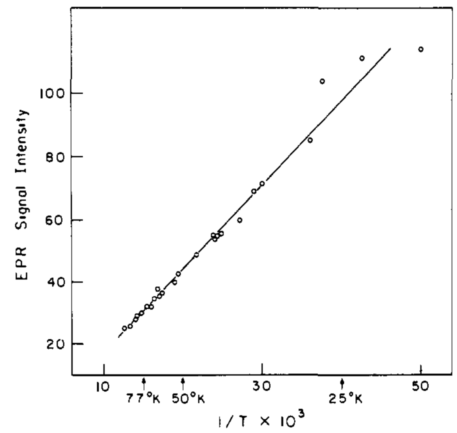

Figure 1. Peak-to-peak height of the low field $\Delta m_s = 1$ (xy) line in the EPR spectrum of trimethylenemethane (I) as a function of reciprocal absolute temperature.

gies.[9,10] Major points of difference among the theoretical treatments arise upon consideration of the magnitudes of the splittings among the several possible singlet and triplet states. This is true not only for the D_{3h} structures, but also for planar singlets and triplets of lower symmetry (e.g., C_{2v}) and for the forms in which one or more of the methylene groups is rotated out of the molecular plane. The most recent theoretical estimates place the lowest excited states 18-25 kcal/mol above the ground triplet state, well above the thermal energy accessible in the present experiments.

A corollary theoretical result is that the ground state triplet of trimethylenemethane is planar (D_{3h}).[9] Although the experimentally observed magnetic parameters ($E = 0$) are consistent with this view, the geometry of the ground state triplet has not been established by experiment.

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(2) See, however, the accompanying communication by M. S. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. E. Potter, and J. A. Berson, *J. Am. Chem. Soc.*, preceding paper in this issue, in which several substituted trimethylenemethanes are demonstrated to be ground state triplet molecules.

(3) Cf. the pentaphenylcyclopentadienyl cation of R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *J. Am. Chem. Soc.*, **89**, 1112 (1967).

(4) Produced by ultraviolet irradiation of 3-methylenecyclobutanone[1a] in methylcyclohexane (ca. 10 mg in 0.5 ml) cooled to below 100 K in the cavity of a Varian E4 EPR spectrometer.

(5) Obtained with a stream of cold helium and measured using a calibrated platinum resistance thermometer immersed in the sample. The temperature range could not be extended to higher values because trimethylenemethane decomposes irreversibly at temperatures only slightly higher than 100 K.

(6) J. H. van Vleck, "The Theory of Electric and Magnetic Susceptibilities", Oxford University Press, London, 1932, p 235.

(7) Double integration of the lines was not necessary since the observed line shape was essentially invariant over the temperature range examined. No saturation effects were observed at the lower temperatures.

(8) Examination of eq 1 reveals that Curie law behavior would also be observed in this temperature range if the absolute value of Δ were less than or equal to approximately 10 cal/mol. This is considered to be unlikely.

(9) M. J. S. Dewar and J. S. Wasson, *J. Am. Chem. Soc.*, **93**, 3081 (1971); W. T. Borden and L. S. Salem, *ibid.*, **95**, 932 (1973); D. R. Yarkony and H. F. Schaefer, *ibid.*, **96**, 3754 (1974); W. T. Borden, *ibid.*, **97**, 2906 (1975); J. H. Davis and W. A. Goddard, *ibid.*, **98**, 303 (1976); W. Hehre, L. S. Salem, and M. R. Wilcott, *ibid.*, **96**, 4328 (1974); W. W. Schoeller, *Tetrahedron Lett.*, 2043 (1973); E. R. Davidson and W. T. Borden, *J. Chem. Phys.*, **64**, 663 (1976). Citation of prior theoretical studies may be found in ref 1.

(10) Qualitative treatments such as the simple Hückel molecular orbital method also predict that the triplet state will be the ground state if Hund's rule is obeyed and electron correlation is taken into account.

