the electron affinities are raised roughly from 1 to 6 kcal/mol. As perturbation arguments suggest, and as found in many other cases, increased stability (of the second-row anions) makes additional stabilization less important. The diminished phenyl-substituent effect in the second-row species relative to the first-row species is also a consequence of the weaker interaction with the phenyl group which arises from the poor overlap of the 3p orbitals of the second-row elements with the 2p orbitals of the ring. The large differences in the effect of phenyl substitution in carbanions vs silyl anions has been attributed[13] to energy mismatch and differences in orbital size, both of which contribute to less stabilization.

Conclusions

We have measured the electron affinities of alkyl- and aryl-substituted phosphide radicals. We have also bracketed the P–H acidity and derived the bracketed P–H bond energy for methylphosphine. Our data extend the existing thermochemical literature addressing substituent effects in the first- and second-row main-group hydrides. We find that replacement of a hydrogen by a methyl group always lowers the electron affinity of the hydride radical by 5–10 kcal/mol; that the hydride bond energies are always lowered upon methyl substitution, except in the case of silane (which remains unaffected); and that the second-row species are always more acidic than their first-row counterparts.

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Theoretical Study of the Low-Lying Triplet and Singlet States of Diradicals. 1. Tetramethyleneethane

Petr Nachtigall and Kenneth D. Jordan*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. Received June 17, 1991

Abstract: The geometry of the lowest energy singlet and triplet states of tetramethyleneethane have been optimized by means of the UHF, ROHF, and MCSCF methods, in order to obtain a better understanding of the importance of electron correlation for the geometries and the singlet–triplet gap. At the MCSCF(6,6)/DZP level of theory, both the singlet and triplet states are predicted to have D_2 structures, with the ground state being the singlet and the triplet state lying 1.36 kcal/mol higher in energy.

I. Introduction

The energy separation between the lowest singlet and triplet states of diradical species is a subject of considerable interest. One of the most studied diradicals is tetramethyleneethane (TME).[1-6] The two frontier orbitals (HOMO and LUMO) of TME are degenerate in the Hückel MO approximation. One triplet and three singlet states result from the various possible ways of distributing the two "frontier" electrons in these two orbitals. Of these four states, the two lowest in energy—the triplet state and one of the singlet states—are diradical in character.[1] The most sophisticated ab initio calculations carried out to date on TME predict a singlet ground state, lying energetically about 1.5 kcal/mol below the triplet state.[2] On the other hand, an ESR spectrum determined from the photodecomposition products of an azo precursor has been attributed to the triplet state of TME,[3] which would seem to imply either that TME has a ground-state triplet or that the singlet–triplet gap is less than 0.2 kcal/mol.

In theoretical studies of TME and other diradicals, it has been standard practice to optimize the geometry of the triplet (T) state by means of the restricted open-shell (ROHF) or unrestricted (UHF) Hartree–Fock methods and either to employ this geometry also for the singlet (S) state or to optimize the geometry of the singlet state by means of the two-configurational SCF (TCSCF) procedure. (A wave function with a minimum of two Slater determinants is required to describe the singlet diradical.[4]) Although, it has been noted that the UHF and TCSCF procedures may prove inadequate for describing the geometries of diradicals,[5] electron correlation effects have generally been included at the Hartree–Fock or TCSCF optimized geometries (see, for example, ref 6). It is possible that geometry optimizations carried out using the multiconfigurational self-consistent field (MCSCF) method could lead to significantly different geometries, which, in turn, could cause an appreciable change in the singlet–triplet gap. In this paper we present the results of MCSCF calculations on the lowest singlet and triplet states of TME. Geometry optimizations were carried out with different choices of active orbital spaces and configuration lists in order to gain a more detailed understanding of the importance of electron correlation effects on the geometries and on the singlet–triplet gap.

