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(4) The CD curve of a binary system consisting of the same two chromophores can be formulated as follows on the basis of the exciton coupling mechanism and a Gaussian distribution for the component CD Cotton effects

$$\Delta\epsilon(\sigma) = \frac{2\sqrt{\pi}\sigma_0^2}{2.296 \times 10^{-33}\Delta\sigma^2}\left(\frac{\sigma_0 - \sigma}{\Delta\sigma}\right) \times \exp\left\{-\left(\frac{\sigma_0 - \sigma}{\Delta\sigma}\right)^2\right\}\vec{R}_{ij}\cdot(\vec{\mu}_{ioa} \times \vec{\mu}_{joa})V_{ij}$$

where σ_0 is excitation frequency of the uv chromophore, $\Delta\sigma$ is standard deviation of Gaussian distribution, R_{ij} is interchromophoric distance, and V_{ij} is interaction energy (cm^{-1}). This shows that the exciton chirality of the system including its sign and amplitude, is essentially definable by the term $R_{ij}\cdot(\vec{\mu}_{ioa} \times \vec{\mu}_{joa})V_{ij}$. Furthermore, since V_{ij} is proportional to R_{ij}^{-3}, the amplitude $\Delta\epsilon$ is proportional to R_{ij}^{-2}, provided the interchromophoric angle remains unchanged.[6]
(5) Computation of the dihedral angle dependency of $\Delta\epsilon$ of a vicinal dibenzoate shows that it resembles a sine curve with its maximum value at *ca.* 70° and zero values at 0 and 180°.[6]
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(12) The shorter wavelength side of a uv band is usually broader than the longer wavelength side (Figure 2); the summation of curves of this type yields a sharp first Cotton effect and broader second Cotton effect.
(13) Supported by NSF GP 40087.
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Nuclear Magnetic Resonance Study of Stereospecific Dimerization of Dicyanohemin

Sir:

The significance of "donor-acceptor" as distinct from hydrophobic interaction in porphyrin-protein linkages in hemoproteins is now widely recognized[1-4] on the basis of a variety of physical and chemical evidence. The propensity for porphyrins to participate in π interactions is evidenced both in their interaction with organic donor and acceptors,[5,6] and by their tendency to dimerize or aggregate in solution.[7-10]

The structure of previously reported[7-10] "loose" porphyrin dimers, characterized by their concentration-dependent intermolecular ring current shifts, is thought to consist of a parallel orientation of the two porphyrin planes with an estimated separation of 8-10 Å, whether or not a metal[8,10] or small axial ligand[10] is present. Minor preferences for orientation of the porphyrin planes have been attributed to either dipole interactions[7] or steric effects.[10] Only in the related magnesium chlorophyll-type system[11] has significant stereospecificity in the dimerization been detected, where it was shown to arise from intermolecular coordination involving basic peripheral substituents. In no porphyrin systems to date has any evidence been found for a "tight" dimer with separations corresponding to distances found in donor-acceptor complexes[12] or hemoproteins.[1,4]

We report here on a proton nmr relaxation study of the dimerization of dicyanohemin,[13] (C in Figure 1), in methanol-d_4 which reveals a "tight" dimer with planar spacing of <4.5 Å that reflects a high degree of stereospecificity in the donor-acceptor interaction.

The "tight" dimer was characterized by the highly stereospecific intermolecular paramagnetic relaxation[14] observed at low temperature. Proton ftnmr traces[15] of the four recently assigned[13] methyl and the two vinyl α-protons are illustrated in A and B of Figure 1 for 0.005 and 0.05 *M* solutions at −80°. At low concentration, the four methyl line widths (and two vinyl) are approximately the same, as observed at 25° at all concentrations. At −80°, the 1-CH_3 and 8-CH_3 methyls broaden selectivity with increasing hemin concentration; the 3-CH_3 and 5-CH_3 are affected very little. Similarly, one vinyl α-H is also broadened. This paramagnetic relaxation (primarily dipolar[14] in origin) is independent of field,[16] and must therefore arise from intermolecular dipolar relaxation of the methyl protons in one porphyrin by the iron of the other porphyrins in the dimer.

