## References and Notes

(1) D. Margerison and J. P. Newport, *Trans Faraday Soc.*, **59**, 2058(1963).
(2) M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, **1**, 654 (1962).
(3) M. Witanowski and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 736 (1966); G. Fraenkel, W. E. Beckenbaugh, and P. P. Yang, *Ibid.*, **98**, 6878 (1976); G. Fraenkel, D. T. Dix, and M. J. Carlson, *Tetrahedron Lett.*, 579 (1968).
(4) See R. L. Kieff and T. L. Brown, *J. Organomet. Chem.*, **77**, 299 (1974); D. P. Novak, and T. L. Brown, *ibid.*, **94**, 3793 (1972).
(5) J. C. P. M. Van Dongen, Ph.D. Thesis, University of Utrecht, 1974.
(6) L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *J. Am. Chem. Soc.*, **96**, 3244 (1968); **91**, 1057 (1969).
(7) G. E. Hartwell and A. Allerhand, *J. Am. Chem. Soc.*, **93**, 4415 (1971).
(8) (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolutions Nuclear Magnetic Resonance," McGraw Hill, New York, 1961, pp 480; (b) F. Wehrli, *J. Magn. Reson.*, **30**, (1978), first report of $^{6}$Li NMR of alkyllithiums.
(9) Li NMR spectra were obtained using a home-built, externally locked, multi-nuclear-pulse spectrometer operating at 23.317 MHz for $^{7}$Li and 8.803 MHz for $^{6}$Li. The spectral width was 2000 Hz (8K points), pulse widths 14 μs ($^{6}$Li) and 2.8 μs ($^{6}$Li), and acquisition time 2.00 s for both. Around 200 transients were collected at 2.2-s intervals. The system was equipped with a Nicholet 1080 computer with disk storage. $^{13}$C NMR data were obtained at 22.03 MHz using the Bruker HX-90 spectrometer. All spectra were obtained with proton decoupling.
(10) Union Carbide Corp., Oak Ridge, Tenn. The lithium was reacted with *n*-propyl chloride in cyclopentane. Synthesis of the $^{13}$C-enriched halide will be described in a later publication. *n*-Propyllithium was distilled over the vacuum line prior to use.
(11) R. Zerger, W. Rhine, and G. Stucky, *J. Am. Chem. Soc.*, **96**, 6048 (1974); T. F. Schaaf, W. Butler, M. D. Glick, and J. P. Oliver, *ibid.*, **96**, 7593 (1974).

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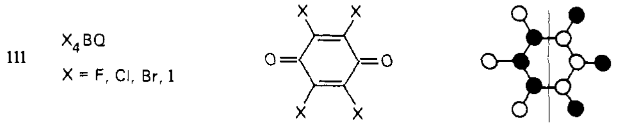
## A New Class of Highly Conducting Organic Materials: Charge-Transfer Salts of the Tetrathiafulvalenes with the Tetrahalo-*p*-benzoquinones

*Sir:*

In organic solids with high electrical conductivity, the acceptor tetracyano-*p*-quinodimethane (TCNQ, I) has played a unique role in that, until now, all charge-transfer salts containing both an organic donor and acceptor in a 1:1 ratio that have exhibited high electrical conductivity ($\sigma > 1\ \Omega^{-1}\,\text{cm}^{-1}$) have contained TCNQ or one of its close derivatives as the acceptor.[1-3]

