State University. The high resolution mass spectrum was obtained on a Kratos MS 50 TC spectrometer purchased with grants from the National Institutes of Health Division of Research Resources (DRR-1S10RR01409) and from the Anheuser-Busch Company.

The 2,3-Dimethylenecyclohexa-1,3-diene Diradical Is a Ground-State Triplet

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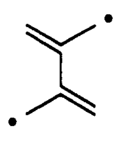
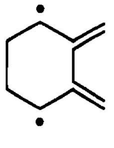
Received April 27, 1987

The properties of the tetramethyleneethane diradical (I) form the focal point of an intense conflict that has developed between theory and experiment.[1,2]



I



II

Since tetramethyleneethane (I) is a disjoint conjugated system, it has been suggested[3,4] on qualitative grounds that the singlet state is the preferred ground state. Disjoint conjugation has provided a basis for understanding the ground-state multiplicity of cyclobutadiene,[4] which adopts a ground singlet state. If the singlet ground state found for cyclobutadiene is due to a lifting of the orbital degeneracy by a rectangular distortion, there is a smaller probability that Hund's rule will be violated by non-Kekulê hydrocarbons, since by definition, such molecules lack one covalent bond and afford less opportunity for covalent bonding in the singlet state than is possible in a Kekulê molecule such as cyclobutadiene.

We recently established that the parent tetramethyleneethane (I) is a ground-state *triplet*, since it yields a linear Curie law plot.[1] Tetramethyleneethane (I) may be viewed in steric terms as a truncated biphenyl; it probably adopts a twisted conformation, and the two halves may even be canted perpendicular to one another (D_{2d}). It seemed probable that the disagreement between theory and experiment had arisen, because we had observed the perpendicular or twisted conformation of tetramethyleneethane (I), while the theoretical work was focused on the planar conformation. However, Du and Borden[2] have recently carried out further calculations and concluded that tetramethyleneethane (I) should be a *ground-state singlet at all conformations*—irrespective of the angle of twist about the central carbon–carbon bond.

In view of this challenge, it was important to examine other conformations, and the diradical II with tetramethyleneethane incorporated into a six-membered ring was available from the work of Roth.[5] With four sp^2-hybridized carbon atoms in a six-membered ring, II is very close to being a planar system. We estimate, using an MM2 procedure,[6] that diradical II deviates from planarity by less than 5°. Accordingly, II becomes an attractive subject for Curie law analysis.

Comparison of the spectrum of tetramethyleneethane (I) with its derivative II is revealing. The tetramethyleneethane (I) spectrum shows no splitting between the x and y lines, a result consistent with the twisted or D_{2d} symmetry. The spectrum of the diradical II differs significantly from that of I. With a D value of 0.024 cm^{-1}, the spectrum is in good agreement with that expected for a tetramethyleneethane (for I, D = 0.025 cm^{-1})[7]. However, the E value of II is 0.0037 cm^{-1}, as expected for a diradical with planar symmetry. The appearance of the latter (Figure 1) supports the idea that diradical I is not planar.

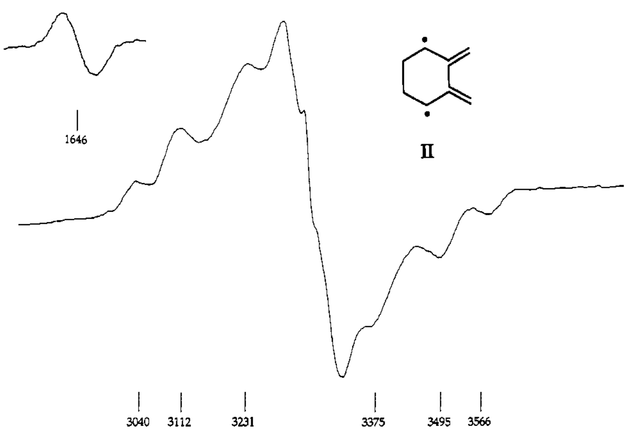


Figure 1. Electron spin resonance spectrum (Δm = 1 lines) of the 2,3-dimethylenecyclohexa-1,3-diene diradical (II). The Δm = 2 line is shown in the inset.

