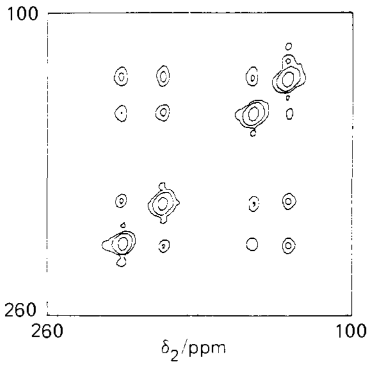

Figure 2. Two-dimensional magnetization transfer ^{15}N CPMAS spectrum (contour plot) of TTAA-$^{15}N_4$ at 300 K with a mixing time of 800 ms. The spectra were obtained at 9.12 MHz by using a Bruker CXP 100 NMR spectrometer. There were 64 by 256 points in the original data, 32 scans per spectrum: 10-ms cross-polarization time, 3-μs ^{1}H-$\pi/2$ pulses, 2.7-s repetition time; reference, external $^{15}NH_4NO_3$.

$- \delta_n$ between the ^{15}N lines m and n, where mn = ab, dc, is given by[6,7]

$$\delta_{mn}/\Delta_{mn} = (1 - K_{mn})/(1 + K_{mn}) \qquad (1)$$

where $K_{mn} = p_n/p_m$. K_{mn} is the equilibrium constant for tautomerism in the ^{15}N pair mn and Δ_{mn} is the intrinsic chemical shift difference. As shown in Figure 1, δ_{dc} decreases more rapidly with increasing temperature than δ_{ab}. Thus, there are two inequivalent proton transfer systems ab and dc present in solid TTAA, with unequal equilibrium constants $K_{ab} < K_{dc} < 1$.[11] Therefore, since $K_{ab} \neq K_{dc}$, the proton motion in system ab cannot take place in concert with the proton motion in system dc.

A central question is whether each TTAA molecule contains both proton transfer systems ab and dc or whether there are two types of molecules in different but equally populated crystallographic sites containing either ab or dc atom pairs. This question was answered by 1D and 2D ^{15}N exchange spectroscopy[12] of solid solutions of TTAA-$^{15}N_4$ in TTAA-$^{14}N_4$. As shown in Figure 2, the 2D spectra contain cross peaks among all four lines, a–d, due to magnetization transfer during the mixing period. These spectra, as well as the magnetization transfer rates obtained by corresponding 1D experiments, did not depend on the TTAA-$^{15}N_4$ mole fraction, which was varied between 0.1 and 1. However, ^{1}H decoupling during the mixing time resulted in a suppression of magnetization transfer, proof that this effect arises from spin diffusion and not from chemical exchange. Since spin diffusion[13] between nuclei decreases with the third power of the internuclear distance, our observation that the spin diffusion rates are independent of TTAA-$^{15}N_4$ mole fraction confirms that the observed spin diffusion is an intramolecular process.

Thus, the observation of four ^{15}N resonances combined with the proof that all four lines come from atoms within the same molecule shows that there is only one type of nonsymmetric molecule in solid TTAA, in agreement with the crystal structure.[5] Consequently, each TTAA molecule contains both proton transfer systems ab and dc and must therefore be able to exist in four tautomeric states, **1**–**4**, which interconvert by single proton transfers as shown in Scheme I. It may be that the "diagonal" processes **1** $\rightleftarrows$ **3** and **2** $\rightleftarrows$ **4** involving concerted two-proton transfer occur as a side reaction. Furthermore, our results show that the rhombic distortion lifts the degeneracy between **2** and **4**, as well as between **1** and **3**.

