ably reliable generalizations. Apical protons are found 0.7 to 1.2 p.p.m. to higher field than tetramethylsilane, whereas basal B–H protons are located 3.6 to 3.0 p.p.m. to lower field. Bridge hydrogens and skeletal C–H protons are found in the regions +2.3 to +2.6 p.p.m. and −6.4 to 5.7 p.p.m., respectively. Approximate "effective" shielding constants[18] for the various carborane groups bonded at a skeletal carbon atom to an alkyl group are: 2,3-dicarbahexaboranyl(8)-, 1.8; 1,6-dicarbaclovohexaboranyl(6)-, 1.1; 2,4-dicarbaclovoheptaboranyl(7)-, 1.8.

Acknowledgments.—The authors wish to express their gratitude to the Office of Naval Research for financial support to this research. They also thank Drs. R. E. Williams and J. Spielman for stimulating and helpful discussions.

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Chemistry of Boranes. XXI.[1] Icosaborane-16[2,3]

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A new volatile boron hydride, icosaborane-16 ($B_{20}H_{16}$), has been synthesized by catalytic pyrolysis of decaborane-14. Icosaborane-16 reacts irreversibly on dissolution in water and in alcohol to form the $B_{20}H_{16}(OH)_2{}^{2-}$ and $B_{20}H_{16}(OC_2H_5)_2{}^{2-}$ ions, respectively. Formally related to these dianions is a class of adducts of the type $B_{20}H_{16}\cdot 2$base which are formed in the reaction of icosaborane-16 with Lewis bases.

Preparation of Icosaborane-16.—Pyrolysis of decaborane-14 at 350° in the presence of methylaminodimethylborane catalyst yields hydrogen, nonvolatile materials, and the icosaborane-16, $B_{20}H_{16}$. Synthesis conditions are quite critical. Short contact times are necessary and oxygen in trace amounts inhibits icosaborane-16 formation. Our best conversions and yields have been in the range of 10 and 15%, respectively, which is superior to the discharge synthesis.[3]

Icosaborane-16 was purified by repeated vacuum sublimation. A rigorous purification was effected by a gas chromatographic procedure. The melting point of icosaborane-16 is 196–199°.

Characterization of Icosaborane-16.—As reported in the original communication,[2] the composition of this new hydride was uniquely determined by a combination of analytical and spectroscopic data. This was an independent solution to the unique characterization provided by the complete crystal structure determination.[3,4] The molecular weight was established fairly precisely from the mass spectrum, unit cell dimensions and density, and isopiestic studies. The B:H ratio was determined precisely from analysis, hydrolytic hydrogen, and B^{11} n.m.r. data. The basic arguments for the characterization were presented[2] earlier, and the complete data are in the Experimental section of this paper.

All of our spectroscopic data[2] suggest the structure presented in Fig. 1, and this is the unique solution obtained from the crystal structure analysis.[3,4]

Derivatives of Icosaborane-16.—Icosaborane-16 dissolves in water with reaction to generate an acidic solution that titrates as a strong acid and gives a neutral equivalent one-half the molecular weight of icosaborane-16. This reaction is irreversible. Removal of solvent water at 25° under vacuum gave $B_{20}H_{16}\cdot 4H_2O$. Attempts to dehydrate this species led to degradation of the B_{20} cage. The tetrahydrate is formulated as the hydronium salt of $B_{20}H_{16}(OH)_2{}^{2-}$ since neutralization with tetraalkylammonium hydroxide gave the corresponding salts of $B_{20}H_{16}(OH)_2{}^{2-}$. These salts behave as strong 2:1 electrolytes. The $B_{20}H_{16}(OH)_2{}^{2-}$ anion slowly hydrolyzes in water; a 0.04 *N* aqueous solution was 3% decomposed in 2 weeks time.

The structure of the $B_{20}H_{16}(OH)_2{}^{2-}$ ion has not been established. However, the strong acceptor properties of icosaborane-16 unquestionably originate at the four unique boron atoms (IV in Fig. 1) which are not bonded to hydrogen. These should be the sites of nucleophilic attack, and it is reasonable to presume that in $B_{20}H_{16}(OH)_2{}^{2-}$ the OH groups are bonded to two of these boron atoms, probably to *trans* boron atoms. The B^{11} n.m.r. spectrum of $B_{20}H_{16}(OH)_2{}^{2-}$ solutions is a broad multiplet centered at about +33 p.p.m. This multiplet shifts to higher fields on addition of acid, and the general contour changes slightly. Because of the small chemical shifts, no structural conclusions can be made from these data, nor from the proton-decoupled B^{11} spectra.