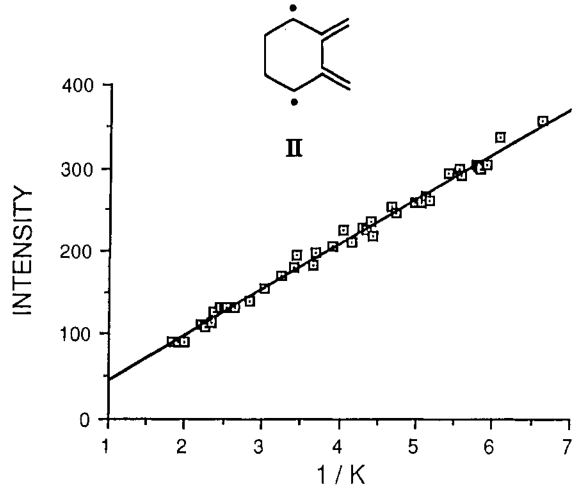


Figure 2. Curie–Weiss plot (least squares, r = 0.996) of the signal intensity of the Δm = 2 line of the 2,3-dimethylenecyclohexa-1,3-diene diradical (II). The temperature range was 15–53 K; the solvent was 2-methyltetrahydrofuran.

A Curie law plot of the intensity of the Δm = 2 line of II vs. temperature from 15–53 K (Figure 2) is linear with a correlation coefficient of 0.996. We conclude that *the planar tetramethyleneethane diradical II is a ground-state triplet.*[10]

It is widely appreciated[8,9] that if the singlet and triplet states are degenerate within 30–40 cal, then a linear Curie law plot will be observed. We estimate that if the singlet and triplet states differ

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

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

(3) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4487.

(4) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 1-72.

(5) Roth, W. R.; Bierman, M.; Erker, G.; Jelich, K.; Gerhartz, W.; Gorner, H. *Chem. Ber.* **1980**, *113*, 586. Roth, W. R.; Erker, G. *Angew Chem., Int. Ed. Engl.* **1973**, *12*, 503.

(6) Imam, M. R.; Allinger, N. L. *J. Mol. Struct.* **1985**, *126*, 345. Kurtz, H. A.; Lloyd, R. V.; Williams, R. V. *J. Org. Chem.* **1987**, *52*, 302.

(7) The reported D and E values of 0.0204 and 0.00159 are slightly different from those we have observed. We observe Δm = 1 lines at 3040, 3112, 3231, 3375, 3495, and 3566 with the Δm = 2 line at 1646 G (microwave frequency 9.256 GHz) following photolysis in a methyltetrahydrofuran matrix at 15 K. The center of the Δm = 1 spectrum is somewhat obscured by a large monoradical impurity.

(8) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 217.

(9) Breslow, R.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1964**, *86*, 5349. Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffman, J. M., Jr.; Perchonock, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. *J. Am. Chem. Soc.* **1973**, *95*, 3017. Breslow, R.; Chang, H. W.; Yager, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 2033. Breslow, R.; Chang, H. W.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112.

(10) Another example of a non-Kekulê molecule whose ground-state multiplicity is at odds with theoretical expectation is provided by the recent work of Roth, W. R.; Langer, R.; Bartmann, M.; Steverman, B.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Müller, W. *Angew Chem., Int. Ed. Engl.* **1987**, *26*, 256.

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in energy by more than 50 calories this can easily be detected by pronounced curvature in the Curie plot. While it is possible that one of the tetramethyleneethane diradicals, I or II, might be characterized by an exact degeneracy between the singlet and triplet states, it is clearly less likely that *both* I and II will exhibit this behavior.

Acknowledgment. This research was generously supported by the National Science Foundation. Acknowledgment is made to the donors of the Petroleum Research Fund, administrated by the American Chemical Society, for partial support of this research.

9-Phenyl-1(9)-homocubene, Probably the Most Twisted Olefin Yet Known, and the Carbene 1-Phenyl-9-homocubylidene, Its Rearrangement Product

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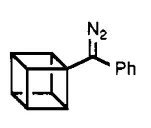
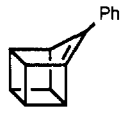
Received March 13, 1987

We have examined the thermal and photochemical decompositions of cubylphenyldiazomethane (**1**) and report here observations which make us believe these processes lead to 9-phenyl-1(9)-homocubene (**2**), the anti-Bredt rule olefin nonpareil.[1] By one phraseology,[2] the double bond in **2** would be called "trans in a five-membered ring". Previous to the present report, double bonds trans in six-membered rings were the limiting examples.[3] Although convenient, the descriptor "trans" is misleading. The relevant dihedral angle (2,1,9,8) in the σ frame of **2** is approximately 41°.[4] Were there no pyramidalization of C-9, the p-orbitals of the "double bond" would be orthogonal to one another.