II. Computational Methodology

The geometries were optimized for structures of D_{2h}, D_{2d}, and D_2 symmetry. Two different active orbital spaces were used in the geometry optimizations carried out using the MSCSF method. The smaller of these has two active electrons in two active orbitals, the HOMO and LUMO, and the larger has six active electrons in six active orbitals, the six valence π and π^* orbitals. Hereafter, these two procedures are referred to as MCSCF(2,2) and MCSCF(6,6), where the first number refers to the number of active electrons and the second to the number of active orbitals. For the singlet state, the MCSCF(2,2) and TCSCF procedures are equivalent, while for the triplet state, the MCSCF(2,2) and ROHF procedures are equivalent. The geometry of the triplet state was also optimized in the UHF approximation.

The MCSCF(6,6) procedure includes all symmetry-allowed configurations in the six orbital active space. The geometry of the singlet state has also been optimized by means of the MCSCF(6,6)SD procedure,

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(1) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

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(3) Dowd, P. *J. Am. Chem. Soc.* **1970**, *92*, 1066. Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416.

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Table I. Energies and Geometries of the Optimized Structures of TME

			ΔE[a]	bond lengths (Å)		angle (deg)
symmetry	state	energy (au)	(kcal/mol)	C_1–C_2	C_1–C_3	$C_1C_2C_3$
			MCSCF(2,2)			
D_{2h}	S	−230.436 31	4.81	1.516	1.376	119.0
	T	−230.434 47	5.96	1.520	1.377	118.6
D_{2d}	S	−230.443 98	0.0	1.505	1.371	123.4
	T	−230.441 31	1.68	1.511	1.372	122.6
D_2	S			minimum not found		
	T	−230.442 20	1.11	1.509	1.373	122.2
			MCSCF(6,6)			
D_{2h}	S	−230.525 94	1.76	1.498	1.398	118.6
	S[b]	−230.522 17		1.498	1.395	118.6
	T	−230.520 35	5.27	1.514	1.396	118.6
D_{2d}	S	−230.528 75	0.0	1.504	1.390	123.4
	T	−230.526 34	1.51	1.510	1.391	122.8
D_2	S	−230.528 95	−0.13	1.502	1.393	122.4
	T	−230.526 83	1.20	1.508	1.392	122.4
			UHF			
D_{2h}	T	−230.479 60	6.94	1.534	1.391	118.9
D_{2d}	T	−230.490 67	0.0	1.511	1.391	122.8
D_2	T			minimum not found		

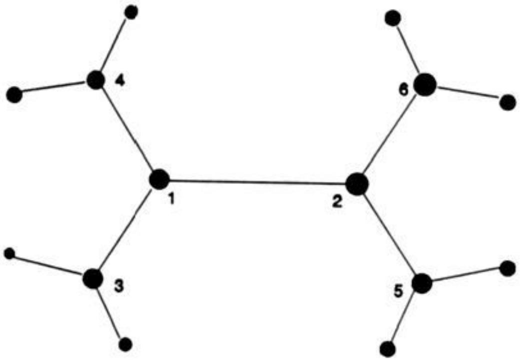
[a] Energies relative to that of the singlet D_{2d} species at the particular level of theory. [b] Energy and geometry obtained by means of the MCSCF-(6,6)SD procedure.

which includes only those excited configurations which are singly or doubly excited with respect to the two configurations in the TCSCF wave function.

The 3-21G basis set[7] was used for all geometry optimizations. At the MCSCF(6,6)/3-21G optimized geometries, additional MCSCF calculations were carried out using Dunning's split-valence basis set with polarization functions on the carbon atoms.[8] Hereafter, this basis set is referred to as DZP. The geometry optimizations were carried out with the Gaussian 90 program,[9] and the single point calculations with the DZP basis set were carried out with the programs of Shepard and co-workers.[10]

III. Results and Discussion

The geometries and energies obtained from the calculations are summarized in Table I. The carbon atoms are labeled as shown in the below. Discussion of the results for the singlet state,



assuming a planar D_{2h} structure, are presented first. The C–C distances obtained from the calculations with the MCSCF(2,2) procedure differ by about 0.02 Å from those obtained with the MCSCF(6,6) and MCSCF(6,6)SD procedures, with the results obtained from the latter two approximations being nearly identical. In the remainder of this study, we consider results obtained at the MCSCF(6,6) rather than the MCSCF(6,6)SD level of theory since, for TME, there is not a significant computational saving associated with use of the latter approximation. However, for larger diradicals, a truncation of the configuration space analogous to that in the MCSCF(6,6)SD procedure for TME could lead to significant reductions in the computational effort.