In order to formulate guidelines for selecting other pairs of donor and acceptor molecules that would form new highly conducting salts, we have been investigating[3,4] those complementary features that the members must possess in order to meet the two essential prerequisites for high conductivity, namely, segregated stacking of donors and acceptors and incomplete transfer of charge between these species.[2,3] The requirement of segregated stakcs is a difficult one to satisfy, since most charge-transfer solids crystallize[1,5] in mixed stacks, i.e., in which donor and acceptor molecules alternate. The approach[4] that we have followed is one of attempting to inhibit good donor-acceptor orbital overlap, thereby minimizing the Mulliken charge-transfer interaction that stabilizes such mixed stacks, with the idea that segregated stacks might be formed by default. One way of creating unfavorable donor-acceptor overlap is to select a pair of molecules such that the relevant frontier orbitals (HOMO of the donor and LUMO of the acceptor, shown schematically (Scheme I) for molecules I, II and III) are of different symmetry with respect to inversion. To meet the criterion of partial charge transfer, we have used[2,3] electrochemical half-wave potentials as a relative measure of the ionization potential of the donor and the electron affinity of the acceptor. These values, combined with consideration of the electrostatic crystalline binding energy, can be used as a crude guide for selecting molecules[3] such that the degree of charge transfer will be between zero (neutral molecular solid) and one (complete charge transfer, fully ionic solid).

Scheme I



One combination of molecules that appears to possess these complementary properties, i.e., frontier orbitals of opposite symmetry and promising match of redox properties, are the tetrathiafulvalene (TTF, II) family of donors and the tetrahalo-*p*-benzoquinone (III) family of acceptors. We have found[6] that TTF and TMTTF (tetramethyl-TTF) form charge-transfer compounds of 1:1 composition with each of the tetrahalo-*p*-benzoquinones. Furthermore, nearly every combination of donor and acceptor forms at least two distinct phases.[4,7] In this communication we shall discuss only those salts which are highly conducting.

The materials discussed here were generally prepared by mixing acetonitrile solutions of the donor and acceptor together at the boiling point of the solvent and cooling to room temperature. The pressed powder conductivities of the resulting salts are summarized in Table I, along with corresponding values measured for TTF-TCNQ[8] and TMTTF-TCNQ.[9] It should be noted that four of these new compounds (Table I)

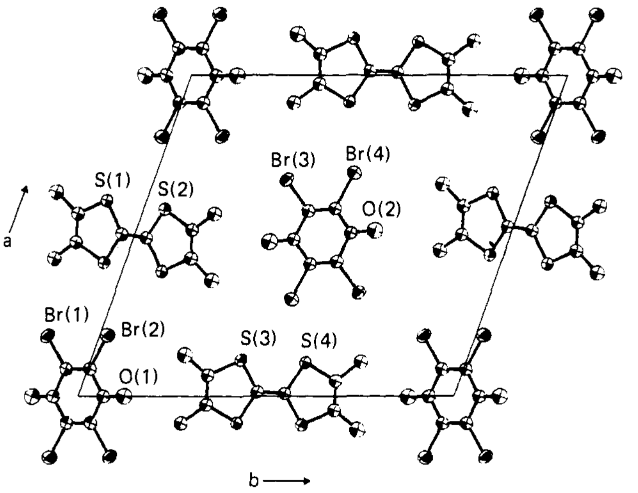


**Figure 1.** Projection of the structure of TMTTF-bromanil onto the *a-b* plane, showing the relationships between the segregated stacks of TMTTF and bromanil (coming out of the plane of the figure).

**Table I.** Values for the Pressed Powder Conductivities at 300 K for the TTF and TMTTF Salts of the Tetrahalo-*p*-benzoquinones (X = halogen) and, for comparison, those of TCNQ. For Salts with Multiple Phases, the Higher Conductivity Is Tabulated

| σ(300 K) | X = F | X = Cl | X = Br | TCNQ |
|---|---|---|---|---|
| TTF | 10 | $8 \times 10^{-4}$ | $6 \times 10^{-4}$ | 70 |
| TMTTF | 7 | 20 | 1 | 35 |

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are the *first highly conducting 1:1 organic charge-transfer salts* that do not contain TCNQ (or a close derivative) as the acceptor. In addition, to the best of our knowledge, TTF and TMTTF-fluoranil are the first stable salts of the fluoranil radical anion.