Icosaborane-16 reacts with ethanol in an analogous fashion to that with water. From these solutions,

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(1) Paper XX: H. C. Miller, N. E. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1456 (1964).

(2) This chemistry was first described in a communication: N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3506 (1963).

(3) Icosaborane-16 was prepared independently by L. F. Friedman, R. D. Dobrott, and W. N. Lipscomb, *ibid.*, **85**, 3505 (1963).

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salts of the $B_{20}H_{16}(OC_2H_5)_2^{2-}$ anion were isolated and characterized. Thus, it would appear that there is a class of ions of the type $B_{20}H_{16}X_2^{2-}$ in which the basic icosaborane-16 framework is retained. These ions are not structurally related to $B_{20}H_{18}^{2-}$, $B_{20}H_{17}(OH)^{2-}$, and $B_{20}H_{16}(OH)_2^{2-}$, which are based on polyhedral B_{10} cages joined by two- or three-center bonds.[5-7] The nonidentity of the two dihydroxy species is readily shown by comparison of ultraviolet, n.m.r., and infrared spectra.

Lewis bases react exothermally with icosaborane-16 to give adducts of the composition $B_{20}H_{16}\cdot 2$base. Such behavior was established for amines, sulfides, ethers, and phosphines. These $B_{20}H_{16}$ derivatives are probably structural analogs of the anionic species $B_{20}H_{16}(OH)_2^{2-}$ and $B_{20}H_{16}(OC_2H_5)_2^{2-}$.

Experimental

Materials.—Trimethylboron was prepared from boron trifluoride (Matheson) and methy magnesium bromide (Arapahoe Chemical) in *n*-butyl ether[8] and purified by distillation in a low-temperature still packed with "Heli-Pak" helices (0.35 × 0.070 × 0.070 in.), b.p. −21 to −17°.

The catalyst, $CH_3NHB(CH_3)_2$, was then prepared from trimethylboron and methylamine (Matheson, anhydrous). A 145-ml. stainless-steel pressure reactor was evacuated, charged with 73 mmoles of trimethylboron and 73 mmoles of methylamine, closed, and heated at 310° for 2 hr.[9] The cylinder contents were then opened to traps maintained at −95° and −196°. The contents of the −95° trap were distilled in an 8-in. packed microcolumn (b.p. 37–37.5°).

Decaborane-14 (Olin Mathieson) was recrystallized from *n*-hexane. Tetramethyl- and tetraethylammonium hydroxides (Eastman) were used without further purification. Ethyl ether (Merck, reagent) was dried over sodium ribbon.

Apparatus.—Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer Model 21 spectrophotometer. Visible and ultraviolet absorption data were secured with a Cary Model 14 spectrometer. Magnetic resonance spectra were observed on a Varian Model V4300 spectrometer. Double irradiation was accomplished with an NMR Specialties Model SD 60 spin decoupler (B^{11} saturation by 19.2 Mc. irradiation while observing H^1 at 60 Mc., and H^1 saturation by 60 Mc. irradiation while examining B^{11} at 19.2 Mc.). H^1 chemical shifts are referred to tetramethylsilane (internal reference), and B^{11} chemical shifts to trimethyl borate (external reference).

Preparation of Icosaborane-16.—A schematic diagram of the apparatus employed for the synthesis of icosaborane-16 is shown in Fig. 2. The pyrolysis was conducted in a 25-mm. diameter Pyrex tube, heated over a 6-in. length with a ceramic furnace, subjected to continuous evacuation by mercury-vapor and mechanical pumps. Decaborane-14 was admitted from a stainless steel cylinder and inlet system maintained at 100°. The decaborane cylinder employed a packless bellows valve, since all packed valves developed leaks at the packing on standing at 100° for short periods. The catalyst inlet system was equipped with a set of solenoid valves periodically activated so that valve 1 opened briefly, followed by brief opening of valve 2. Both valves then remained closed for preset periods of time which could be varied from 0.5 to 60 min. Good yields were achieved with fresh catalyst admitted every 8 min. from a catalyst supply maintained at 0°. Initially the vapor pressure of fresh catalyst at 0° is 193 mm. As the catalyst stood for prolonged periods, its vapor pressure diminished, apparently due to polymerization.

