other reported crystal modifications,[4] suggests that the massive amorphous boron deposit is possibly a microcrystalline deposit of β-rhombohedral boron. Some evidence for this hypothesis is presented in the series of X-ray diffraction patterns of heated silica-core filaments summarized in Table II. Since the X-ray diffraction pattern of boron in these filaments was not partially obscured by the lines due to tungsten borides in the core, a clear picture of the initial stages of development of crystalline boron was obtained. In pattern A the diffuse halos at *d* spacings of 4.4, 2.5, and 1.4 A are characteristic of massive amorphous boron. In pattern B sharp lines at *d* spacings of 2.58 and 2.40 A, clearly associated with the 2.5-A halo and part of the β-rhombohedral pattern[11] illustrated in pattern F as obtained in this work, have appeared as a result of heating the filament at 950° for 30 min. A differentiation of the 1.4-A halo is apparent in pattern C, and sharp lines in the vicinity of the 4.4-A halo appear in the filament heated at 1000° for 5 min. The stepwise development of the β-rhombohedral diffraction pattern is clearly indicative of recrystallization and grain growth and suggests that the massive amorphous boron may be a microcrystalline deposit of β-rhombohedral boron.

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The Interaction of Iodine with Aminoboranes

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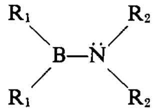
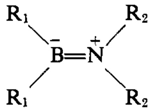
Abstract: The spectra of solutions containing mixtures of piperdinodimethylborane, (dimethylamino)dimethylborane, or (dimethylamino)di-*n*-propylborane with iodine in carbon tetrachloride exhibit absorption bands in the near-ultraviolet region that are not characteristic of either of the components and are assigned to complexes. The intensities of these bands depend upon the mole ratio of the components. The values of the equilibrium constants and heats of formation of these complexes, determined from spectral data, indicate that the aminoboranes act as amine donors rather than π donors toward iodine in these complexes.

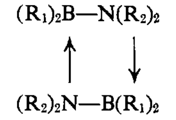
Although the B–N bond in aminoboranes (I) is isoelectronic with the carbon–carbon double bond, there is only indirect evidence that electron delocalization (II) occurs in these systems. The position of the B–N stretching mode in the infrared spectra of aminoboranes is dependent upon the nature of the substituents and occurs over a wide range of frequencies (1300–1500 cm^{-1}).[2] Several attempts have been made to relate the degree of double bond character of the B–N bond to the frequency of this absorption;[2] the absorption at lower energies has been assigned to a B–N single bond suggesting that the electron pair is localized (I) in this type of compound. In addition, many aminoboranes are dimeric,[2b,d] the dimers presumably forming by intermolecular N–B bonding (III). In the case of (dimethylamino)dimethylborane (II, $R_1 = R_2 = CH_3$) the B–N stretching vibration occurs[3] at 1530 cm^{-1} and the compound is monomeric.[4] Thus theoretically it would appear that aminoboranes could act as either π-electron donors (II) or amine-type donors (I) when they interact with Lewis acids. In either case it might be expected that aminoboranes would form complexes with iodine in solution since both olefins (eq 1)[5] and amines (eq 2)[6] form complexes under these conditions. Therefore, the interaction between aminoboranes and iodine was studied in an attempt to elucidate the nature of the B–N bond in these compounds.



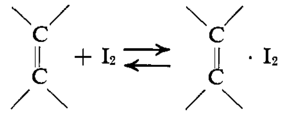
I



II



III



(1)

$$R_3N\colon + I_2 \rightleftharpoons R_3N\colon I_2 \qquad (2)$$

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[1] Welch Foundation Fellow, 1961–1962; Dow Chemical Co. Fellow, 1962–1963.

[2] (a) K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81**, 5553 (1959); (b) K. Niedenzu and J. W. Dawson, *ibid.*, **82**, 4223 (1960); (c) G. M. Wyman, K. Niedenzu, and J. W. Dawson, *J. Chem. Soc.*, 4068 (1962); (d) G. E. Coates and J. G. Livingston, *ibid.*, 1000 (1961).

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[5] J. G. Traynahm and J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959).

