ventional Patterson and Fourier techniques and refined by full-matrix least-squares calculations (Table I). All phenyl groups in the two structures were treated as rigid bodies[14] with the hydrogen atoms attached and the individual carbon temperature factors refined (C-C = 1.390 Å, C-H = 0.95 Å). Nongroup atoms were refined anisotropically. Structural details for the two complex anions are presented in Table II. See paragraph at end of paper regarding supplementary material.

The Fe(II) ions in both structures are four coordinate. The FeS_4 units are distorted tetrahedra and the distortions present in the two structures are remarkably similar. To a first approximation these distortions can be envisioned as a compression of each of the tetrahedra along one of their twofold axes. On closer examination, the compression appears to affect two of the sulfur atoms to a greater extent than the other two. This significant difference, present in both structures, is clearly evident in the S_1-Fe-S_3 angle compared to the S_2-Fe-S_4 angle and the S_1-S_3 and S_2-S_4 distances, respectively (Table II, Figure 1). The relatively short S_1-S_2 and S_3-S_4 distances are very similar in both structures and suggest that in the case of the $Fe(Dts)_2{}^{2-}$ complex ligand-"bite" constraints probably are not responsible for the observed distortion of the FeS_4 unit. It should be noted that the observed intraligand S-S distances in the coordinated Dts ligands (Table II) are *shorter* than the one expected for the free ligand.[15] Since it seems highly unlikely that the same crystal packing forces are present in both lattices, the very similar distortions found in both structures most probably are due to inherent electronic characteristics of the Fe(II) ions,[16] and quite likely are a manifestation of a pseudo-Jahn-Teller effect expected for tetrahedral iron(II). The average Fe-S bond length (2.389 Å) in I is significantly longer than the average Fe-S bond length (2.355 Å) in III. Both of these values are similar to the one reported[7] for $Fe[(SPMe_2)_2N]_2$, but are appreciably longer than the Fe(III)-S bond length in the $Fe(S_2\text{-}o\text{-xylyl})_2{}^-$ anion[5b] or the Fe-S_4 core in Rd_{ox}.[2] The structural parameters of the two independent dithiosquarate ligands in I are similar to those reported for the $Ni(Dts)_2{}^{2-}$ complex.[9a]

It is apparent that the observed differences in the Mössbauer spectra[10] between I and III cannot be accounted for solely on the basis of deviations from tetrahedral symmetry. Electron delocalization properties of the ligands and charge density at the sulfur donors must be important. The longer Fe-S bond lengths in I compared to III may indicate differences in these properties for the dithiosquarate and thiophenolate ligands, respectively.

Acknowledgments. The financial support of this project by a grant (1R01 GM 18144-01A1) from the U.S. Public Health Service is gratefully acknowledged. The authors also are thankful to Dr. C. Murphy for growing the single crystals which were used for the collection of data.

Supplementary Material Available: Observed structure factors (24 pages). Ordering information is available on any current masthead page.

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(16) To establish this point we are presently undertaking a crystal structure determination of the x-ray isomorphous Co(II) complex.
(17) Alfred P. Sloan Fellow, 1972–1974.

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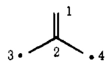
The Influence of Substituents on the Molecular Orbital Energies and Ground Electronic States of Substituted Trimethylenemethanes[1]

Sir:

In the simple Hückel approximation, π-electron molecular orbital (MO) theory predicts a degenerate pair of nonbonding energy levels (ψ_2 and ψ_3) for D_{3h} unsubstituted trimethylenemethane, **1**,[2] in accord with the experimental observation[3] of a triplet ground state. However, although unsymmetrical substitution or geometric distortion from threefold symmetry can lift the simple Hückel orbital degeneracy, membership in a highly symmetrical molecular point group is neither in principle[4] nor in fact a necessary condition for a triplet ground state, as the case of the diyl **2d** demonstrates.[5]



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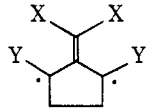
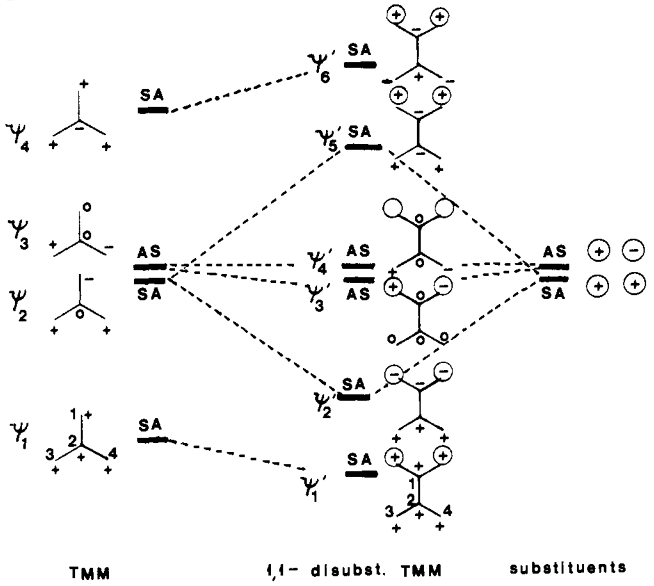