Table II. C_1–C_2 and C_2–C_3 Bond Lengths of Butadiene

		bond length (Å)	
method	basis set	C_1–C_2	C_2–C_3
SCF	3-21G	1.321	1.467
MCSCF	3-21G	1.342	1.466
SCF	DZP	1.329	1.472
MCSCF	DZP	1.350	1.470
expt[a]		1.341	1.463

[a] The experimental geometry is from ref 12.

Because the MCSCF(6,6) procedure neglects correlation effects involving the σ electrons and because the 3-21G basis set does not include polarization functions, it is not obvious that the resulting geometrical parameters are necessarily closer to the exact values than those obtained from the MCSCF(2,2) calculations.

In order to gain more insight into the reliability of full π-space MCSCF calculations, employing the 3-21G basis set, for predicting geometries, the geometry of *trans*-butadiene has been optimized in both the HF and MCSCF(4,4) approximations,[11] and using both the 3-21G and DZP basis sets. As may be seen from the results summarized in Table II, the C–C bond lengths obtained from MCSCF(4,4)/3-21G calculations are in closer agreement with the experimental values than are those obtained at either the HF/3-21G or MCSCF (4,4)/DZP levels of theory. Although, this is in part fortuitous, we conclude that π-space MCSCF calculations, employing the 3-21G basis set, will generally give geometries closer to experiment than do HF/3-21G calculations.

At both the MCSCF(2,2) and MCSCF(6,6) levels of theory and for both the singlet and triplet states, the D_{2d} structure of TME is predicted to lie energetically below the D_{2h} structure, with the singlet state lying lower in energy. Moreover, at the MCSCF(6,6) level of theory, both the singlet and triplet states are found to be slightly more stable in twisted D_2 structures than in the D_{2d} structures. However, at the MCSCF(2,2) level of theory, only the triplet state is found to give a D_2 minimum, and the UHF approximation fails to give a D_2 minimum for the triplet state.

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(7) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(8) The DZP basis set employs a [9s5p1d/3s2p1d] set of contracted functions on the carbon atoms and a [4s/2s] set of contracted functions on the hydrogen atoms: Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

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(11) The four active orbitals in the MCSCF(4,4) calculations on butadiene consist of the two π and two valence π^* orbitals.

(12) Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1967**, *1*, 463.

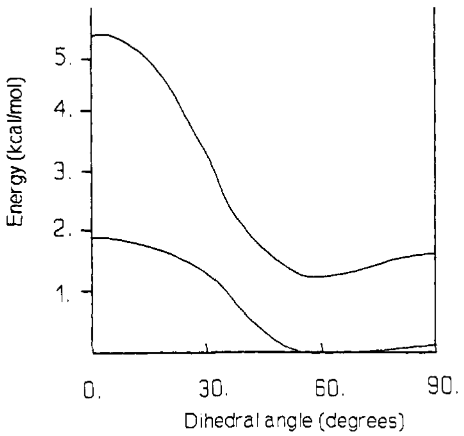

Figure 1. Potential energy (in kcal/mol) as a function of the dihedral angle for the singlet (S) and triplet (T) states. These results are obtained from MCSCF(6,6) calculations using the 3-21G basis set. The curves are fit to the energies for four dihedral angles, those corresponding to the optimized D_{2h}, D_{2d}, and D_2 structures (~59°) as well as that at 30°. For each dihedral angle, the other geometrical parameters were fully optimized under the constraint of the appropriate point group (D_{2h}, D_{2d}, or D_2).

The dihedral angle between the two allyl groups is predicted in the MCSCF(6,6) procedure to be 58.0° and 59.0° for the singlet and triplet states, respectively. The MCSCF(2,2) method gives a dihedral angle of 56.7° for the triplet state. Apparently, neither the D_{2d} nor D_{2h} structures for the singlet or triplet states correspond to potential energy minima at the MCSCF(6,6) level of theory.