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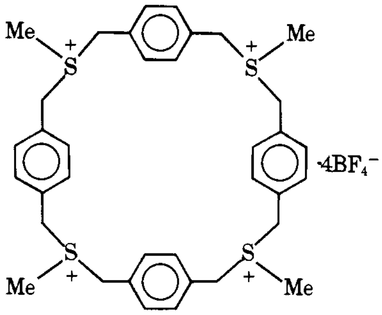
Water Soluble Heterocyclophane as a Novel Class of Inclusion Host

Sir:

During the past decade the cyclodextrins have attracted extensive attention as (almost) the sole class of inclusion hosts that form 1:1 complexes with a variety of hydrophobic guest molecules.[1] Recently, another class of inclusion hosts, the crown family, has been added to the list, some of whose members exhibit chiral recognition in complexation of both ground and transition states[2] and give promise of interesting and versatile applications to organic chemistry. To further develop and generalize "host-guest" chemistry it is important that still other novel classes of inclusion hosts be studied, and it is to this goal that we are currently investigating polyparacyclophanes[3] and we wish to report here a water soluble heterocyclophane that strongly binds hydrophobic guests *in aqueous solution.*

The tetrasulfide II was synthesized from xylylene bromide and xylylene dithiol in benzene-ethanol solution and obtained as colorless crystals, mp 199-200 °C. II possessed these properties: ir (KBr), 3050, 2950, 1510, 1420, 1230, 1010, 850, 760, 720 cm^{-1}; mass m/e (relative intensity), 544 (M$^+$, 21), 512 (4), 440 (6), 272 (18), 240 (26), 137 (52), 136 (52), 105 (85), 104 (100). Anal. Found: C, 70.51; H, 5.79. Calcd: C, 70.54; H, 5.92. NMR ($CDCl_3$), δ 3.55 (singlet, methylene protons 16 H), 7.18 (singlet, aromatic protons 16 H).



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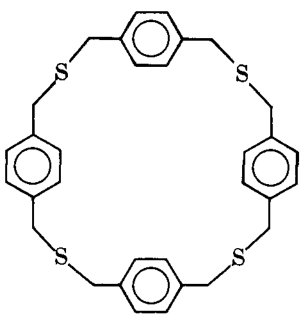

II

Treatment of the tetrasulfide II with $Me_3O^+BF_4^-$ produced S,S′,S″,S‴-tetramethyl-2,11,20,29-tetrasulfonium[3.3.3.3]-paracyclophane (heterocyclophane I), as colorless crystals, mp 164-166 °C. I possessed these properties: ir (KBr), 3000, 2960, 1518, 1425, 1200 1000, 860, 760, 720 cm^{-1}. Anal. Found: C,

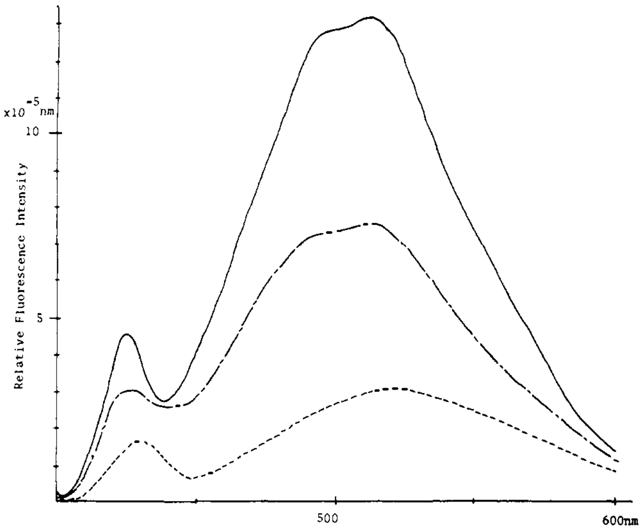

Figure 1. Fluorescence spectrum of 0.5 × 10^{-4} M, 1,8-ANS (- - -) on addition of 1 × 10^{-3} M β-cyclodextrin (– – –) and 1 × 10^{-3} M I (—) at pH 6.98. The exitation wavelength was 375 nm. The fluorescence intensity (nm^{-1}) is given so that the quantum yield (quanta emitted/quanta absorbed) was represented by the peak area measured by the wavelength on the horizontal axis (nm).

