

propane due to the similar ring strain of both molecules.

### Conclusions

The  $C_4H_9^+$  potential energy surface has been investigated thoroughly at correlated levels of ab initio molecular orbital theory. A  $C_s$  symmetric structure **1** of the *tert*-butyl cation represents the global minimum on the  $C_4H_9^+$  PES with a  $C_{3h}$  isomer being very close in energy. Both species benefit from C-H hyperconjugative stabilization, as shown by the elongation of the C-H bonds aligned parallel to the formally vacant 2p orbital on the central carbon and the decrease of the corresponding (HCC) angles. The 2-butyl cation, the second stable  $C_4H_9^+$  species, is 13.4 kcal/mol less stable than the *tert*-butyl cation. 2-Butyl cation favors a symmetrically H-bridged  $C_2$  structure, a protonated *trans*-2-butene **5**. A methyl bridged isomer of the 2-butyl cation **4**, which profits from C-C hyperconjugative stabilization, is only marginally higher in energy. Agreement between  $^{13}C$  chemical shifts computed with the IGLO method for the *tert*-butyl and 2-butyl cation with the experimental data confirm this assignment. Several other stationary points have been located on the  $C_4H_9^+$  surface, but only two additional minima could be found: one, **14**, corresponds to an edge protonated cyclobutane, 35.9 kcal/mol above the *tert*-butyl cation, the other, **10**, is a corner protonated methylcyclopropane, 22.0 kcal/mol above the *tert*-butyl cation. All other stationary points located, such as the isobutyl cation **12** and the 1-butyl cation **13**, are saddle points. Proton and carbon scrambling in the 2-butyl cation occurs either through an edge protonated cyclopropane with an activation barrier of 8.5 kcal/mol (exptl:  $7.5 \pm 0.1$  kcal/mol) or via a corner protonated cyclopropane with a calculated activation barrier of

8.9 kcal/mol. Rearrangement from 2-butyl to the more stable *tert*-butyl cation has a theoretically predicted activation energy of 19.6 kcal/mol, also in good agreement with the experimental estimate of ca. 18 kcal/mol.

The computed relative stabilities of the various  $C_4H_9^+$  species and the predicted proton affinities of *trans*-2-butene and isobutene are in good agreement with the experimentally known data. Considerable deviations are found only for protonated cyclobutane **14**. It seems likely that the experimental determination underestimated the stability of this cation by about 20 kcal/mol.

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**Supplementary Material Available:** A complete list of the computed harmonic frequencies (scaled by 0.93<sup>42</sup>) and IR intensities of the four minimum ion structures (4 pages). Ordering information is given on any current masthead page.

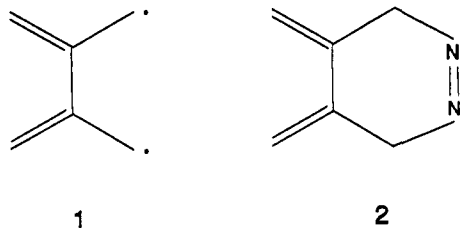
## Theoretical Study of the Low-Lying Triplet and Singlet States of Tetramethyleneethane: Prediction of a Triplet below Singlet State at the Triplet Equilibrium Geometry

P. Nachtigall and K. D. Jordan\*

Contribution from the Department of Chemistry and Materials Research Center, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. Received July 13, 1992

**Abstract:** CI calculations are used to characterize the twisting potentials of the lowest singlet and triplet states of tetramethyleneethane. It is found that the triplet state, at its optimized geometry, lies 1.0–1.5 kcal/mol below the singlet state.

The two frontier orbitals of tetramethyleneethane (TME) (**1**) are close in energy, and, as a result, TME has low-lying singlet (S) and triplet (T) states.<sup>1</sup> The photochemical decomposition of the azo precursor (**2**) in low-temperature matrices gives rise to an EPR spectrum which has been attributed to the triplet state of TME.<sup>2</sup> The Curie-Weiss plot indicates that either the triplet state is the ground state or lies only slightly ( $\leq 0.1$  kcal/mol) above



the singlet state. On the other hand, the theoretical calculations carried out to date have predicted that TME has a singlet ground state, lying about 1.4 kcal/mol below the triplet state.<sup>3,4</sup>

A common feature of the previous theoretical studies of TME is that electron correlation effects involving excitations external to the valence space were excluded. In the present study it is shown that the inclusion of such correlation effects stabilizes the T state relative to the S state and that at the minimum in its twisting potential (for rotation of one allyl fragment relative to the other) the T state lies energetically below the S state.