It is tempting to correlate the nonconcerted proton motion with noncoplanarity[5] of the H-chelate units sterically induced by the methyl groups. This effect could lead to a reduced repulsion of the inner protons of TTAA states **2** and **4** and to reduced electronic interaction of the two H-chelate units. The latter effect is supported by the electronic spectra: the lowest energy transition in the spectrum of the methyl-free compound appears at 452 nm[14] while that of TTAA is at 342 nm.[8]

We have shown here that the protons in the solid malonaldehyde derivative TTAA move rapidly in asymmetric double-minimum potentials between four different tautomeric states which interconvert by single proton transfers according to Scheme I. Further experiments are under way to examine the effect of the removal of the methyl groups on the tautomerism.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, the Stiftung Volkswagenwerk, Hannover, and the Fonds der Chemische Industrie, Frankfurt, for financial support.

---

[11] We calculate the enthalpy differences $\Delta H_{ab} = 1.01 \pm 0.04$ kcal/mol and $\Delta H_{dc} = 1.09 \pm 0.04$ kcal/mol and the entropy differences $\Delta S_{ab} = 0.6 \pm 0.1$ cal K^{-1} mol^{-1} and $\Delta S_{dc} = 1.1 \pm 0.1$ cal K^{-1} mol^{-1}. The K_{mn} can be expressed in terms of equilibrium constants for the tautomers: $K_{ab} = K_{12}(1 + K_{23})/(1 + K_{14})$ and $K_{dc} = K_{14}(1 + K_{43})/(1 + K_{12})$. $K_{ij} = x_j/x_i$ where x_i is the molefraction of the ith tautomer. We have arbitrarily assigned the lowest energy to tautomer **1**.

[12] Jeener, J.; Meier, B. H.; Buchmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546. Szeverenyi, N. M.; Sullivan, M. J.; Maciel, G. E. *J. Magn. Reson.* **1982**, *47*, 462. Szeverenyi, N. M.; Bax, A.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 2579.

[13] Suter, D.; Ernst, R. R. *Phys. Rev. B* **1982**, *25*, 6038. Caravati, P.; Deli, J. A.; Bodenhausen, G.; Ernst, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 5506.

[14] Hiller, H.; Dimroth, P.; Pfitzer, H. *Justus Liebigs Ann. Chem.* **1968**, *717*, 137.

Ab Initio Calculations Predict a Singlet Ground State for Tetramethyleneethane

Ping Du and Weston Thatcher Borden*

Department of Chemistry, University of Washington
Seattle, Washington 98195

Received August 18, 1986

Tetramethyleneethane (TME) is the simplest non-Kekulé hydrocarbon whose nonbonding molecular orbitals (NBMOs) can be localized to different regions of space.[1] The localizability of the NBMOs of TME leads to the prediction of a singlet ground state for the planar diradical.[2-4]

In 1970, Dowd reported the first preparation of TME and the observation of a triplet EPR signal for this diradical.[5] Roth and co-workers have also detected a triplet EPR signal[6a] from a TME derivative,[6] but the Curie law studies necessary to establish whether the triplet was the ground state were not reported. Very recently, Dowd and co-workers measured the temperature dependence of the EPR signal intensity for the parent TME, and from the linearity of a Curie–Weiss plot, they concluded that TME has a triplet ground state.[7]

Dowd's finding does not necessarily conflict with the theoretical prediction of a singlet ground state for the *planar* diradical.[3,4] In fact, the results of the ab initio calculations reported here show, in agreement with previous computational studies,[8,9] that both the

---

[1] The simplest conjugated hydrocarbon whose NBMOs have this property is cyclobutadiene,[2] which is an antiaromatic annulene.

[2] Review: Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 1–72.

[3] Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

[4] See also: (a) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297. (b) Dohnert, D.; Koutecy, J. *J. Am. Chem. Soc.* **1980**, *102*, 1789. (c) Klein, D. J.; Nelin, C. J.; Alexander, S.; Matsen, F. A. *J. Chem. Phys.* **1982**, *77*, 3101. (d) Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273. (e) Karafiloglou, P. *J. Chem. Phys.* **1985**, *82*, 3728.

[5] Dowd, P. *J. Am. Chem. Soc.* **1970**, *92*, 1066.

