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(4) Alfred P. Sloan Research Fellow.

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Preparation and Structure of a New Boron Hydride, $B_{20}H_{16}$

Sir:

A new boron hydride, $B_{20}H_{16}$, m.p. 195–197°, has been prepared by slow passage of $B_{10}H_{14}$ and H_2 through an a.c. discharge of 1700 v. between Cu electrodes spaced 16.3 cm. apart.¹ The composition and molecular structure were established by a complete three-dimensional X-ray diffraction study.

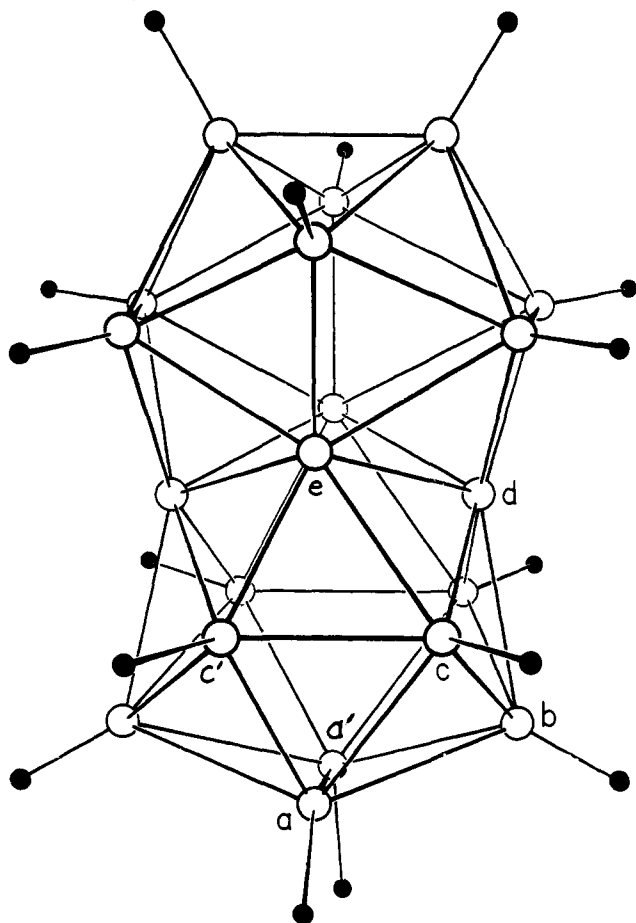


Fig. 1.—Molecular structure of $B_{20}H_{16}$. Bond distances are $a-a' = 1.76$, $a-b = 1.81$, $a-c = 1.79$, $b-c = 1.81$, $b-d = 1.76$, $c-c' = 1.78$, $c-d = 1.87$, $c-e = 1.80$, and $d-e = 1.78$, all ± 0.01 Å. The primes refer to bonded atoms related by the D_{2d} symmetry, which the molecule has within experimental error.

Beautiful single crystals, easily obtained by sublimation, were shown to be tetragonal in the space group $I4_1/acd$. There are eight molecules in a unit cell having dimensions $a = 9.65$ and $c = 29.64$ Å., and the space group requires molecular symmetry of D_2 or S_4 . The intensities were well fitted by placement of the B_{20} unit (Fig. 1) of D_{2d} symmetry of the sites of S_4 symmetry, but not at the sites of D_2 symmetry. All H atoms were located unambiguously, without chemical

(1) R. N. Grimes and W. N. Lipscomb, *Proc. Natl. Acad. Sci.*, **48**, 496 (1962).

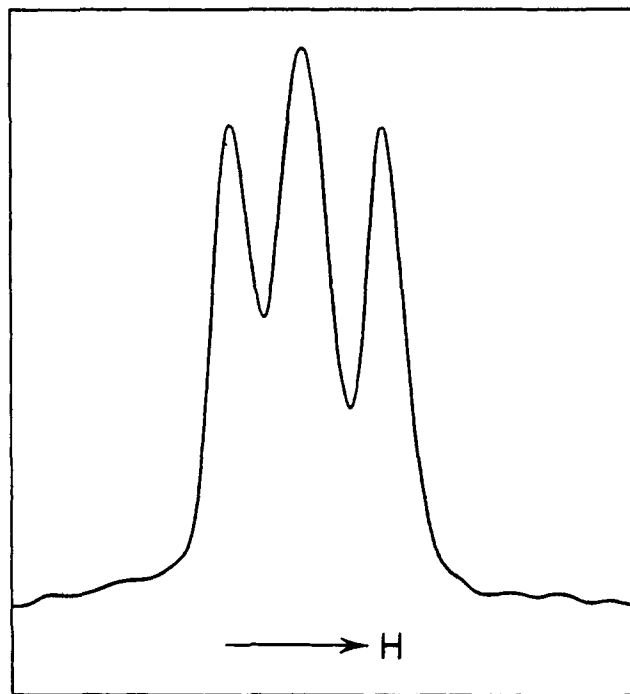


Fig. 2.— B^{11} n.m.r. spectrum of $B_{20}H_{16}$.