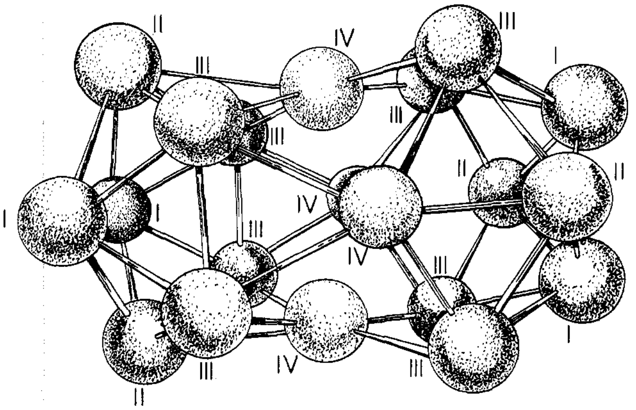

Fig. 1.—Structure of icosaborane-16.

Variation of catalyst supply showed that no icosaborane-16 was formed in the absence of catalyst; once the system was exposed to catalyst, product formation continued for nearly 1 hr. after the catalyst supply had been closed. Excess catalyst appeared to lower yields. Catalyst recovered in the cold traps possessed an infrared spectrum nearly the same as that of freshly prepared $CH_3NHB(CH_3)_2$.

The product deposited as a yellowish solid just outside the hot zone of the pyrolysis tube and was purified by repeated sublimation. In the best runs, conversions of up to 0.1 g./hr. and yields up to 10% were obtained at a pyrolysis temperature of 350°. Other products included hydrogen and a nonvolatile, brown-black solid found in the hot zone of the tube. The presence of oxygen, even in trace amounts, prevented formation of icosaborane-16.

Characterization of Icosaborane-16.—The crude product on repeated vacuum sublimations at 100–120° left traces of residue and yielded icosaborane-16 as a white, hygroscopic, crystalline solid. Elemental analyses on a triply-sublimed sample were in agreement with the proposed formulation.

Anal. Calcd. for $B_{20}H_{16}$: C, 0.0; H, 6.9; B, 93.0. Found: C, 0.3, 0.3; H, 7.1, 7.2; B, 92.9, 92.5.

Icosaborane-16 melts without significant decomposition at 196–199° in a sealed, evacuated capillary and is soluble in carbon tetrachloride, paraffinic hydrocarbons, and alcohols. Molecular weight determinations by the isopiestic method yielded values of 239 and 235, using azobenzene and dicarbaclovodecaborane-12, respectively, as standards and pentane as solvent (calcd. for $B_{20}H_{16}$, 232).

Gas chromatographic analysis on a 1-m. Apiezon (20%) firebrick (60–80 mesh) column at 175–260° showed trace peaks at 0.3 and 12.5 min. and a large peak at 14.55 min. The mass spectral analysis of the material from the major chromatographic cut provided further molecular weight data. The fragmentation pattern included peaks up to *m/e* 236 (calcd. for $B^{11}{}_{20}H_{16}$, 236). There were peaks of low intensity at *m/e* 246 and 260; however, these varied in intensity with sample and were essentially absent in one gas chromatographic cut.

Additional molecular weight data were obtained by Dr. John Whitney from a single crystal X-ray study. With a floatation density of 1.13 g./cc., the X-ray molecular weight is 231. These studies have established the crystals to be tetragonal with cell dimensions of $a = 9.60 \pm 0.05$ and $c = 29.4 \pm 0.1$ Å. and space group $I4_{1/acd}$. There are eight molecules per unit cell and the required molecular symmetry is $\bar{4}$ or 222. These data agree with those of Dobrott, Friedman, and Lipscomb.[4]

Complete hydrolysis established the number of hydrogen atoms in icosaborane-16.[10] Samples of approximately 30 mg. of icosa-

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(10) This hydrolysis technique was suggested by H. C. Miller, personal communication.

