_2SO$-$d_6$) δ 8.27, 8.22 (s, 7.84 H, aromatic), 4.53 (s, 4.15 H, $CH_2CN$); IR (KBr) 3042 (w), 2957 (m), 2913 (m), 2248 (m), 1612 (m), 1448 (m), 1412 (m), 1368 (m), 926 (m), 868 (s), 806 (m), 712 (s), 703 cm$^{-1}$ (m).

**2,2′-(2,7-Pyrenediyl)bis[(carboethoxy)propanedinitrile] (14).** Sodium ethoxide was prepared from sodium metal (1.0 g, 0.044 mol) and 48 mL of absolute EtOH in an oven-dried, argon-flushed, 250-mL, three-necked, round-bottomed flask containing a magnetic stirrer and connected to a still head, condenser, receiver, and argon inlet. A septum sealed another of the flask's necks. The EtOH was distilled off, and 100 mL of dry toluene was added. Diethyl carbonate (20.4 g, 0.173 mol) and the dinitrile 13 (5.05 g, 0.018 mol) were added, and the mixture was vigorously stirred and heated while the solvent distilled and the temperature reached 110 °C. The solution was then cooled in ice, CNCl (8 mL, 10 g, 0.16 mol) was distilled in over a 2-h period, and the reaction mixture was then stirred at 60 °C for 2 h and at room temperature overnight. After the mixture cooled, the precipitate was collected, washed with toluene, stirred with 200 mL of ice–$H_2O$, collected again, washed with $H_2O$, and dried in a vacuum desiccator (0.1 mm). The crude product was then taken up in 600 mL of boiling toluene containing Norit, filtered, concentrated to 200 mL, and cooled, affording the product as white needles, which were collected and dried: 5.54 g (65%); mp 274–275 °C dec; $^1H$ NMR ($CDCl_3$) δ 8.54, 8.26 (s, 7.94 H, aromatic), 4.49 (q, 4.06 H, $J$ = 7.08 Hz, $OCH_2CH_3$), 1.32 (t, 6.00 H, $J$ = 7.08 Hz, $OCH_2CH_3$); IR (KBr) 2989 (w), 2252 (w), 1765 (s, $CO_2Et$), 1605 (m), 1448 (m), 1414 (m), 1296 (m), 1270 (m), 1234 (s), 1159 (m), 1114 (m), 1042 (m), 1011 (m), 883 (m), 870 (m), 850 (m), 712 (m), 690 cm$^{-1}$ (m).

**2,2′-(2,7-Pyrenediyl)bis[propanedinitrile] (2).** The diester 14 (5.54 g, 0.012 mol) was added to a 500-mL round-bottomed flask containing a magnetic stirrer and 195 mL of a 10% KOH/$H_2O$ solution. The mixture was stirred for 20 min at room

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temperature and then acidified with dilute HCl while cooling. The initial red color turned to yellow and then white. After the mixture was cooled in ice, a solid precipitate was collected, washed with $H_2O$, and dried under vacuum (0.1 mm). Taken up in 2 L of boiling $CH_3CN$ containing Norit, filtered, concentrated to 1 L, and cooled, it gave a first crop, and after concentration to 250 mL, a second was obtained for a total yield of tetranitrile **2** amounting to 3.15 g (81%): mp 325–330 °C dec (lit.[2] mp >360 °C); $^1H$ NMR ($Me_2SO$-$d_6$) $\delta$ 8.38, 8.28 (s, 7.75 H, aromatic), 6.68 (s, 2.26 H, $C(CN)_2\mathbf{H}$); IR (KBr) 3025 (w), 2944 (s), 2255 (w, saturated CN), 1608 (m), 1448 (w), 1408 (w), 1327 (m), 1002 (m), 900 (s), 875 (s), 712 (s), 694 (m), 382 $cm^{-1}$ (m). UV ($CH_3CN$) $\lambda_{max}$ 273 nm (log $\epsilon$ 4.53), 246.5 (4.73), 264 (4.33), 275 (4.39), 309 (4.26), 323 (4.65), 337 (4.60), 372 (3.83). Anal. Calcd for $C_{22}H_{10}N_4$: C, 79.99; H, 3.05; N, 16.96. Found: C, 80.22; H, 3.21; N, 16.75.