Single crystals have so far been obtained only for TMTTF-bromanil. The single crystal conductivity is 5 $\Omega^{-1}$ $cm^{-1}$ at 300 K and is thermally activated with an activation energy of 0.11 eV (1200 K). This compound is found to crystallize[10] in the triclinic space group $P\bar{1}$, with cell parameters $a = 15.754$, $b = 17.520$, $c = 3.939$ Å; $\alpha = 83.64$, $\beta = 82.84$, $\gamma = 70.54°$; $Z = 2$. The packing motif is one of segregated stacks of donors and acceptors arrayed along *c*. Figure 1 shows the (001) projection of the structure. The overlap between adjacent TMTTF molecules is essentially the same as that found in TMTTF-TCNQ.[11] In both cases the mean interplanar spacing is ~3.53 Å. The acceptor stacks in TMTTF-bromanil and TMTTF-TCNQ are similar in that the exocyclic double bond of one molecule lies directly over the quinoid ring of the adjacent molecule. However, the interplanar spacing between acceptors in the bromanil complex is 3.39 Å compared with 3.29 Å in the TCNQ complex. This increased spacing between the bromanils, due probably to the bulk of the bromine atoms, may be partially responsible for the lower conductivity of TMTTF-bromanil compared with that of TMTTF-TCNQ and TMTTF-chloranil (Table I).

Some insight into the degree of charge transfer can be gained from a study of the optical absorption spectrum. The spectra of powdered samples (dispersed in KBr) of all the compounds in Table I have been measured. In addition to intramolecular excitations of the ions in the visible region, the highly conducting compounds each have a broad, intense infrared band centered near 0.5 eV (4000 $cm^{-1}$) which we ascribe to a mixed-valence charge-transfer transition, characteristic[12,13] of salts such as TTF-TCNQ which exhibit incomplete charge transfer. Thus, the criteria of segregated stacks and partial charge transfer have both been met.

There are two significant conclusions to be drawn from the discovery of this new class of highly conducting organic solids. First, the fact that segregated stacks and incomplete charge transfer were achieved tends to support the guidelines used in selecting the pairs of donors and acceptors. Second, this discovery makes it clear that the field of highly conducting organic solids is not restricted to TCNQ salts but, in fact, may involve a much wider variety of materials than previously believed.

## References and Notes

(1) Z. G. Soos, *Annu. Rev. Phys. Chem.*, **25**, 121 (1974).
(2) R. C. Wheland, *J. Am. Chem. Soc.*, **98**, 3926 (1976).
(3) J. B. Torrance, *Acc. Chem. Res.*, **12**, 79 (1979); J. B. Torrance, in "Molecular Metals", NATO Conference Series VI, W. E. Hatfield, Ed., Plenum Press, New York, 1979, p 7.
(4) J. J. Mayerle, J. B. Torrance, V. Y. Lee, J. I. Crowley, and R. M. Metzger, unpublished work; R. M. Metzger, J. B. Torrance, J. J. Mayerle, and J. I. Crowley, *Bull. Am. Phys. Soc.*, **23**, 356 (1978).
(5) F. H. Herbstein in "Perspectives in Structural Chemistry", Vol. IV, J. D. Dunitz and J. A. Ibers, Eds., Wiley, New York, 1971, p 166.
(6) This work has been presented, in part, at the International Conference on Quasi-One-Dimensional Conductors, Dubrovnik, Yugoslavia, Sept 1978; at the 176th National Meeting of the American Chemical Society, Miami Beach, Fla., Sept 1978; and at the 1978 Pacific Conference on Chemistry and Spectroscopy, San Francisco, Calif., Sept 1978.
(7) J. J. Mayerle, J. B. Torrance, and J. I. Crowley, *Acta Crystallogr.*, in press.
(8) J. Ferraris, D. O. Cowan, V. V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).
(9) J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, *Tetrahedron Lett.*, **27**, 2552 (1973).
(10) The structural relationship between like stacks suggests the possibility that a glide plane exists in the lattice. Indeed, a C-centered monoclinic cell can be formulated, related to the triclinic cell by the matrix 201/001/110. Attempts to determine whether the cell is truly monoclinic or just nearly so have thus far been inconclusive. We are pursuing this point. In any case, higher symmetry would have little effect on the gross structural features reported here.
(11) T. E. Phillips, T. J. Kistenmacher, A. N. Bloch, J. P. Ferraris, and D. O. Cowan, *Acta Crystallogr. Sect. B*, **33**, 422 (1977).
(12) J. B. Torrance, B. A. Soctt, and F. B. Kaufman, *Solid State Commun.*, **17**, 1369 (1975).
(13) J. Tanaka, M. Tanaka, T. Kawai, T. Takabe, and O. Maki, *Bull. Chem. Soc., Jpn.*, **49**, 2358 (1976).
(14) H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark.