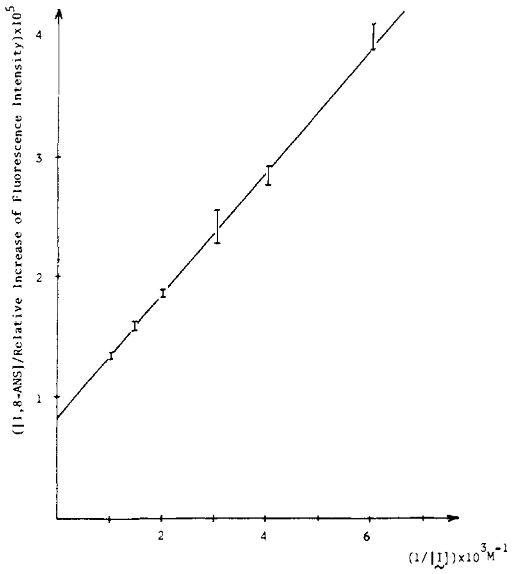

Figure 2. The Benesi–Hildebrand plot of 1,8-ANS and I. Error in the figure was calculated by the sum of the error of the mechanical recording noise and dependence of the observed value on the wavelength (between 500 and 540 nm).

45.55; H, 4.58. Calcd: C, 45.39; H, 4.66.

Space-filling models (CPK) of compound I shows it to have an approximately square hydrophobic cavity surrounded by four benzene "walls", the size of the cavity (distance between opposite walls in "face" conformation[4]) being about 7 Å which is large enough to occlude a phenyl or a naphthyl moiety.

An important feature of heterocyclophane I is its solubility in water at pH 7, which introduces a *hydrophobic cavity into the water phase* and facilitated the inclusion of hydrophobic compounds. That this does, indeed, occur was demonstrated through the use of a fluorescent hydrophobic guest, sodium 1-anilino-8-naphthalenesulfonate (1,8-ANS).[5] As shown in Figure 1, there is a strong enhancement in the fluorescence intensity of this compound in the presence of the heterocyclophane I, an enhancement greater than that produced by β-cyclodextrin.[1b,6] Plotting the fluorescent intensity against the reciprocal of the concentration of I (Benesi–Hildebrand plot[6]) produces a straight line from which the association constant of I and 1,8-ANS can be calculated to be 1.6 × 10^3 M^{-1}, a value that is 28 times greater than that for β-cyclodextrin. Experiments are currently under way to test compound I or its derivatives as inclusion catalysts.

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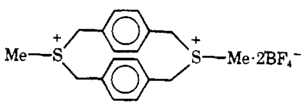
(4) "Face" conformation is concluded to be favored for paracyclophanes based on the NMR study. See ref 3e.

(5) Such fluorescence enhancement often has been observed for 1,8-ANS, when it is bound to enzymes[5a] or cyclodextrin.[1b,5b] (a) D. C. Turner and L. Brand, *Biochemistry*, 7, 3381 (1968). (b) Only slight enhancement of fluorescence of 1,8-ANS was observed on addition of standard compound, *S,S'*-dimethyl-2,11-disulfonium[3.3]paracyclophane difluoroborate (III).



III

The Benesi-Hildebrand treatment gave K_{ass}, which was smaller than 50 M^{-1}

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Freezing Out the Fluxional Behavior in Fe(CO)$_5$ and Other Metal Carbonyls

Sir:

There has been considerable interest over the years in the fluxional behavior of iron pentacarbonyl (Fe(CO)$_5$). While gas phase electron diffraction results[1] show a trigonal bipyramidal geometry, exchange of all CO ligands occurs rapidly on the ^{13}C NMR time scale down to the lowest possible solution temperature.[2]

In an elegant study of the ^{13}C NMR spectra of *solid* Fe(CO)$_5$, Spiess and co-workers[3] have concluded from both T_1 and line-shape measurements that down to at least 100 K Fe(CO)$_5$ is nonrigid, probably via an axial/equatorial exchange mechanism. Below about 100 K T_1 becomes extremely long and the difference between the line-shape for a rigid molecule and a slowly exchanging one becomes more difficult to establish. Extrapolation from exchange rates at higher temperatures (213 K, $\tau^{-1} \sim 24$ kHz; 155 K, $\tau^{-1} \sim 13$ kHz; 100 K, $\tau^{-1} \sim 6$ kHz), which allows estimation of an activation energy ~1 kcal mol^{-1}, suggests that below about 30 K, the motion will be frozen out.

We have recently prepared a partially oriented sample of d^6 chromium pentacarbonyl[4] in solid argon at 20 K, by using polarized visible photolysis. The very fact that this sample did not lose its polarization properties for the duration of the experiment means that the square pyramidal Cr(CO)$_5$ molecule is essentially nonfluxional under these conditions. We have now