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Large Electron Acceptors for Molecular Metals: 13,13,14,14-Tetracyano-4,5,9,10-tetrahydro-2,7-pyrenoquinodimethane (TCNTP) and Anions of 13,13,14,14-Tetracyano-2,7-pyrenoquinodimethane (TCNP)

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The acceptor, TCNTP, prepared by oxidation of dimalonitrile VIII or IX, is reversibly ionized by two one-electron reductions at a platinum electrode in butyronitrile with 0.1 M tetrabutylammonium tetrafluoroborate at half-wave potential $E_{1/2}(1)$ red = −0.145 V and $E_{1/2}(2)$ = −0.449 V vs. an $Ag/AgNO_3$ reference electrode. Allylic bromination of metacyclophane III followed by treatment with sodium cyanide provides diacetonitrile VI, which acts with potassium hydride and diethyl carbonate to form a bis(cyanoacetate) dianion for reaction with cyanogen chloride. Base hydrolysis and decarboxylation of diacetate VII leads to VIII and IX. Dehydrogenation of TCNTP in chlorobenzene with 10% palladium on carbon under reflux produces pyrene X, which is deprotonated with base and the dianion precipitated by the addition of tetraalkylammonium hydroxide. Cyclic voltammetry of $(TBA)_2(TCNP)$ (TBA = tetrabutylammonium) shows a reversible oxidation of $E_{1/2}$ = −0.342 V vs. $Ag/AgNO_3$ and a largely irreversible oxidation at $E_{1/2}$ = −0.032 V.

Metallic conduction in organic charge-transfer salts generally occurs along chains of stacked planar molecular ions. By exploiting the flexibility of organic synthesis, ions can be modified systematically to control solid-state properties.[1-3] For example, by use of substituent groups to determine interchain spacings,[2] of heteroatoms to alter intrachain bandwidths,[3] and of both to adjust ionization potentials and electron affinities,[1] we have produced a family of materials whose properties vary progressively from Mott insulators to metals and even superconductors. Less active attention has been given the potential effects of controlling still another molecular variable, the spatial extent of the molecular orbitals which are the basis states for the electronic conduction band.

Specifically, in a series of acceptor molecules whose sizes increase while their first electron affinities (A_1) increase only slightly, we expect to find systematic decreases in the strength of the intramolecular Coulomb repulsion (U) between two conduction electrons in the same frontier molecular orbital. Since molecular size also affects the degree to which U is screened in the metallic solid state, we expect these variations to be manifested in the magnetic and electrical properties of corresponding charge-transfer salts. Further, since the value of U also bears directly upon the cohesive energy and the degree of charge transfer from donor to acceptor, we expect the chemistry of charge-transfer salt formation in these systems to be especially interesting.

In this paper we report the detailed synthesis and characterization, and some charge-transfer chemistry, of two large electron-acceptor molecules on the basis of the prototype 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ). The two, 13,13,14,14-tetracyano-4,5,9,10-tetrahydro-2,7-pyrenoquinodimethane (TCNTP) and 13,13,14,14-tetracyano-2,7-pyrenoquinodimethane (TCNP) (Figure 1), are designed so as to retain the basic structure of TCNQ but to increase the separation between the two electron-withdrawing dicyanomethylene groups which largely determine A_1. In TCNP further delocalization of the conduction electrons is achieved by adding an additional four carbon atoms to the π-system.

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(1) See, for example: Torrance, J. B. *Acc. Chem. Res.* **1977**, *12*, 79–86. Berlinsky, A. J. *Contemp. Phys.* **1976**, *17*, 331–354. Garito, A. F.; Heeger, A. J. *Acc. Chem. Res.* **1974**, *7*, 232–240.

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(3) 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*, 1–26. 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.

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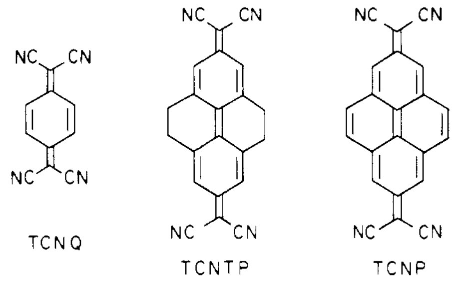


Figure 1.

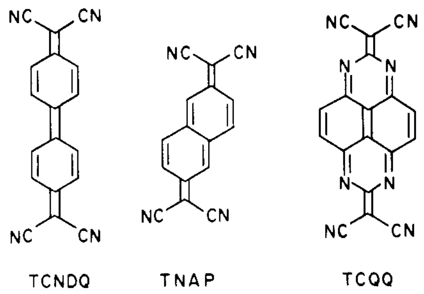


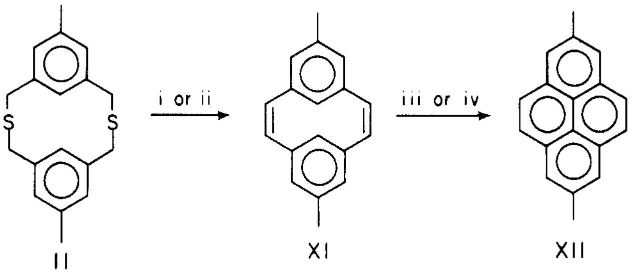
Figure 2.

The study of large analogues of TCNQ began at least by 1963 with the synthesis of 11,11,12,12-tetracyano-2,6-naphthoquinodimethane (TNAP),[4] a stable, planar oxidizing agent whose first electron affinity, A_1, is 2.88 eV by our measurement (see the section on electrochemistry) compared to 2.84 eV for TCNQ. The difference between electrochemical half-wave potentials, $\Delta E_{1/2}$, for the first and second reductions of TNAP is about 70% as large as TCNQ's $\Delta E_{1/2}$, indicating the relative magnitudes of their free molecular U.

After the report of metallic conductivity observed in (TTF)(TCNQ) (TTF = tetrathiafulvalene)[5] improvements in the TNAP synthesis were reported by Sandman,[6] using the Du Pont scheme for making substituted TCNQ's,[7] and by Wilson and co-workers.[8] These improvements led to several TNAP salts similar to their respective TCNQ analogues plus single crystals of (TTF)(TNAP) which are metallic at medium temperatures but undergo a sharp metal–insulator transition below 185 K.[9] The thermally activated conductivity at low temperature has been ascribed, in part, to the lower symmetry of TNAP and to the disparity in size of donor and acceptor (Figure 2).

Another large acceptor, the biphenyl analogue of TCNQ, has been pursued since 1964. The dianion of tetracyanodiphenoquinodimethane (TCNDQ) was prepared first at Du Pont[10] and later by Weiler et al.[11] who determined its spectroscopic and solution electrochemical properties. In 1979, a group at Osaka University reported resistivities of its sodium, *N*-methylquinolinium, and *N*-methylphenazinium salts, all of which are insulating at room temperature.[12] Neutral TCNDQ has not been isolated; yet, its A_1 is substantially lower than TCNQ contrary to predictions for a large π-system. This suggests that the ortho–ortho hydrogen repulsions force a twist about the central double bond such that there is incomplete delocalization between the rings. The very small $\Delta E_{1/2} = 0.16$ eV reported may not be representative of a divalent acceptor with an extended π-system but rather two monovalent acceptors covalently bonded.