[6] (a) Roth, W. R.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 503. (b) Roth, W. R.; Biermann, M.; Erker, G.; Jelich, K.; Gerhartz, W.; Gorner, H. *Chem. Ber.* **1980**, *113*, 586. (c) Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1982**, *115*, 1197.

[7] Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416. We are indebted to Professor Dowd for sending us a preprint of his manuscript.

[8] (a) Odell, B. G.; Hoffmann, R.; Imamura, A. *J. Chem. Soc. B* **1970**, 1675. (b) Schoeller, W. W. *Tetrahedron Lett.* **1973**, *23*, 2043. (c) Dixon, D. A.; Foster, R.; Halgren, T. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 1359.

0002-7863/87/1509-0930$01.50/0

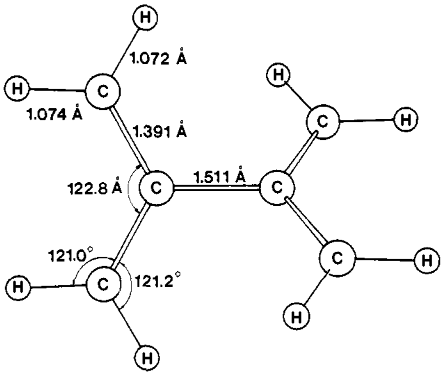

Figure 1. Triplet UHF optimized geometry for TME. The dihedral angle between the planes of the allyl groups is 44.9°.

Table I. Calculated Singlet and Triplet Energies for TME

geometry	calcn	$E(^1A_1)^a$	$E(^3B_3)^a$	ΔE^b
planar (D_{2h})	TCSCF/RHF	-231.7575	-231.7546	1.8
planar (D_{2h})	SD-CI	-232.0447	-232.0403	2.8
triplet minimum (D_2)	TCSCF/RHF	-231.7599	-231.7600	-0.1
triplet minimum (D_2)	SD-CI	-232.0443	-232.0437	0.4
perpendicular (D_{2d})	TCSCF/RHF	-231.7634	-231.7594	2.5
perpendicular (D_{2d})	SD-CI	-232.0464	-231.0428	2.2

[a] Energies in hartrees. [b] $E(^3B_3) - E(^1A_1)$ in kcal/mol.

lowest singlet and triplet state of TME prefer nonplanar geometries. However, our calculations find the singlet to lie below the triplet at all the geometries investigated. Thus, the computational results reported here stand in direct conflict with the experimental finding of a triplet ground state.[7]

The lowest triplet state of planar (D_{2h}) and perpendicular (D_{2d}) TME was optimized with UHF calculations. These calculations were performed with Gaussian 82,[10] with use of the 3-21G basis set.[11] However, the UHF triplet geometry of lowest energy, shown in Figure 1, was found to have only D_2 symmetry with a dihedral angle of 44.9° between the planes of the allyl groups. A vibrational analysis showed this geometry to be a true energy minimum.

CI calculations were performed at all three geometries, using the Dunning split-valence basis set, augmented by a set of polarization functions on carbon.[12] The calculations were carried out with MELD,[13] starting from an RHF wave function for the triplet and a two-configuration (TC) SCF wave function for the singlet. The CIs involved all single and double excitations within the conceptual minimal basis set of valence orbitals. In D_2 symmetry this generated 32 561 spin-adapted configurations for $^3B_3$ and 16 570 for $^1A_1$. In order to provide the maximum amount of electron correlation with the virtual orbitals used, the virtual space was transformed to K orbitals.[14]

The TCSCF/RHF and CI energies are given in Table I. The calculations at the TCSCF/RHF level do not include the effects of dynamic spin polarization,[2] since spin polarization requires intraallylic electron correlation. Dynamic spin polarization, which is included at the CI level, results in enhanced π bonding in the lowest singlet state between the central carbons of the allylic moieties[2,3] and, hence, is largest at planar geometries.

