Table I. Predicted Singlet–Triplet Separations for Trimethylenemethane

level of theory	$E(^3A_2')$, hartrees	$\Delta E(^3A_2' - {}^1B_1)$, kcal/mol
DZ SCF	−154.8295	15.1
DZ + central d SCF	−154.8482	14.9
DZ + d SCF	−154.8844	14.9
DZ 4e⁻ CI[a]	−154.8787	17.6
DZ 8e⁻ CI[a]	−154.9167	17.3
DZ 10e⁻ CI[a]	−154.9396	14.6
DZ 14e⁻ CI[b]	−154.9871	14.3
DZ 14e⁻ CI[a]	−155.0063	

[a] Four highest virtual orbitals excluded from CI. [b] Eight highest virtual orbitals excluded from CI.

slightly, to 14.9 kcal.

The effects of electron correlation frequently change predicted electronic excitation energies by 10 kcal/mol or more.[25] In the present research, the configuration interaction (CI) method was used to describe correlation effects, and the DZ basis set was adopted since d functions had little effect on ΔE at the SCF level of theory. All Hartree–Fock interacting[26] single and double excitations were included in the CI, and a series of ΔE values was predicted by respectively correlating the 4, 8, 10, and 14 outermost valence electrons. The largest calculation included 8723 triplet configurations, spatially adapted for the C_{2v} subgroup. The predicted singlet–triplet separation of 14.3 kcal suggests that electron correlation lowers $\Delta E(^3A_2' - {}^1B_1)$ by only 0.8 kcal. Combining this with our DZ + d SCF result of 14.9 kcal suggests a "final" prediction of 14.1 kcal for the singlet–triplet separation.

One should be cautious about concluding that the theoretical prediction of $\Delta E(^3A_2' - {}^1B_1) = 14$ kcal is in conflict with the 7.3-kcal experimental activation energy[9] for TMM ring closure. Davidson and Borden have pointed out[27] that the 7-kcal experimental energy may not refer to the orthogonal singlet equilibrium geometry at all. They suggested that the 7 kcal might be the height (above the lowest vibrational state for the triplet surface) at which the triplet is crossed by one of the two singlet surfaces arising from the planar $^1E'$ state. However, preliminary calculations[28] have not yet provided substantive support for this possibility.

