proton transfer having occurred in the transition state (*i.e.*, low degree of positive character of the O–H protons) and, concommitantly, (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 (−d log k_C/dH_0 is around unity for a number of alkenes[1]). 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-β,β-d_2 and of styrene-α-d is consistent with mechanism I. The α-C–D isotope effect would be minimized by the α-carbon being trigonal in the transition state as well as the ground state. In mechanism I, the change that occurs at the β-carbon resembles that of σ-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. I, 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 $\beta = 110°5'$. $Z = 8$ 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

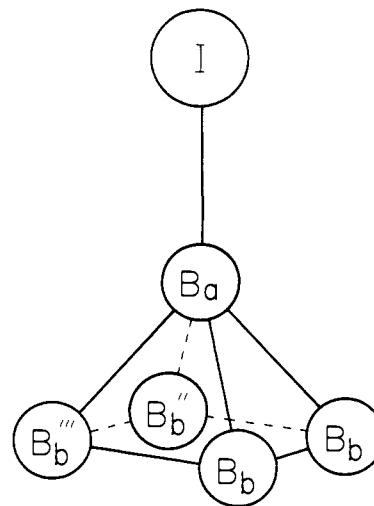(1) L. H. Hall, W. S. Koski, and V. V. Subbanna, *J. Am. Chem. Soc.*, **86**, 1304 (1964).

Fig. 1.—Molecular structure of B_5H_8I: bond distances are B_a–I = 2.20 ± 0.03, B_a–B_b = 1.71 ± 0.05, B_b–B_b = 1.84 ± 0.05 Å.; bond angles are $\angle B_b$–B_a–B_b' = 65.0 ± 1.5°, $\angle$I–B_a–B_b = 130.5 ± 1.5°, and $\angle B_b$–I–B_b = 30.0 ± 1.0°. 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 pentaborane(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]

(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).
(4) Department of Chemistry and Physical Sciences, Florida Atlantic University, Boca Raton, Fla.

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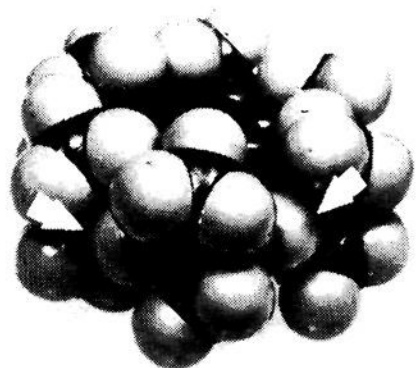(4) E. M. Arnett and M. E. Strem, *Chem. Ind.* (London), 2008 (1961).

Fig. 1.—Model of hexaisopropylbenzene from about 20° above plane of ring. Note two methine hydrogens (arrows) in plane of ring and in "clockwise" alignment. Note, also, how ring is protected from above and below by alignment of methyl groups.

groups are pointed in the same direction, clockwise or counterclockwise, around the perimeter of the ring. Once the model has been put together in this way, it is impossible to rotate the isopropyl groups more than a few degrees without breaking it. The model, therefore, suggests that an extreme case of hindered rotation exists in the molecule, and spectral evidence indicates that this may actually be so.

The n.m.r. spectrum of hexaisopropylbenzene shows the expected sharp methyl doublet at τ 8.73 p.p.m., nearly the same position (τ 8.79 p.p.m.) as in cumene. However, the methine septet is shifted over 0.7 p.p.m. downfield (center at τ 6.39 p.p.m.) relative to that for cumene[5] (τ 7.12 p.p.m.).

Such a shift is just what would be expected if the methine hydrogens were forced into such close proximity to neighboring isopropyl groups that strong dispersion interactions could occur.[6] The methine peaks are sharp, suggesting equivalence of the methine hydrogens.

A striking feature of the infrared spectrum of hexaisopropylbenzene is a very sharp band of medium intensity at 3070 cm.$^{-1}$. Since there are no aromatic hydrogens, this cannot be a shifted 3030-cm.$^{-1}$ band. Indeed, we know of only one precedent for such a band in a hydrocarbon, and that is for the crowded methylene hydrogens in the "bird-cage hydrocarbons" described by Winstein and de Vries.[7,8] This band is absent from other isopropylbenzenes and also from tetraisopropylcyclopentadienone (see below), whose model is relatively free of the rotational limitation on hexaisopropylbenzene. We propose that this should be assigned to the methine hydrogens which are forced into close proximity to their neighboring isopropyl groups.

A logical conclusion from the above spectral interpretation is that the model is correct in showing that rotation of the isopropyl groups is almost completely blocked in this molecule, but that there is no unusual restriction to normal rotation of the methyl groups around their own axes.