Scheme I[a]



[a] (i) (1) $(CH_3O)_2CHBF_4$, (2) $KO(t\text{-}C_4H_7)$, (3) $(CH_3O)_2CHBF_4$, (4) $n\text{-}(C_4H_7)Li$; (ii) (1) $n\text{-}(C_4H_7)Li$ then CH_3I, (2) $(CH_3O)_2CHPF_6$, (3) $n\text{-}(C_4H_7)Li$; (iii) $FeCl_3(aq)\text{-}CH_3Cl$; (iv) UV irradiation, O_2.

In order to overcome the steric shortcomings evident in TCNDQ, Wudl and co-workers prepared tetracyanoquinazolinoquinazoline (TCQQ).[13] TCQQ is relatively stable as its di- and trianion, but its metathesis products have yet to be reported. It is nonetheless a rigid π-system capable of multiple oxidation states and is compatible in size and symmetry with many of the large sulfur and selenium heterocyclic donors.

Work in our laboratories to synthesize TCNP in its various oxidation states began in 1975 and produced TCNTP[14a] en route to the pyrene analogue of TCNQ. An independent synthesis of TCNTP has been reported by Aharon-Shalom, Becker, and Agranat.[14b] TCNP was expected to provide a large planar and symmetric acceptor that is stable as the dianion, radical anion, and neutral species. It was also anticipated to be somewhat more strongly oxidizing than TNAP with a smaller $\Delta E_{1/2}$ signifying a further reduction in its free molecular U.

Results and Discussion

Initial Approach to TCNP. The initial approach to make the fully conjugated pyrene acceptor was to prepare 2,7-dimethylpyrene (XII in Scheme I) and apply Du Pont's methods for functionalizing the terminal methyls.[7] Whereas pyrene does not lend itself to substitution at the 2- and 7-positions, the appropriately substituted compound XII is known to be the principal oxidation product of diene XI via ferric chloride[15] or photoinduced air dehydrogenation.[16] Several routes were tried to arrive at XI all starting from thiacyclophane II prepared by a high-dilution coupling reaction of 3,5-bis(mercaptomethyl)toluene and its corresponding dibromide described by Mitchell and Carruthers.[16] Two modifications of a Ramberg-Bäcklund ring contraction of the corresponding sulfone were un-

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(5) Ferraris, J.; Cowan, D. O.; Walatka, V., Jr.; Perlstein, J. *J. Am. Chem. Soc.* **1973**, *95*, 948–949.

(6) Sandman, D. J.; Garito, A. F. *J. Org. Chem.* **1974**, *39*, 1165–1166.

(7) Martin, E. L. U.S. Patent 3 504 001, 1975.

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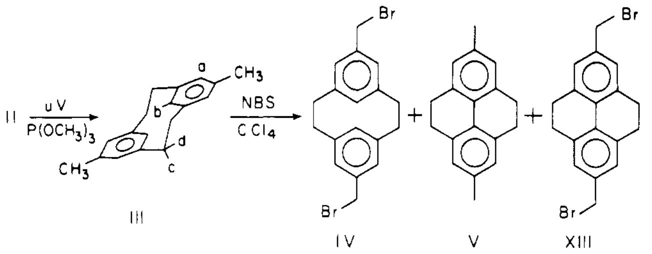
Scheme II



successful,[17,18] but the longer Stevens reaction followed by a Hoffmann elimination[19] did produce XI as did the Wittig rearrangement described by Mitchell et al.[20] Attempts to halogenate XII were frustrated by its low solubility in suitable solvents, and this approach was abandoned in favor of preparing and functionalizing the more soluble metacyclophane III.

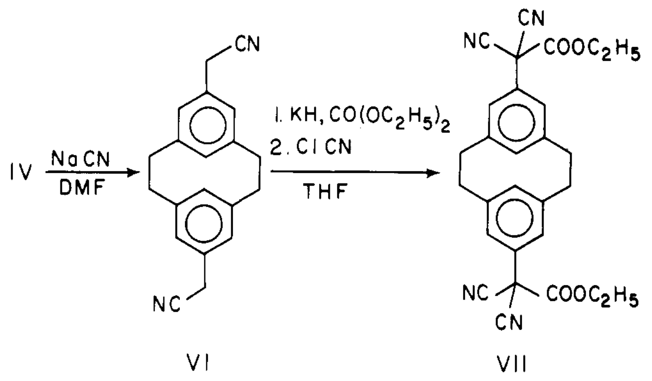
Synthesis of TCNTP. A photochemical sulfur extrusion from II using neat trimethyl phosphite provided III in 48% yield.[21] Careful purification to remove the partially reacted monothiacyclophane and the thiophosphate byproduct, completed by sublimation, made a substantial improvement in the steps that followed. The proton magnetic resonance signals of III form a distinctive pattern, consistent with a "chair" conformation, which remains in the spectra of the next four intermediates.[22] For the unsubstituted metacyclophane III, external aromatic proton resonances (a) appear at δ 6.98 (from Me$_4$Si), internal aromatic protons (b) at δ 4.02, equatorial bridge protons (c) at δ 3.07 (d, J = 7 Hz), and axial bridge protons (d) at δ 2.09 (d, J = 7 Hz), ppm.

Treatment of III with *N*-bromosuccinimide (NBS) in carbon tetrachloride resulted in a mixture of the desired bromination product IV (typical yields ranged 42–50%), the oxidation product 2,7-dimethyl-4,5,9,10-tetrahydropyrene (V, 5–12%), and varying amounts (as high as 30% yield from III) of 2,7-bis(bromomethyl)-4,5,9,10-tetrahydropyrene (XIII) as well as monobromination products (Scheme II). The NMR of the more nearly planar hydrocarbon, V, is marked by a disappearance of the internal aromatic proton signal and the coalescence of the methylene protons into a singlet at δ 2.84[22] Further treatment of V with NBS or pyridinium hydrobromide perbromide gave only XII. Compound XIII underwent the reaction sequence without significant variation from the conditions and yields reported for the cyclophane intermediates.

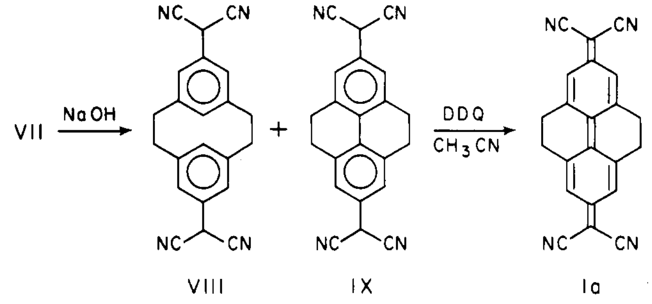
Displacement of the benzylic bromide by excess sodium cyanide in dimethylformamide[8] yielded (at least 90%) diacetonitrile VI, mp 191–192.5 °C. A weak absorption at 2245 cm^{-1} in its infrared spectrum indicates an unconjugated cyanide group.