References and Notes

(1) For an interesting discussion of Moffitt and Coulson's 1948 theoretical research on trimethylenemethane, see C. A. Coulon, "Wave Mechanics: The First Fifty Years", W. C. Price, S. S. Chissick, and T. Ravendsdale, Ed., Wiley, New York, 1973, p 268.
(2) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966).
(3) P. Dowd, *Acc. Chem. Res.*, **5**, 242 (1972).
(4) W. R. Roth and G. Wegener, *Angew. Chem., Int. Ed. Engl.*, **14**, 758 (1975).
(5) M. S. Platz, J. M. McBride, R. D. Little, A. Shaw, J. J. Harrison, S. E. Potter, and J. A. Berson, *J. Am. Chem. Soc.*, **98**, 5725 (1976).
(6) M. S. Platz, D. R. Kelsey, J. A. Berson, N. J. Turro, and M. Mirbach, *J. Am. Chem. Soc.*, **99**, 2010 (1977).
(7) P. Dowd and M. Chow, *J. Am. Chem. Soc.*, **99**, 2825 (1977).
(8) M. S. Platz and J. A. Berson, *J. Am. Chem. Soc.*, **99**, 5178 (1977).
(9) P. Dowd and M. Chow, *J. Am. Chem. Soc.*, **99**, 6438 (1977).
(10) D. Cichra, M. S. Platz, and J. A. Berson, *J. Am. Chem. Soc.*, **99**, 8507 (1977).
(11) M. J. S. Dewar and J. W. Wasson, *J. Am. Chem. Soc.*, **93**, 3081 (1971).
(12) The first ab initio study of TMM was that of D. R. Yarkony and H. F. Schaefer, *J. Am. Chem. Soc.*, **96**, 3754 (1974).
(13) W. J. Hehre, L. Salem, and M. R. Willcott, *J. Am. Chem. Soc.*, **96**, 4328 (1974).
(14) D. R. Yarkony and H. F. Schaefer, *Chem. Phys. Lett.*, **35**, 291 (1975).
(15) E. R. Davidson and W. T. Borden, *J. Chem. Phys.*, **64**, 663 (1976).
(16) J. H. Davis and W. A. Goddard, *J. Am. Chem. Soc.*, **98**, 303 (1976).
(17) E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, **99**, 2053 (1977).
(18) J. H. Davis and W. A. Goddard, *J. Am. Chem. Soc.*, **99**, 4242 (1977).
(19) D. A. Dixon, R. Foster, T. A. Halgren, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **100**, 1359 (1978).
(20) D. M. Hood, R. M. Pitzer, and H. F. Schaefer, *J. Am. Chem. Soc.*, **100**, 2227 (1978).
(21) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 2906 (1975).
(22) E. R. Davidson, the 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug 28–Sept 2, 1977, plenary lecture, Symposium on the Reliability of Quantum Chemical Predictions.
(23) F. W. Bobrowicz and W. A. Goddard, "Modern Theoretical Chemistry", Vol. 3, H. F. Schaefer, Ed., Plenum Press, New York, 1977, pp 79–127.
(24) This basis set is conventionally labeled C(9s5p/4s2p), H(4s/2s): S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965); T. H. Dunning, *ibid.*, **53**, 2823 (1970).
(25) R. R. Lucchese and H. F. Schaefer, *J. Am. Chem. Soc.*, **99**, 6765 (1977); D. M. Hood and H. F. Schaefer, *J. Chem. Phys.*, **68**, 2985 (1978).
(26) R. R. Lucchese and H. F. Schaefer, *J. Chem. Phys.*, **68**, 769 (1978).
(27) E. R. Davidson and W. T. Borden, presented at the Conference on the Spin States of Organic Molecules, University of Colorado, Boulder, Colo., June 22–24, 1978.
(28) E. R. Davidson, K. Tanaka, and W. T. Borden, personal communication.

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**Optical Rotatory Dispersion Studies. 125.[1]
Independent Evidence for Preference of Axial
Deuterium vs. Axial Hydrogen through
Variable-Temperature Circular Dichroism Spectra of
(4S)-2,2-Dimethyl-4-deuteriocyclohexanone and
(3S)-3-Deuterio-4,4-dimethylcyclohexanone**

Sir:

In a recent communication[2] we reported on the temperature-dependent circular dichroism spectra of (3R)-2,2-dimethyl-3-deuteriocyclohexanone (1) and (5S)-2,2-dimethyl-5-deuteriocyclohexanone (11) and concluded that the observed intensity changes reflect a shift of the equilibrium toward that conformer in which the deuterium is in the axial orientation.
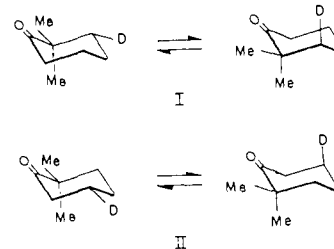
The enthalpy differences between both conformations were calculated to be −7.2 and −2.1 cal/mol, respectively,[3] and represent the first quantitative estimates for the slight preference of axial deuterium vs. axial hydrogen. We now present independent and additional evidence supporting our earlier conclusions[2] through the synthesis and variable-temperature CD measurements of (4S)-2,2-dimethyl-4-deuteriocyclohexanone (111)—a substance with axial or equatorial deuterium in a symmetry plane but possessing a *gem*-dimethyl "chiral probe"[2]—and (3S)-3-deuterio-4,4-dimethylcyclohexanone (1V)—a compound in which the *gem*-dimethyl group cannot act as a "chiral probe"[2] since it lies in a symmetry plane.

