

To a solution of 200 ml. of 1.67 *M* borane in tetrahydrofuran^{6,7} in a 500-ml. flask (nitrogen atmosphere) was added 25.8 g. (200 mmoles) of *N,N*-dimethylpivalamide in 100 ml. of tetrahydrofuran over 15 min. The temperature was maintained at approximately 0° during the addition. The colorless solution was then refluxed for 1 hr. The flask was permitted to cool to room temperature and 50 ml. of 6 *M* hydrochloric acid was added. The tetrahydrofuran was removed by distillation at atmospheric pressure as hydrogen was evolved (15.5 l., 0.60 mole) from the hydrolysis of excess reagent. Sodium hydroxide pellets were added to saturate the aqueous phase, and the latter was extracted three times with a total of 100 ml. of ether. After drying over sodium sulfate, distillation yielded 18.2 g. (79% yield) of dimethylneopentylamine, b.p. 95–96°, n_D^{20} 1.3982.

In extending this procedure to primary and secondary amides, the amount of borane used was increased by 1 equiv. for each equivalent of "active" hydrogen present in the amide. The reduction of primary amides appears to be considerably slower than that of secondary and tertiary. Consequently, it was found desirable to increase the reaction time to 2 hr. for primary aliphatic amides and to 8 hr. for primary aromatic amides (Table I).

Acknowledgment.—This investigation was made possible by Grant GM 10937 from the National Institutes of Health.

(6) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

(7) One molar solution of borane in tetrahydrofuran is now commercially available from Metal Hydrides Incorporated, Beverly, Mass.

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Phase Transitions and the Radiative Neutron Capture in Solid Organic Media

Sir:

During recent studies in this laboratory of the radiative neutron capture (Szilard-Chalmers effect¹) in solid organic halides, it was found that the organic yield of ⁸⁰Br presents a marked dependence on the phase transitions of the corresponding solid organic media.

Figure 1 shows the organic yield as a function of irradiation temperature in solid CH₂BrCH₂Br. There appears to be an abrupt change of the yield at 10° (melting point) and at -24° (transition point). The same figure shows the dependence of the heat capacity on temperature as determined by Pitzer.² The discontinuity of the heat capacity curve at the transition point is characteristic for a 2I-type transition³ and was interpreted to mean that the dibromoethane molecules undergo hindered rotation around their symmetry axis in the temperature range between 10 and -24°.²

Figure 2 shows the organic yield of ⁸⁰Br in CCl₃Br as a function of the irradiation temperature (some of the data was taken from ref. 4). This halide is known to

(1) L. Szilard and Chalmers, *Nature*, **134**, 462 (1934).

(2) K. S. Pitzer, *J. Am. Chem. Soc.*, **62**, 331 (1940).

(3) E. F. Westrum, Jr., and J. P. McCullough in "Physics and Chemistry of the Organic Solid State," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, p. 80.

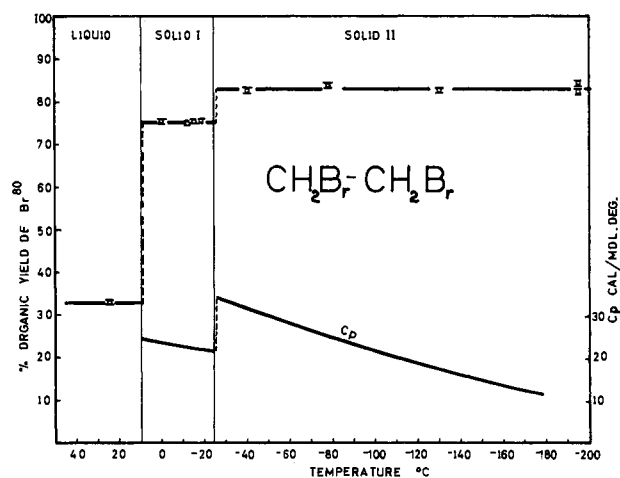


Fig. 1.—CH₂BrCH₂Br: upper curve, the organic yield of the (n, γ) reaction as a function of temperature; lower curve, the heat capacity as a function of temperature (taken from ref. 2).

