

Figure 1. Curie plot observed on an irradiated frozen benzene solution of 3d.

spin delocalization onto the aryl rings. Since the diyls all lack threefold symmetry, the approximately zero E value observed for 2e must be accidental.

The signal intensities of the four diyls 2c–2f in frozen solutions (80–150 K) and of diyl 2f in a single crystal of 3f (14–268 K) decrease with increasing temperature. The changes in each case are reversible and correspond to strict adherence to the Curie law, $IT = \text{constant}$, where I is the ESR signal intensity, as measured by the $\Delta m_s = 1$ peak height, and T is the absolute temperature. A typical Curie plot is exemplified by the behavior of the signal for diyl 2d (Figure 1). These results require either that the triplet and singlet have nearly identical enthalpies in each case, or more plausibly, that the triplet is the ground state.

Presumably, there are variations in the size of the singlet–triplet gap in the series 2a–f, but the preference for the triplet is strong enough to push such variations “off-scale” with respect to the limit of the present (not very sensitive) experimental techniques. The results contrast strikingly with the fine balance between singlet and triplet observed in another 4-electron- π -system, cyclopentadienylium cation,^{7a–d} where small changes in substitution shift the ground state from one multiplicity to the other. It is interesting and possibly significant that the most sophisticated calculations now available^{8–14} for TMM suggest a singlet–triplet gap of 18–21 kcal/mol, which is substantially greater than the 7 kcal/mol indicated by a Pariser–Parr–Pople calculation^{7b} for cyclopentadienylium cation.

References and Notes

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Matthew S. Platz, J. M. McBride, R. Daniel Little,
James J. Harrison, Andrew Shaw,¹⁵ Stephen E. Potter,¹⁶
Jerome A. Berson*

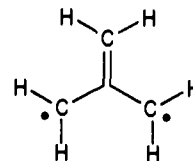
Department of Chemistry, Yale University
New Haven, Connecticut 06520

Received April 5, 1976

Trimethylenemethane. Experimental Demonstration That the Triplet State is the Ground State

Sir:

Trimethylenemethane (I), as it is generated photolytically at the boiling point of liquid nitrogen, exhibits a triplet state electron paramagnetic resonance (EPR) spectrum which persists for extended periods of time at that temperature.¹ As a result, it is widely assumed that the triplet state of trimethylenemethane (I) is the ground state. In fact, there exists no experimental evidence² which distinguishes this possibility from one in which the triplet is an excited state, thermally populated from a ground singlet state.³



I

In order to provide the firmest possible foundation for present and future studies of this reactive intermediate, it is essential that this fundamental feature of the trimethylenemethane system be made clear. Accordingly, we have examined the variation in intensity of the EPR spectrum of the triplet trimethylenemethane (I)⁴ as a function of temperature over the range 20–80 K.⁵ The results were plotted according⁶ to eq 1, where I is the peak-to-peak height⁷ of the EPR

$$IT = \text{constant}[1 + \frac{1}{3} \exp(-\Delta/RT)]^{-1} \quad (1)$$

signal, T is the absolute temperature, and Δ is the difference in energy between the triplet and a (higher) singlet state. Some representative data are shown in Figure 1. From this graph, it is evident that the triplet state of trimethylenemethane (I) is the ground state⁸ and that $\Delta \ll RT$ in the temperature range examined. That is, $IT = \text{constant}$. Curie law behavior was also observed for the relatively stable monoradicals produced in the course of photolysis.

Because of its symmetry, relative simplicity, experimental accessibility, chemical reactivity, and rare four π -electron configuration, trimethylenemethane (I) has been extensively investigated from a theoretical standpoint.⁹ That the triplet state is the ground state is the unanimous conclusion of all theoretical treatments capable of distinguishing between the singlet and triplet states on the basis of their relative ener-

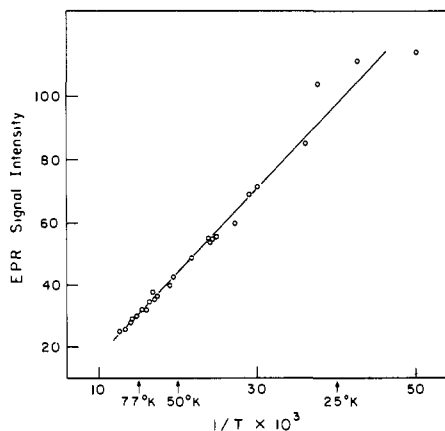


Figure 1. Peak-to-peak height of the low field $\Delta m_s = 1$ (xy) line in the EPR spectrum of trimethylenemethane (I) as a function of reciprocal absolute temperature.

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.

Acknowledgment. This work was generously supported by the U.S. Energy Research and Development Administration (E-(11-1)-3435) and by the National Science Foundation (NSF Grant No. MPS74-07864). The authors are indebted to Professor J. A. Berson and his colleagues for graciously making possible the simultaneous publication of this work with theirs.²

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

Robert J. Baseman, David W. Pratt*
Mudan Chow, Paul Dowd*

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

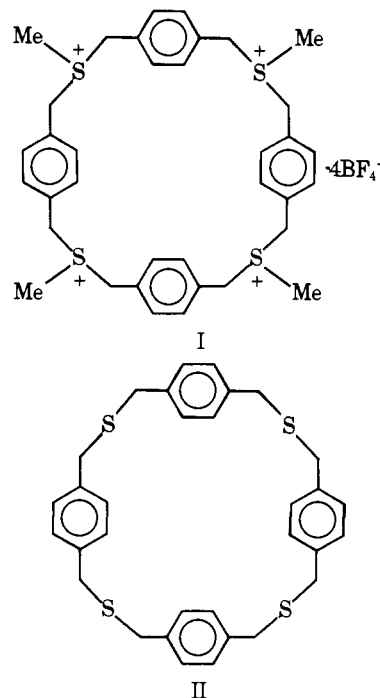
Received May 7, 1976

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 states² 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 polyparacyclophanes³ 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).



Treatment of the tetrasulfide II with $\text{Me}_3\text{O}^+\text{BF}_4^-$ produced $\text{S,S',S'',S'''}\text{-tetramethyl-2,11,20,29-tetrasulfonium[3.3.3.3]-paracyclophane}$ (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,