Figure 1 depicts the MCSCF(6,6) potential energy curves of the lowest S and T states of TME as a function of the dihedral angle. From this figure it is seen that the $D_{2d} \rightarrow D_2$ distortion leads to a greater decrease in the energy of the triplet state than that of the singlet state (0.31 versus 0.13 kcal/mol). In addition, the energy gap between the D_2 and D_{2h} structures is much greater for the triplet than for the singlet state (4.07 versus 1.89 kcal/mol). The singlet D_2 species is 1.33 kcal/mol more stable than the triplet D_2 species at the MCSCF(6,6)/3-21G level of theory.

For both the singlet and triplet states, regardless of the dihedral angle, the C_1–C_3 bond lengths of TME are found to increase by about 0.02 Å in going from the MCSCF(2,2) to the MCSCF(6,6) level of theory. However, only for the planar singlet species does the inclusion of electron correlation prove important for the C_1–C_2 bond length, leading to a 0.018-Å decrease. With this exception, these trends are similar to those discussed above for butadiene. The UHF procedure gives a C_1–C_2 distance for the D_{2h} triplet species about 0.036 Å longer than the MCSCF(6,6) value.

The energy lowering due to the inclusion of electron correlation effects is nearly the same for the triplet D_{2h}, D_{2d}, and D_2 structures as well as for the singlet D_{2d} structure but is appreciably larger for the singlet D_{2h} structure. The importance of electron correlation for the singlet D_2 species is intermediate between that for the D_{2h} and D_{2d} structures. This result is deduced from calculations at the MCSCF(2,2) optimized structure for the triplet rather than for the singlet, which does not have a D_2 minimum at this level of theory. Thus, electron correlation effects prove particularly important for determining the twisting potential for the singlet state as well as for singlet–triplet energy gap in the case of the D_{2h} and D_2 structures. The energy gap between the singlet and triplet D_{2h} structures is almost three times larger in the MCSCF(6,6) than in the MCSCF(2,2) procedure (3.49 versus 1.15 kcal/mol).

Although the results discussed above show that the singlet–triplet gap for the D_{2h} structure (and to a lesser extent, also for the D_2 structure) is appreciably larger in the MCSCF(6,6) approximation, there remains the question as to whether the geometry changes induced by the inclusion of electron correlation are largely responsible for this behavior. In order to resolve this issue, MCSCF(6,6) calculations have been carried out at the UHF and MCSCF(2,2) optimized geometries. Figure 2 presents a correlation diagram of the energies obtained at the MCSCF(6,6)/MCSCF(6,6), MCSCF(2,2)/MCSCF(2,2), MCSCF(6,6)/MCSCF(2,2), and MCSCF(6,6)/UHF levels of theory, where the procedure indicated on the left is that used to calculate the energy and that on the right specifies the geometry used. The MCSCF(6,6)/UHF calculations have been carried out using the triplet UHF geometries for both the singlet and triplet states, and the MCSCF(6,6)/MCSCF(2,2) and MCSCF(2,2)/MCSCF(2,2) calculations on the D_2 species used the MCSCF(2,2) triplet state geometry for both the singlet and triplet states (since the MCSCF(2,2) level of theory does not give a D_2 minimum for the singlet state). For each set of calculations, the energies are reported relative to that of the singlet D_{2d} species. From Figure 2, it is seen that for both the D_{2h} and D_2 structures, as well as for the previously discussed D_{2d} structures, the energy differences are relatively insensitive as to whether the MCSCF(2,2), UHF, or MCSCF(6,6) geometries are employed.