Activation of the benzylic cyanocarbanion with a carbethoxy group, as described by Wheland and Martin,[7,23] proved to be a necessary condition for the substrate to react with cyanogen chloride. Distilling cyanogen chloride into a mixture of potassium hydride and VI in tetrahydrofuran (THF) gave no reaction. Likewise cyanogen bromide was unreactive toward VI under any circumstances. When an ice-cold solution of VI in THF is added to a cold slurry of potassium hydride in diethyl carbonate and THF,[24] a vigorous reaction ensues producing a dark brown sticky slurry. The NMR spectrum of an aliquot of reaction mixture, quenched at this point with acid, is consistent with diethyl α,α'-dicyano[2.2]metacyclophane-5,13-diacetate. Addition of a large excess of cyanogen chloride appeared to be essential to complete conversion of the dianion of the diacetate to VII (30–70%), mp 235–238 °C (Scheme III). NMR of VII indicates the loss of benzylic hydrogens other than bridge hydrogens and the appearance of the ethoxy pattern at δ 4.36 (q, J = 6 Hz) and 1.26 (t, J = 6 Hz). Infrared (KBr) absorptions at 2245 and 1760 cm^{-1} indicate an unconjugated cyanide and an ester carbonyl, respectively.

Scheme III



Scheme IV



Hydrolysis and decarboxylation of VII by aqueous sodium hydroxide[6] under rigorously degassed conditions provided a good yield (80–90%) of nearly pure metacyclophane VIII, mp 224–226 °C, plus some IX (less than 5%). The IR (KBr) of VIII shows the 2245-cm^{-1} absorption and its NMR records the aryl malononitrile hydrogen at δ 5.08. Less air-free conditions for the decarboxylation led to higher proportions of IX to VIII, and bubbling oxygen through the reaction mixture gave about 85% IX. Ferric chloride in water was stirred in a chloroform solution[15] of the metacyclophane to oxidize it to IX (93%) for purposes of characterization, mp 280 °C dec. Its NMR shows the aryl malononitrile hydrogen as a singlet at δ 5.06 and bridge hydrogens as a singlet at δ 2.97 instead of the pair of doublets characteristic of the cyclophanes. The electronic spectrum of IX (THF) has absorbance maxima at 292 (log ϵ = 3.90) and 355 nm (3.15).

Both VIII and IX react with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing acetonitrile to give (75–87%) TCNTP, Ia, mp >360 °C (Scheme IV). NMR

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[17] Paquette, L. A.; Wingard, R. E., Jr.; Philips, J. C.; Thompson, G. L.; Read, L. K.; Clardy, J. *J. Am. Chem. Soc.* **1971**, *93*, 4508–4512.

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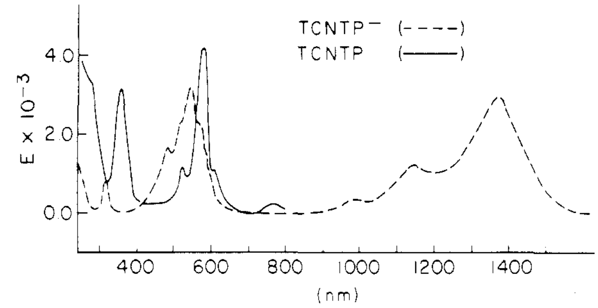


Figure 3. Electronic spectra of Ia in acetonitrile with 0.1 M (TBA)(BF_4) before and after reduction at −0.30 V vs. an Ag/$AgNO_3$ reference electrode.

signals appear only at δ 7.53 and 3.02 reflecting the vinylic and bridge hydrogens, respectively. The cyanide absorption in the IR is shifted to longer wavelength, 2205 cm^{-1}, due to conjugation with the π-system. A band appears in the visible region of the electronic spectrum, shown in Figure 3, at 571 nm (log ε = 3.63), consistent with the violet-blue color, as well as maxima at 265 (3.55) and 349 nm (3.50).

Mass spectra were obtained for several samples of TCNTP produced by various oxidation methods from VIII or IX. All samples gave an $M^+ + 2$ (*m/e* 334) peak of comparable intensity to the molecular ion peak (*m/e* 332). On one sample, time–intensity graphs of total ion current, ion current at 334, and ion current at 332 show that M^+ and $M^+ + 2$ have identical profiles. This is consistent with the 332 and 334 peaks originating from the same species. Apparently the acceptor Ia picks up an equivalent hydrogen in the probe in the same way that solutions of TCNTP in water-soluble solvents revert to IX within a day.

Hydrogenation and dehydrogenation both appear to be occurring with this structure in the mass spectrometer. This is suggested by the absence of heavy isotope peaks, e.g., M^+ (*m/e* 336), in the spectrum of 4,5,9,10-tetrahydro-2,7-pyrene(dimalononitrile-d_2) or TCNTP-d_2. Instead, the mass spectrum was identical with that of IX or TCNTP(H_2). The deuterium-enriched analogue of IX was prepared by decarboxylation of VII in 10% KOD/D_2O with oxygen bubbling followed by quenching with DCl produced by the reaction of D_2O and benzoyl chloride. The NMR ($CDCl_3$) was identical with that of IX except for a marked depletion of malononitrile hydrogens.

In order to test the reactivity of TCNTP (see also the section on electrochemistry) with various donors, three complexation regimes were adopted. Diffusion techniques were abandoned quickly owing to the low solubility of the acceptor at moderate temperatures. Slow cooling of sealed solutions of TCNTP in chlorobenzene, nitrobenzene, and butyronitrile plus equimolar TTF, Me_4TTF, tetramethyltetraselenafulvalene (TMTSF), hexamethylenetetraselenafulvalene (HMTSF), quinolinium iodide, morpholinium iodide, and triethylammonium iodide produced recoverable salts of TMTTF only. Combining boiling solutions of TCNTP in chloroform with solutions of TTF and TMTTF in hot chloroform produced a black powder (compaction σ_{RT} about 10^{-8} ohm^{-1} cm^{-1}) and black needles (compaction σ_{RT} = 0.2 ohm^{-1} cm^{-1}), respectively. Metathesis reactions were tried by combining electrochemically generated tetrafluoroborate salts of TTF, TMTTF, and dithiophenotetrathiafulvalene with (TBA)(TCNTP) without recovering any donor–acceptor salt.

Our observation is that, for most donors used in organic metals, the difference between the first ionization potential and the first electron affinity of TCNTP ($I_1 - A_1$) is too large and positive to react with sufficient charge transfer to stabilize segregated stacks. The possible exception is TMTTF, which is the strongest reducing agent of the donors employed. In addition, lowering the $\Delta E_{1/2}$ from those of previous acceptors seems to exaggerate the tendency for TCNTP to revert to its hydrogenated precursor, IX, in water-soluble solvents.

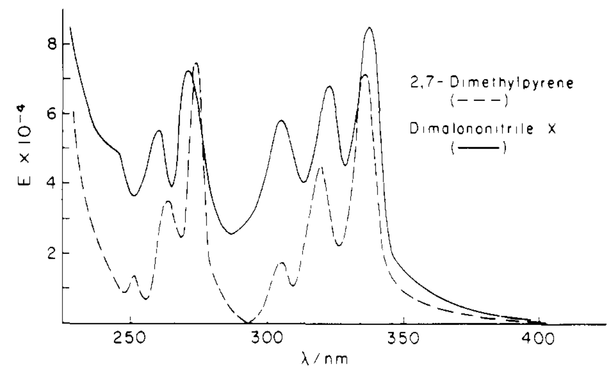
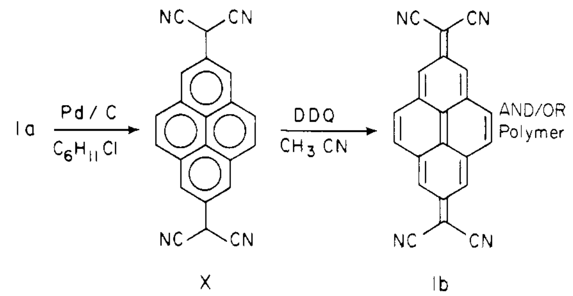


Figure 4. Electronic spectrum of X in acetonitrile superimposed on that of 2,7-dimethylpyrene, also in acetonitrile, prepared by the initial synthetic scheme.