The evidence given here suggests (but does not demand) that the time of rotation is long on the n.m.r. time scale. If this is correct, it presents a novel stereochemical situation in which a conformation is "frozen" at room temperature by virtue of cooperative nonbonded repulsions of the whole molecule instead of

through covalent bonds. A natural consequence of this would be the existence of stable enantiomers related to hexaisopropylbenzene in which the symmetry, with respect to the ring, is destroyed, provided that the average time for rotation is long enough to allow resolution. We are examining this possibility.

We prepared hexaisopropylbenzene by treatment of diisopropylacetylene[9] (0.26 mole) with dicobalt octacarbonyl (0.02 mole) at reflux temperature in Skellysolve C for three days, at the end of which time the solution had a greenish color. Work-up resulted in a 12% yield of hexaisopropylbenzene which melts at the high temperature of 286°, compared to hexa-n-propylbenzene[11] (m.p. 101°). Anal. Calcd. for $C_{24}H_{42}$: C, 87.19; H, 12.81; mol. wt., 330. Found (two independent analytical laboratories): C, 87.29, 86.92; H, 12.81, 13.01; mol. wt., 295 (vapor pressure osmometer), 330 (mass spectrometer). The n.m.r. spectrum was very simple, showing, in addition to the methine septet referred to above, a doublet centered at τ 8.73 p.p.m. whose integrated area was six times that for the septet. This agrees with an n.m.r. spectrum reported for this compound in a very recent article[12] which, however, gives no other structural data.

Except for the peculiar band at 3070 cm.$^{-1}$, which we have assigned to crowded methine hydrogen, the infrared spectrum was simple and consistent with the proposed structure. Like the n.m.r. spectrum, it gave no indication of olefinic groups, and the isopropyl doublet at 1385 and 1370 cm.$^{-1}$ was normal. A band at 433 cm.$^{-1}$ falls within the small range characteristic of hexasubstituted benzenes.[13] The ultraviolet spectrum was very similar to that of hexamethylbenzene showing a typical aromatic band at 273 mμ (ϵ 188) (ϵ 218 at 270 mμ for HMB). This gives a greatly reduced K value (0.57) for hexaisopropylbenzene relative to that (1.35) for hexamethylbenzene, in conformity with the more crowded structure proposed for the former.

Three other compounds were isolated from the filtrate after removal of hexaisopropylbenzene. Complete discussion of the structural evidence for them will be given in a full paper. The result is presented in preliminary form here because of its relevance to the mechanism of acetylene trimerization.

As might be expected,[14] one of the compounds isolated from the filtrate is tetraisopropylcyclopentadienone. The other two are assigned the following structures, which can be derived by one and two hydrogen shifts, respectively, from tetraisopropylcyclobutadiene.

The products which we have found indicate that a cobalt carbonyl–tetraisopropylcyclobutadiene complex

(5) Spectra of both compounds were determined in carbon disulfide and peaks were invariant to dilution.

(6) A. A. Bothner-By, J. Mol. Specty., 5, 52 (1960).

(7) D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, J. Am. Chem. Soc., 83, 2938 (1961).

(8) I. de Vries and P. R. Ryason, J. Org. Chem., 26, 621 (1961).

(9) This was made by mercuric oxide oxidation of the bishydrazone of diisobutyryl which in turn was prepared by rearrangement of 2,5-dimethylhexynediol-2,5 in 80% sulfuric acid. It boiled at 105–106°[10] and was homogeneous to gas chromatography.

(10) R. Levina and Y. Shaborov, Chem. Abstr., 47, 3219e (1953).

(11) E. Wertyporoch and T. Firla, Ann., 500, 287 (1933).

(12) H. Hopff, Chimia, 18, 140 (1964).

(13) R. J. Jakobsen, Technical Documentary Report ASD-TDR-62-895, Battelle Memorial Institute, Columbus, Ohio.

(14) U. Krüerke and W. Hübel, Chem. Ber., 94, 2829 (1961).

has probably been formed as an intermediate.[14] Because of the strain and steric protection of the cyclobutadiene ring by the isopropyl groups, the cyclobutadiene isomers shown above may be formed before insertion of a carbonyl group (to give tetraisopropylcyclopentadienone) or of another diisopropylacetylene moiety (to give hexaisopropylbenzene) can occur.

Acknowledgments.—We wish to express our gratitude to Mr. A. G. Sharkey, Jr., of the U. S. Bureau of Mines for determining mass spectral molecular weights and to Drs. Aksel Bothner-By, of Mellon Institute, and R. A. Friedel, of the U. S. Bureau of Mines, for discussion of the spectral evidence presented here. Mellon Institute provided facilities for the preparation of this manuscript.