2a, X = OMe; Y = H
b, X = acceptor; Y = donor
c, X = donor; Y = acceptor
d, X = CH_3; Y = H

Recent more elaborate quantum mechanical calculations[6-12] suggest that the lowest singlet state of **1** may lie as much as 18–21 kcal/mol above the triplet. If this is correct, one might expect ground state triplet character to survive rather severe perturbations of the parent trimethylenemethane (TMM) structure. We report here qualitative arguments and semiempirical quantitative calculations that provide a theoretical basis for the discussion of substituent effects on the ordering of spin states and on the chemical behavior of TMM derivatives. Other papers[13,14] contain experimental tests of some of the conclusions.

The degeneracy of ψ_2 and ψ_3 persists even in C_{2v} TMM at the simple Hückel (HMO) level. At a higher level of approximation, contraction of one C-C-C angle lifts the degeneracy because of the resulting nonnearest neighbor interaction.[9b] However, it can be shown by a zero differential overlap (ZDO) calculation[8,15] that the effect remains too small to reverse the singlet–triplet ordering, even for unique angles as small as 90°. Moreover, a graph theoretical procedure[16] now shows that substitution of any combination of alternant hydrocarbon residues (e.g., phenyl, vinyl, etc.) is without effect on the HMO orbital degeneracy, even when such substitution removes all

Scheme I



molecular symmetry elements (other than the nuclear plane).

Hetero substituents, however, do lift the degeneracy, with consequences that may be deduced from perturbation theory. The argument presented here parallels the treatment of substitution in cyclobutadiene,[17,18] a molecule which resembles TMM in having a degenerate nonbonding pair of HMO's, but which differs from it in MO symmetries.

Scheme I shows the effects of 1,1-substitution. The substituents are represented by a pair of $2p\pi$ orbitals (not necessarily on carbon) which can be taken as in-phase or out-of-phase combinations and which are π electron acceptors when empty or donors when each is doubly occupied. Note that the point group symmetry of TMM is reduced from D_{3h} to C_{2v} by the extra atomic orbitals. The MOs are classified as symmetric (S) or antisymmetric (A) with respect to the reflection plane σ_v and the rotation axis C_2, respectively, the only two C_{2v} operations of significance here.

The resulting set of MO's is, of course, similar to those of tetramethylenethane,[19] but not identical because of the lower symmetry of the present system. In particular, the two AS orbitals ψ_3' and ψ_4' are not degenerate unless the substituent p orbitals are on carbon. When the substituents are electron withdrawing, there is a total of 4 π electrons in the system, so that the highest occupied MO (HOMO) is ψ_2', which is symmetric with respect to σ_v, and the lowest unoccupied MO (LUMO) is the antisymmetric ψ_3'. For electron releasing substituents, 8 π electrons must be accommodated, which makes the HOMO (ψ_4') antisymmetric and the LUMO (ψ_5') symmetric. The effect of 1,1-disubstitution thus is to remove the orbital degeneracy of TMM by a perturbation of the SA component ψ_2, which is stabilized by electron acceptors and destabilized by donors. Substituents at carbon 1 do not perturb the AS component ψ_3 appreciably because it has a node there.

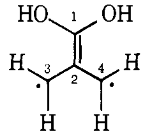
An analogous treatment of 3,4-disubstitution leads to the conclusion that π electron acceptors stabilize the AS orbital ψ_3 more than ψ_2, because ψ_3 has larger coefficients at C_3 and C_4. Similarly, π electron donors destabilize ψ_3 more than ψ_2. Thus, both 1,1- and 3,4-disubstitution remove the orbital degeneracy, but the effects on the ordering of the orbitals are in opposite directions.

The results may be contrasted with those in the cyclobutadiene (CBD) case, where to first order, 1,2-disubstitution does not lift the degeneracy, but 1,3-disubstitution does.[17,18] In the 1,2-disubstituted CBD system, the degenerate π orbitals and the substituent orbitals have matching symmetries, so that *both* ψ_2 and ψ_3 are perturbed, but in the 1,3 case, the degeneracy is broken because the symmetry of *only one* of the substituent orbital combinations matches that of a CBD degenerate orbital.