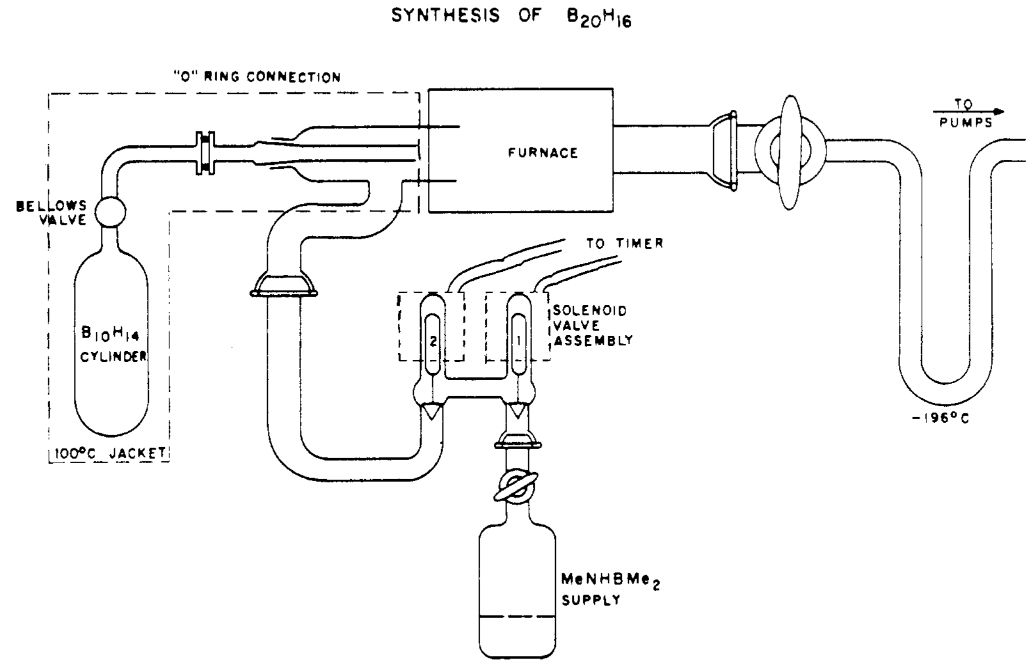

Fig. 2.—Apparatus employed for synthesis of icosaborane-16.

borane-16 in a platinum boat were placed in the side arm of a Kjeldahl-shaped reaction vessel equipped with a water condenser. The vessel, containing 0.1 g. of platinum black (Englehard Industries) and 20 ml. of 4 *N* hydrochloric acid, was then cooled to $-196°$ and evacuated to less than 1 μ. The aqueous acid was then allowed to melt, and the platinum boat dislodged from the side arm into the acid, initiating hydrogen evolution. The volume of the system was such that, on complete hydrolysis, the total pressure approached, but did not exceed, 760 mm. The reaction mixture was heated at reflux until no increase in pressure was noted for 15 min. The hydrolysis mixture was cooled to $-196°$ and the generated gas passed through a liquid nitrogen trap to a known volume with a Toepler pump. Hydrolytic hydrogen values of 163.8 ± 0.8 and 164.4 ± 0.8 mmoles/g. were obtained using 31.6 and 31.2 mg. samples, respectively (calcd. for $B_{20}H_{16}$, 163.5 mmoles/g.). The final solutions did not reduce aqueous silver ion.

Spectra of Icosaborane-16.—The infrared spectrum of $B_{20}H_{16}$ as a Nujol mull (Fig. 3) has a strong terminal B–H stretching frequency at 2600 cm.$^{-1}$. The splitting in the BH stretching frequency (as a Nujol mull) is primarily a solid-state phenomenon, since there is only a weak shoulder at 2570 cm.$^{-1}$ in carbon tetrachloride solution. Other bands in the Nujol mull are at 960 (s), 915 (w), 890 (w), 870 (m), 840 (w), 790 (m), 765 (w), and 720 (s, triplet) cm.$^{-1}$.

The H^1 magnetic resonance spectrum at 60 Mc. of icosaborane-16 in carbon tetrachloride was an approximately equivalent but unequally spaced broad quartet spanning 600 c.p.s. On simultaneous irradiation at 19.2 Mc., the quartet collapsed to a nearly equivalent doublet at -3.42 and -2.75 p.p.m. The upfield singlet was perceptibly more broad. The B^{11} n.m.r. spectrum at 19.2 Mc. consisted of three broad peaks of relative intensities 1:1.3:1 at +7.8, +18.5, and +27.3 p.p.m. (Fig. 4). On effective decoupling of the hydrogen atoms by simultaneous irradiation at 60 Mc., the peak at +7.8 p.p.m. was not significantly altered (Fig. 4b), indicating that these boron atoms are not directly bonded to hydrogen atoms. On sweeping with the saturating proton field, two other boron resonances were detected at +15.6 and +22.4 p.p.m. Relative intensities in Fig. 4b are approximately 4, 4, and 12 for the resonances at +7.8, +15.6, and +22.4 p.p.m., respectively. On varying the decoupling frequency slightly (Fig. 4c) the low-field peak again remained unchanged. This peak continued to account for one-fifth of the total boron (A/B = 1/4). The B^{11} resonance data indicate that there are at least three types of boron atoms in addition to those four boron atoms not bonded to hydrogen.