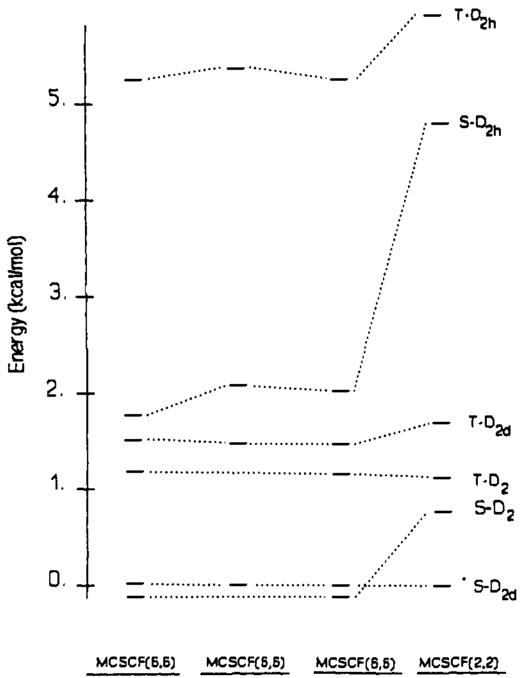

Figure 2. Relative energies (in kcal/mol) of the singlet and triplet states for the D_{2h}, D_{2d}, and D_2 species. Energies are given relative to that of the singlet D_{2d} state. At the bottom of the figure both the method used for the calculation of the energy (upper designation) and the geometry employed (lower designation) are indicated. All calculations are carried out with 3-21G basis set.

The MCSCF(6,6) calculations with the 3-21G basis set give an adiabatic singlet–triplet gap of 1.33 kcal/mol, somewhat smaller than that (1.5 kcal/mol) reported by Du and Borden.[2] Even though these two values for the singlet–triplet gap are quite close, the singlet twisting potential obtained in the present study differs appreciably from that of Du and Borden. Although we find that the optimized structure for the singlet is of D_2 symmetry, Du and Borden reported that the D_2 structure lies energetically above both the D_{2h} and D_{2d} structures for the singlet state, with the lowest energy structure having D_{2d} symmetry. Hence, although the adiabatic and vertical S → T excitation energies obtained in the present study are very close, those of Du and Borden differ appreciably.

There are several differences between the present calculations and those presented in ref 2.[13] The CI calculations of ref 2 used

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(13) In ref 2 it was reported that the UHF/3-21G procedure gave a D_2 minima (with a dihedral angle of 44.9°) for the triplet state. In the present study it was found that the D_2 structure is not a minimum in the UHF/3-21G approximation, but that at this level of theory, the minimum is of D_{2d} symmetry. The bond lengths obtained here for the D_{2d} structure at the UHF level of theory agree precisely with those tabulated in ref 2 for the D_2 structure. A check with the authors of this paper revealed that their UHF calculations actually gave as the lowest energy form of the triplet the D_{2d} structure, and that their report of a lower energy D_2 structure was incorrect.

Table III. Total Energies and Singlet–Triplet Splittings Obtained from MCSCF Calculations on TME Using the DZP Basis Set[a]

method	symmetry	total energies (au)		S–T splitting (kcal/mol)
		singlet	triplet	
MCSCF(2,2)	D_{2h}	−231.748 612	−231.745 853	1.72
	D_{2d}	−231.755 784	−231.751 720	2.54
	D_2	−231.753 981	−231.752 884	0.65
MCSCF(6,6)	D_{2h}	−231.833 391	−231.827 246	3.84
	D_{2d}	−231.835 212	−231.832 139	1.92
	D_2	−231.835 270	−231.833 097	1.36

[a] All energies in this table are obtained at the MCSCF(6,6)/3-21G optimized geometries.

a basis set with d functions on the carbon atoms, employed the triplet UHF optimized geometries for both the singlet and triplet states, included all single-plus-double excitations within the valence space, and employed orbitals generated from MCSCF(2,2) calculations on the singlet and triplet states. Our calculations, described above, were carried out using the 3-21G basis set, used separately optimized MCSCF(6,6) geometries for the singlet and triplet states, and treated electron correlation effects by means of the MCSCF(6,6) procedure, which includes only a subset of the valence orbitals in the active space.