[6] (a) C. Reed and R. S. Mulliken, *ibid.*, **76**, 3869 (1954); (b) S. Nagakura, *ibid.*, **80**, 520 (1958).

Experimental Section

All operations were conducted in an atmosphere of dry, prepurified nitrogen.[7]

Reagents. Benzene, dimethylamine, piperidine, triethylamine, ether, and carbon tetrachloride were the purest commercially available reagents. The reagents were dried over calcium hydride, distilled, and kept over calcium hydride in especially designed storage bottles containing provisions for deoxygenation.[7] Reagent grade iodine was sublimed from a finely ground mixture of iodine and potassium iodide; the iodine was resublimed and stored over calcium chloride.

Aminoboranes. The aminoboranes were prepared on a half-mole scale by the method of Niedenzu and Dawson[2a] which involves the transformations shown in eq 3–5.

$$BCl_3 + NHR_2 \longrightarrow R_2NHBCl_3 \quad (3)$$

$$R_2NHBCl_3 + (C_2H_5)_3N \longrightarrow R_2NBCl_2 + (C_2H_5)_3N\cdot HCl \quad (4)$$

$$R_2NBCl_2 + 2R'MgBr \longrightarrow R_2NBR'_2 + 2MgBrCl \quad (5)$$

Piperidinodimethylborane (bp 143–145°, ν_{BN} 1476 cm^{-1}) was prepared in 58% yield. *Anal.* Calcd for $C_5H_{10}NB(CH_3)_2$: B, 8.65; mol wt, 125. Found: B, 8.75; mol wt, 128 (freezing point depression, C_6H_6).

(Dimethylamino)di-*n*-propylborane (bp 136–138°, ν_{BN} 1511 cm^{-1}) was prepared in 60% yield. *Anal.* Calcd for $(CH_3)_2NB(C_3H_7)_2$: N, 9.93. Found: N, 10.00.

(Dimethylamino)dimethylborane was prepared in 55% yield: bp 63° (lit.[4] 65°). The infrared spectrum of the product was identical with that reported in the literature.[3]

Since aminoboranes react rapidly with air yielding a series of decomposition products, it was necessary to establish the effect of these products on the spectra of the aminoboranes. Accordingly, the decomposition of piperidinodimethylborane was studied under a variety of conditions. The aminoborane decomposes in air to a yellow liquid from which a white solid separates; sublimation of the solid yields white crystals melting at 69.5°.

Anal. Calcd for $(C_5H_{10}NH)_2\cdot H_3BO_3$: C, 51.74; H, 10.86; N, 12.07; mol wt, 232. Found: C, 51.73; H, 11.91; N, 12.05; mol wt, 218 (freezing point depression, C_6H_6).

The BN vibration characteristic of piperidinodimethylborane (1476 cm^{-1}) was absent from the infrared spectrum of the decomposition product; however, bands were observed at 1206 and 1302 cm^{-1} which could be assigned to B–O vibrations.[8] The decomposition product yielded piperidinium borate upon heating. *Anal.* Calcd for $C_5H_{10}NH_2BO_2$: N, 10.86; mol wt, 129. Found: N, 10.82; mol wt, 130 (freezing point depression, C_6H_6).

The original decomposition product was not obtained when the aminoborane was hydrolyzed (in a nitrogen atmosphere) and then oxidized; however, the product formed when the pure aminoborane was oxidized (in a stream of dry oxygen) and then hydrolyzed. Both the decomposition product and the parent aminoborane interact with iodine in carbon tetrachloride solution, and the interaction can be easily detected by the marked difference in ultraviolet spectra of the two systems.

Spectral Measurements. The spectra of the aminoboranes are featureless in the region studied (300–600 mμ). Since the aminoboranes studied are very sensitive to water and/or oxygen, the solutions used for the spectral measurements were prepared, the necessary dilutions made, and the cells filled in a nitrogen atmosphere.[7] Spectra were determined with a Beckman Model DU spectrophotometer incorporating a thermostated cell compartment.