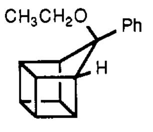
1



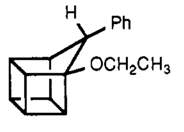
2

Cubylphenyldiazomethane was prepared by thermolysis of the sodium salt of the tosylhydrazone of cubyl phenyl ketone,[5] itself obtained by reaction of cubane carboxylic acid[6] with phenyllithium in ether. Its tosylhydrazone precipitated analytically pure on reaction of the ketone overnight at room temperature with excess tosylhydrazine in ethanol. When the tosylhydrazone was refluxed in ethanol with excess sodium ethoxide, it decomposed fairly rapidly. The solution turned red; aliquots showed the generation of a diazo compound (IR 2037 cm^{-1}), but it was not stable under these conditions and after 5 h was gone completely. Pyrolysis under vacuum (80–120 °C/0.005 Torr) of the dry sodium salt of the tosylhydrazone below a liquid N_2 cold finger gave 27–39% yield on the condensing surface of neat cubylphenyldiazomethane.[7] It is a red oil, labile at room temperature but stable for several days when stored at −20 °C in pentane.

Thermolysis of the tosylhydrazone in ethanolic sodium ethoxide and, separately, photolysis (Hg arc, Pyrex filter) of the diazo compound itself in ethanol gave good conversions to a 1.5:1 mixture of isomeric ethers of formula corresponding to addition of ethanol to cubylphenylcarbene. However, it was completely clear from their NMR spectra that the symmetry of the cubyl skeleton had been lost and that rearrangement into the homocubane system had occurred.[7] Whether (for the major product) this rearrangement occurred concommitantly with the loss of nitrogen or happened after cubylphenylcarbene was generated is yet a moot point.[8] The major isomer was assigned structure **3**, it being apparent from its proton and carbon NMR spectra that a single plane of symmetry bisects the molecule. This is the compound expected from addition of ethanol in the Markovnikov sense to 9-phenyl-1(9)-homocubene (**2**). The minor ether was first thought to be **4**, formed perhaps by ethanolysis with rearrangement[8] of the diazo compound or, instead, by addition of ethanol in the anti-Markovnikov sense to **2**. Although this assignment was reasonably consistent with the elementary NMR data,[7] it is in fact wrong; the true structure is **5**. The distinction between **4** and **5** was made unambiguously by using homonuclear coupled ^{13}C NMR methodology by which it was demonstrated that the quaternary carbon of the phenyl group is *not* attached to an adjacent aliphatic carbon which bears hydrogen. The origin of **5** is addressed later in this paper.



3



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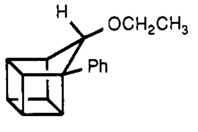

5

Following first the traditional approach, we attempted to trap the highly strained olefin **2** as a Diels–Alder adduct. Thermolysis of its precursor tosylhydrazone salt in monoglyme containing 9,10-diphenylisobenzofuran did indeed give an adduct of the expected formula, but it was obvious from its NMR spectra that it had not been formed by a 4 + 2 cycloaddition. The cyclohexadiene component of the isobenzofuran had not been aromatized; addition had occurred instead to one of the double bonds of this ring. This led us to use simple monoolefins as trapping agents.

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[1] For an excellent review of anti-Bredt olefins and previous references, See that of Szeimies, G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; pp 329–359.

[2] Wiseman, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 5966.

[3] Examples: 1-norbornene (Keese, R.; Krebs, E. P. *Angew. Chem.* **1971**, *83*, 254.); adamantene (Conlin, R. T.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 7637. Martella, D. J.; Jones, M., Jr.; Schleyer, P. v. R.; Maier, W. F. *J. Am. Chem. Soc.* **1979**, *101*, 7634); see ref 1 for others.

[4] Allinger, N. L. *Quantum Chemistry Program Exchange*, program MMP2(85).