(4S)-2,2-Dimethyl-4-deuteriocyclohexanone (111) was synthesized by methylation (Ireland's method[4]) of (+)-(2R,4R)-2-methyl-4-isopropenylcyclohexanone[5] (optical purity >95%) to (4R)-2,2-dimethyl-4-isopropenylcyclohexanone, ethylene ketal formation and successive ozonolysis,
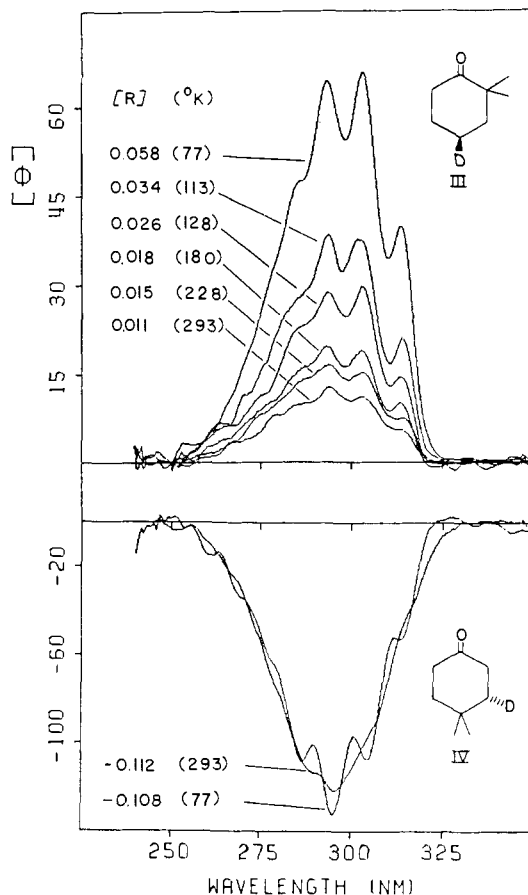
Figure 1. Circular dichroism spectra of (4S)-2,2-dimethyl-4-deuterio-cyclohexanone (III) (upper curves) and (3S)-3-deuterio-4,4-dimethyl-cyclohexanone (IV) (lower curves) at various temperatures in EPA ($c \sim$ 0.05 mol/L).

Figure 2. Configuration and their corresponding octant diagrams for (4S)-2,2-dimethyl-4-deuteriocyclohexanone (III) and (3S)-3-deuterio-4,4-dimethylcyclohexanone (IV) (methyl groups are indicated by ●).

Baeyer–Villiger oxidation (*m*-chloroperbenzoic acid), tosylate formation, LiAlD$_4$ reduction, and deketalization.[6] (3S)-3-Deuterio-4,4-dimethylcyclohexanone (IV) was obtained by L-Selectride reduction of (5R)-(+)-2,2-dimethyl-5-isopropenylcyclohexanone (optical purity >95%),[2] column chromatographic separation of both diastereoisomeric alcohols on silica gel, and conversion of the isopropenyl group of (+)-(1R,5R)-2,2-dimethyl-5-isopropenylcyclohexanol[7] to acetyl as in the above-outlined synthesis of III, followed by mesylation of the free hydroxyl group, LiAlD$_4$ reduction, and reoxidation.[6]

The CD spectra of III and IV at various temperatures are given in Figure 1. A significant increase is observed for III by lowering the temperature ($[R]^{293}_{obsd} = 0.011$; $[R]^{77}_{obsd} = 0.058$),[8] whereas the rotational strength for IV remains virtually unchanged over the same temperature range. The two chair conformations involved in the equilibrium and their octant diagrams together with the estimated $[R]_{ax}$ and $[R]_{eq}$ values[9] are given in Figure 2. In (4S)-2,2-dimethyl-4-deuteriocyclohexanone (III) both conformers have large and oppositely signed rotational strengths because of the α,α-dimethyl "chiral probe"[2] so that even a small shift in the equilibrium will result in a measurable change of $[R]^{T}_{obsd}$.