Scheme V



X Ib

Synthesis of TCNP^{2-}. Anhydrous ferric chloride, NBS, DDQ, bromine plus pyridine,[25] and bromine water can each oxidize dimalononitriles VIII and IX to give acceptor Ia with varying ease; but none of these reagents acted to dehydrogenate the bridge methylenes to give the fully unsaturated acceptor Ib (Scheme V). However, 10% palladium on carbon was able to fully aromatize the pyrene structure of TCNTP in refluxing chlorobenzene over 4 days (refluxing 1,2,4-trichlorobenzene effected reaction more quickly and butyronitrile very slowly) to yield 2,7-pyrenedimalononitrile (X, 60–64%), mp > 360 °C. The infrared spectrum of X includes the 2250-cm^{-1} absorption and its electronic spectrum (acetonitrile), compared to that of 2,7-dimethylpyrene in Figure 4, has maxima at 260 (log ε = 4.75), 270 (4.86), 305 (4.76), 323 (4.84), and 338 nm (4.93). Compounds VIII and IX were unchanged by the treatment with palladium on carbon in chlorobenzene.

Tetraalkylammonium salts of Ib were precipitated from a solution of X in aqueous sodium hydroxide by addition of tetraethyl- or tetrabutylammonium hydroxide. $(TBA)_2$(TCNP) exhibits a proton resonance at δ 7.80 plus the pattern due to the ethyl hydrogens. The bis(tetrabutylammonium) salt is more resistant to air oxidation and was used for further characterization. Its IR (KBr) shows two sharp, equally intense absorptions at 2160 and 2120 cm^{-1} due to two asymmetric modes of CN vibration. Its electronic spectrum is shown in Figure 5.

Reaction of $(TBA)_2$(TCNP) with a solution of $(TTF)_3(BF_4)_2$[26] in acetonitrile promptly gave a brown solid with

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[25] Acker, D. A.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370–3374.

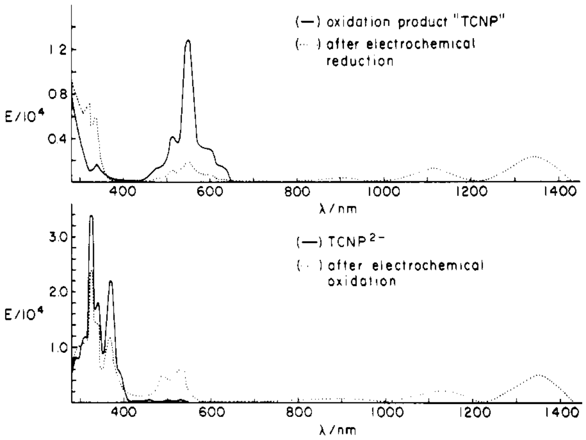

Figure 5. (Top) Electronic spectra of the oxidation product of X in butyronitrile with 0.1 M (TBA)(BF_4) before and after partial reduction at −0.15 V vs. an Ag/$AgNO_3$ reference electrode. (Bottom) Electronic spectra of a solution of $(TBA)_2$(TCNP) in butyronitrile with 0.1 M (TBA)(BF_4) before and after partial oxidation at −0.02 V vs. an Ag/$AgNO_3$ reference electrode.

a room temperature compaction resistivity of about 10^6 Ω cm. The material was presumed to be a (TTF)(TCNP) salt that does not have a segregated stack morphology.

Chemical Oxidation of TCNP(H_2). As soon as DDQ in acetonitrile was added to a refluxing solution of X in acetonitrile, a blue solid precipitated, mp > 360 °C. The infrared (KBr) of the solid shows two cyanide vibrations at 2255 and 2205 cm^{-1} (5:1 relative intensity). Whereas the poor solubility of the solid prevented complete characterization, some of it was sparingly soluble in butyronitrile. The electronic spectrum of this fraction, shown in Figure 5, reveals λ_{max} at 557 nm (log ϵ = 4.12) in the visible region as well as at 243 (4.60) and 340 nm (3.31). The mass spectrum of the solid is the same as that of X except for the addition of peaks at *m/e* 329 (13% relative intensity; $M^+ + 1$ assuming $TCNP^0$ is the product), 328 (10%, M^+), and 164 (2%, M^{2+}) and the omission of the 202 (330 − C_6N_4) peak. Precise mass measurement of the *m/e* 328 peak is consistent with $C_{22}H_8N_4$, TCNP.

Acton et al.[27] reported the chemical oxidation of X plus the electrochemical oxidation of $TCNP^{2-}$ and observed only the 2255-cm^{-1} CN vibration in the infrared of the products. They concluded that $TCNP^0$ is unstable relative to a polymerization product. A precedent for partial polymerization was observed in the final step of a TNAP synthesis when 2,6-naphthalenedimalononitrile, TNAP(H_2), is oxidized TNAP.[4] We concur that a majority of the oxidation product is polymeric but feel that monomeric TCNP is produced under our conditions. The strongest evidence for stable $TCNP^0$ is that $TCNP^{-}\cdot$ can be electrochemically generated from the oxidation product (see the section on electrochemistry). Whether or not the neutral acceptor can be produced, its expected insolubility would most likely preclude its use in the formation of complexes. The best route for the formation of TCNP complexes is via metathesis reactions with the soluble, stable TCNP dianion.

Characterization of Acceptor Reactivity. The reactivity of an electron donor or acceptor is in part characterized by its cyclic voltamogram (CV). The numerical values generally reported for acceptors are the half-wave reduction potentials, $E_{1/2}$, determined as the mean values between the cathodic current peak voltages and their corresponding anodic peaks representing one-electron reductions and subsequent reoxidations. Although the CV gives evidence for the reversibility of electron transfers and relative reactivity in a particular solvent, its peak voltages can vary dramatically due to variations in solvent, electrolyte, reference electrode bridge, and temperature. For this reason, unless the electrochemical conditions are scrupulously duplicated, a meaningful measure of acceptor oxidizing strength cannot be achieved by comparing their $E_{1/2}$ values. We recommended that acceptors be characterized by converting their first reduction $E_{1/2}(1)$ values to electron affinities (A_1) and that $\Delta E_{1/2}$ (equal to $E_{1/2}(2) - E_{1/2}(1)$) values be compared only when obtained under identical conditions. The second electron affinity (A_2) has a bearing on $E_{1/2}(2)$, but there are insufficient data on A_2 to make a quantitative relation between them.

