transmitted inductive effects not buried in the mathematics of eq. 2 and 3. Likewise, inclusion of restricted rotation will act in the direction of giving better fit.

According to this simple approximation, it appears that each atom or group makes a more-or-less fixed contribution to the chemical shift, with this contribution being attenuated in proportion to $1/R^3$, where R is the distance of separation measured through space, not through the molecular chain. Refinement of the C_y values into the respective $\Delta\chi$ contributions[5] of eq. 1 is not given here because of the approximation involved in eq. 2 and 3. A more complete theory should include electronic effects propagated through the molecular chain itself.

(5) *E.g.*, A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad Sci.*, **70**, 833 (1958); R. W. Lenz and J. D. Heeschen, *J. Polymer Sci.*, **51**, 247 (1961); J. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 2105 (1961); see also J. Guy and J. Tillieu, *J. Chem. Phys.*, **24**, 1117 (1956).

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Preparation, Isolation, and Structure of B_8H_{12}

Sir:

One of the important predictions[1,2] of the valence theory of boron hydrides is the existence of B_8H_{12} and its structural possibilities. We report here the isolation of this thermally unstable material in pure crystalline form in small yields from the electric discharge of a mixture of diborane-6 and pentaborane-9, and the proof of chemical composition and structural formula from a complete three-dimensional X-ray diffraction study of single crystals at low temperatures (Fig. 1).

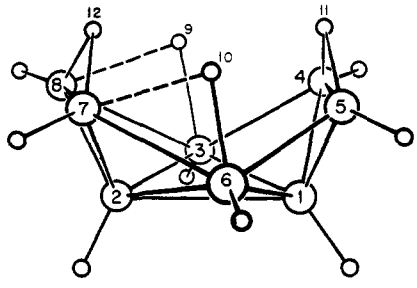

Fig. 1.—Molecular structure of B_8H_{12}. The B_8 unit is an icosahedral fragment. The B–B distances are 1–3 = 1.793, 1–6 = 1.783, 1–4 = 1.684, 1–5 = 1.696, 2–3 = 1.791, 2–6 = 1.796, 2–7 = 1.718, 2–8 = 1.721, 3–4 = 1.790, 5–6 = 1.787, 3–8 = 1.800, 6–7 = 1.793, 1–2 = 1.803, 4–5 = 1.672, and 7–8 = 1.706, all ±0.003 A. Average B–H (terminal) is 1.10 ± 0.03 Å. Some other B–H distances are 3–9 = 1.30, 6–10 = 1.27, 8–9 = 1.48, 7–10 = 1.46, 4 · · · 9 = 1.98, and 5 · · · 10 = 1.99 Å.

Diborane-6 and pentaborane-9 in a 2:1 ratio were swept in a carrier of H_2 at 12 mm. into a cylindrical discharge tube containing two parallel circular electrodes of copper, 90 mm. in diameter and 80 mm. apart maintained at 2700 v. a.c. The product gases were passed through traps at −80, −131, −196, and −196°, and the material condensing at −80° was then repeatedly slowly passed through two −57° traps until the sample was free of pentaborane-9. A series of rapid fractionations through a −45° trap passed hexaborane-10, at first mixed with pentaborane-9 and later with octaborane-12. After a sufficient number of fractionations, small amounts of pure octaborane-12 passed through the trap, but rapid passes were necessary in order to ensure that the nonaborane-15 and the decaborane-16 were retained in the −45° trap. All fractionations were carefully followed by mass spectrometric measurements, which indicated a final product showing a maximum mass number of 100 atomic units (Fig. 2).

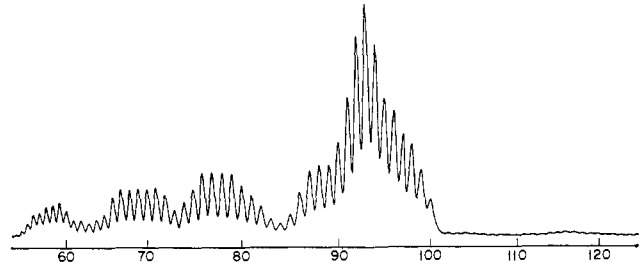

Fig. 2.—Mass spectrum of B_8H_{12}; intensities are plotted on the vertical scale and mass numbers on the horizontal scale.

Each single crystal examined by X-ray diffraction methods was grown in a thin-walled cylindrical capillary maintained at about −20° or lower by a cold nitrogen stream. Complete Weissenberg photographs taken about two axes indicated the space group Pbca and the unit cell dimensions, a = 13.61, b = 10.41, and c = 10.41, all ±0.01 Å. The structure shown in Fig. 1 was obtained from three-dimensional superposition procedures, and all H atoms were located without chemical assumptions in three dimensional electron density maps from which the B atoms had been subtracted. The present value of $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ is 0.11 for the 1571 reflections.