The increase of $[R]^{T}_{obsd}$ with lowering the temperature *leads to the unambiguous conclusion that the conformer with the deuterium in the axial position is energetically preferred;* $\Delta H°$ was calculated to be -3.3 cal/mol.[10] Comparing this value with those for I (-7.2 cal/mol) and II (-2.1 cal/mol), we note that $\Delta H°$ is dependent on the proximity of deuterium with respect to the *gem*-dimethyl group; i.e., it is largest when deuterium is in the 3 and smallest when in the 5 position.

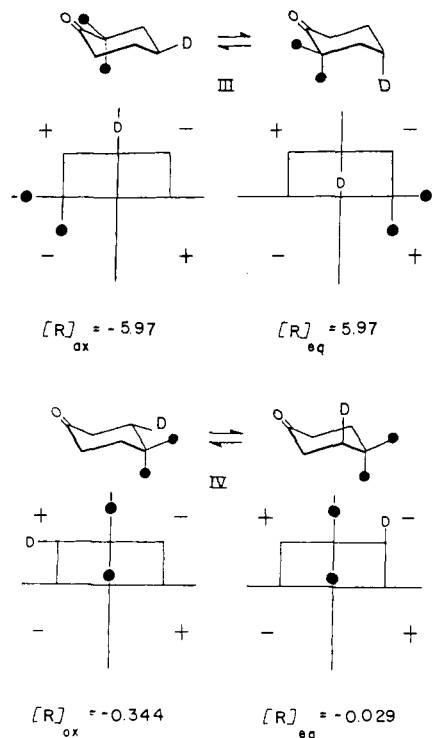Qualitatively these results are consistent and in agreement

with the general observation that deuterium is of "smaller size" than hydrogen[11] originating from the somewhat shorter bond length (~ 0.003 Å) and smaller vibrational amplitudes of the C–D bond.[12] Quantitatively, however, one would have expected the largest energy difference in favor of axial deuterium in the 4 position (III) and equal values for the 3 (I) and 5 (II) positions, since III contains, in addition to 1–3 diaxial deuterium–hydrogen interaction, one 1–3 diaxial deuterium–methyl interaction. Obviously additional factors play a role and we expect to cover this aspect in our detailed paper.

In contrast to III, the $[R]_{ax}$ and $[R]_{eq}$ values for IV are now very small numbers since the methyl groups lie in a symmetry plane in both conformations and do not contribute to the rotational strength. Even though a small equilibrium shift could be expected based on our previous results for I and II,[2] the associated changes of $[R]^{T}_{obsd}$ are well below the accuracy of measurement.[13] The temperature-independent CD of IV is of particular relevance since it *excludes the alternative possibility that the observed changes of the rotational strength in I, II, and III are associated with the presence of twist conformations.*[14]

References and Notes

(1) For part 124 see P. Sundararaman and C. Djerassi, *Tetrahedron Lett.*, 2457 (1978).
(2) S.-F. Lee, G. Barth, K. Kieslich, and C. Djerassi, *J. Amer. Chem. Soc.*, **100**, 3965 (1978).
(3) These values were calculated with the deuterium contributions obtained from ref 1 and differ slightly from those in ref 2.
(4) R. E. Ireland and J. A. Marshall, *J. Amer. Chem. Soc.*, **81**, 6336 (1959).
(5) Y. Takagi, Y. Nakahara, and M. Metsui, *Tetrahedron*, **34**, 517 (1978). We are indebted to Dr. Takagi for a generous gift of this starting material.
(6) All intermediates and final products were fully characterized including high resolution mass spectra.
(7) The configuration of the hydroxyl group in each diastereoisomer was assigned by NMR (D. H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry", McGraw-Hill, New York, 1973, p 104). (+)-(1S,5R)-2,2-Dimethyl-5-isopropenylcyclohexanol was subjected to the

same reaction sequence yielding (3R)-3-deuterio-4,4-dimethylcyclohex-anone whose CD spectrum was the mirror image of IV and showed the same temperature independence.

