whereas **2c** opposes it. Although the geometric effect is small (see above), **2b** is the substitution pattern most likely to produce a planar closed shell singlet ground state TMM in this series.[22]

References and Notes

(1) The support of this work by the National Science Foundation (GP-33909X and CHE 76-00416) is gratefully acknowledged.

(2) W. E. Moffitt, as cited by C. A. Coulson, *J. Chem. Phys.*, **45**, 243 (1948); *Trans. Faraday Soc.*, **45**, 373 (1949).

(3) P. Dowd, *Acc. Chem. Res.*, **5**, 242 (1972), and references cited there.

(4) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969, p 97.

(5) (a) J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Am. Chem. Soc.*, **93**, 1544 (1971). (b) On the other hand the failure of 4-chloromethylene-3,3,5,5-tetramethylpyrazoline to generate a triplet electron spin resonance (ESR) spectrum upon irradiation has been attributed to the absence of threefold symmetry in the corresponding diyl: S. D. Andrews and A. C. Day, *J. Chem. Soc. B*, 1271 (1968).

(6) M. J. S. Dewar and J. S. Wasson, *J. Am. Chem. Soc.*, **93**, 3081 (1971).

(7) W. W. Schoeller, *Tetrahedron Lett.*, 2043 (1973).

(8) W. T. Borden and L. Salem, *J. Am. Chem. Soc.*, **95**, 932 (1973).

(9) (a) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 2906 (1975); (b) *Tetrahedron Lett.*, 259 (1967).

(10) W. J. Hehre, L. Salem, and M. R. Willcott, *J. Am. Chem. Soc.*, **96**, 4328 (1974).

(11) J. H. Davis and W. H. Goddard, III, *J. Am. Chem. Soc.*, **98**, 303 (1976).

(12) D. R. Yarkony and H. F. Schaefer, *J. Am. Chem. Soc.*, **96**, 3754 (1974).

(13) M. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. Potter, and J. A. Berson, following paper in this issue.

(14) J. A. Berson, A. Shaw, R. D. Little, and G. O'Connell, *J. Am. Chem. Soc.*, paper in preparation.

(15) Cf. (a) R. G. Parr, "The Quantum Theory of Molecular Electronic Structure", W. A. Benjamin, New York, N.Y., 1963; (b) H. E. Zimmerman, "Quantum Mechanics for Organic Chemists", Academic Press, New York, N.Y., 1975, p 172; (c) we thank Professor W. T. Borden for a further enlightening discussion of this procedure.

(16) I. Gutman and N. Trinajstic, *Fortschr. Chem. Forsch.*, **42**, 49 (1973).

(17) R. Hoffmann, *Chem. Commun.*, 240 (1969).

(18) W. T. Borden, "Modern Molecular Orbital Theory for Organic Chemists", Prentice-Hall, Englewoods Cliffs, N.J., 1975, pp 52–55.

(19) B. G. Odell, R. Hoffmann, and A. Imamura, *J. Chem. Soc. B*, 1675 (1970).

(20) H. J. Kopineck, *Z. Naturforsch.*, **5a**, 420 (1950); **6a**, 177 (1951).

(21) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.

(22) Angular Jahn–Teller distortion in singlet TMM might be expected to be less effective in lifting the degeneracy than bond length distortion would be in singlet cyclobutadiene, where the effect is directly on the nearest-neighbor resonance integral.

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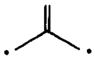
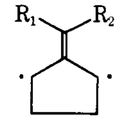
Triplet Ground States of Trimethylenemethanes[1]

Sir:

Since Dowd's original demonstration[2] of a stable triplet electron spin resonance (ESR) spectrum for parent trimethylenemethane (TMM, **1**), the only new triplet TMM observed by ESR has been 2-isopropylidenecyclopentane-1,3-diyl, **2f**.[3a] To evaluate experimentally the effect of substituents on the ordering of the lowest TMM spin states, and to test some theoretical predictions,[3b] we have prepared a series of new diyls **2a–e** and have investigated their ESR spectra.