Results and Discussion

The addition of an aminoborane to a solution of iodine in carbon tetrachloride causes the characteristic violet color of iodine to change to red-brown. The spectra of these solutions exhibit an absorption band in the near-ultraviolet region (*i.e.*, 390 mμ for piperdinodimethylborane, 365 mμ for (dimethylamino)di-*n*-propylborane, 388 mμ for (dimethylamino)dimethylborane) that is not characteristic of either of the components and is assigned to an aminoborane–iodine complex. The intensity of the new band depends upon the mole ratio of the aminoborane to iodine; application of the method of continuous variations[9] suggests that 1:1 complexes are formed (eq 6) and the presence of an isosbestic

$$R_2NBR'_2 + I_2 \longrightarrow R_2NBR'_2\cdot I_2 \quad (6)$$

point indicates that two absorbing species are present at equilibrium in solution. When the aminoboranes are decomposed by air in the presence of iodine, the isosbestic point disappears and the spectrum is markedly different from that of the pure aminoborane and iodine.

The equilibrium constants, K, for the formation of the aminoborane–iodine complexes (eq 6) were calculated using the method of Rose and Drago[10] from eq 7

$$K^{-1} = -(C_D + C_I) + \frac{A - A_I - A_D}{a_C - a_I - a_D} + \frac{C_D C_I}{A - A_I - A_D}(a_C - a_I - a_D) \quad (7)$$

where C_D and C_I are the analytical (initial) concentrations of the aminoborane and iodine; a_D, a_I, and a_C are the molar absorptivity of the aminoborane, iodine, and complex, respectively, at a given wavelength; A_D, A_I, and A are the absorbances of the aminoborane, iodine, and the solution, respectively, at the same wavelength. When it is possible to find a wavelength at which one or more of the species does not absorb, eq 7 can be simplified considerably. For the piperdinodimethylborane– and (dimethylamino)dimethylborane–iodine systems both A_D and A_C are equal to zero at 517 mμ, and eq 7 simplifies to eq 8 which contains only one

$$K^{-1} = -(C_D + C_I) + \frac{A_I - A}{a_I} + \frac{C_D C_I}{A_I - A}(a_I) \quad (8)$$

unknown, K^{-1}. However, a convenient wavelength was not found at which $A_C = 0$ for the (dimethylamino)di-*n*-propylborane–iodine complex, and eq 9 (derived from eq 7) was used.

$$K^{-1} = -(C_D + C_I) + \frac{A - A_I}{a_C - a_I} + \frac{C_D C_I}{A - A_I}(a_C - a_I) \quad (9)$$

Although eq 9 contains two unknowns, K^{-1} and a_C, the data for two independent experiments can be used to set up two equations which can then be solved simultaneously; an alternative graphical method[10a] can be used to evaluate K^{-1}. The latter approach was used in this investigation.

The appropriate equation (eq 7, 8, or 9) was used to calculate the equilibrium constant for each group of aminoborane–iodine solutions at a series of temperatures between 5.0 and 25.0°; the equilibrium constants are summarized in Table I. The heats of formation, determined from the least-squares slope of the plot of K *vs.* $1/T$, the free energies of formation at 25°, and the

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[7] A variety of special handling techniques involving specially designed equipment were used in conjunction with this investigation. For a complete description see I. D. Eubanks, Ph.D. Dissertation, The University of Texas, 1963.

[8] W. Gerrard, "The Organic Chemistry of Boron," Academic Press Inc., New York, N. Y., 1961, Chapter XVI.

[9] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 48.

[10] (a) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959); (b) R. S. Drago and N. J. Rose, *ibid.*, **81**, 6141 (1959); (c) N. J. Rose, Ph.D. Dissertation, University of Illinois, 1960.