(8) $[R]^T_{obsd}$, $[R]$, and $[R]_{eq}$ refer to the observed rotational strength or to the one calculated for the conformer with the deuterium in the axial and equatorial position, respectively.

(9) The contributions for the axial and equatorial α-methyl groups were taken from D. N. Kirk and W. Klyne, *J. Chem. Soc., Perkin Trans. 1*, 1076 (1974).

(10) Obtained by a linear least-squares fit (standard deviation 10%) to the data points in an Arrhenius diagram. The experimental error associated with the $[R]^T_{obsd}$ values was ±0.0015.

(11) R. E. Carter and L. Melander, *Adv. Phys. Org. Chem.*, **10**, 1 (1973).

(12) K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2470 (1962).

(13) A ±1% shift in the equilibrium would result in a change of $[R]^T_{obsd}$ = ±0.003.

(14) C. Djerassi and W. Klyne, *Proc. Natl. Acad. Sci. U.S.A.*, **48**, 1093 (1962).

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Evidence for "Naphtharadialene" (1,2,3,4,5,6,7,8-Octakis(methylene)-Δ⁹-octalin)[1]

Sir:

Various precursors have recently been converted by pyrolysis to the reactive and theoretically interesting hydrocarbon hexaradialene (**1**).[2-4] There is no indication yet that **1** cyclizes to the isomeric tricyclobutabenzene (**2**). We describe here novel pyrolysis results which suggest the intermediacy of "naphtharadialene" (**3**),[1] although the isolated product is a cyclized isomer.
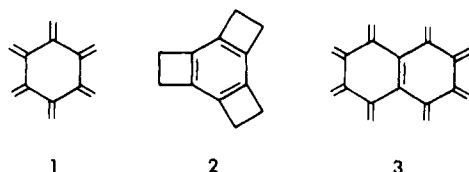

Pyrolysis[5] of either 1,4,5,8-tetrakis(chloromethyl)-2,3,6,7-tetramethylnaphthalene (**4**)[6] or its isomer **5**,[7] in which the relative positions of the methyl and chloromethyl groups are interchanged, in a quartz apparatus[8] at 620–640 °C and 10^{-4} Torr gave the same product, in ~15% yield. The product was best separated from the crude pyrolyzate by sublimation at 150 °C and 10^{-3} Torr.[9] It is a yellow crystalline compound (cubes from benzene) which may be handled at room temperature, although samples darken and decompose gradually, particularly in solution. Gradual heating gave no melting point because of progressive decomposition. However, a sample sealed in a capillary and plunged into a bath at 160 °C, and then heated rapidly, melted reproducibly at 175–176 °C.

The product had the following spectral properties. The high resolution mass spectrum showed a parent and base peak at *m/e* 232.12509 (calcd for $C_{18}H_{16}$ 232.12520). The ¹H NMR spectrum (CDCl₃, 180 MHz) consisted of two singlets with equal intensity at δ 3.24 and 3.26,[10] and the ¹³C NMR spectrum (CDCl₃) had aliphatic carbon signals at δ 29.12 and 29.49 and aromatic carbon signals at δ 132.67, 137.39, and 139.95.[11]

These NMR data do not permit an unequivocal choice between structures **6** and **7** for the pyrolysis product (Scheme I). Both compounds have D_{2h} symmetry and the proton and carbon-13 chemical shifts of model compounds are similar.[12,13] Consequently it was necessary to carry out an X-ray structure determination on a crystal. The correct structure is **7**. The molecule is essentially planar, with the bond angles and distances shown.[14]