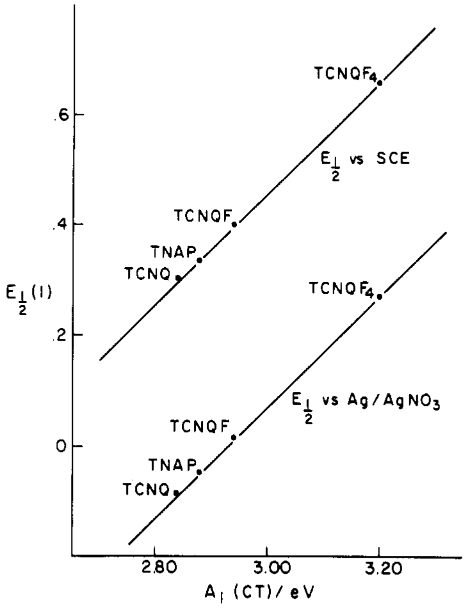

Figure 6. Plot of acceptor electron affinity calculated from the charge-transfer band λ_{max}, by eq 1, vs. first reduction half-wave potentials, vs. a saturated calomel electrode and an Ag/$AgNO_3$ reference electrode. The lines are described by the equation

$$A_1(E_{1/2}) = (E_{1/2})_1 - \Delta G_{sol} - C \qquad (2)$$

where ΔG_{sol} = 2.53 eV for butyronitrile and C = −5.07 eV for the SCE and −5.45 eV for the Ag/$AgNO_3$ electrode.[28]

Table I. Reduction Half-Wave Potentials for TCNTP, TCNP, and Known Acceptors and Their Electron Affinities

acceptor	h/λ(CT), eV	A_1(CT),[a] eV	$A_1(E_{1/2})$,[b] eV	$(E_{1/2})(1)$,[c] V	$-\Delta E_{1/2}$,[c] V
TCNTP			2.79	−0.145	0.304
TCNQ	1.67	2.84	2.84	−0.083	0.642
TNAP	1.63	2.88	2.88	−0.047	0.458
TCNP			2.90	−0.032[d]	0.310[d]
TCNQF	1.57	2.94	2.95	+0.017	0.643
$TCNQF_4$	1.31	3.20	3.20	+0.270	0.602

[a] Calculated from eq 1, with esd ±0.02 eV. [b] Calculated from eq 2, with esd ±0.01 eV. [c] Vs. Ag/$AgNO_3$ reference electrode. [d] Estimated from the second oxidation waves of $(TBA)_2$(TCNP) at E_{Pa} = +0.026 V and E_{Pc} = −0.09 ± 0.02 V.

In order to establish a reliable calculation of A_1 from $E_{1/2}(1)$, A_1's for four known acceptors were determined spectrophotometrically and plotted vs. their $E_{1/2}(1)$'s (Figure 6) obtained under identical conditions. Chen and Wentworth[28] have demonstrated that the A_1, calculated

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from the charge transfer energy of an acceptor complexed with a donor of known ionization potential I_1, is as accurate as electron affinities measured by photodetachment[29] and magnetron[30] methods. The procedure of Merrifield and Phillips[31] was employed to determine the charge transfer energy of TCNQ, TNAP, TCNQF,[32] and TCNQF$_4$[23] with pyrene in methylene chloride. The $\lambda_{\max}$ of the resulting charge transfer bands, pyrene's I_1 = 7.41 eV, and an empirical constant C = -2.90 eV[28] were used in eq 1 derived

$$A_1(\mathrm{CT}) = I_1 + C - h/\lambda_{\max}(\mathrm{CT}) \qquad (1)$$

by Chen and Wentworth to calculate A_1(CT)'s, listed in Table I. The linearity of the relationship between A_1(CT) and $E_{1/2}(1)$ suggests that A_1, for closely related compounds, can be determined directly from its CV if the electrochemistry is performed without deviation from the procedures used to measure the standards.

Solution Electrochemistry of TCNTP and TCNP^{2-}. A solution of TCNTP in butyronitrile with 0.1 M tetrabutylammonium tetrafluoroborate (TBA)(BF$_4$) undergoes two reversible reductions at $E_{1/2}(1)$ = -0.145 V and $E_{1/2}(2)$ = -0.449 V vs. a silver/silver nitrate reference electrode. Its $E_{1/2}(1)$ corresponds to A_1 = 2.79 eV, if the larger size of TCNTP can be assumed to have negligible effect on the solvation energy change in going from the neutral species to the radical anion. This assumption appears to be valid for TNAP and may be extended to TCNTP. The $E_{1/2}(1)$ is surprisingly negative considering TCNTP's large π-system. The extended conjugation is reflected in the electronic spectrum of its radical anion, generated by passing 1 Faraday per mol of TCNTP from the working electrode at -0.30 V vs. Ag/AgNO$_3$. Near-infrared bands at 980 (log ϵ = 2.57), 1135 (3.09), and 1358 nm (3.48) appear (Figure 3) as predicted by extended Hückel calculations.[14b] On the basis of the extent of its π-system, the $E_{1/2}(1)$ of TCNTP would be expected to be less negative than those of TCNQ and TNAP under the same conditions (-0.083 and -0.047 V, respectively). Instead, the potential required for electrochemical reduction of TCNTP is more negative than either owing perhaps to insufficient overlap between the rings caused by the twist about the central double bond.

Both the large distance between dicyanomethylene groups and the apparent electronic isolation of the rings of TCNTP make the second one-electron reduction very easy; its $\Delta E_{1/2}$ at 0.30 V is less than half of that for TCNQ.

The cyclic voltammogram of (TBA)$_2$(TCNP) in butyronitrile with 0.1 M (TBA)(BF$_4$) has anodic current peaks at $E_{\mathrm{Pa}}(1)$ = -0.278 and $E_{\mathrm{Pa}}(2)$ = +0.026 V vs. Ag/AgNO$_3$. The first oxidation is reversible ($E_{1/2}(2)$ = -0.342 V), but the second appears nearly irreversible and the first reduction half-wave potential can be only estimated at $E_{1/2}(1)$ = -0.032 V corresponding to A_1 = 2.90 eV. The $\Delta E_{1/2}$ = 0.310 V, related to molecular U, is also an estimate based upon a barely perceptible cathodic wave at -0.090 V. The irreversible process in the second oxidation may be the precipitation of TCNP^0 or the formation of an electrode-passive polymer as suggested by Katz and coworkers.[27]

The electronic spectrum of the TCNP^{2-} solution was recorded before and after partial oxidation at 0.02 V vs. Ag/AgNO$_3$ (Figure 5, lower graph). The oxidation resulted in the decline of bands at 371 and 327 nm ascribed to the dianion and the appearance of bands at 910, 1124, and 135 nm. We propose that these new electronic transitions are due to the formation of the TCNP radical anion. Gerson, Cowan and co-workers[33] have recently characterized the radical anion of TCNTP and the radical anion and trianion of TCNP via ESR and ENDOR techniques. The assignments of the 545- and 490-nm bands are unclear.

The generation of TCNP radical anion was likewise approached via the partial reduction of the neutral oxidation product of X. Although the solution of the oxidation product (TCNP and/or polymer) in butyronitrile was too dilute to register a CV, its electronic spectrum was detectable before and after partial reduction at -0.15 V midway between $E_{1/2}(1)$ and $E_{1/2}(2)$ (Figure 5, upper graph). The bands at 600, 557, and 515 nm associated with the neutral material were diminished by the reduction and the same near-IR bands appeared that were described above. The single reduction of monomeric TCNP^0, rather than the reductive cracking of a TCNP polymer, is suggested as the source of TCNP$^{-\cdot}$ since the cathodic reduction of an aromatic molecule requires a potential more negative than the -0.15 V employed (e.g., reduction of pyrene in butyronitrile requires ca. -2.2 V vs. Ag/AgNO$_3$).

