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## Structure of the New Boron Hydride $B_{16}H_{20}$

*Sir:*

The pyrolysis of $B_9H_{13}S(CH_3)_2$ has recently been shown[1] to yield a mixture of boranes, including a new compound characterized as $B_{16}H_{20}$. We report here preliminary results of an X-ray diffraction study of this compound, which we find to be the first structurally characterized neutral borane without molecular symmetry.

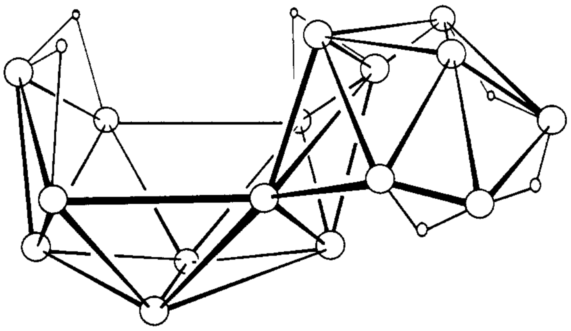

Figure 1. Structure of $B_{16}H_{20}$. Terminal hydrogen atoms are not included in the drawing.

A small sample of $B_{16}H_{20}$ was supplied by Drs. Jaromír Plešek and Stanislav Heřmánek of the Institute of Inorganic Chemistry, Prague-Řež, Czechoslovakia. Single crystals were grown by sublimation and were found to belong to the monoclinic space group $C_{2h}^5$-$P2_1/c$. The assumption that the unit cell with dimensions $a = 5.85 \pm 0.01$, $b = 13.67 \pm 0.02$, $c = 16.75 \pm 0.03$ Å, $\beta = 100° 50' \pm 5'$ contains four molecules of $B_{16}H_{20}$ leads to a calculated crystal density of 0.98 g cm$^{-3}$. This value is in reasonable agreement with experimental measurements (flotation technique) which bracket the density between 0.94 and 1.00 g cm$^{-3}$. The high solubility of the compound and the limited amount of sample preclude a more accurate density determination.

Intensities of diffraction maxima were measured on a Picker automated X-ray diffractometer, and the boron positions were found by iterative application of Sayre's equation[2] using the multiple solution program of Long[3] which had been appropriately modified for the local computer. All hydrogen atoms were located unambiguously in a three-dimensional electron density map from which the contribution of the boron atoms had been subtracted. At the current stage of refinement, with isotropic thermal parameters, the conventional crystallographic discrepancy factor, $R$, is 0.08 for the 1059 observations.

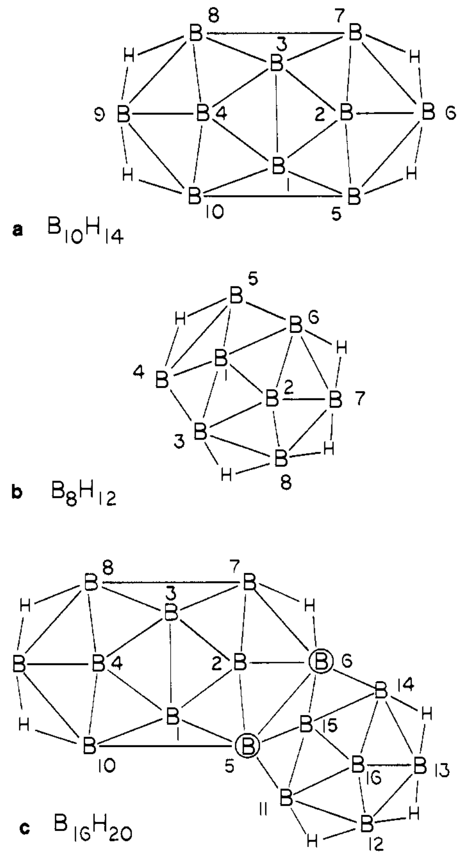

Figure 2. Projection drawings and numbering schemes for (a) $B_{10}H_{14}$, (b) $B_8H_{12}$, (c) $B_{16}H_{20}$. One terminal hydrogen atom has been omitted from each boron atom except for the encircled B-5 and B-6 of $C_{16}H_{20}$, which do not have terminal hydrogen atoms.