To facilitate comparison of our results and those of Du and Borden, MCSCF(6,6) and MCSCF(2,2) calculations have also been carried out using the DZP basis set and the MCSCF(6,6)/3-21G optimized geometries. The results of these calculations, summarized in Table III, show that the inclusion of carbon d functions has relatively little effect on the singlet–triplet splitting; with the MCSCF(6,6) procedure the calculations using the DZP basis set give a splitting of 1.36 kcal/mol as compared the 1.33 kcal/mol splitting obtained with the 3-21G basis set. However, the inclusion of d functions proves important for determining the shapes of the twisting potentials, particularly for the singlet state, causing the energy of the D_{2h} species relative to that of the singlet D_2 species to decrease from 1.9 to 1.2 kcal/mol. Even with the inclusion of d functions, the singlet twisting potential obtained from the MCSCF(6,6) calculations differs appreciably from that obtained by Du and Borden. We believe that the CI calculations of these authors place the D_2 structure too high in energy due to the use of MCSCF(2,2) orbitals and a relatively small CI space.[15]

IV. Conclusions

The geometries of the singlet and triplet states of TME were optimized by means of the MCSCF, ROHF, and UHF methods and using the 3-21G basis set. In the MCSCF(6,6) procedure, with all π and π^* orbitals active, the singlet and triplet states are predicted to have D_2 structures, with dihedral angles between the two allyl groups of 58.0° and 59.0°, respectively. The present calculations, in agreement with those of Borden and co-workers, place the singlet state below the triplet, with the singlet–triplet gap being 1.36 kcal/mol in the MCSCF(6,6)/DZP approximation. Moreover, it is found that the singlet state is below the triplet state at all dihedral angles.

The twisting potential of the singlet state is particularly shallow, with the energy difference between the D_2 and D_{2d} structures being only about 10 cm^{-1} in the MCSCF(6,6)/DZP approximation. Exploratory calculations with larger basis sets and recovering more of the electron correlation energy do not give a D_2 minimum for the singlet state, but indicate that the potential for twisting away from the D_{2d} structure is very shallow. TME in its lowest singlet state thus undergoes very large amplitude motion in its zero-point vibrational level. The twisting potential is much steeper for the triplet state, with the D_2 structure being predicted to be 120 and 210 cm^{-1} below the D_{2d} structure in MCSCF(6,6) calculations using the 3-21G and DZP basis sets, respectively, and the zero-point level should lie well below the D_{2d} barrier in the case of the triplet state.

With the exception of the dihedral angle, the geometries obtained with the MCSCF(6,6) procedure are fairly close to those obtained neglecting electron correlation effects: for the D_{2h} and D_{2d} structures the changes in the geometries do not prove very important for the singlet–triplet gap. However, in order to reliably calculate the energy separation between the singlet and triplet states at their D_2 structures, it is important to employ accurate values for the dihedral angles. In this regard use of the UHF procedure for the triplet state or the RHF procedure for the singlet state is inadequate since D_2 minima are not obtained at these levels of theory. This is particularly serious for the triplet state due to the larger D_2–D_{2d} energy difference in this case. On the other hand, the use of the MCSCF(2,2) (i.e., ROHF) optimized geometry for the triplet state for subsequent MCSCF(6,6) calculations on the singlet and triplet state does not introduce a large error in the singlet–triplet gap.

The singlet–triplet energy gap of TME calculated by means of the MCSCF(6,6) procedure is relatively insensitive to the basis set employed. In addition to the calculations employing the 3-21G and DZP basis sets discussed in the main body of the text, calculations were also carried out with basis sets containing diffuse s, p, and d functions on the carbon atoms. These extensions to the basis set proved relatively unimportant for the singlet–triplet splitting.