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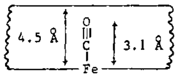
## Cyclophane Porphyrin. 2. Models for Steric Hindrance to CO Ligation in Hemoproteins[1,2]

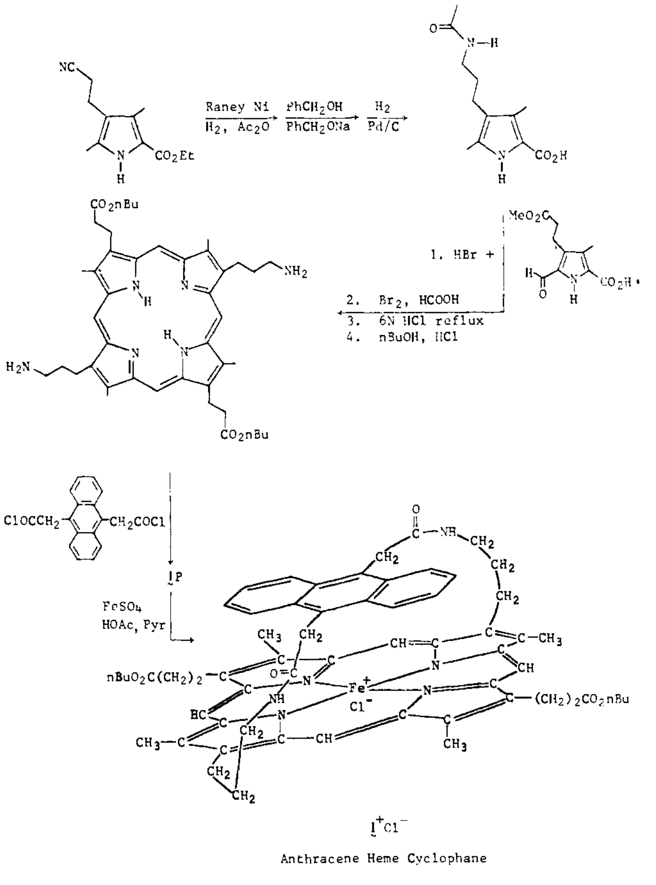
*Sir:*

The distorted geometry of bound CO or $CN^-$ in hemoproteins and the close proximity of certain protein residues to the ligation site on iron have been interpreted to indicate steric hindrance toward CO or $O_2$ ligation of the hemoproteins.[3-6] The nature of this "distal side" steric effect has been the subject of numerous recent theoretical[9-11] and experimental[12,13] studies in hemoproteins. However, no model system has displayed this effect.

We report here the synthesis and preliminary dynamic study of two model heme compounds, **1** and **2**, in which large distal side steric effects are seen. In order to present an entering ligand with steric interference similar to that provided by the distal imidazole or other groups in myoglobin, we devised a porphyrin cyclophane[2] whose two aromatic rings are <5 Å apart. This means that a linear Fe-CO bond would encounter



**Scheme I**



Anthracene Heme Cyclophane