1



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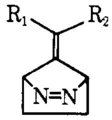


3

a, R_1, R_2 = H
b, R_1 = H; R_2 = Ph
c, R_1 = H; R_2 = Cl
d, R_1, R_2 = Ph
e, R_1, R_2 = OMe
f, R_1, R_2 = Me

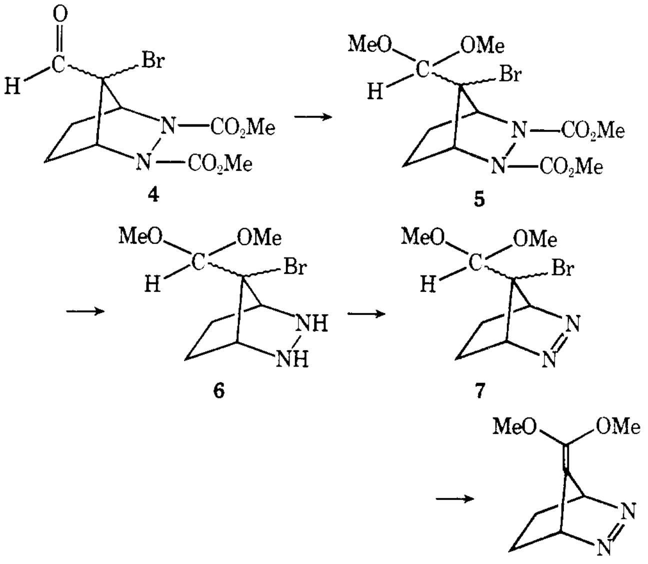
Table I. Zero-Field ESR Splitting Parameters[a] (cm^{-1})

Species	D	E
2a	0.0265	0.00550
2b[b]	0.0196	0.004
2c[c]	0.0266	0.0051
2d[b]	0.0180	0.0013–0.0032
2e	0.0278	<0.00133
2f	0.0256	0.00340

[a] Values calculated by matching the experimental spectrum using a computer program (P. Kottis and R. Lefebvre, *J. Chem. Phys.*, **41**, 379 (1964)) to refine the values obtained by visual inspection. [b] Hyperfine anisotropy caused poorer computer simulation leading to uncertainty in *E*. [c] *g*-Factor anisotropy caused poorer than usual computer simulation.

The syntheses of **3b, 3c,** and **3d,**[5] the azo compound precursors of diyls **2b, 2c,** and **2d,** parallel that of the dimethyl compound **3f.**[3] Semi-hydrogenation of the Diels–Alder adduct of dimethyl azodicarboxylate with the appropriate 6-substituted fulvene,[4] saponification of the carbamate functions, decarboxylation to the hydrazine, and oxidation give the azo compounds, which decompose just above room temperature. The dihydro analogue **3a** results when the hydrazine precursor of the azo compound **3c** in the chloro series is reduced with sodium in liquid ammonia and the resulting dechlorinated hydrazine is oxidized.

The synthesis of the dimethoxy compound requires a special route, which starts from the known[5a] bromo aldehyde **4.** The corresponding acetal **5** is converted by saponification and decarboxylation to the hydrazine **6.** Oxidation with mercuric oxide gives the crystalline bromoacetal azo compound **7**, which upon treatment with $NaNH_2$ in Et_2O at −50 °C gives a solution of the azo compound **3e.** This substance[5b] is extremely unstable and decomposes at temperatures above −20 °C.



The diyls **2a–f** result from irradiation (>320 nm) of 2-methyltetrahydrofuran or benzene solutions of the azo compounds **3a–f** cooled to <100 K in the cavity of a Varian E-line ESR spectrometer. In each case, we observe a clear triplet ESR spectrum which persists with undiminished intensity for at least 30 min after irradiation is stopped. The spectra are free of signals due to doublet impurities. For **2a, 2c, 2d,** and **2f,** we observe weak $\Delta m = 2$ transitions at approximately half the field of the main absorption. The zero field splitting parameters[6] are given in Table I.