Conclusions

The carbethoxy activation scheme of Martin and Wheland, modified by the sundry improvements described here, is of general utility for the preparation of "TCNQ-type" molecules. In seeking to optimize the solid-state properties of the acceptor in charge-transfer complexes, we have encountered practical problems related to the solubility of the unreacted acceptors and their tendency to polymerize and to pick up hydrogen from water-soluble solvents. Metathetical procedures using onium salts of TCNP may be the only viable approach to donor-TCNP conducting complexes. Unlike its precursor, TCNTP, and its biphenyl analogue, TCNP fulfills our expectations that it is a slightly stronger oxidant than TNAP, yet well below the threshold established by Ferraris and Saito[34] for electron affinities, and that its apparent $\Delta E_{1/2}$ is very low, yet representative of a rigid planar π-system.

Experimental Section

NMR spectra were recorded on a Varian A-60 or T-60 spectrometer. Data are reported in δ (ppm) relative to tetramethylsilane. A KRATOS MS-50 mass spectrometer fitted with a 23-kG magnet and DS-50 data system was used for both high-resolution mass measurements and low-resolution spectra utilizing direct exposure electron impact ionization.[35,36] Low-resolution mass spectra were also recorded on a Perkin-Elmer/Hitachi RMU-6. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. Electronic spectra were recorded on a Cary 14 recording spectrophotometer and absorption intensities are reported as the log of the extinction coefficient. Melting point determinations were performed by using sealed capillaries in a Thomas-Hoover apparatus with no correction necessary. Cyclic voltammetry was performed on a Princeton Applied Research 173 potentiostat in conjunction with a PAR 175 universal programmer and plotted on a Houston Instrument Omnigraphic 2000 X-Y recorder. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. The sparing production of compounds VIII, IX, X, and the target compounds precluded exhaustive purification for elemental analysis. Instead,

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high-resolution mass spectrometry was performed on the M^+ peaks of the target materials. All reaction solvents were purified prior to use: benzene, hexanes, and THF were distilled from sodium benzophenone; acetonitrile, butyronitrile, and chlorobenzene were distilled from phosphorus pentoxide; nitrobenzene and diethyl carbonate were fractionally distilled from calcium chloride; trimethyl phosphite was fractionally distilled from potassium hydroxide.

6,15-Dimethyl-2,11-dithia[3.3]metacyclophane (11). A solution of 8.4 g (43 mmol) of 3,5-bis(mercaptomethyl)toluene and 12 g (43 mmol) of 3,5-bis(bromomethyl)toluene is added at eight drops per min to 7 g (85%, 0.11 mol) of potassium hydroxide in 1.5 L of 95% ethanol under reflux.[16] An argon atmosphere and vigorous stirring is maintained throughout the 4-day addition to minimize oligomerization and oxidation of sulfides. Six hours after the addition is completed, solvents are removed leaving 200 mL of oil to be taken up in 700 mL of chloroform, filtered, and washed with water. The organic layer is dried over $MgSO_4$, reduced in volume, and eluted on silica gel with benzene–hexanes (1:3). Removing solvent from the eluent leaves white crystals of II, mp 102–103 °C. Recrystallization from cyclohexane yields 8.0 g (60%) of colorless prisms: mp 103.5–105 °C; IR (KBr) 3010, 2900, 1605 1455, 1380 cm^{-1}; NMR ($CDCl_3$) δ 6.68 (br s, 4), 6.60 (br s, 2), 3.68 (s, 8), 2.15 (s, 6).

5,13-Dimethyl[2.2]metacyclophane (III). Dithiacyclophane II (4.5 g, 15 mmol) is dissolved in 150 mL of trimethyl phosphite and irradiated by a 450-W Hanovia medium-pressure mercury arc lamp in a water-cooled Vycor immersion well for 24 h while being flushed with argon. Solvent and volatile byproducts are removed by vacuum distillation. The residue is eluted onto silica gel with carbon tetrachloride. Evaporation of the first fraction yields 1.75 g of crude hydrocarbon, which is recrystallized in ethanol–acetone (4:1) to give 1.5 g (48%) of III, mp 145–146 °C. Sublimation at 60 °C and 2 torr further purifies III: NMR ($CDCl_3$) δ 6.98 (s, 4), 4.02 (br s, 2), 2.41 (s, 6), 3.07 (d, $J \sim 8$ Hz, 4), 2.09 (d, $J \sim 8$ Hz, 4).

5,13-Bis(bromomethyl)[2.2]metacyclophane (IV). As soon as 1.12 g (4.3 mmol) of metacyclophane III in 150 mL of dry carbon tetrachloride is brought to 70 °C, 1.69 g (9.5 mmol) of NBS along with 50 mg of azobis[isobutyronitrile] (AIBN) is added in four portions over 6 h. After two additional hours, the solvent is removed completely and the residue stirred with 300 mL of warm water. The water is decanted and the residue is taken up in 300 mL of methylene chloride and washed 3 times with 150-mL portions of fresh water. The organic layer is dried, reduced to 20 mL, and eluted onto silica gel with methylene chloride–hexanes (1:3). The oily crystals from the concentrated eluent are triturated with a minimum of chloroform and recrystallized in carbon tetrachloride to yield 1.80 g (48%) of IV as white crystals: mp 207–208 °C (lit. 205–206 °C);[35] NMR ($CDCl_3$) δ 7.10 (br s, 4), 4.22 (br s, 2)8 4.51 (s, 4), 3.11 (d, $J \sim 8$ Hz, 4), 2.10 (d, $J \sim 8$ Hz, 4). Anal. Calcd for $C_{18}H_{18}Br_2$: C, 54.85; H, 4.60. Found: C, 54.76; H, 4.52.

The washings from the above trituration are eluted on a fresh silica gel column with methylene chloride–hexanes (1:4) and concentrated to yield colorless crystals, mp 139–141 °C. Recrystallization from aqueous ethanol yields 0.12 g (12%) of 2,7-dimethyl-4,5,9,10-tetrahydropyrene (V): mp 145–147 °C (lit. 146.5–148 °C);[22] NMR ($CDCl_3$) δ 6.89 (br s, 4), 2.84 (s, 8), 2.33 (s, 6).

Larger ratios of NBS to III lead to oxidation of IV to give 2,7-bis(bromomethyl)-4,5,9,10-tetrahydropyrene (XIII) mp 226–228 °C; NMR ($CDCl_3$) δ 7.14 (br s, 4), 4.54 (s, 4), 2.86 (s, 8).