Despite this fact, the singlet is found to prefer the perpendicular to the planar geometry. However, this preference is reduced from 3.7 kcal/mol at the TCSCF level to 1.1 kcal/mol at the CI level of theory. Since the triplet also has a lower energy at the perpendicular than at the planar geometry, it is likely that in both states this energetic preference is due to the smaller interallylic, steric repulsion at the former geometry.

The UHF triplet minimum occurs near the geometry of minimum electronic interaction between the allyl NBMOs. At this geometry, the singlet and triplet are essentially degenerate in energy at the TCSCF/RHF level of theory. When CI is included, dynamic spin polarization causes the singlet to fall 0.4 kcal/mol below the triplet, since at this geometry there is still appreciable overlap between the π orbitals on the central carbons.

The CI energy of the singlet at its optimal geometry (D_{2d}) is 1.3 kcal/mol lower than that at the optimal UHF triplet geometry (D_2), so that the adiabatic singlet-triplet energy separation is computed to be 1.7 kcal/mol.[15] The calculated energy separation allows the possibility that a thermally populated triplet might be observable by EPR, but the singlet is unequivocally predicted to be the ground state.

It is, of course, conceivable that higher level calculations could reverse the energy ordering of these two states. However, there is a simple physical argument in favor of a singlet ground state. If TME is regarded as two allyl radicals, any long-range bonding between the allyl NBMOs will selectively stabilize the singlet. Moreover, even at geometries where there is no long-range bonding, dynamic spin polarization in the singlet will still stabilize it with respect to the triplet.[3]

Although there are several possible explanations for the apparent conflict between the theoretical prediction of a singlet ground state for TME and the experimental finding of a linear Curie-Weiss plot for this diradical, the correct resolution remains to be determined.

Acknowledgment. We thank the National Science Foundation for support of this research. Some of the calculations were performed on a Convex C-1 computer, whose purchase was made possible by Grant CHE-85501 from the National Science Foundation.

---

(9) For experimental studies of singlet TME, see: Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981; pp 138-149.

(10) Binkley, J.; Frisch, S.; Raghavachari, M.; Fluder, E.; Seeger, R.; Pople, J. A., Carnegie-Mellon University.

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

(12) Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schafer, H. F., III, Ed.; Plenum: New York, 1977; Vol. 2.

(13) Developed by E. R. Davidson and co-workers at the University of Washington.

(14) Feller, D.; Davidson, E. R. *J. Chem. Phys.* **1981**, *74*, 3977.

(15) With both the RHF and CI calculations, the triplet minimum, found by rigid rotation of the allyl groups in Figure 1, occurs at a dihedral angle of 53.2° between the planes of the allyl groups. At this geometry the $^3B_1$ CI energy of -232.0440 hartrees is 0.5 kcal/mol above that of $^1A_1$ and gives an adiabatic singlet-triplet splitting of 1.5 kcal/mol.

Nucleophilic Addition Reactions of Hindered Unsaturated Boranes. A New Synthesis of Organoboranes

Manning P. Cooke, Jr.,* and R. K. Widener

Department of Chemistry, Washington State University
Pullman, Washington 99164

Received August 8, 1986

Olefin activation to nucleophilic addition by virtue of the presence of polarizing substituents is of fundamental importance. Conspicuously absent are examples of such activation by boron-containing groups owing to their normally facile formation of ate complexes with nucleophiles.[1] We wish to report the first examples of boron-activated nucleophilic additions to olefins made possible by the steric suppression of ate complex formation.

It has been shown previously that ate complex formation can be sterically retarded in appropriately substituted arylboranes.[2]

---

(1) Pelter, A.; Smith, K. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon: New York, 1979; Vol. 3, Section 14.

(2) Brown, H. C.; Dodson, V. H. *J. Am. Chem. Soc.* **1957**, *79*, 2304. Blount, J. F.; Finocchiaro, P.; Gust, D.; Mislow, K. *Ibid.* **1973**, *95*, 7019. Glogwski, M. E.; Zumbulyadis, N.; Williams, J. L. R. *J. Organomet. Chem.* **1982**, *231*, 97.

0002-7863/87/1509-0931$01.50/0