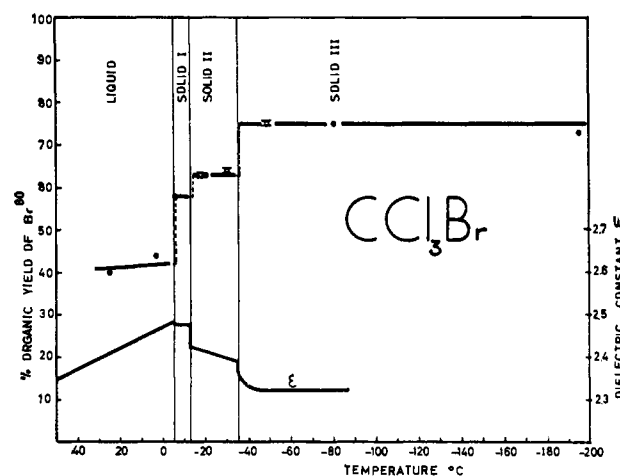


Fig. 2.—CCl₃Br: upper curve, the organic yield of the (n, γ) reaction as a function of temperature (●, points taken from ref. 4; ○ this work); lower curve, the dielectric constant as a function of temperature (taken from ref. 6).

have two phase transitions which appear to affect in a drastic way the chemical effect of the neutron capture.⁵ The data obtained from the neutron irradiation is compared in the same figure with the variation of the measured dielectric constant as given by Miller and Smyth.⁶ These authors interpreted their findings as meaning that in the solid state the CCl₃Br molecules undergo "rotation around at least one axis, presumably the C-Br... with decrease of freedom at the higher transition point and disappearance below the lower."

The connection between phase transition and the Szilard-Chalmers effect might give a rationale for the apparently erratic variations of the organic yield with temperature in the organic solid state.⁷

Further studies are on the way to test the generality of this effect and to find a phenomenological explanation of the latter.

(4) S. Goldhaber, R. S. Chiang, and J. E. Willard, *J. Am. Chem. Soc.*, **73**, 2271 (1951).

(5) It is interesting to note at this point that the $G(\text{Br}_2)$ value from the γ -ray decomposition of CCl₃Br showed no such dependence on solid-phase transition; see R. F. Firestone and J. E. Willard, *ibid.*, **83**, 3551 (1961).

(6) R. C. Miller and C. P. Smyth, *ibid.*, **79**, 20 (1957).

(7) For a review of the problem and references see: T. D. Jones, R. H. Luebke, Jr., J. R. Wilson, and J. E. Willard, *J. Phys. Chem.*, **62**, 6 (1958).

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The Boron-11 Nuclear Magnetic Resonance Spectrum of $B_{20}H_{18}^{-2}$ at 60 Mc./sec.

Sir:

We have recently had occasion to employ an experimental nuclear magnetic resonance (n.m.r.) spectrometer for the observation of ^{11}B spectra at 60 Mc./sec. (43.9 kgauss). The experimental spectrometer employed a cryogenic solenoid and was recently described elsewhere.¹ The very high level of resolution obtained prompts us to present results bearing on the structure of the $B_{20}H_{18}^{-2}$ ion.

The known chemistry of the $B_{20}H_{18}^{-2}$ ion and its electron balance suggest that this ion is formally composed of two $B_{10}H_9^-$ ions joined by two bonds of the three-center type.²⁻⁷ The simplest suggested structure in keeping with the known centrosymmetric³ character of $B_{20}H_{18}^{-2}$ and previously recorded³ ^{11}B n.m.r. spectra (19.3 Mc./sec.) employed two B-H-B bridge bonds as the required three-center linkages between $B_{10}H_9^-$ units.^{2,3} Each B-H-B bridge bond in this postulated structure linked an apical boron atom in one polyhedral B_{10} unit with an equatorial boron of the other B_{10} unit as in Fig. 1. The presence of a low-

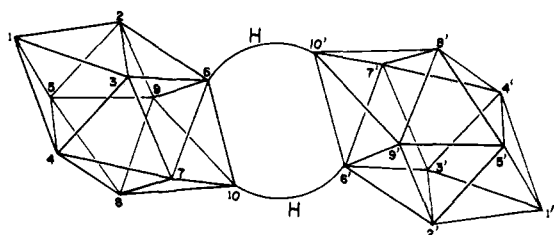


Fig. 1.—Structure of the $B_{20}H_{18}^{-2}$ ion previously proposed^{2,3} on the basis of the 19.3 Mc./sec. ^{11}B n.m.r. spectrum and the centrosymmetric character of the ion.

field singlet of area 2 in the earlier ^{11}B n.m.r. spectra was attributed to the apical boron atoms (10 and 10') involved in these B-H-B bridge bonds.³ Following this suggestion further, one would expect to observe a similar singlet of area 2 due to the B-H-B bonded equatorial boron atoms (6 and 6') in the high-field array if sufficient resolution were obtained. In addition, the high-field region should also contain four doublets of area 2:4:4:4 due to the 8-8', 7-9-7'-9', 2-3-2'-3',