The three very similar probable structures[2] have symmetries C_{2v}, C_s, and C_2. Of these, the structure of symmetry C_s is the correct one, and is, moreover, the structure which is most closely related to that[3] of $C_2H_5NH_2B_8H_{12}NHC_2H_5$. There are two symmetrical H bridges across the B_4–B_5 and the B_7–B_8 distances which differ from one another by ten times their standard deviations. The bridges across the B_3–B_8 and B_6–B_7 distances are unsymmetrically displaced toward B_3 and B_6, respectively, probably in order to prevent the $H_9 \cdot \cdot \cdot H_{12}$ = 1.87 Å. and $H_{10} \cdot \cdot \cdot H_{12}$ = 1.95 Å. distances from becoming too short. For comparison, we note that the $H_9 \cdot \cdot \cdot H_{11}$ and $H_{10} \cdot \cdot \cdot H_{11}$ contacts of 2.20 and 2.23 Å., respectively, indicate a very significant distortion from an idealized C_{2v} symmetry toward the observed structure of C_s symmetry. Theoretical studies of the energies involved in these distortions are underway.

An early report[4] of a possible B_8 hydride has been reconsidered recently[5] to favor B_9H_{15}. Vapor pressure anomalies in the B_9H_{15} preparation[6,7] as well as mass spectroscopic studies[8–10] have supported the probable

(1) R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 212 (1957).

(2) W. N. Lipscomb, "Boron Hydrides," The W. A. Benjamin Co., New York, N. Y., 1963, p. 59.

(3) R. Lewin, P. G. Simpson, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 478 (1963); *J. Chem. Phys.*, **39**, 1532 (1963); also ref. 2, pp. 52–53 (Principle 7).

(4) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **55**, 4009 (1933).

(5) A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

(6) R. Schaeffer, private communication, 1953.

(7) R. E. Dickerson, P. J. Wheatley, P. A. Howell, W. N. Lipscomb, and R. Schaeffer, *J. Chem. Phys.*, **25**, 606 (1956).

(8) I. Shapiro and B. Keilin, *J. Am. Chem. Soc.*, **76**, 3864 (1954).

(9) R. E. Dickerson, P. J. Wheatley, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957).

(10) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehman, "Borax to Boranes," Advances in Chemistry Series, American Chemical Society, Washington, D. C., 1961, p. 127.

existence of a B_8 hydride. The maximum of 100, also observed by the authors, in the mass spectrum of a B_8 hydride,[10] which was not isolated,[11] is apparently an unsafe criterion of the formula B_8H_{12} inasmuch as the maximum masses observed[10] for B_4H_{10}, B_5H_{11}, and B_9H_{15} are all less by two mass units than the maximum permitted by each of these compounds.

Besides the hydrides B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$ discovered by Stock, the known structurally characterized boron hydrides now include[2] B_8H_{12}, B_9H_{15}, $B_{10}H_{16}$, $B_{18}H_{22}$, *i*-$B_{18}H_{22}$, and $B_{20}H_{16}$.[12] In addition, the composition of B_6H_{12} has been reported.[13]

The unexpected lowering of symmetry of B_8H_{12} from C_{2v} to C_s suggests to us that the theory of boron hydride structures may become applicable to carbonium ion chemistry, where the somewhat smaller size of C, as compared with B, also appears to lead to lowering of symmetry in complex carbonium ions.

Acknowledgment.—We wish to acknowledge the assistance of Dr. W. E. Streib and support of this research by the National Science Foundation, the Office of Naval Research, and the U. S. Army Research Office (Durham).

(11) R. E. Williams, private communication, 1963.

(12) L. B. Friedman, R. D. Dobrott, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 3505 (1963).

(13) D. F. Gaines and R. Schaeffer, *Proc. Chem. Soc.*, 267 (1963).

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The Hydrogen Chloride-Catalyzed Racemization of Sulfoxides[1]

Sir:

We have found that sulfoxides are rapidly and cleanly racemized at room temperature by solutions of hydrogen chloride in organic solvents such as benzene, dioxane, and THF. The presence of water slows the rate of racemization; nevertheless, we have found that for many purposes an effective medium may be prepared most conveniently[2] by mixing one volume of 12 *M* aqueous hydrochloric acid and two volumes of dioxane. Typically, a colorless solution of 100 mg. of (+)-phenyl *p*-tolyl sulfoxide[3] (I) in 5.0 ml. of the above medium was allowed to stand at room temperature under nitrogen for 24 hr. The acid was neutralized with aqueous sodium hydroxide or sodium carbonate (alternatively, with magnesium oxide) and the sulfoxide was extracted with ether; removal of the organic solvents under reduced pressure left a white, crystalline residue of the racemic sulfoxide (100 mg.), m.p. 67–68.5° (lit.[4] m.p. 69–70°), infrared spectrum identical with that of starting material.