The relatively small D values observed for the phenyl-substituted diyls **2b** and **2d** are consistent with the expected[6,7a,c-g]

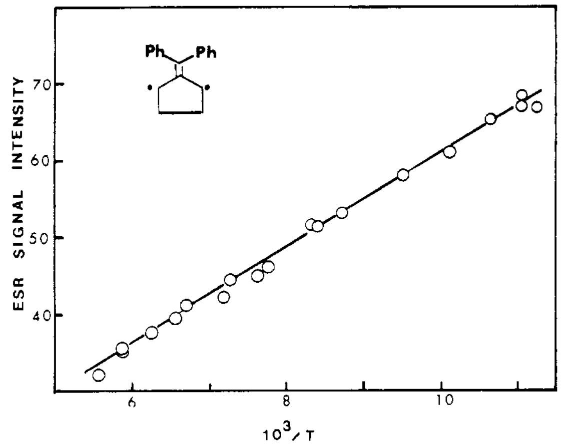


Figure 1. Curie plot observed on an irradiated frozen benzene solution of **3d.**

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 = 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

(1) The support of this work by the National Science Foundation (GP-33909X and CHE 76-00416) and the National Institutes of Health (GM-16962) is gratefully acknowledged.

(2) (a) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966); (b) R. J. Baseman, D. W. Pratt, M. Chow, and P. Dowd, *ibid.*, following paper in this issue, recently have shown that the ESR signal of **1** obeys the Curie law. We thank Professor Dowd for an advance copy of his paper.

(3) (a) J. A. Berson, R. J. Bushby, M. Tremelling, and J. M. McBride, *J. Am. Chem. Soc.*, **93**, 1544 (1971); (b) B. K. Carpenter, R. D. Little, and J. A. Berson, *ibid.*, preceding paper in this issue.

(4) For preparation of 6-chlorofulvene, see R. G. Bergman and M. D'Amore, *Chem. Commun.*, 461 (1971).

(5) (a) B. M. Trost and R. M. Cory, *J. Org. Chem.*, **37**, 1106 (1972). (b) The azo compounds and their precursors in the syntheses are characterized by their nuclear magnetic resonance (NMR) spectra. Precursors which are new compounds also give correct combustion analyses.

(6) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969, p 99.

(7) (a) R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *J. Am. Chem. Soc.*, **89**, 1112 (1967); (b) M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffman, Jr., C. Perchonock, E. Wasserman, R. S. Hutton, and V. J. Kuck, *ibid.*, **95**, 3017 (1973); (c) W. Broser, H. Kurreck, and P. Siegle, *Chem. Ber.*, **100**, 788 (1967); (d) W. Broser, P. Siegle, and H. Kurreck, *ibid.*, **101**, 69 (1968); (e) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962); (f) R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1963); (g) E. Wasserman, G. Smolinsky, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 129 (1965).

(8) M. J. S. Dewar and J. S. Wasson, *J. Am. Chem. Soc.*, **93**, 3081 (1971).

(9) W. W. Schoeller, *Tetrahedron Lett.*, 2043 (1973).

(10) W. T. Borden and L. Salem, *J. Am. Chem. Soc.*, **95**, 932 (1973).

(11) (a) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 2906 (1975); (b) *Tetrahedron Lett.*, 259 (1967).

(12) W. J. Hehre, L. Salem, and M. R. Willcott, *J. Am. Chem. Soc.*, **96**, 4328 (1974).

(13) J. H. Davis and W. H. Goddard, III, *J. Am. Chem. Soc.*, **98**, 303 (1976).

(14) D. R. Yarkony and H. F. Schaefer, *J. Am. Chem. Soc.*, **96**, 3754 (1974).

(15) NATO Postdoctoral Fellow, 1972–1973, sponsored by the Science Research Council of Great Britain.

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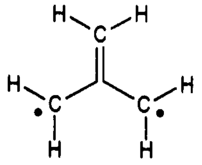
Trimethylenemethane. Experimental Demonstration That the Triplet State is the Ground State

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 evidence[2] 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 according[6] to eq 1, where I is the peak-to-peak height[7] of the EPR

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

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 state[8] and that $\Delta \ll RT$ in the temperature range examined. That is, IT = 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-