[2.2]Metacyclophane-5,13-diacetonitrile (VI). Sodium cyanide (0.4 g, 8.3 mmol) in 8 mL of water is added to a solution of 0.46 g (1.2 mmol) of dibromide IV in 40 mL of DMF at 40 °C. After 4 h the mixture is cooled, poured into 100 mL of ice water, and filtered. The filter cake is washed with fresh water, dried in vacuo, and recrystallized in THF to give 0.30 g (96%) of pale yellow needles: mp 191–192.5 °C; NMR ($CDCl_3$) δ 7.01 (br s, 4), 4.22 (br s, 2), 3.70 (s, 4), 3.13 (d, $J \sim 8$ Hz, 4), 2.12 (d, $J \sim 8$ Hz, 4); IR (KBr) 3000, 2920, 2845, 2245, 1590, 1445, 1400 cm^{-1}; MS, *m/e* (relative intensity, fragment) 285 (13%, M^+), 258 (7%, $M^+ - C_2H_4$), 246 (24%, $M^+ - C_2H_2N$), 206 (100%, $M^+ - C_4H_4N_2$). Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.76; H, 6.43; N, 9.69.

Diethyl $\alpha,\alpha,\alpha',\alpha'$-Tetracyano[2,2]metacyclophane-5,13-diacetate (VII). A three-necked round bottom is fitted with a graduated pressure-equalizing addition funnel, topped by a cold finger condenser, and vented to a Chlorox trap. While the reaction vessel is flushed with argon, 0.6 g (23.6% in oil, 3.5 mmol) of potassium hydride is introduced and washed 4 times with 15-mL portions of hexanes. The excess hexanes are removed, the vessel cooled to 0 °C and 0.51 g (3.5 mmol) of diethyl carbonate is syringed in. An ice-cold solution of 0.1 g (0.35 mmol) of diacetonitrile VI in 15 mL of THF is added slowly and stirred in an ice bath for 1 h. The addition funnel is chilled with ice and a 0.5% mixture of salt and ice water is put into the cold finger. Cyanogen chloride, introduced at the top of the condenser, condenses and drops into the addition funnel until 1 mL (19 mmol) accumulates and then is added at once. After 2 h at 0 °C the mixture is warmed to room temperature for 8 h, poured into ice water, and extracted with three 50-mL portions of methylene chloride. The organic portions are combined, dried, and evaporated under argon at room temperature. The residue is evacuated for 2 days to pull off excess diethyl carbonate. Recrystallization from acetone gives 0.10 g (60%) of VII as off-white crystals: mp 235–238 °C; NMR ($CDCl_3$) δ 7.33 (br s, 4), 4.36 (q, $J = 6$ Hz, 4), 4.29 (br s, 2), 3.27 (d, $J \sim 8$ Hz, 4), 2.18 (d, $J \sim 8$ Hz, 4), 1.26 (t, $J = 6$ Hz, 6); IR (KBr) 3000, 2930, 2845, 2245, 1760, 1710, 1590, 1440 cm^{-1}; MS (chemical ionization) *m/e* (relative intensity, fragment) 481 (20%, MH^+), 454 (100%, $M^+ - CN$), 437 (12%, $MH^+ - C_2H_4O$), 409 (9%, $MH^+ - C_3H_4O_2$), 382 (6%, $MH^+ - C_4H_5O_2N$), 343 (10%, $M^+ - C_6H_5N_2O_2$, 316 (17%, $M^+ - C_7H_5N_3O_2$). Anal. Calcd for $C_{28}H_{24}N_4O_4$: C, 69.09; H, 5.03; N, 11.66. Found: C, 69.02; H, 5.01; N, 11.45.

[2.2]Metacyclophane-5,13-dimalononitrile (VIII). After degassing 10 mL of 5% sodium hydroxide, the solution is added to 186 mg (0.39 mmol) of diester VII under argon. The suspension is stirred and warmed to 40 °C until it becomes homogeneous. After filtering, the solution is neutralized with 6 N hydrochloric acid to precipitate the crude product, which is washed several times with fresh water and dried in vacuo. The crude product is taken up in methylene chloride and eluted on silica gel with methylene chloride–hexanes (1:3). According to their NMR, the yellow crystals (120 mg, 90%) obtained by concentrating the eluent are 95% VIII and 5% 4,5,9,10-tetrahydro-5,13-pyrenedimalononitrile (IX). When air is not rigorously excluded, mixtures favoring IX result from the decarboxylation of VII. Recrystallization from ethanol–acetone (3:1) gives nearly pure VIII: mp 224–226 °C; NMR ($CDCl_3$) δ 7.24 (br s, 4), 5.08 (s, 2), 4.33 (br s, 2), 3.25 (d, $J \sim 8$ Hz, 4), 2.35 (d, $J \sim 8$ Hz, 4).

4,5,9,10-Tetrahydro-2,7-pyrenedimalononitrile (IX) from VIII. A mixture of VIII and IX (3:2) (56 mg, 0.17 mmol) in 40 mL of chloroform is combined with 200 mg (0.72 mmol) of hydrated ferric chloride in 40 mL of water and stirred 6 h at room temperature. After washing the organic layer several times with fresh water, the solvent is dried and removed. The residue is taken up in 200 mL of diethyl ether, filtered, and reduced in volume until 52 mg (93%) pale yellow needles of IX precipitate: mp 280 C dec; NMR ($CDCl_3$) δ 7.28 (br s, 4), 5.06 (s, 2), 2.97 (s, 8); IR (KBr) 3010, 2930, 2890, 2245, 1595, 1460, 1428 cm^{-1}; electronic spectrum (THF) 292 (3.90), 355 nm (3.15); MS, *m/e* (relative intensity, fragment) 334 (20%, M^+), 308 (8%, $M^+ - CN$), 206 (100%, $M^+ - C_6N_4$), 204 (28%, $M^+ - C_6H_2N_4$), 203 (24%, $M^+ - C_6H_3N_4$), 202 (20%, $M^+ - C_6H_4N_2$).

13,13,14,14-Tetracyano-4,5,9,10-tetrahydro-2,7-pyrenoquinodimethane, TCNTP (Ia). Both metacyclophane VIII and tetrahydropyrene IX can be efficiently converted to acceptor Ia by the following procedures.

To 300 mg (0.9 mmol) of IX in 100 mL of refluxing dry acetonitrile is added 800 mg (3.6 mmol) of DDQ. The mixture turns deep blue and is refluxed under argon for 6 h and cooled overnight to precipitate the product. The mixture is filtered and the filter cake is washed with cold acetonitrile, water, and ether. Finally, it is taken up in 400 mL of boiling butyronitrile, which is reduced in volume to 100 mL to precipitate 260 mg (87%) of Ia as a blue powder: mp >360 °C; NMR ($CDCl_3$) δ 7.53 (s, 4), 3.02 (s, 8); IR (KBr) 3000, 2935, 2885, 2205, 1562, 1462, 1430 cm^{-1}; electronic spectrum (acetonitrile) 265 (3.55), 349 (3.50), 571 nm (3.63); MS, *m/e* (relative intensity, fragment) 334 (62%, $M^+ + 2$), 332 (65%, M^+), 208 (11%, 334 − CN), 306 (12%, $M^+ - CN$), 266 (20%, M^+

$- \mathrm{C_3H_2N}$), 265 (28%, $\mathrm{M^+ - C_3H_3N_2}$), 240 (28%, $\mathrm{M^+ - C_5H_4N}$), 202 (100%, $\mathrm{M^+ - C_6H_4N_4}$), 101 (22%, $\mathrm{M^{2+} - C_6H_4N_4}$), high-resolution MS of the molecular ion calcd for $\mathrm{C_{22}H_{12}N_4}$ 332.1061, measured 332.1064.