In order to obtain estimates of the dependence of the energies of the S and T states on the dihedral angle,  $\alpha$ , between the two allyl fragments (described below) were carried out for the planar ( $D_{2h}$ ,  $\alpha = 0^\circ$ ), perpendicular ( $D_{2d}$ ,  $\alpha = 90^\circ$ ), and  $D_2$  ( $\alpha = 59^\circ$ ) structures. In each case, geometrical parameters obtained from MCSCF(6,6)/3-21G<sup>5</sup> optimizations of the singlet

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

(3) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* 1987, 109, 930.

(4) Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* 1992, 114, 4743.

(5) The MCSCF(6,6) procedure allows for all arrangements of the six  $\pi$  electrons in the space of the six  $\pi$  and  $\pi^*$  orbitals.

Table I. S/T Gaps (kcal/mol) for TME<sup>a</sup>

basis set	method	structure		
		$D_{2d}$	$D_2$	$D_{2h}$
DZ	MCSCF	1.70	1.37	3.83
	CI	1.53	0.30	1.96
	CI + DV2	0.81	-0.14	2.22
DZP	MCSCF	1.91	1.37	3.89
	CI	1.75	0.22	1.81
	CI + DV2	0.82	-0.50	1.57
TZ2P	MCSCF	2.01	1.38	3.95
	CI	1.94	-0.12	1.91
	CI + DV2	0.96	-0.50	1.56

<sup>a</sup> A positive energy for the S/T gap means that the S state lies below the T state.

state were used. (The minimum in the MCSCF(6,6)/3-21G triplet potential occurs at  $\alpha = 59^\circ$ .)

The CI calculations<sup>6</sup> employed a single reference configuration for the T state and two reference configurations<sup>7</sup> for the S state and included all symmetry-allowed single and double excitations from the reference configurations, with the restriction that excitations were excluded from the six "C(1s)" MOs. The CI calculations were performed with double- $\zeta$  (DZ), double- $\zeta$ -plus polarization (DZP), and triple- $\zeta$ -plus double polarization (TZ2P) basis sets.<sup>8</sup> The hydrogen atoms are described using a DZ basis set.<sup>9</sup> For each basis set used, MCSCF(6,6) calculations were carried out on the S and T states in order to determine the orbitals for the CI calculations.

The S-T gaps obtained at various levels of theory are summarized in Table I. The results obtained for the  $\alpha = 59^\circ$   $D_2$  structure are considered first. Consistent with the findings of prior studies,<sup>4</sup> the S-T gap calculated by means of the MCSCF(6,6) procedure is relatively insensitive to the basis set, with the S lying about 1.4 kcal/mol below the T for each of the basis sets employed. The CI calculations place the S and T states much closer in energy, with the S state lying below the T state by about 0.3 and 0.2 kcal/mol with the DZ and DZP basis sets, respectively, and the T state lying below the S by about 0.1 kcal/mol with the TZ2P basis set. Upon inclusion of the DV2 size-consistency correction,<sup>10</sup> the T state is found to lie below the S state by 0.14, 0.50, and 0.50 kcal/mol with DZ, DZP, and TZ2P basis sets, respectively.

CI calculations were also carried out for both the S and T states at  $\alpha = 49.5^\circ$ ,<sup>11</sup> the value of  $\alpha$  at which the triplet potential has its minimum at a MP2/TZ2P<sup>12</sup> level of theory. Spline fits of the CI + DV2/TZ2P energies at  $\alpha = 0, 49.5, 59$ , and  $90^\circ$  were used to generate the twisting potentials shown in Figure 1. The minimum in the T potential falls energetically within 0.1 kcal/mol