- (1) *Chem. Eng. News*, **42**, No. 23, 55 (1964).
- (2) W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **47**, 1791 (1961).
- (3) A. Kaczmarek, R. Dobrott, and W. N. Lipscomb, *ibid.*, **48**, 729 (1962).
- (4) A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3218 (1962).
- (5) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin Co., New York, N. Y., 1963.
- (6) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *J. Am. Chem. Soc.*, **85**, 3704 (1963).
- (7) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *ibid.*, **85**, 3704 (1963).

and 4-5-4'-5' boron atoms, respectively. Figure 2 presents the ^{11}B spectrum of $B_{20}H_{18}^{-2}$ obtained at 60 Mc./sec. in which the high-field resonances are well resolved. Also included in Fig. 2 is the similar spectrum of $B_{20}D_{18}^{-2}$. These two spectra clearly show the high-field group to be composed of *five* doublets with areas 2:4:4:4:2 reading upfield. The greater apparent height of the area 4 singlet f in $B_{20}D_{18}^{-2}$ is attributed to a smaller line width and not to a greater intensity. The presence of only one singlet of area 2 in the spectrum of $B_{20}H_{18}^{-2}$ is not compatible with the simplest proposed structure^{2,3} unless the bridge hydrogen atoms are strongly coupled only with one type of boron atom involved in the B-H-B bridge bonds. Such strong and specific coupling interactions have not been previously observed, and it appears likely that $B_{20}H_{18}^{-2}$ may contain two B-B-B three-center linkages.

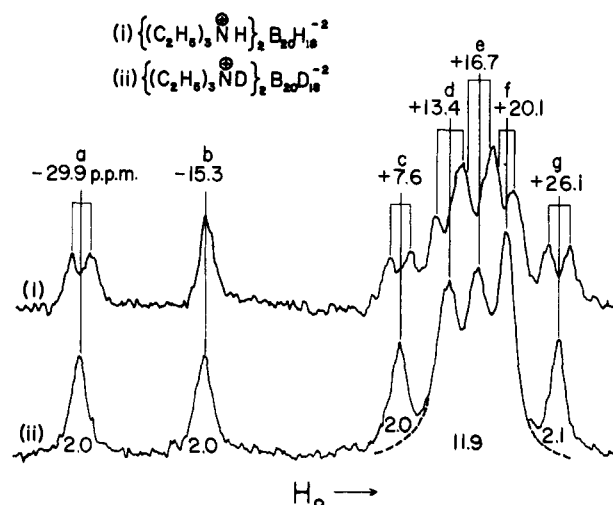


Fig. 2.— ^{11}B n.m.r. spectra at 60 Mc./sec. in acetonitrile of (i) $\{(C_2H_5)_3NH\}_2B_{20}H_{18}^{-2}$, and (ii) $\{(C_2H_5)_3ND\}_2B_{20}D_{18}^{-2}$. Chemical shifts in parts per million (p.p.m.) from $BF_3 \cdot O(C_2H_5)_2 = 0$ were extrapolated from chemical shift values obtained at 32.1 Mc./sec. for the doublet a and the singlet b. Integrated areas, normalized to give a total of 20 atoms, are indicated below the peaks.

The low-field singlet b of area 2 could equally well represent an apical or equatorial set of boron atoms which carry no terminal hydrogens, and thus two other possible $B_{20}H_{18}^{-2}$ structures based upon B-B-B linkages could be considered. Each of these structures might utilize a pair of three-center interactions, each of which involves a terminal apical or terminal equatorial orbital and an edge of the other B_{10} polyhedral located between apical and equatorial boron atoms. Thus, atoms 10 and 10' might be bonded to the 6'-10' and 6-10 edges, respectively, with preservation of the required center of symmetry.⁵ Alternatively, boron atoms 6 and 6' could be bonded with the 6'-10' and 6-10 edges, respectively. The latter model is much preferred due to the presence of more favorable angles between bonding orbitals. Either of these models would provide a strong basis for the framework fusion observed in the $B_{18}H_{22}$ hydrides^{4,8-10} and the ultra-

- (8) P. G. Simpson and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 1490 (1962).
- (9) P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 26 (1963).
- (10) P. G. Simpson, K. Folting, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 1879 (1963).