The principal deficiency of the MCSCF(6,6) method employed in the present investigation is the neglect of correlation effects involving the σ electrons. However, the calculations of Du and Borden[2] which recovered part of the σ-electron correlation also predict the singlet state to lie energetically below the triplet state. Given the relative insensitivity of the singlet–triplet gap to the basis set and to the inclusion of valence space σ electron correlation effects, it is tempting to conclude that TME has a singlet ground state, lying over 1 kcal/mol below the triplet state, in apparent contradiction to the ESR results. However, preliminary CI calculations carried out in our group indicate that correlation effects not recovered in either the MCSCF(6,6) calculations or in the valence space CI calculations of Du and Borden stabilize the triplet state relative to the singlet.[16] Indeed, SD–CI calculations at the MCSCF(6,6)/3-21G optimized D_2 singlet structure, using a triple-zeta-plus polarization quality basis set,[17] employing a single reference configuration for the triplet state and two reference configurations for the singlet state, and allowing for excitations from all occupied valence orbitals into the entire virtual space, place the triplet state only 0.21 kcal/mol above the singlet state. With the inclusion of the Davidson correction,[18] the triplet state drops to 0.57 kcal/mol below the singlet state. Thus it appears that with the inclusion of correlation effects not recovered in approaches correlating only valence electrons, the singlet and triplet states are likely to be very close in energy, with the triplet perhaps lying lower in energy. It is anticipated that the inclusion of excitations external to the valence space would not drastically alter the shapes of the twisting potentials from those obtained with the MCSCF(6,6) procedure and that the major effect of these

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(14) The CI calculations on the singlet and triplet D_2 structures of TME reported in ref 2 used a structure with a dihedral angle of 44.9° (see ref 13) and with the other geometrical parameters taken to be those of the triplet D_{2d} species, optimized in the UHF/3-21G approximation.

(15) Full CI calculations, in the space of the six π orbitals, on the three structures considered for the singlet state, were performed using orbitals determined from MCSCF(2,2) calculations on the singlet state. (The π and π^* orbitals were obtained from diagonalization over the MCSCF(2,2) Fock operator.) These calculations placed the D_2 and D_{2d} structures over 3.5 kcal/mol above the D_{2h} structure, in contrast to the situation found with the MCSCF(2,2) or MCSCF(6,6) approximations. This indicates that sizable errors in the energies of the D_{2d} and D_2 structures result from the use of non-optimized orbitals. This problem is expected to persist to some extent in SDCI calculations carried out in the valence space using MCSCF(2,2) orbitals, as this approach will permit only partial relaxation of the occupied orbitals. This, together with the use of dihedral angle 45° instead of optimized dihedral angle (~60°), is expected to be partially responsible for the relatively high energy reported for the D_2 structure in ref 2.

(16) Nachtigall, P.; Jordan, K. Unpublished results.

(17) The CI calculations were carried out using a (10s5p1d/4s3p1d) set of contracted Gaussian functions on the carbon atoms, with the s and p functions being from Dunning (Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007) and exponent of the d function chosen to be 0.55. Dunning's (4s/2s) contracted basis set was used on the hydrogen atoms.

(18) Davidson, E. R.; Silver, D. W. *Chem. Phys. Lett.* **1978**, *52*, 403.

correlation effects will be to uniformly stabilize the twisting potential of the triplet state relative to that of the singlet state.

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Theoretical Study of the Low-Lying Triplet and Singlet States of Diradicals. 2. Cyclopentadienyltrimethylenemethane

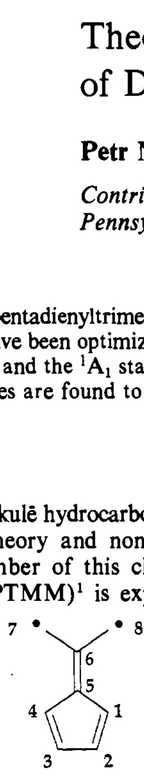
Petr Nachtigall, Paul Dowd, and Kenneth D. Jordan*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. *Received September 23, 1991*

Abstract: Cyclopentadienyltrimethylenemethane has low-lying singlet and triplet states of A_1 and B_2 symmetry. The geometries of these states have been optimized by means of the ROHF, UHF, and MCSCF methods. The two lowest energy states—the $^3B_2$ ground state and the $^1A_1$ state, lying 4.9 kcal/mol above the ground state—are predicted to be planar. The higher-lying $^3A_1$ and $^1B_2$ states are found to have nonplanar structures.

Introduction

Nonalternant, non-Kekulē hydrocarbons have received relatively little attention from theory and none from an experimental standpoint. As a member of this class, cyclopentadienyltrimethylenemethane (CPTMM)[1] is expected to have low-lying singlet and triplet electronic states, with considerable diradical character. On the basis of Hückel MO calculations, it has been predicted that the ground state should be a singlet.[2,3] CPTMM has not been studied experimentally or by means of ab initio electronic structure methods.