assumptions, in three-dimensional electron density maps from which B atoms had been subtracted. The present value of $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ is 0.143 for the 610 observations.²

These results confirm our tentative conclusions³ based upon the molecular symmetry required by the space group, the crystal density of 1.130 g. cm.⁻³ obtained while the crystal was dissolving rapidly, and the B^{11} nuclear magnetic resonance spectrum (Fig. 2) which suggested B atomic electronic environments more like those in $B_{12}H_{12}^{-2}$ rather than those in $B_{10}H_{14}$, $B_{10}H_{14}^{-2}$, or $B_{10}H_{10}^{-2}$. In particular, the B^{11} n.m.r. spectrum suggests that there are no bridge H atoms, and that some B atoms should not have terminal H atoms. However, the coupling anomaly associated^{3,4} with the apex BH_2 unit of B_5H_{11} raised sufficient doubt about the uniqueness of this interpretation of the B^{11} n.m.r. spectrum that we waited until the completion of chemical analysis by three-dimensional X-ray diffraction techniques before reporting this compound and its structure.

Further studies, now in progress, of the reactions of this compound will be reported later. It forms a strongly acid solution upon reaction with water, and, although thermally very stable, is very hygroscopic.

Acknowledgments.—We wish to acknowledge a recent private communication from E. L. Muetterties in which he reports in collaboration with N. E. Miller the independent synthesis, by pyrolysis, of $B_{20}H_{16}$ and its B^{11} n.m.r. spectrum. We also acknowledge support of this research by the National Science Foundation, the Office of Naval Research, and the National Institutes of Health. Assistance of R. N. Grimes and H. A. Beall in the experimental studies is gratefully acknowledged.

(2) If the four largest reflections, which were difficult to correlate to the same scale as the others, are omitted, and if a single parameter correction for secondary extinction is also made, R then becomes 0.107.

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

(4) L. R. Lavine and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 2087 (1953).

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A New Boron Hydride, B₂₀H₁₆

Sir:

We wish to report the synthesis and characterization of a new boron hydride, B₂₀H₁₆, which is the first example of a volatile borane that has fewer hydrogen than boron atoms.¹ Preparation was effected by catalytic pyrolysis of decaborane-14 at 350° (<1 mm.). With methylaminodimethylborane as the catalyst, yields of B₂₀H₁₆ averaged about 10%. The product was purified by repeated vacuum sublimation. The new hydride is a white, hygroscopic crystalline solid that melts at 196–199°, sublimes at 100–120° (<1 mm.), and is soluble in most common organic solvents.

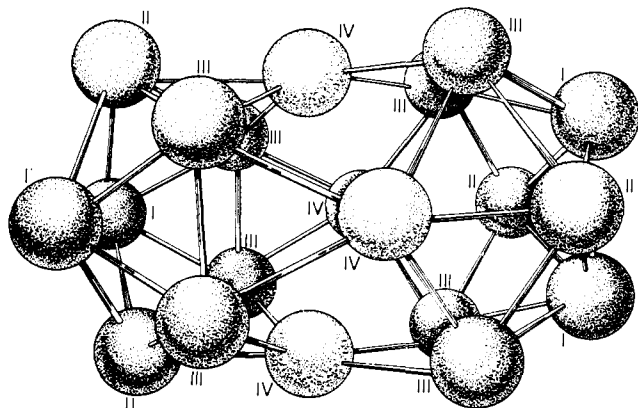


Fig. 1.—Proposed boron atom arrangement in B₂₀H₁₆. The unique boron atoms not directly bonded to hydrogen atoms are the central four atoms labeled IV.

Characterization is based on a thrice-sublimed sample of B₂₀H₁₆ which showed only one peak of any significance on gas chromatographic analysis using a 1 m. apiezon-on-firebrick column.

Anal. Calcd. for B₂₀H₁₆: B, 93.1; H, 6.9; C, 0.0; mol. wt., 232.5. Found: B, 92.9; H, 7.1; C, 0.3.