To a solution of 60 mg (0.18 mmol) of VIII or IX in 100 mL of butyronitrile under reflux is added 122 mg (0.72 mmol) of anhydrous ferric chloride dissolved in 20 mL of butyronitrile. After 5 h the mixture is cooled, washed with four 100-mL portions of water, and reduced in volume to 20 mL. The electronic spectrum and IR of the resulting precipitate, 40 mg (80%), are identical with those above.

Crystal Growth Techniques Tried with TCNTP. The slow cooling method entailed combining 3 mg (0.01 mmol) of TCNTP with an equimolar amount of donor in an 8-mm heavy-wall Pyrex tube with a magnetic stir bar, adding 3–5 mL of butyronitrile, chlorobenzene, or nitrobenzene, degassing the tube by four freeze–thaw cycles, and sealing the tube under vacuum during a final freeze. The tube is immersed in an oil bath, stirred, and heated to 180 °C. After 1 h the bath is cooled at a uniform rate over 4 days to 60 °C. In the case of TMTTF, the residue from the tube was washed with acetonitrile and ethyl ether, dried, and pressed into a pellet having a room temperature dc conductivity of 0.2 $\mathrm{ohm^{-1}\ cm^{-1}}$. Similar results were obtained by combining 2 mL of boiling chloroform saturated with TCNTP with 2 mg (0.01 mmol) of TMTTF dissolved in 2 mL of hot chloroform. In all other cases, the residue consisted of unreacted TCNTP sometimes mixed with donor (HMTSF, TMTSF).

Metathesis experiments started by passing 1 Faraday per mol of TCNTP into 15 mL of acetonitrile with 5 mg (1.6×10^{-2} mmol) of TCNTP and 0.1 M (TBA)($\mathrm{BF_4}$) at the working electrode to generate (TBA)($\mathrm{TCNTP^-}$). Similarly, one-electron oxidation of acetonitrile solutions of equimolar amounts of TTF, TMTTF, HMTSF, and dithiophenotetrathiafulvalene was carried out and the solutions were combined. No donor–acceptor salts were recovered.

2,7-Pyrenedimalononitrile (X). Acceptor Ia (20 mg, 0.06 mmol) is taken up in 40 mL of dry chlorobenzene along with 50 mg of 10% palladium on carbon and refluxed under argon 4 days. The suspension is filtered hot and the filtrate cooled slowly to allow white platelets of X to come out of solution, 12.8 g (64%): mp >360 °C; IR (KBr) 3000, 2925, 2900, 2245, 1510, 1440, 1405 $\mathrm{cm^{-1}}$; electronic spectrum (acetonitrile) 247 (4.69), 260 (4.75), 272 (4.86), 305 (4.76), 323 (4.84), 338 nm (4.93); MS, *m/e* (relative intensity, fragment) 330 (100%, $\mathrm{M^+}$), 304 (10%, $\mathrm{M^+ - CN}$), 265 (25%, $\mathrm{M^+ - C_3HN_2}$), 238 (15%; $\mathrm{M^+ - C_5H_4N_2}$), 202 (12%, $\mathrm{M^+ - C_6N_4}$), 200 (8%, $\mathrm{M^+ - C_6H_2N_4}$).

13,13,14,14-Tetracyano-2,7-pyrenoquinodimethane, TCNP (Ib), plus Polymer. A solution of 4.3 mg (1.3×10^{-2} mmol) of X in 12 mL of dry acetonitrile is refluxed under argon and combined with 23 mg (0.1 mmol) of DDQ in 2 mL of acetonitrile, turning the clear solution deep purple and causing a blue precipitate to fall out. After 2 h, the suspension is cooled and filtered. The filter cake is washed with acetonitrile and ethyl ether and dried: mp >360 °C; IR (KBr) 3000, 2930, 2255, 2205, 1595, 1401 $\mathrm{cm^{-1}}$; MS, *m/e* (relative intensity, fragment) 330 (100%, $\mathrm{M^+ + 2}$), 329 (13%, $\mathrm{M^+ + 1}$), 328 (10%, $\mathrm{M^+}$), 304 (9%, 330 − CN), 265 (25%, 330 − $\mathrm{C_3HN_2}$), 238 (15%, 330 − $\mathrm{C_5H_4N_2}$), 200 (9%, $\mathrm{M^+ - C_6N_4}$); precise mass measurement calcd for $\mathrm{C_{22}H_8N_4}$ 328.0748, measured 328.0753.

Butyronitrile dissolves some but not all of the filter cake. The soluble fraction (ca. 5–15%) is combined with TBA·$\mathrm{BF_4}$ and its electronic spectrum obtained before and after cathodic reduction: before reduction 243 (4.60), 340 (3.31), 557 nm (4.12).

($\mathrm{R_4N^+}$)$_2$($\mathrm{TCNP^{2-}}$) (R = Alkyl). Dimalononitrile X (2 mg, 3×10^{-3} mmol) is taken up in 0.5 mL of 5% sodium hydroxide, filtered, and precipitated with 0.5 mL of 20% tetraethylammonium hydroxide in water. The pink solid is washed with fresh water, dried under inert atmosphere, and taken up in degassed acetonitrile-d_3 for NMR: δ 7.80 (br s, 8), 3.42 (q, $J \sim 7$ Hz, 16), 1.45 (t, $J \sim 7$ Hz, 24).

Similarly, when 2 mg of X, taken up in 5% sodium hydroxide, is precipitated with tetrabutylammonium hydroxide (40% in water) a pink-orange solid results which is more resistant to air oxidation. (TBA)$_2$($\mathrm{TCNP^{2-}}$): IR (KBr) 3010, 3000, 2160, 2120, 1604, 1450 $\mathrm{cm^{-1}}$; electronic spectrum (butyronitrile) 292 (3.91), 312 (4.08), 327 (4.52), 341 (4.26), 371 nm (4.36).

Reaction of (TBA)$_2$(TCNP) with (TTF)$_3$($\mathrm{BF_4}$)$_2$. The tetrafluoroborate salt of TTF is prepared by Wudl's procedures.[26] The tetrabutylammonium salt of TCNP (5 mg, 6×10^{-3} mmol) dissolved in 2 mL of acetonitrile is placed in one side of an "H" tube and 2 mg (8×10^{-3} mmol) in 2 mL of acetonitrile in the other. An additional 2 mL of acetonitrile fills the bridge of the tube and, after 2 days at room temperature under argon, a brown solid is collected and dried. The salt has a room temperature dc pellet resistivity of about $10^6\ \Omega$ cm.

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Registry No. Ia, 73120-72-6; Ib, 64535-30-4; II, 42082-65-5; III, 10549-23-2; IV, 19391-17-4; V, 10549-25-4; VI, 73120-73-7; VII, 73120-74-8; VIII, 73120-75-9; IX, 73120-76-0; X, 76357-78-3; X·2NEt$_4$, 95674-00-3; X·2NBu, 80294-06-0; XIII, 57703-27-2; 3,5-bis(thiomethyl)toluene, 42082-63-3; 3,5-bis(bromomethyl)toluene, 19294-04-3; tetraethylammonium hydroxide, 77-98-5; tetrabutylammonium hydroxide, 2052-49-5; (TTF)$_3$($\mathrm{BF_4}$)$_2$, 55492-86-9; TCNP·2TTF, 95739-47-2.