There were no maxima in the ultraviolet spectrum of a solution of 0.84 mg. of $B_{20}H_{16}$ in 10 ml. of cyclohexane; however, there was end-absorption beginning at about 350 mμ.

Reaction with Water.—Icosaborane-16 dissolved in water without evolution of gas to yield a strongly acidic solution. Titration of the latter with 0.1 *N* aqueous sodium hydroxide yielded a curve typical of the neutralization of a strong acid. The equivalent weights observed in two titrations (end point at pH 6–6.5) were 116.3 ± 1 and 117 ± 1. Addition of aqueous silver nitrite to the solution immediately gave a white precipitate which rapidly darkened.

$(H_3O)_2B_{20}H_{16}(OH)_2$.—Icosaborane-16 (1.0 g., 4.27 mmoles) was dissolved in 80 ml. of water and the resultant solution was filtered. Evaporation to dryness by vacuum pumping through a $-196°$ trap for 2 days left an extremely hygroscopic, white solid.

Anal. Calcd. for $(H_3O)_2B_{20}H_{16}(OH)_2$: H, 7.92; B, 71.0. Found: H, 8.09, 7.93; B, 70.2, 72.1.

Infrared absorptions as a Nujol mull included the following: 3600 (s), 2625 (m, shoulder), 2550 (s), 1675 (m), 1600 (m), 1300 (m), 1150 (m), 1090 (s), 975 (s, br), and 890 (m) cm.$^{-1}$.

The B^{11} resonance spectrum at 19.2 Mc. in acetonitrile consisted of a broad absorption with peaks at +6.8, +20.8, +28.6, +38.3, and +48.2 p.p.m. from trimethyl borate. The peak at +28.6 p.p.m. was the most intense.

Irreversibility of this reaction with water was indicated by the observation that icosaborane-16 could not be regenerated either by standing in the presence of phosphoric anhydride or by thermal treatment. Heating $B_{20}H_{24}O_4$ to 150° in a closed, evacuated system caused hydrogen evolution and left a tan, intractable residue. No sublimate was formed.

$[(CH_3)_4N]_2B_{20}H_{16}(OH)_2$.—Doubly-sublimed icosaborane-16 (1.5 g., 6.5 mmoles) was dissolved in 70 ml. of water. The solution was filtered and titrated potentiometrically to pH 7 with an aqueous solution of tetramethylammonium hydroxide (0.05 g./ml.). Upon initiation of the titration, a precipitate formed which dissolved as the pH rose toward the neutralization point. The solution was evaporated under vacuum at room temperature, then dried at 80° over phosphoric anhydride for 2 days. The infrared spectrum of the resultant solid included absorptions at 3700 (m), 3450 (m), 2550 (s, sh), 2500 (s), 1380 (s), 1100 (m, br), 1000 (m), 980 (m), and 950 (s) cm.$^{-1}$.

Anal. Calcd. for $[(CH_3)_4N]_2B_{20}H_{16}(OH)_2$: C, 22.2; H, 10.5;

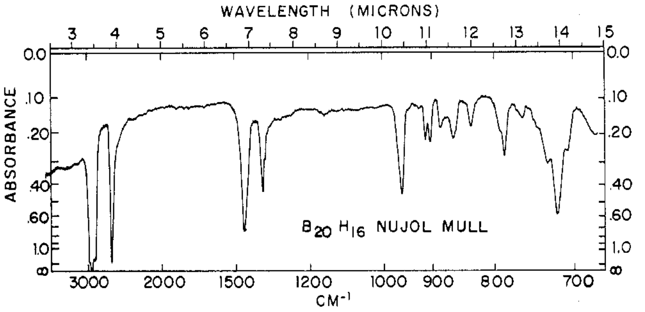

Fig. 3.—Infrared absorption spectrum of icosaborane-16.

N, 6.47; B, 49.9. Found: C, 22.9; H, 10.5; N, 6.74; B, 50.6.

The B^{11} resonance spectrum consisted of absorptions at +12.7, +20.2, +33.6, and +37.2 p.p.m. in acetonitrile. That at +33.6 p.p.m. was by far the most intense. Proton resonance measurements in deuterated dimethyl sulfoxide showed a sharp singlet due to the methyl group at −2.9 p.p.m. and the hydroxy singlet at −2.0 p.p.m.

A molecular weight determination by freezing point in dimethyl sulfoxide yielded 185 (calcd., 414), indicating partial, but not complete, ionization.