CP-TMM

CPTMM can be viewed as being derived from cyclopentadienyl and allyl fragments. Figure 1 presents a correlation diagram of the energies of the Hückel MO's of cyclopentadienyl, allyl, and CPTMM, and Figure 2 compares the Hückel energies and MO's of CPTMM and tetramethyleneethane (TME), a prototypical diradical.[4,5] At the Hückel level of theory CPTMM differs from TME in that the two frontier orbitals of TME are degenerate and nonbonding and also are energetically well separated from the other MO's, while for CPTMM the HOMO and the LUMO have rather different energies ($\alpha + 0.504\beta$ and α, respectively) and the second highest occupied orbital (SHOMO), with a Hückel energy of $\alpha + 0.618\beta$, is only slightly more stable than the HOMO. The symmetries of the three orbitals in question for CPTMM are: LUMO (a_2), HOMO (b_1), SHOMO (a_2), assuming a planar C_{2v} structure. As a consequence of the similar energies of the HOMO and SHOMO, CPTMM is expected to have low-lying $^3A_1$, $^1A_1$, $^3B_2$, and $^1B_2$ states.

The origin of the nearly degenerate a_2 SHOMO and b_2 HOMO in the Hückel model for CPTMM is readily apparent from consideration of the cyclopentadienyl plus allyl fragment model. The ground state of the allyl radical has a $1b_1^2 1a_2$ configuration, and cyclopentadienyl radical has two low-lying states, with $1b_1^2 2b_1^2 1a_2$ and $1b_1^2 1a_2^2 2b_1$ configurations. The degenerate $1a_2$ and $2b_1$ orbitals of the cyclopentadienyl fragment correlate with the $1a_2$ and $3b_1$ orbitals of CPTMM. Although the latter pair of orbitals are not degenerate, they lie close in energy providing all C–C bond lengths are assumed equal (as is done implicitly in the Hückel model).

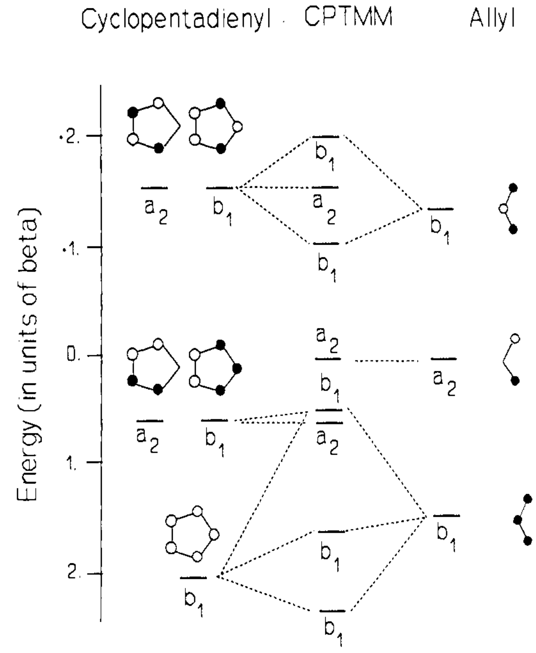


Figure 1. Correlation diagram showing the derivation of the π orbitals of CPTMM from the π orbitals of cyclopentadienyl and allyl radicals. Hückel orbital energies are employed.

The B_2 states of CPTMM, due to the $1b_1^2 1a_2^2 2b_1$ occupancy of the cyclopentadienyl fragment, should distort so as to stabilize the $1a_2$ MO and to destabilize the $3b_1$ MO (of CPTMM). Based on the MO's depicted in Figure 1, this should involve a shortening of the C_1–C_2 and C_3–C_4 bonds and a lengthening of the C_2–C_3 bond in the cyclopentadienyl fragment. Conversely, the A_1 states, due to the $1b_1^2 2b_1^2 1a_2$ occupancy of the cyclopentadienyl fragment,

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[1] An alternative name for this compound is 2-(1′-cyclopentadienyl)allyl.

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