Table I. Equilibrium Constants of Aminoborane–Iodine Complexes at Various Temperatures

	$K \times 10^{-2}$		
t, °C	$C_5H_{10}NB(CH_3)_2$	$(CH_3)_2NB(C_3H_7)_2$	$(CH_3)_2NB(CH_3)_2$
5.0	14.5 ± 0.9	6.33 ± 0.50	2.48 ± 0.23
10.0	14.1 ± 0.7	3.80 ± 0.41	2.65 ± 0.47
15.0	13.8 ± 0.7	2.80 ± 0.36	2.75 ± 0.34
20.0	13.5 ± 0.7	1.90 ± 0.12	2.72 ± 0.42
25.0	13.1 ± 0.7	1.54 ± 0.90	2.87 ± 0.45

Table II. Thermodynamic Quantities of Aminoborane–Iodine Complexes

Aminoborane	$K \times 10^{-2}$, l./mole	$-\Delta H$, kcal/mole	$-\Delta F$, kcal/mole	ΔS, eu
$C_5H_{10}NB(CH_3)_2$	13.1 ± 0.7	0.8 ± 0.6	5.62 ± 0.03	16 ± 2
$(CH_3)_2NB(C_3H_7)_2$	1.54 ± 0.09	11.6 ± 0.9	2.86 ± 0.04	−29 ± 3
$(CH_3)_2NB(CH_3)_2$	2.87 ± 0.45	−1.5 ± 1.5	3.36 ± 0.09	16 ± 5

Table III. Thermodynamic Quantities of Olefin–Iodine and Amine–Iodine Complexes at 25°

Donor	K, l./mole	$-\Delta H$, kcal/mole	ΔS, eu
Cyclopentene[5]	2.58	0.43	−0.6
Cyclohexene[5]	3.04	2.18	4.9
Cycloheptene[5]	2.80	1.95	4.3
cis-Cyclooctene[5]	1.00	0.48	1.4
Triethylamine[6b]	4.65×10^3	12.0	−23.5
Pyridine[6a,a]	2.90×10^2	7.8	−15.5
	1.01×10^2[b]	...	...

[a] Determined at 17°. [b] A. I. Popov and R. H. Rygg, *J. Am. Chem. Soc.*, **79**, 4622 (1957).

entropies of formation at 25° for the aminoborane–iodine complexes are shown in Table II.

Although the double bond character of the B–N bond in certain tetraorganoaminoboranes, *e.g.*, $(CH_3)_2BN(CH_3)_2$, has been demonstrated,[2b,11] the thermodynamic data reported here suggest that these compounds, as well as the aminoboranes which contain B–N single bonds (I), exhibit aminoid character when they interact with iodine. A comparison of the equilibrium constants for the formation of olefin–iodine complexes with those for the formation of amine–iodine complexes (Table III) indicates that the latter are markedly more stable than the former. The equilibrium constants for the aminoborane–iodine complexes reported here (Table II) are of the same order of magnitude as those of the amine–iodine complexes. Thus it would appear from these data that tetraorganoaminoboranes behave as amine-type donors *when they interact* with iodine. The equilibrium constants would not be expected to be vastly different from the olefin–iodine complexes if the aminoboranes behaved as olefins. In addition, relatively little variation in the values for the different aminoborane–iodine complexes would be expected, as has been observed for a variety of olefins with a range of steric requirements (Table III).

Since both the nonassociated and associated aminoboranes behave as amine-type donors, the formation of a complex requires either the breaking of the π component of the boron–nitrogen bond (II) or the dissociation of the dimer (III). Either process, in the absence of steric effects, introduces a degree of freedom (rotation about the B–N bond) not present previously. This effect would be expected to contribute a substantial positive term to the entropy of the system. Where large steric effects are possible, rotation would be more hindered and the positive contribution to the entropy would not be observed. (Dimethylamino)dimethylborane and piperidinodimethylborane both exhibit a much more positive entropy term than either olefin–iodine or amine–iodine complexes. For (dimethylamino)di-*n*-propylborane–iodine complexes the entropy change and other thermodynamic quantities are much nearer to the values for amine–iodine systems.

Thus in the case of the aminoboranes, as for the borazines,[12] a variety of measurements which do not appreciably perturb the molecule indicates an increase in the B–N bond order over that expected for a single bond; however, both of these systems of compounds give reaction products which appear to be the result of aminoid-type reactions.

Acknowledgment. We gratefully acknowledge the support of the Robert A. Welch Foundation.

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(12) E. K. Mellon, Jr., and J. J. Lagowski, *Advan. Inorg. Chem Radiochem.*, **5**, 259 (1963).