Conductivity measurements were made on $[(CH_3)_4N]_2B_{20}H_{16}(OH)_2$ by Dr. Y. T. Chia. The salt (0.8393 g.) was diluted to 100 ml. with conductivity water, to give a 4.093×10^{-2} *N* solution. This solution was then diluted to 9.771×10^{-3} *N* and titrated. The conductivity curve obtained from the data in Table I was characteristic of a 2:1 electrolyte. The linearity of the plot indicated a high degree of purity. Only an impurity with an equivalent conductance very close to that of the major constituent could be present. Boric acid does not possess an appropriate equivalent conductance value.

TABLE I

CONDUCTANCE OF AQUEOUS SOLUTIONS OF $[(CH_3)_4N]_2B_{20}H_{16}(OH)_2$

Concn., *N*	Equiv. conductance, ohm.$^{-1}$ cm.^{2} equiv.$^{-1}$
1.031×10^{-4}	94.18
1.042×10^{-3}	89.67
2.140×10^{-3}	85.71
3.438×10^{-3}	82.47
5.648×10^{-3}	79.02
7.542×10^{-3}	76.74
9.771×10^{-3}	74.60

Two 10-ml. portions of the original solution were run through a strongly acidic exchange column and titrated with 0.1003 *N* sodium hydroxide. Neutralization was accomplished with 4.079 ml. of the base, indicating an equivalent weight of 205.2 for the salt (calcd. for $[(CH_3)_4N]_2B_{20}H_{16}(OH)_2$, 207). The second titration was made 6 hr. after the first, yet the curves were superimposable, ruling out any significant decomposition of the salt in aqueous solution under these conditions.

The stability of the solution was further studied by titration of an aliquot from the 4.093×10^{-2} *N* solution for boric acid after 1 week and after 2 weeks. After 1 week, there was 0.45 mg. of boric acid per ml. (7.3×10^{-3} *M* in boric acid) in the solution which had originally contained 83.93 mg. of $[(CH_3)_4N]_2B_{20}H_{16}(OH)_2$ per ml. After a second week, hydrolysis had increased markedly, there being 1.65 mg. of boric acid per ml. of solution (2.7×10^{-2} *M*).

The infrared spectrum of $[(CH_3)_4N]_2B_{20}H_{16}(OH)_2$ remained unchanged after heating the salt at 150° for 1.5 hr. Noncondensable gases were evolved at 200°; however, the infrared spectrum of the yellow residue after 16 hr. at 200° was generally unchanged, but with loss of definition. Further heating at 300° (3 hr.) and 350° (1 hr.) caused more hydrogen evolution and left a grossly decomposed residue.

$[(C_2H_5)_4N]_2B_{20}H_{16}(OH)_2$.—A solution of 1.5 g. (6.7 mmoles) of $B_{20}H_{16}$ in 70 ml. of water was filtered and titrated to pH 7 with aqueous tetraethylammonium hydroxide. The neutral solution was then evaporated to dryness at room temperature and vacuum dried over phosphoric anhydride at 80° for 2 days.

Anal. Calcd. for $[(C_2H_5)_4N]_2B_{20}H_{16}(OH)_2$: C, 36.3; H, 11.1; B, 41.2; N, 5.32. Found: C, 35.3; H, 11.1; B, 40.1; N, 5.36.

The infrared pattern consisted of the following absorptions: 3650 (m), 3450 (m), 2550 (s, sh), 2500 (vs), 1170 (s), 1120 (m), 1080 (m), 1000 (s), 975 (m), 950 (m), and 780 (m) cm.$^{-1}$. The salt did not melt on heating to 400° in a sealed, evacuated capillary. The molecular weight by freezing point depression in dimethyl sulfoxide was 216 (calcd. for $[(C_2H_5)_4N]_2B_{20}H_{16}(OH)_2$, 526), indicating partial, but not complete, ionization.

$B_{20}H_{16} \cdot 3.5(C_2H_5OH)$.—Icosaborane-16 (1.0 g., 4.3 mmoles) was dissolved in 70 ml. of absolute ethanol. The clear solution was filtered, then evaporated under vacuum to a liquid nitrogen trap for 2 days.

Anal. Calcd. for $B_{20}H_{16} \cdot 3.5(C_2H_5OH)$: C, 21.4; H, 9.48; B, 54.9. Found: C, 21.2, 21.3; H, 9.62, 9.57; B, 54.7, 54.6.