Table I. Relative Energies (eV) of Various States of **3**

Electronic state	Geometry	Calcd energy above ground state: ZDO	INDO (opt)	INDO (105°)
Triplet	Planar	0.00	0.00	0.00
Closed shell singlet	Planar	2.70	2.30	3.25
Closed shell singlet	Bisected	2.95	1.55	2.90
Open shell singlet	Planar	3.40		
Open shell singlet or triplet	Bisected	3.80		

The qualitative argument must be supplemented by more detailed calculations in order to determine whether heteroatom substitution of TMM can convert the ground state from triplet to singlet. The hypothetical 1,1-dihydroxytrimethylenemethane **3** serves as a model for the experimentally accessible[13,14] diyl **2a**, and we calculate the properties of **3** by two independent methods.



3

The first uses the HMO wave functions to compute electron repulsion integrals $\gamma_{\mu\nu}$ by the ZDO approximation, as has been done for TMM itself,[8] according to eq 1, where γ is in electron volts,[15a] and $r_{\mu\nu}$, the internuclear distance, is in angstrom. The resonance ($\beta_{\mu\nu}$) and Coulomb (α_μ or α_ν) integrals are in electron volts and are given by eq 2. The overlap integrals S are taken from Kopineck's tables.[20]

$$\gamma_{\mu\nu} = \frac{\gamma_{\mu\mu} + \gamma_{\nu\nu}}{2 + 0.80537 r_{\mu\nu}} \tag{1}$$

$$\beta_{\mu\nu} = 0.75 S(\alpha_\mu + \alpha_\nu)/2 \tag{2}$$

$$\beta_{C\text{-}C} = -2.367 \text{ eV}; \ \beta_{C\text{-}O} = -1.350 \text{ eV}$$

These parameters give an ordering of states for the parent unsubstituted D_{3h} TMM (**1**) which is the same as that predicted by a variety of more sophisticated calculations,[6-12] In particular, they predict a triplet ground state and a bisected open shell singlet as the next highest state. The results for the substituted case **3** are given in Table I.

Two calculations use the INDO method,[21] one including geometry optimization by minimization of the energy with respect to independent variations of bond lengths (C_1-O, C_1-C_2, and C_2-C_3) and bond angles (O-C-O, C_3-C_2-C_4, and H-C_3-H). An alternative INDO calculation fixes the C_3-C_2-C_4 angle at 105° in simulation of the five-membered ring of **2a.** The results are given in Table I.

Of course, it would be unjustified to place much weight on the quantitative results of such approximate techniques. Nevertheless, it seems clear that the triplet ground state for 1,1-dialkoxy TMM derivatives should be preferred over any singlet, in agreement with the experimental result for **2a.**[13]

If a singlet ground state TMM can be achieved it will probably be through the cooperative action of 1,1- and 3,4-substituents. For the methylenecyclopentane-2,5-diyl series, substitution patterns **2b** or **2c** superficially would seem to be equally effective. However, **2b** reinforces the ψ_2 stabilization[9b] caused by the angular contraction in the five-membered ring, 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]

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(23) NATO Postdoctoral Fellow, 1973-1975, sponsored by the Science Research Council of Great Britain.

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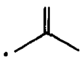
Triplet Ground States of Trimethylenemethanes[1]

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.



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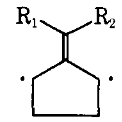

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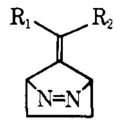


3

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

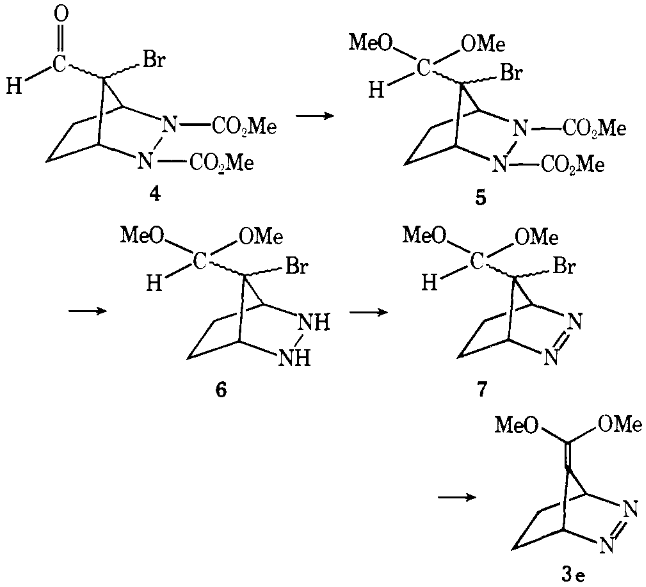
Table I. Zero-Field ESR Splitting Parameters[a] (cm^{-1})

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,e-g]