Scheme I
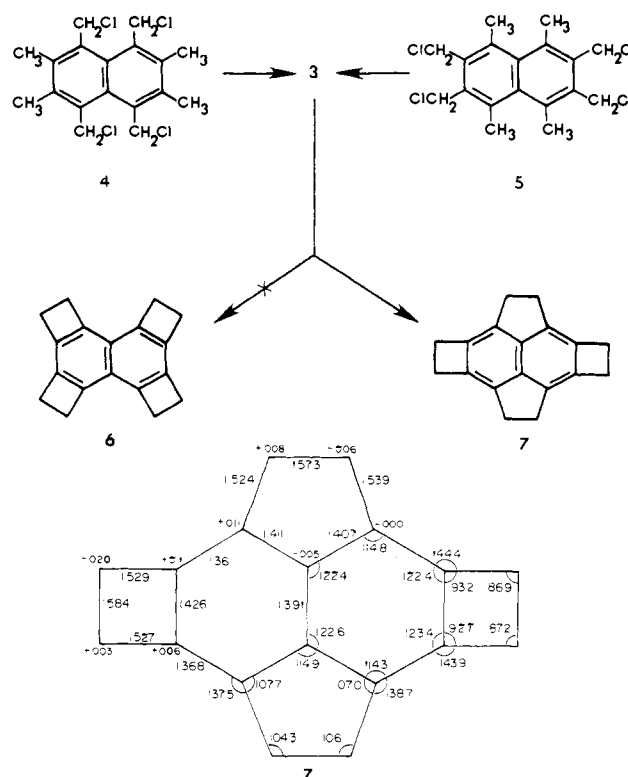
The formation of **7** from both **4** and **5** is striking, since it requires bond formation between methyl carbons in the precursors. This result strongly suggests the intermediacy of **3**, since stepwise elimination of hydrogen chloride and ring closure can only lead to **6**. Experiments designed to isolate and/or trap **3** are under way.[15]

In partial support for the intermediacy of **3**, pyrolysis of the bis(chloromethyl)naphthalene **8**[16] at 540 °C and 10^{-4} Torr gave a good yield of the relatively stable radialene type product **9**: ¹H NMR δ 2.13 (s, 6 H), 2.31 (s, 6 H), 4.92 (d, 2 H, J = 1.5
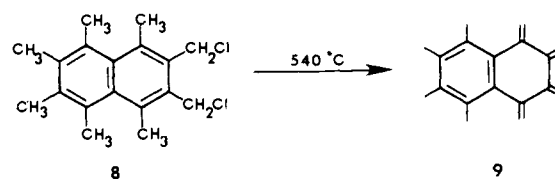
Hz), 5.17 (br s, 2 H), 6.30 (br s, 2 H), 5.48 (d, 2 H, J = 1.5 Hz).

References and Notes

(1) The term "radialene" generally refers to a single carbocyclic ring, each carbon of which is part of an exocyclic carbon–carbon double bond. Although the trivial name "naphtharadialene" which we suggest here for **3** does not adhere strictly to this definition, it is descriptive and much simpler than the systematic name.

(2) A. J. Barkovich, E. S. Strauss, and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **99**, 8321 (1977).

(3) P. Schiess and M. Heitzmann, *Helv. Chim. Acta*, **61**, 844 (1978).

(4) L. G. Harruff, M. Brown, and V. Boekelheide, *J. Am. Chem. Soc.*, **100**, 2893 (1978).

(5) We follow here the elegant experimental design of others[3,4] and also our own earlier interest in benzocyclobutene synthesis via hydrogen chloride eliminations: H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 749 (1960); H. Hart, J. A. Hartlage, R. W. Fish, and R. R. Rafos, *J. Org. Chem.*, **31**, 2244 (1966).

(6) H. Hart, J. L. Reilly, and J. B.-C. Jiang, *J. Org. Chem.*, **42**, 2684 (1977).

(7) Compound **5** was obtained by chloromethylation of 1,4,5,8-tetramethyl-naphthalene: mp 263–266 °C dec; NMR (CDCl₃) δ 2.62 (s, 12 H), 4.83 (s, 8 H). We are indebted to Mr. David Makowski for this preparation, and for