The infrared spectrum was broad, with peaks at 2590 (m), 2500 (s), 1150 (s, br), and 950 (s, br) cm.$^{-1}$. The B^{11} resonance spectrum in acetonitrile showed peaks at +1.6, +20.3, +28.1 (strongest), +38.0, and +48.2 p.p.m.

$Cs_2B_{20}H_{16}(OC_2H_5)_2$.—A solution of 1.1 g. (4.7 mmoles) of icosaborane-16 in 70 ml. of absolute ethanol was filtered and allowed to stand at room temperature for 3 hr. It was then titrated to pH 7 with 25% aqueous cesium hydroxide. The solution was cooled to 0° and the precipitate filtered off. The solid was air-dried, then dried under vacuum over phosphoric anhydride at 80° for 1 day. The infrared pattern, as a Nujol mull, included the following absorptions: 3500 (s), 2460 (s), 1575 (m), 1290 (m), 1170 (s), 1130 (s), 1040 (m), and 1000 (m) cm.$^{-1}$.

Anal. Calcd. for $Cs_2B_{20}H_{16}(OC_2H_5)_2$: C, 8.17; H, 4.45; B, 36.7. Found: C, 7.10; H, 4.76; B, 37.0.

$B_{20}H_{16} \cdot [O(C_2H_5)_2]_2$.—Diethyl ether (250 ml.) was added with stirring to a solution of 0.84 g. (3.6 mmoles) of icosaborane-16 in 175 ml. of pentane. A white solid formed. The mixture was

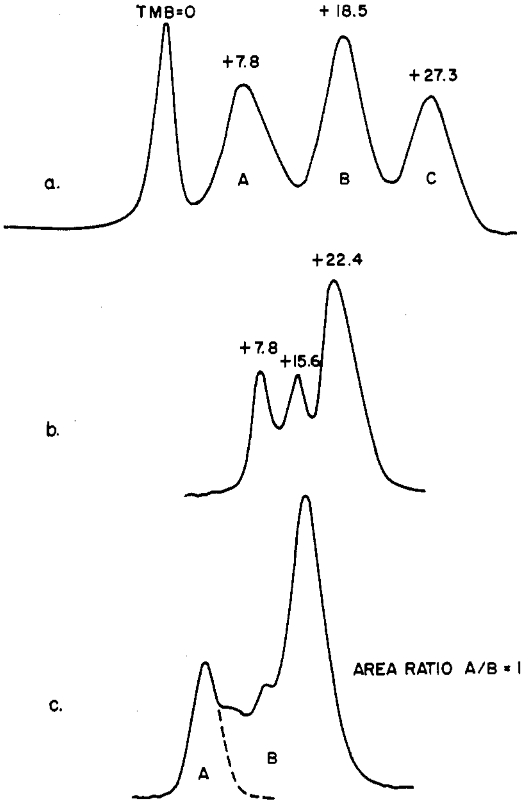

Fig. 4.—B^{11} resonance spectra of icosaborane-16 in CCl_4: (a) at 19.2 Mc., (b) simultaneous irradiation at 60 Mc., and (c) also doubly irradiated, slight difference in H^1 irradiation.

stirred overnight in an inert atmosphere. The white solid was filtered off, washed with pentane to remove any unchanged starting material, and dried by pumping at room temperature. The product is soluble in acetone and acetonitrile, moderately soluble in carbon tetrachloride.

Anal. Calcd. for $B_{20}H_{16}\cdot[O(C_2H_5)_2]_2$: C, 24.9; H, 9.45; B, 56.2. Found: C, 24.8; H, 9.89; B, 55.7.

Infrared absorptions as a Nujol mull included: 3550 (w), 2600 (s, sh), 2525 (s), 1330 (m), 1280 (m), 1140 (m), 1090 (s), 1050 (m), 1010 (s), 970 (s), 960 (s), 930 (s), and 790 (m) cm.$^{-1}$. When heated at 125° under vacuum, the solid decomposed, as confirmed by the infrared spectrum of the residue.

Molecular weight determinations by osmometry in acetonitrile yielded 356 on the basis of a curve plotted with three points (calcd. for $B_{20}H_{16}\cdot[O(C_2H_5)_2]_2$, 380.6).

The B^{11} resonance pattern in acetonitrile showed a broad weak absorption centered at +10.1 p.p.m. and a group of four peaks at +20.8, +27.8, +34.8, and +41.4 p.p.m. In deuterated dimethyl sulfoxide, the H^1 resonance spectrum consisted of a methyl multiplet at −1.3 p.p.m. and a methylene multiplet at −3.8 p.p.m. No protons bonded to boron were observable. Double irradiation at 19.2 Mc. gave rise to a new broad peak at −2.0 p.p.m.