[5] For a detailed review of the Bamford–Stevens reaction for the synthesis of diazo compounds, see: Maas, G.; Regitz, M. *Diazo Compounds*; Academic: New York, 1986; pp 257–272.

[6] Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 962, 3157.

[7] The analytical and spectra data are in accord with expectation. Only the critical NMR data are given here (PMR at 500 MHz; CMR at 100 MHz; shifts in ppm from TMS; $CDCl_3$ solutions). Aromatic resonances are not included. **1**: PMR 4.10 (m); CMR 58.4 (s, br, weak), 51.7 (1 C, s), 49.9 (3 C, d, 155 Hz), 47.9 (1 C, d, 157.5 Hz), 45.0 (3 C, d, 157.5 Hz). **3**: PMR 3.65, 3.47, 3.26, 3.19 (2 H each, multiplets), 3.13 (2 H, q), 1.04 (3 H, t); CMR 102.0 (1 C, s), 61.1 (1 C, t, 140 Hz), 50.5 (2 C, d, 148 Hz), 44.4 (2 C, d, 151 Hz), 43.0 (2 C, d, 153 Hz), 41.1 (2 C, d, 156 Hz), 16.2 (1 C, q, 126.5). **5**: PMR 4.11 (1 H, d, 2), 3.91 (1 H, m), 3.81 (1 H, m), 3.56 (1 H, m), 3.46 (2 H, m), 3.38 (2 H, m), 3.35 and 3.47 (2 H, AB of ABX_3; J_{AB} 9.6, $J_{AX} = J_{BX} = 7$), 1.13 (3 H, t, 7); CMR 96.5 (1 C, d, 140), 65.5 (1 C, t, 143), 61.3 (1 C, s), 48.6 (1 C, d, 156), 48.3 (1 C, d, 157.5), 47.2 (1 C, d, 146.5), 44.85 (1 C, d, 156), 41.9 (1 C, d, 156), 41.8 (1 C, d, 156), 40.1 (1 C, d, 155), 15.7 (1 C, q, 126). **6**: PMR 3.68 (2 H, m), 3.45 (3 H, m), 3.18 (1 H, m), 3.10 (1 H, m), 0.92 (6 H, m), 0.28 (2 H, m); CMR 61.8 (1 C, s), 51.6, (1 C, s), 50.2 (2 C, d, 150), 45.7 (1 C, d, 145), 43.7 (2 C, d, 150), 42.5 (1 C, d, 154), 40.2 (1 C, d, 150), 12.2 (2 C, d, 154 to H at ∂ 0.28), 9.41 (2 C, q, 127). **7**: 3.80 (2 H, m), 3.23 (2 H, m), 3.17 (1 H, m), 3.10 (1 H, m), 2.47 (1 H, m), 0.98 (2 H, m), 0.72 (6 H, m); CMR 59.6 (1 C, s), 58.8 (1 C, d, 144), 52.3 (2 C, d, 145), 48.2 (1 C, s), 41.7 (2 C, d, 153), 40.6 (1 C, d, 157.5), 40.4 (1 C, d, 155), 16.7 (2 C, d, 153 to H at ∂ 0.98), 9.35 (2 C, q, 127). **8**: PMR 4.01 (1 H, m), 3.62 (1 H, m), 3.52 (1 H, m), 3.44 (1 H, m), 3.27 (1 H, m), 3.20 (1 H, m), 2.99 (1 H, m), 1.14 (3 H, d, 6.3), 0.63 (2 H, m), 0.48 (3 H, d, 6.3); CMR 60.3 (1 C, s), 55.0 (1 C, d, 153), 51.9 (1 C, s), 51.4 (1 C, d, 145), 47.6 (1 C, d, 149), 43.4 (2 C, d, 159), 41.1 (1 C, d, 156), 40.5 (1 C, d, 155), 21.8 (1 C, d, 154 to H at ∂ 0.63), 18.9 (1 C, d, 154 to H at ∂ 0.63), 15.6 (1 C, q, 127), 14.2 (1 C, q, 127).

[8] Solvolyses of cubylcarbinylbenzoates and the like are assisted anchimerically and occur with ring expansion (Cole, T. W., Jr. Ph.D. Thesis, The University of Chicago, 1964.). There is no evidence for solvolysis without expansion even for diphenylcubylcarbinyl derivatives (Stock, L.; Cole, T. W., Jr.; Luh, T. Y., unpublished results.).