The concentration dependence of the line widths suggests that a single type of species exists in solution, whose structure reflects stereospecific interaction involving predominantly pyrroles I and IV. An estimate of the separation of the porphyrin planes in the dimer[17] can be made on the basis of the relative importance of inter- *vs.* intramolecular paramagnetic dipolar relaxation for the methyl groups. At the lowest temperature where the two low-field resonances can be resolved, (*ca.* −95°) the 8-CH_3 line width is ~60-80% greater than the 5-CH_3 line width. This requires that in the dimer, $[P^1Fe^1(CN)_2^-]$-$[P^2Fe^2(CN)_2^-]$, the 8-CH_3 of P^1 is about as close to Fe^2 as to Fe^1, ($r(Fe^1$-8-$CH_3^1) \simeq$ 5.6 Å). The proposed structure consistent with this distance is depicted in D in Figure 1. Consideration of the steric interaction between 8-CH_3 and CN^- (1-CH_3 and CN^-) leads to an estimated interplane separation of <4.5 Å, which is

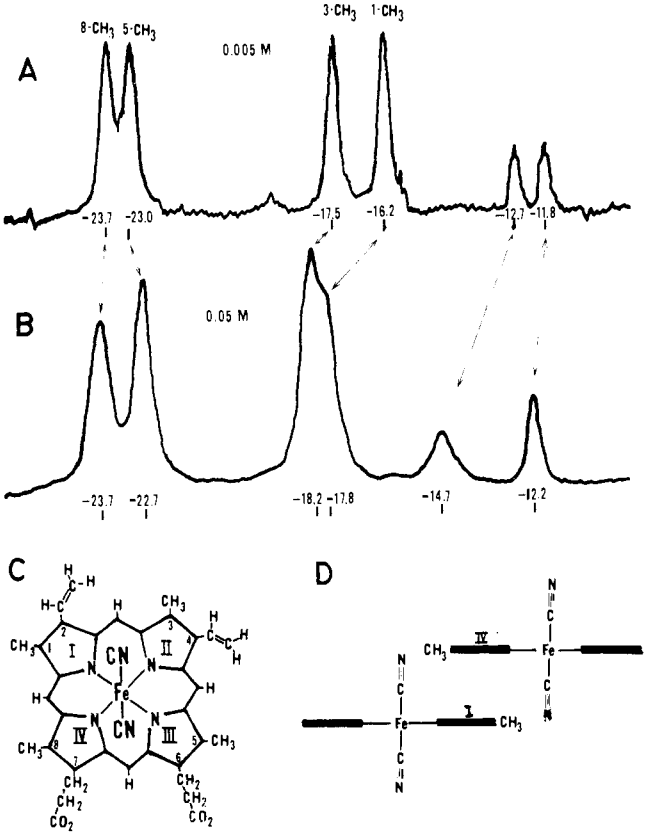

Figure 1. Proton ftnmr traces of (A) 0.005 *M* and (B) 0.05 *M* solutions of dicyanohemin (protoporphyrin IX ferric dicyanide), in methanol-d_4 at −80°. C represents the structure of dicyanohemin and D the configuration of the proposed dimer.

close to that observed in ordinary donor-acceptor complexes.[12] The lesser broadening of 1-CH_3 relative to 8-CH_3 and the broadening of a vinyl α-H[18] can yield detailed information on how the pyrroles I and IV aromatic skeletons actually overlap.

The stereospecific dimer formation suggests that the four pyrroles in protoporphyrin IX differ significantly in their donor or acceptor capabilities, with I the best donor and IV the best acceptor.[19] These differential donor-acceptor capabilities of the individual pyrroles may be crucial for efficient porphyrin-protein linkages in hemoproteins.[1-4]

A detailed study of this dimerization in a variety of porphyrin derivatives in several solvents is in progress and will be reported in the near future. The relevance of the dimerization to the interpretation[20] of the methyl shifts in low-spin hemes and hemoproteins will be discussed in detail elsewhere.

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(16) The authors are indebted to M. P. Klein, University of California, Berkeley, for 220-MHz proton spectra.
(17) The estimated separation from the relaxation data depends on the degree of association. We cannot exclude higher aggregates than dimers at this time. Higher aggregates would still require the stereospecific stacking indicated in D of Figure 1.
(18) The broadening of the downfield vinyl α-H peak identifies it as 2-vinyl. The differential broadening of 1-CH_3 and 8-CH_3, in addition to the broadening of 2-α-vinyl-H but *not* 7-α-CH_2, must reflect some asymmetry in the overlap of the I and IV pyrroles.
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Tricyclo[2.2.0.0^{2,6}]hexan-3-one