**Bis(tetra-*n*-butylammonium) Salt of 2 (15).** The tetranitrile **2** (0.203 g, 0.62 mmol), tetra-*n*-butylammonium hydroxide (0.352 g, 1.36 mmol, 40% solution/$H_2O$), and 50 mL of $CH_3CN$ were added to a nitrogen-flushed 100-mL round-bottomed flask containing a stirring bar. The reaction mixture was stirred until all the solid had dissolved (ca. 45 min), and $H_2O$ (125 mL) was added to precipitate the product, which was collected and dried under vacuum (0.1 mm), giving an orange solid, 0.41 g (82%). An analytical sample was prepared by recrystallization from 2:3 $EtOH/H_2O$: mp 209–210.5 °C (red liquid); $^1H$ NMR ($CD_3CN$) $\delta$ 7.69, 7.50 (s, 7.94 H, aromatic), 3.02 (t, asymmetric, skewed, 16.05 H, $J$ = 8.64 Hz, $N^+CH_2$), 1.72–1.08 (m, br, 32.10 H), 0.94 (t, asymmetric, skewed, 23.91 H, $J$ = 6.40 Hz, $CH_2CH_3$); IR (KBr) 2957 (s), 2870 (m), 2157 (s, $^-C(CN)_2$), 2120 (s, $^-C(CN)_2$), 1600 (s), 1578 (m), 1478 (m), 1450 (s), 1377 (m), 1318 (s), 1208 (m), 1150 (m), 764 (m); UV ($CH_3CN$) $\lambda_{max}$ 234 nm (log $\epsilon$ 4.43), 295 (4.38), 310 (4.75), 323 (5.18), 337 (4.83), 365 (4.83). Anal. Calcd for $C_{54}H_{80}N_6$: C, 79.75; H, 9.92; N, 10.33. Found: C, 79.82; H, 9.73; N, 10.28.

**Purple Solid.** Tetranitrile **2** (0.119 g, 0.36 mmol) and 140 mL of dry $CH_3CN$ were added to a flame-dried, $N_2$-flushed, 250-mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser with a $N_2$ gas inlet. The suspension was heated to reflux until **2** dissolved, and DDQ (0.40 g, 1.76 mmol) in 1 mL of dry $CH_3CN$ was then syringed in over a 1-min period. A purple precipitate formed, and the reaction mixture was refluxed further for 15 min. After the mixture cooled, the solid was collected, washed with $CH_3CN$, and dried under vacuum (0.15 torr), yielding a purple solid: 0.101 g (85%, assuming mol wt 328); mp >330 °C. The product was too insoluble for the $^1H$ NMR spectrum (Fourier transform, 80 MHz) to be measured: IR (KBr) 3055 (w), 3025 (w), 2924 (w), 2255 (w), 1605 (m), 1598 (m, sh), 1470 (w), 1450 (m), 1402 (m), 1385 (w), 1317 (m), 1212 (m), 1162 (m), 1137 (w), 1008 (m, br), 910 (m), 874 (vs), 808 (m), 738 (w), 724 (m), 704 (s), 570 (w), 532 (vw), 497 $cm^{-1}$ (w).

The purple solid was also prepared by chemical oxidation with *N*-chloro-, *N*-bromo-, or *N*-iodosuccinimide/TEA/$CH_3CN$ or DMF, with pyridinium hydrobromide perbromide/$CH_3CN$, with $Br_2$ or $I_2/NaH/CH_3CN$ or DMF, and with DDQ/dioxane under $N_2$. In each case it was identified by the IR spectrum which was identical with that obtained in the DDQ/$CH_3CN$ reaction. Elemental analysis of four different samples are shown in Table III.

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# Mechanisms of Bromination of Uracil Derivatives. 6.[1] Cytosine and N-Substituted Derivatives

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The reactions of bromine with cytosine, 1-methylcytosine, cytidine, and 3-methylcytosine in acidic aqueous solutions have been studied. Initially adducts (5-bromo-5,6-dihydro-6-hydroxycytosines) are produced which are clearly observable by proton NMR, albeit in their protonated forms in the acidic media used. In time the adducts undergo elimination of water to give substitution products, 5-bromocytosines. Kinetic measurements of the initial reaction in the pH range 0–5 are consistent with the adducts resulting from rate-determining attack of bromine on the free base form of the cytosine substrates followed by capture of the cation so produced by water. An alternative mechanism involving first hydration and then bromine attack can be ruled out.

Simple uracils undergo electrophilic bromination in aqueous solution by an addition–elimination mechanism, as first proposed by Wang.[2] The validity of his proposal was shown by studies carried out in this laboratory.[1,3] Kinetic studies provided details of both the addition step[1] and the elimination step,[3] and the postulated adducts were clearly observed by proton NMR.[3] The product of the addition–elimination sequence is a 5-bromouracil which can also react with aqueous bromine to undergo the formal addition of HOBr and give a 5,5-dibromo derivative.[1-3]

During the course of our earlier studies[3] Banerjee also observed by NMR the formation of an adduct, **2a**, resulting from the reaction of aqueous bromine with cytosine (**1a**).[4] It seemed probable, therefore, that bromination of cytosines also proceeded by an addition–elimination mechanism such as shown in Scheme I, and so we undertook a study of the reaction by methods similar to those used in our earlier work on uracils.[1,3] While this study was in

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