The boron framework, illustrated in Figure 1, may be described as a $B_{10}$ icosahedral fragment which shares an edge with a $B_8$ fragment in such a way that the two fragments open in opposite directions. It is convenient to regard the $B_{16}H_{20}$ molecule as a $B_{10}H_{14}$ unit[4] and a $B_8H_{12}$ unit[5] with the shared edge consisting of B-5 and B-6 from $B_{10}H_{14}$ and B-4 and B-5 from $B_8H_{12}$. The symmetry observed for $B_{10}H_{14}$ and for $B_8H_{12}$ is lost in the unsymmetrical fusion of the two units. There are six bridging hydrogen atoms in $B_{16}H_{20}$, three of which occupy positions corresponding to those found in $B_{10}H_{14}$, and the other three occupying positions corresponding to those in $B_8H_{12}$. Projection drawings of $B_{16}H_{20}$, $B_{10}H_{14}$, and $B_8H_{12}$ are included in Figure 2.

The 14 terminal hydrogen atoms of $B_{16}H_{20}$ are distributed one per boron atom, with the two boron atoms (B-5 and B-6) connecting the two icosahedral fragments lacking terminal hydrogens. The B–B bond distances are in the range from 1.7 to 1.8 Å, except for the B-5–B-6 value of 1.68 Å, which compares well with the corresponding value of 1.67 Å in the $B_8H_{12}$ molecule,[5] and the predictably[4,6] large values of 1.91 and 2.02 Å

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[3] R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis (Part III), UCLA, 1965.

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for B-5–B-10 and B-7–B-8, respectively. Average values for the B–H bond distances of 1.1 and 1.3 Å for terminal and bridging hydrogen atoms, respectively, are consistent with values from other boranes.[7] Each boron atom is six-coordinate, and B-5 is coordinated to boron atoms only. In the *n*-$B_{18}H_{22}$ molecule[6b] there are two boron atoms each surrounded by six boron atoms; however, these atoms also participate in bridge hydrogen bonding and are thus seven-coordinate.

The $B_{16}H_{20}$ molecule is highly relevant to the chemistry of the $B_{10}H_{14}$, *n*-$B_{18}H_{22}$, and *i*-$B_{18}H_{22}$ molecules.[4,6,7] Both $B_{10}H_{14}$ and *n*-$B_{18}H_{22}$ are products of the same reaction which produces $B_{16}H_{20}$, and $B_{16}H_{20}$ reacts[1] with dimethyl sulfide and triphenylphosphine to yield $B_{10}H_{14}$. In addition, the formal removal of B-9′ and B-10′ from *either* *n*-$B_{18}H_{22}$ or *i*-$B_{18}H_{22}$, followed by minor shifts of boron atoms and appropriate rearrangement of bridge hydrogen atoms, yields the $B_{16}H_{20}$ molecule.

Full details of the structural study, as well as chemical implications of the results, will be published in the near future.

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(7) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

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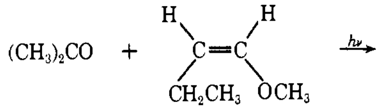
## Molecular Photochemistry. X. The Photocycloaddition of Acetone to 1-Methoxy-1-butene. A Comparison of Singlet and Triplet Mechanisms and Biradical Intermediates[1]