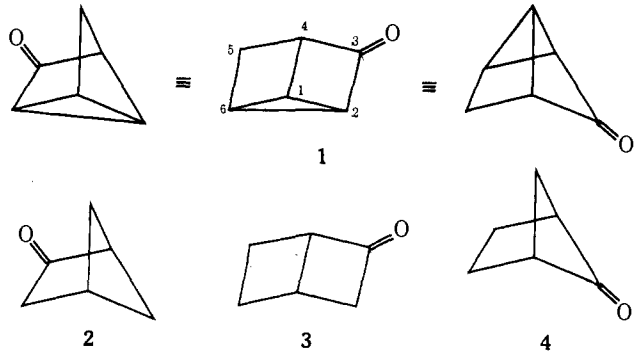
Sir:

The chemistry of highly strained small ring compounds continues to be of great interest. We report here the synthesis and structure proof of the title compound **1**, a derivative of a rare ring system.[1,2] With the preparation of **1**, ring functionalized derivatives of the simple tricyclo[2.2.0.0^{2,6}]hexane system become available for the first time. Ketone **1** is formally a dehydro derivative of the already strained ketones bicyclo[2.1.1]hexan-2-one[3] (**2**), bicyclo[2.2.0]hexan-2-one[4] (**3**), and bicyclo[2.1.1]hexan-5-one[5] (**4**).

Table I. Pmr (220 MHz) Assignments to **1**[a]

Assignment	δ (shape)	Coupling constants (Hz)
H_1	3.58 q (broad)	$J_{1-4} = 4, J_{1-5'}$(endo) $= 4.5, J_{1-6} = 3.8$
H_2	2.88 d of d	$J_{2-6} = 10, J_{2-4} = 4$
H_4	2.70 q	$J_{4-1} = J_{4-2} = J_{4-5} = 4$
H_5(exo)	2.78 m	$J_{5-4} = 4, J_{5-5'} = \pm 7.5, J_{5-6} = 3.5$
$H_{5'}$(endo)	1.91 d of d	$J_{5'-1} = 4.5, J_{5'-5} = \pm 7.5$
H_6	2.46 m	$J_{6-1} = 3.8, J_{6-2} = 10, J_{6-5} = 3.5$

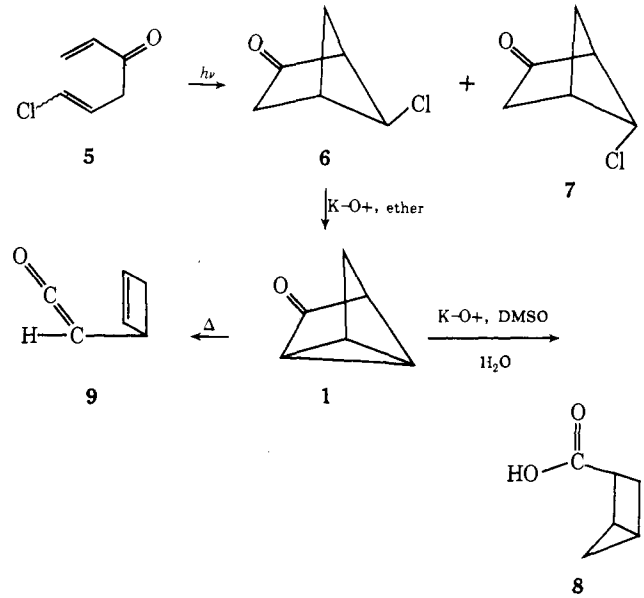
[a] Eu(Fod)$_3$ titration studies showed that the 2.70 and 2.88 patterns shifted most dramatically, the 1.91 and 3.58 peaks an intermediate amount, and the 2.46 and 2.78 peaks the least.



1

2 **3** **4**

Photolysis of a cis-trans mixture of 6-chlorohexa-1,5-dien-3-one[6,8] (**5**) affords an approximately 1:1 mixture[9] of *exo*-5-chlorobicyclo[2.1.1]hexan-2-one (**6**) and its endo isomer **7**. Treatment of the exo isomer **6** with potassium *tert*-butoxide in ether at 0°, followed by rapid work-up in the cold, affords **1** in about 80% yield. Purification by glpc at temperatures below 50° removes final traces of *tert*-butyl alcohol. Thermal rearrangement to **9** occurs readily at higher temperatures.



5 **6** **7**

9 **1**

8

Tricyclo[2.2.0.0^{2,6}]hexan-3-one (1) has the nmr spectrum reported in Table I. Assignments were made by comparison with nortricyclanone,[11] Eu(Fod)$_3$ shift reagent