

proton transfer having occurred in the transition state (*i.e.*, low degree of positive character of the O-H protons) and, concomitantly, (2) a good distribution of positive charge in the organic portion of the transition state. The transition state in the hydration of aliphatic olefins appears to be more strongly solvated since the acidity dependence of the rates is less steep ($-\log k_c/dH_0$ is around unity for a number of alkenes¹). Perhaps this is due to the proton having been transferred to a lesser extent in the transition state; *i.e.*, the transition state has greater oxonium ion character. This would be consistent with the small solvent isotope effects found.¹ On the other hand, the small isotope effect in the hydration of aliphatic olefins has been attributed to nearly complete proton transfer in the transition state.³ In that event, proton transfer in the transition state of styrene hydration may be less complete. The steeper acidity dependence of styrene hydration then could be attributed to a more efficient distribution of the positive charge in the organic portion of the transition state.

The lack of a detectable isotope effect in the hydration of styrene- $\beta,\beta\text{-}d_2$ and of styrene- $\alpha\text{-}d$ is consistent with mechanism I. The $\alpha\text{-C-D}$ isotope effect would be minimized by the $\alpha\text{-carbon}$ being trigonal in the transition state as well as the ground state. In mechanism I, the change that occurs at the $\beta\text{-carbon}$ resembles that of $\sigma\text{-complex}$ formation in aromatic substitution. Secondary isotope effects in the latter reaction also are absent or very small.⁹

(9) E. A. Halevi, "Secondary Isotope Effects," in "Progress in Physical Organic Chemistry," Vol. 1, Interscience Publishers, Inc., 1963, p. 109, and references therein.

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The Molecular Symmetry of Iodopentaborane

Sir:

The compounds formed by the direct attack of elemental iodine on pentaborane(9) in excess pentaborane(9) at 70°¹ has been shown to be 1-iodopentaborane(9); that is, the iodine atom is bonded to the apical boron of the tetragonal boron pyramid as shown in Fig. 1.

Since the compound is sensitive to air, single crystals were grown from the melt in thin-walled Pyrex capillaries. The unit cell is monoclinic with $a = 11.24$, $b = 10.03$, $c = 13.14$ Å, and $\beta = 110^\circ 5'$. $Z = 8$ and the space group is $C2/c$.

The structure was solved by the heavy atom technique using partial three-dimensional data obtained on a Buerger precession camera at -25° . The R value with individual isotropic temperature factors is 13.0 for the 529 reflections.

The space group places no symmetry requirements on the molecule. However, the measured bond distances and bond angles show that within experimental

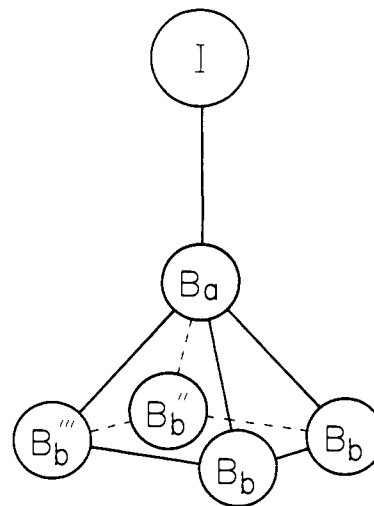


Fig. 1.—Molecular structure of B_5H_8I : bond distances are $B_a-I = 2.20 \pm 0.03$, $B_a-B_b = 1.71 \pm 0.05$, $B_b-B_b = 1.84 \pm 0.05$ Å; bond angles are $\angle B_b-B_a-B_b' = 65.0 \pm 1.5^\circ$, $\angle I-B_a-B_b = 130.5 \pm 1.5^\circ$, and $\angle B_b-I-B_b = 30.0 \pm 1.0^\circ$. The listed errors are estimated errors.

error the molecule nearly possesses a four-fold axis. The boron(apical)-boron(basal) average bond distance is 1.71 Å, with values ranging from 1.70 to 1.72 Å. The boron(basal)-boron(basal) average bond distance is 1.84 Å, with values ranging from 1.78 to 1.95 Å. A complete discussion will be presented in a later paper.

These results confirm the n.m.r. work of Schaeffer, *et al.*,² who concluded that the monoiodide of penta-borane(9) is apically substituted. It is to be noted that the boron-iodine bond distance in B_5H_8I , 2.20 Å, is somewhat longer than the boron-iodine distance in BI_3 , 2.10 Å.³

Acknowledgments.—The computations performed in this study were carried out on an IBM 7094 computer with the aid of a system of crystallographic programs developed at the University of Maryland and the University of Washington.

(2) R. Schaeffer, J. N. Shoolery, and R. Jones, *ibid.*, **80**, 2670 (1958).

(3) M. A. Ring, J. D. H. Donnay, and W. S. Koski, *Inorg. Chem.*, **1**, 109 (1962).

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Blocked Rotation in Hexaisopropylbenzene. Evidence for Cyclobutadiene Intermediates in the Trimerization of Diisopropylacetylene by Dicobalt Octacarbonyl^{1,2}

Sir:

The Fisher-Hirschfelder model of hexaisopropylbenzene (see Fig. 1) can only be constructed with great difficulty because of the requirement that each isopropyl group exactly interlock with its neighbors on either side. This can only be accomplished if (as shown) all of the

(1) Crowded Benzene Compounds. III. Ref. 3 and 4 are parts I and II in this series.

(2) This work was supported at various stages by NIH Grant CA-05512 and NSF Grant GP-2014, for which we are most grateful.

(3) E. M. Arnett, M. E. Strem, and R. A. Friedel, *Tetrahedron Letters*, No. 19, 658 (1961).

(4) E. M. Arnett and M. E. Strem, *Chem. Ind. (London)*, 2008 (1961).

(1) L. H. Hall, W. S. Koski, and V. V. Subbanna, *J. Am. Chem. Soc.*, **86**, 1304 (1964).