These data establish a hydrogen deficiency; the B–H ratio is about 20:16.3. Isopiestic molecular weight determinations in *n*-pentane gave values of 235 and 239 using as standards B₁₀C₂H₁₂ and azobenzene, respectively. The mass spectrum showed positive ions of every mass up to 236, and those clustered around the 100% peak at 232 were by far the most abundant. The highest mass of any significance is 236 which corresponds to ¹¹B₂₀H₁₆. Additional molecular weight data were obtained from a preliminary single crystal X-ray study (*vide infra*). With a measured density of 1.13 g./cc., the X-ray molecular weight is 231.

With the number of boron atoms determined by molecular weight and elemental analysis data, the hydrogen atom number was confirmed as 16 by aqueous acid hydrolysis. Values of 163.9 ± 0.8 and 164.4 ± 0.8 check with that of 163.4 mmoles of H₂/g. required for B₂₀H₁₆. Since B₂₀H₁₆ is diamagnetic, odd hydrogen atom numbers are excluded. Formulations as B₂₀H₁₄ and B₂₀H₁₈ fall well outside the precision and accuracy of the acid hydrolysis experiment; respective hydrolysis values would be 160.5 and 166.2 mmoles of H₂/g. Thus the B₂₀H₁₆ composition is fully established.

The infrared spectrum of B₂₀H₁₆ shows no evidence of a bridge hydrogen stretching absorption. In the spectrum of the solid (Nujol mull), the B–H stretch at

(1) L. F. Friedman, R. D. Dobrott, and W. N. Lipscomb, have independently found and characterized B₂₀H₁₆, *J. Am. Chem. Soc.*, **85**, 3505 (1963). This information was kindly given to us before publication by W. N. Lipscomb.

2600 cm.⁻¹ has just discernible fine structure. This splitting must be a crystalline lattice effect, since it is absent in solution spectra. No ultraviolet absorption maxima were detected in cyclohexane solution.

The B¹¹ n.m.r. spectrum at 19.2 Mc. in CCl₄ solution consists of three peaks of unequal intensity at +7.8, +18.5, and +27.4 p.p.m.² On irradiation of the hydrogen nuclei at 60 Mc., the peak at +7.8 p.p.m. was not significantly altered, indicating these boron atoms are not directly bonded to hydrogen. On sweeping with the saturating proton field, two other boron resonances are detected at +15.6 and +22.4 p.p.m. Relative intensities in the decoupled B¹¹ spectra are ~4, 4, and 12 for the 7.8, 15.6, and 22.4 resonances, respectively.

X-Ray studies have shown the crystals to be tetragonal with the cell dimensions of *a* = 9.60 ± 0.05 Å. and *c* = 29.4 ± 0.1 Å. and space group I4₁/acd. There are eight molecules per unit cell and the required molecular symmetry is $\bar{4}$ or 222.

The X-ray and n.m.r. data indicate a model of D_{2h} symmetry formed by joining two decaborane cages so that the 6 and 9 boron atoms of each decaborane cage contact the 5,10 and 7,8 boron atoms of the other cage (Fig. 1). Four boron atoms in the center plane are not bonded to hydrogen in agreement with analysis of the B¹¹ n.m.r. spectrum.³

The chemistry of this novel boron hydride is under study. We have established that B₂₀H₁₆ dissolves with reaction in water. No hydrogen is evolved and a strongly acidic solution is generated. The titration curve of the aqueous solution is typical of that of a strong acid. Equivalent weight determined by titration was 116 ± 2 indicating that the species in solution is a diprotic acid.

Acknowledgments.—We wish to thank Dr. John Whitney for the X-ray data, and Mr. W. B. Askew and Mr. R. J. Berndt for the mass spectral information.

(2) Trimethyl borate external reference.

(3) In the model in Fig. 1, there is a total of 4 boron atom environments. This requires accidental coincidence of two boron chemical shifts. B¹¹ n.m.r. assignments are I (or II), 15.6 p.p.m.; II (or I) and III, 22.4 p.p.m.; and IV, 7.8 p.p.m.

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Reactions of Unsaturated Free Radicals with Nitric Oxide. Radical-Induced Scission of Carbon–Carbon Triple Bonds

Sir:

We have recently examined the gas phase reactions, at room temperature, of nitric oxide with vinyl and substituted vinyl radicals, where the radicals were formed *in situ* by the addition of an inducer radical (Y·) to an alkyne (X–C≡C–Z). The results suggest a new family of free-radical reactions involving degradation, at the triple bond, of the parent alkynyl structure. The general reaction to be exemplified may be written