The marked effect of water on the rate of racemization may be illustrated by the following observation: under the above described conditions the half-life ($t_{1/2}^{25}$) of I is 2.4 hr., whereas in *anhydrous* dioxane, 4.0 *M* in hydrogen chloride, $t_{1/2}^{25}$ is less than 30 sec. Conversely, $t_{1/2}^{25}$ is 27 hr. in a 1:1 v./v. mixture of 9 *M* aqueous hydrochloric acid and dioxane. The rate is also highly dependent on the concentration of the acid.

The specificity of hydrogen chloride as an effective catalyst is remarkable. Thus the rotation on a solution of I in a 2:1 v./v. mixture of dioxane and 48.8% hydrofluoric acid remains unchanged for 11 days at 25°. In a 2:1 or 1:1 v./v. mixture of dioxane and 47% aqueous hydrobromic acid, decomposition (with evolution of bromine) of I is an important side reaction and racemization studies were therefore vitiated.

The rate of racemization is extraordinarily sensitive to the steric requirements of the groups attached to the asymmetric sulfur atom. As seen in Table I, the specific rate constants of racemization of methyl and *t*-butyl *p*-tolyl sulfoxides differ in this medium by a factor of greater than 3.5×10^5.

TABLE I

RATE CONSTANTS OF RACEMIZATION OF p-$CH_3C_6H_4$–SO–R[a]

R[b]	$k_1^{25} \times 10^5$, sec.$^{-1}$	$[\alpha]_D$ (acetone)
Methyl	3700	+145°
Ethyl	957	+188°
Isopropyl	29.3	+177°
(*R*)-2-Octyl[c]	23.7	+118°
(*S*)-2-Octyl[c]	22.3	+138°
Phenyl	8.00	+25°
m-Tolyl	7.53	+15°
o-Tolyl	4.53	−89°
Mesityl	0.0418	−284°
t-Butyl	0.0105	+161°

[a] In a 2:1 v./v. mixture of dioxane and 12 *M* aqueous HCl. [b] All compounds were prepared from (−)-menthyl (−)-*p*-toluenesulfinate by the Andersen synthesis [K. K. Andersen, *Tetrahedron Letters*, **No. 3**, 93 (1962)] and gave satisfactory elemental analyses. [c] Rates of mutarotation. The diastereomeric sulfoxides were separated by chromatography and the configurations were established by oxidation to the sulfones. For phenyl 2-octyl sulfoxide of m.p. 21° [(D. J. Cram and S. H. Pine, *J. Am. Chem. Soc.*, **85**, 1096 (1963)] we observe the comparable value of $k_1^{25} = 20.8 \times 10^{-5}$ sec.$^{-1}$.

The mildness of the conditions employed and the freedom from side reactions present distinct advantages over previous approaches. Thermal stereomutations[5,6] are inconvenient since elevated temperatures are required and we find that partial decomposition cannot be easily avoided. Although sulfoxides racemize in 97% sulfuric acid,[7] the development of a pronounced color in this medium contrasts sharply with the absence of color in our hydrogen chloride solutions.[8] The action of hydrogen bromide requires further study.[9]

It should be pointed out that some sulfoxides are reported to suffer decomposition in hydrochloric acid[5,8,10] and it is therefore advisable to isolate the

(1) We gratefully acknowledge support by the National Science Foundation (Grant No. GP-757).

(2) We reported on the efficacy of this medium at the Eighteenth National Chemistry Symposium of the American Chemical Society, Columbus, Ohio, June 19, 1963 (Abstracts, p. 81).

(3) K. Mislow, A. L. Ternay, Jr., and J. T. Melillo, *J. Am. Chem. Soc.*, **85**, 2329 (1963).

(4) H. Burton and W. A. Davies, *J. Chem. Soc.*, 528 (1948).

(5) K. Fries and W. Vogt, *Ber.*, **44**, 756 (1911); *Ann.*, **381**, 312 (1911).

(6) G. Farina, F. Montanari, and A. Negrini, *Gazz. chim. ital.*, **89**, 1548 (1959).

(7) S. Oae, T. Kitao, and Y. Kitaoka, *Chem. Ind.* (London), 291 (1961).

(8) The chemical instability of aromatic sulfoxides in concentrated sulfuric acid has been discussed by H. J. Shine and L. Piette [*J. Am. Chem. Soc.*, **84**, 4798 (1962)], and by R. J. Gillespie and R. C. Passerini [*J. Chem. Soc.*, 3850 (1956)].

(9) We must distinguish between racemization and the mere loss of optical activity (which could be due to decomposition). Thus J. Holloway, J. Kenyon, and H. Phillips [*ibid.*, 3000 (1928)] observed the loss of optical activity of (+)-ethyl *m*-carboxyphenyl sulfoxide in 3.3 *N* hydrobromic acid at 25° ($k_1 \sim 6 \times 10^{-7}$ sec.$^{-1}$) but the product was not isolated.

(10) J. A. Smythe, *ibid.*, **95**, 349 (1909); M. Zincke and P. Jörg, *Ber.*, **42**,