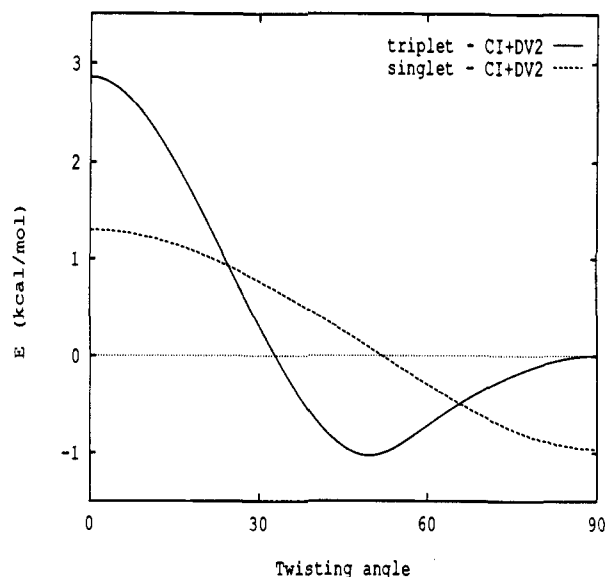


Figure 1. Potential energy (in kcal/mol) of the lowest singlet and triplet states of TME as a function of the dihedral angle between the two allyl groups.

of that in the S potential, which occurs at  $\alpha = 90^\circ$ . More importantly, at the minimum in the CI + DV2 triplet potential (near  $\alpha = 50^\circ$ ), the T state lies about 1.0 kcal/mol below the S state. The use of the geometry of the T state rather than that of the S state in carrying out the CI + DV2/TZ2P calculations leads to an additional 0.5 kcal/mol stabilization of the T state.

Although, the prediction of the relative stability of states lying within 2 kcal/mol of one another is a difficult proposition, the present calculations provide strong evidence that the minimum energy structure for the lowest triplet state of TME lies energetically about 1.0–1.5 kcal/mol below the lowest singlet state at the geometry of the triplet.

The barrier for rotation about the central C-C bond in the triplet state is predicted to be about  $400\text{ cm}^{-1}$  at the CI + DV2/TZ2P level of theory. MP2/DZP calculations give a value  $89\text{ cm}^{-1}$  for the frequency of the twisting mode (in the harmonic approximation), which places the zero-point level near  $45\text{ cm}^{-1}$ . We conclude, therefore, that at the temperature (10 K) at which Dowd and co-workers obtained their EPR spectra,<sup>2</sup> the majority of the TME molecules should be vibrationally unexcited.

Although the results of the present calculations are consistent with the detection via EPR spectroscopy of the triplet state of TME,<sup>2</sup> there remains the puzzle that the EPR measurements give a zero value of the  $\epsilon$  parameter, which would seem to imply a  $D_{2d}$  structure, while the calculations give a  $D_2$  structure for the triplet state. Theory and experiment could be reconciled if tunneling between the minima in the triplet potential were rapid on the EPR time scale. Calculations using the Numerov-Cooley method<sup>13</sup> give a splitting energy of only  $10^{-10}\text{ cm}^{-1}$  between the two lowest vibrational levels of the one-dimensional double minimum twisting potential. This splitting is far too small for significant tunneling on the EPR time scale. However, these calculations neglected any possible role of mixing between the singlet and triplet states. Conceivably such mixing could facilitate tunneling between the triplet minima.

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(6) The MCSCF and CI calculations were performed with the COLUMBUS suite of programs, described in the following reference. Shepard, R.; Shavitt, I.; Pitzer, R. M.; Comeau, D. C.; Pepper, M.; Lischka, H.; Szalay, P. G.; Ahlrichs, R.; Brown, F. B.; Zhao, J. G. *Int. J. Quantum Chem. Symp.* **1988**, *22*, 149.

(7) The two frontier orbitals of TME are nearly degenerate, and as a result the zeroth-order wave function for the singlet state requires two configurations.

(8) The carbon basis sets are from Dunning, T. H., Jr. *J. Chem. Phys.* **1969**, *90*, 1007. The DZ basis set used is derived from the DZP basis set by removing the d function. The hydrogen basis set is from Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(9) Exploratory calculations showed that the S-T splitting is relatively unaffected by inclusion of p polarization functions on the hydrogen atoms.

(10) The DV2 approximation of the COLUMBUS programs is a modification of the procedure described in Davidson, E. R.; Silver, D. W. *Chem. Phys. Lett.* **1978**, *52*, 403.

(11) The MCSCF and CI calculations on TME at  $\alpha = 49.5^\circ$  were carried out using the geometrical parameters optimized for the  $\alpha = 59^\circ$  structure. A justification of this approximation is provided by the fact that for the T state, the frequency of the twisting mode determined analytically in the MP2 approximation (using the MP2 optimized geometry) is close to that obtained numerically from the CI potential.

(12) The MP2 calculations were performed using the Gaussian 90 program: Gaussian 90; Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1990.

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