$B_{20}H_{16}\cdot[N(CH_3)_3]_2$.—Anhydrous trimethylamine was bubbled through a solution of 0.63 g. of icosaborane-16 in 200 ml. of pentane kept under nitrogen. A yellow precipitate formed at once. After the amine had been admitted for 2 hr. at room temperature, the precipitate was filtered off and recrystallized from acetonitrile.

Anal. Calcd. for $B_{20}H_{16}\cdot[N(CH_3)_3]_2$: C, 20.5; H, 9.76; B, 61.6; N, 8.05. Found: C, 20.8; H, 9.66; B, 59.6; N, 8.30, 8.42.

Infrared absorptions occur at 3600 (m), 3200 (m), 2550 (s), 1310 (m), 1260 (m), 1100 (s), 980 (s), 850 (m), 800 (m), and 720 (m) cm.$^{-1}$. H^1 resonance measurements in acetonitrile showed a singlet at −2.7 p.p.m.

$B_{20}H_{16}\cdot[P(C_6H_5)_3]_2$.—A solution of 0.1 g. of icosaborane-16 in 30 ml. of pentane was mixed at room temperature with a solution of 0.5 g. of triphenylphosphine in 50 ml. of pentane in an inert atmosphere. A white precipitate formed at once. After the solution had been stirred for 0.5 hr., the precipitate was collected.

Anal. Calcd. for $B_{20}H_{16}\cdot[P(C_6H_5)_3]_2$: C, 57.2; H, 6.13; B, 28.6; P, 8.19. Found: H, 6.66; B, 30.8; P, 7.30.

Infrared absorptions included 2550 (s), 1190 (w), 1160 (m), 1100 (s), 995 (m), 930 (w), 740 (s), 720 (s), and 690 (s) cm.$^{-1}$. The H^1 resonance spectrum in acetonitrile showed a broad singlet at −7.3 p.p.m.

$B_{20}H_{16}[S(CH_3)_2]_2$.—Dimethyl sulfide (25 ml.) was added with stirring to a solution of 0.84 g. (3.6 mmoles) of icosaborane-16 in 175 ml. of pentane. A white solid formed. The mixture was stirred for 2 hr. in an inert atmosphere. The solid was filtered off, washed three times with pentane, and recrystallized from acetonitrile.

Anal. Calcd. for $B_{20}H_{16}\cdot[S(CH_3)_2]_2$: C, 13.4; H, 7.91; B, 60.6; S, 18.0. Found: C, 13.4; H, 7.91; B, 59.8; S, 17.4.

Infrared absorptions included 2640 (s, sh), 2550 (s), 1090 (m), 1040 (m), 970 (s), 925 (m), and 840 (w) cm.$^{-1}$.

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Polarization and Complexation Effects in Solutions of Borazine Derivatives

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Polarization measurements were made on solutions of hexamethylborazine in *n*-heptane, *p*-xylene, and hexafluorobenzene at 25°, in benzene at 15, 20, and 25°, and on the pure substance from 29.8 to 104.9°. The data suggest that the hexamethylborazine molecule is nonpolar and that the apparent dipole moment for the molecule arises from large values of the atom polarization. The absence of significant solute–solvent interaction in these systems is also suggested by spectral studies.

Although X-ray, electron diffraction, and infrared spectral studies indicate that the borazine ring is planar and has D_{3h} symmetry,[1] the results of two polarization investigations suggest that this ring system possesses a dipole moment significantly greater than zero. On the basis of the earliest measurement (gas phase),[2] borazine was assigned a dipole moment of 0.67 D.; however, there is evidence that the sample had undergone partial decomposition, rendering this measurement suspect. More recently, dipole moments in the range 0.2–0.7 D. were obtained for borazine and six of its derivatives in benzene.[3] The moments were attributed to either the nonplanarity of the borazine ring or very low-frequency molecular vibrations which cause high atomic polarizations. The possibility that the moments are due to π-complexation between the solute and solvent molecules, as occurs in benzene solutions of iodine,[4] was not considered.

Experimental

Materials.—Hexamethylborazine was prepared in 85% yield by the reaction of B-trichloro-N-trimethylborazine (prepared from boron trichloride and methylammonium chloride[5–7]) with methylmagnesium bromide; m.p. 98.9–99.3° (cor.). The ultraviolet spectrum of hexamethylborazine in *n*-heptane is featureless above 230 mμ and the infrared spectra of benzene, carbon tetra-

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