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Gas Chromatographic Separation of the Hydrogen Isotopes[1]

Sir:

Considerable interest has been shown in the gas chromatographic separation of the six molecular species of hydrogen: H_2, HD, D_2, HT, DT, and T_2. The most recent work was summarized by Carter and Smith[2] and by King.[3] Since previous work was done at low levels of tritium, it was of interest to see whether comparable results could be obtained at higher tritium concentrations where radiation effects might impair separation factors. Glueckauf reported a decrease in the separation factor of radiokrypton and radioxenon with increasing radioactive power.[4]

Separation of the six hydrogen molecular species in a mixture that contained 2.4 c. of tritium is shown in Fig. 1. The column, ferric oxide coated alumina at 77°K., was similar to that described by Carter and Smith and by King. Separation factors calculated from this chromatogram and compared with those of Carter and Smith ($\sim$0.5 mc. of tritium) and King ($\sim$70 mc. of tritium) show no significant effect from the tritium radiation.

The separation factors in Table I were calculated in the manner described by Carter and Smith, *viz.*

$$\alpha_{1,2} = d_2/d_1$$

where d_2 and d_1 represent the distances from zero time to the peak maxima for respective components on the chromatograms. Direct comparison of separation factors defined in this manner is complicated by the decrease in retention times for peak maxima with increasing amounts of components, even for nonradioactive components. These decreases result from curvature of the sorption isotherms. The concentration dependence is particularly noticeable when comparing the separations of the five other species from H_2 in Table I. The higher separation factors reported by Carter and Smith are attributable to the shorter retention time for the H_2 peak as a consequence of increased

(1) The information contained in this paper was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

(2) E. H. Carter and H. A. Smith, *J. Phys. Chem.*, **67**, 1512 (1963).

(3) J. King, *ibid.*, **67**, 1397 (1963).

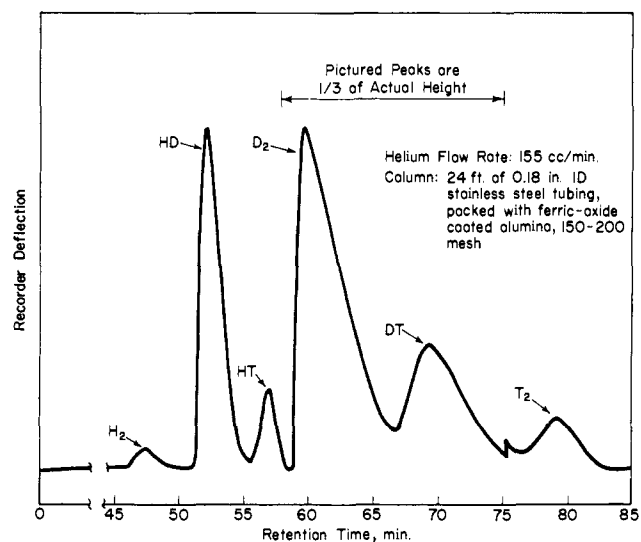(4) E. Glueckauf, *Ann. N. Y. Acad. Sci.*, **72**, 562 (1959).

Fig. 1.—Chromatogram of 5-cc. sample of hydrogen isotopes.

H_2 content of their sample (see Table II). When allowance is made for the effects of gross compositional differences, good agreement is observed between the separation factors derived by all three experimenters. In no case was there indication that the tritium radiation level had significantly affected the separation factor.

TABLE I

COMPARISON OF SEPARATION FACTORS FOR HYDROGEN SPECIES

α	This work	King[3]	Carter and Smith[2]
HD/H_2	1.09	1.13	1.22
HT/H_2	1.20	1.23	1.42
D_2/H_2	1.26	1.38	1.49
DT/H_2	1.45		1.85
T_2/H_2	1.66	1.68	2.08
HT/HD	1.10	1.09	1.22
D_2/HD	1.15	1.22	1.17
DT/HD	1.33		1.52
T_2/HD	1.52	1.48	1.71
D_2/HT	1.05	1.12	1.05
DT/HT	1.21		1.30
T_2/HT	1.38	1.30	1.47
DT/D_2	1.15		1.24
T_2/D_2	1.32	1.22	1.40
T_2/DT	1.14		1.13

TABLE II

COMPOSITION OF SAMPLES FOR HYDROGEN ISOTOPE SEPARATIONS

	Sample size, cc.[a]		
Component	This work	King[b]	Carter and Smith[b]
H_2	0.025	0.09	1.6
HD	0.48	0.08	0.7
HT	0.12	0.03	10^{-4}
D_2	2.8	0.08	1.0
DT	1.4	—	10^{-4}
T_2	0.16	0.01	10^{-5}
Total sample, cc.	4.985	0.29	3.3
Total activity, c.	2.4	0.07	0.0005

[a] At STP. [b] Concentrations estimated from information in ref. 2 and 3.

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