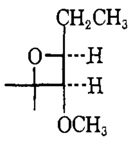
*Sir:*

The photocycloaddition of ketones to ethylenes has attracted considerable synthetic[2] and mechanistic[3] attention recently. Although triplet ketones are generally the chemically active states in these reactions,[3] cases are now known in which the ketone singlets initiate attack on the ethylene.[3b,e,f] To date, however, there have been no studies which answer the questions: (a) What are the relative reactivities[4] of the $S_1$ and $T_1$ states of a given ketone toward a single olefin? (b) What effect, if any, will spin differences have on attack of an excited ketone on an ethylene? (c) If biradical intermediates[5] are formed by attack of $S_1$ and $T_1$ on an ethylene, are these intermediates different or comparable in their structures and chemical properties? The last question is particularly intriguing because it examines the nature of spin correlation (spin memory) in a 1,4 biradical, a problem of considerable theoretical[6] and practical[7] interest since, if spin inversion is slow relative to competing processes, biradicals of different multiplicities may exhibit different chemistry.

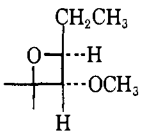
The photoaddition of acetone to *cis*-1-methoxy-1-butene (*c*-**1**) discussed below appears to be a particularly attractive case to study in order to answer questions a–c. Both $S_1$ (n,π*) and $T_1$ (n,π*) states of acetone (*vide infra*) attack *c*-**1** to produce[8] the isomeric oxetanes **2**–**5**. In order to simplify analyses, **4** and **5** were conveniently eliminated by treatment of the photolysate with dilute (0.01 *M*) HCl.[9] The ratio and absolute yields of **2** and **3** were then able to be determined accurately. Stern–Volmer plots of $\phi^0/\phi$ for the formation of **2** and **3** *vs.* 1,3-pentadiene (**6**) are shown in Figure 1. At low concentrations of **6** these plots yield a straight line with a slope of 126 and a limiting ratio of **2**:**3** of 1.1. However, at high concentrations of **6** the ratio of **2**:**3** steadily increases and then reaches a limit of 4.1. *The same limiting ratio is approached as the concentration of c-**1** is increased.* A Stern–Volmer plot ($1/\Phi_2$ *vs.* $1/[c\text{-}\mathbf{1}]$) of the quantum yield for the formation of **2** as a function of *c*-**1** in the presence of 0.3 *M* **6** yields a straight line with a slope of 142 and an intercept of 75. (Preliminary results



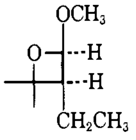
$$(CH_3)_2CO + \underset{CH_2CH_3\ \ OCH_3}{\overset{H\ \ \ \ H}{C{=}C}} \xrightarrow{h\nu}$$



**2**



**3**



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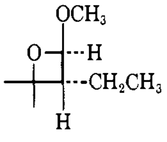

**5**

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(1) (a) The authors gratefully acknowledge support of this work by the Air Force Office of Scientific Research (Grant AFOSR-68-1381). We also thank the Ciba Co. for a genrous gift. (b) Part IX: N. J. Turro and R. Engel, *Molecular Photochem.*, in press.

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(4) Direct measurement of comparative bimolecular reactivities of $S_1$ and $T_1$ of alkyl ketones have not been previously measured. See, however, ref 1a and 11 for related studies.

(5) Biradical intermediates have long been assumed to be intermediates in the photocycloaddition of ketones to olefins, but only recently[3e] has this point been examined experimentally; for a review see ref 2 and N. J. Turro, "Molecular Photochemistry," W. A. Benjamin Co., New York, N. Y., 1965, p 208.

(6) For theoretical work on the related trimethylene biradical see R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968); W. B. DeMore and S. W. Benson, *Advan. Photochem.*, 2, 219 (1964); P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, p 235.

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(8) Compounds **2**–**4** were unambiguously identified from spectral data. The assignments of stereochemistry in **2** and **3** are made on the basis of the nmr coupling constants of the ring hydrogen (*J* = 6.5 and 5.5 Hz, respectively) and the correlation of the stereospecific singlet addition of acetone to *c*-**1** and *t*-**1** with predominant formation of **2** and **3**, respectively.

(9) Compound **5** elutes with **3** during vpc analysis. Compounds **2** and **3** were totally unaffected by the addition of a trace of HCl.