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 Ω^{-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; α = 83.64, β = 82.84, γ = 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.

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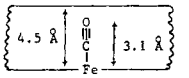
Received January 22, 1979

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

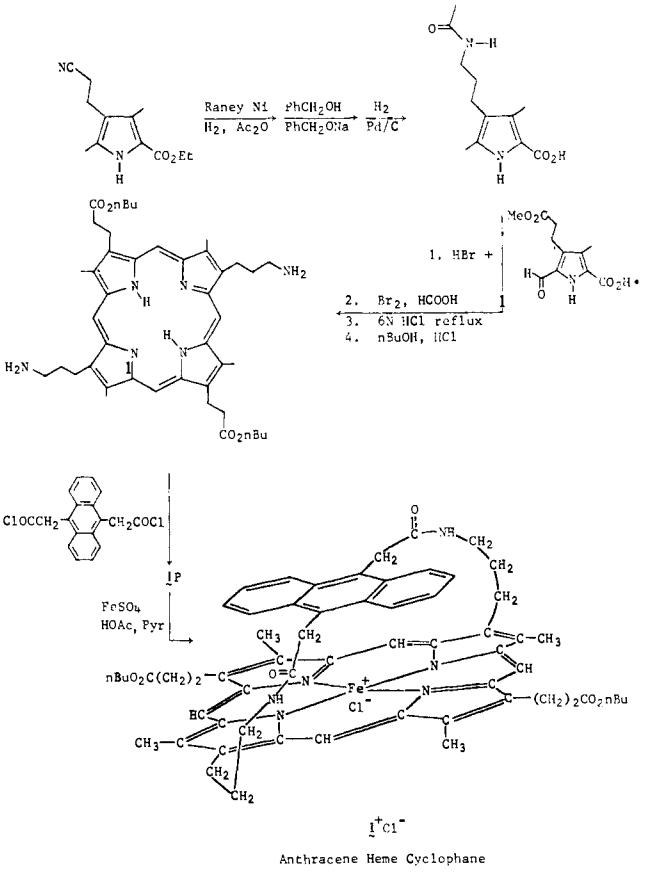
Sir:

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

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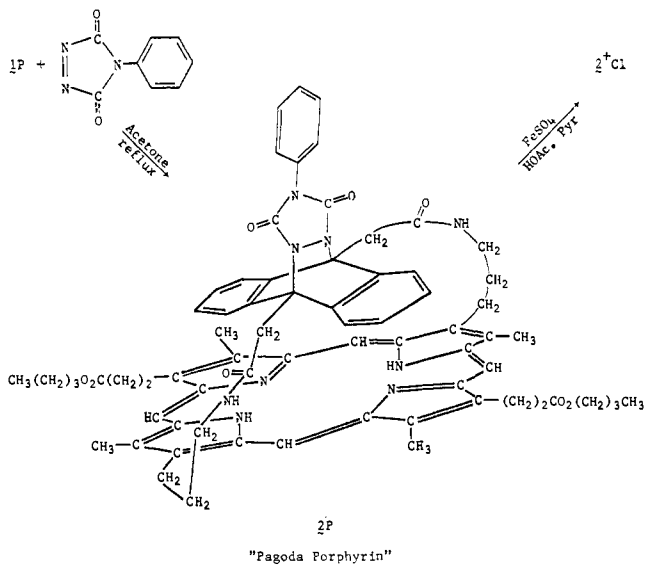
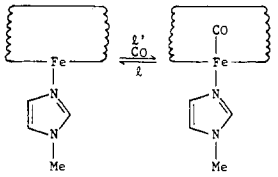
Scheme II



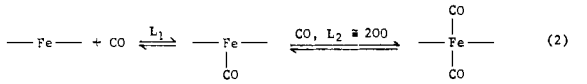
steric hindrance with the second aromatic group. To reduce the flexibility of the cyclophane ring, we have used two strategies. First, by using anthracene connected at the 9,10 positions, the tilting of this ring is severely limited. Secondly, by performing a Diels–Alder addition to the anthracene–porphyrin cyclophane, an even further restriction and tighter pocket is achieved. The syntheses are outlined in Schemes I and II.[14]

Properties of Anthracene–Heme [6.6]Cyclophane (1). The first striking property of this heme is its behavior toward 1-methylimidazole. At 1 M 1-methylimidazole in methylene chloride, the spectrum of this heme shows a five-coordinated spectrum at 418 and 543 nm, previously observed with "capped heme" by Baldwin et al.[17] Under these conditions the binding constant for a second imidazole would be $\sim 10^4$ M^{-1}.[18a]

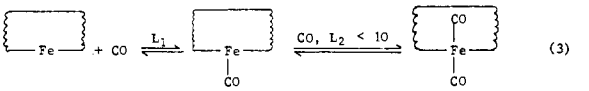


(1)

A more pertinent steric effect of the anthracene ring was demonstrated by preparing the CO complex in dry benzene by the method of Rougee and Brault.[18b] At 1 atm of CO pressure the spectrum showed a single Soret band at 394 nm corresponding to pure monocarbonyl heme. Under these conditions deuteroheme was reported to be ~50% monocarbonyl and 50% dicarbonyl heme.[18b] Therefore, the anthracene has greatly reduced the affinity of the second CO.



(2)



(3)

Additional evidence for distal side steric effects comes from kinetic measurements. Kinetic measurements in methylene chloride containing 0.2 M 1-methylimidazole were complex but clearly demonstrated that the second-order rate constants, l', for CO combination according to eq 1 were $<10^4$ M^{-1} s^{-1} for the anthracene heme cyclophane **1** and $<10^3$ M^{-1} s^{-1} for the "pagoda" heme **2.** These compare with 10^7 M^{-1} s^{-1} for chelated hemes without the steric effect.[7c] These drastic reductions in CO association rates can be attributed to the steric hindrance in the synthetic heme pocket. We have previously shown that solvent effects are not important in heme–CO kinetics or equilibria.[7a]

Further studies of steric hindrance to CO, CN^-, and O_2 binding are in progress.

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Received April 3, 1979

Macrolide Antibiotics. 1. Total Synthesis of the Prelog–Djerassi Lactone and Methynolide

Sir:

Efforts directed toward the total synthesis of the macrolide antibiotic methymycin[1] have evolved around the Prelog–Djerassi lactone **1**,[2] a key degradation product of methymycin retaining the original four chiral centers present in the C(1)–C(7) segment of the aglycone methynolide **2.** Since the first synthesis of (±)-**1** by Masamune[3] which was employed in the only total synthesis of methymycin recorded to date,[4] two additional syntheses of (±)-**1** have appeared.[5] In this communication we report our work in this area which has resulted in a total synthesis of methynolide (**2**). In addition, we record

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