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Preparation and Properties of Sterically Overcrowded Aminoboranes

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Several aralkylaminoboranes have been prepared with large substituents on boron and nitrogen, designed to introduce steric overcrowding in the electronically favorable planar conformation (B–N π-interorbital angle $\cong 0°$). The purpose was to produce compounds with a ground-state nonzero B–N π-interorbital angle. From infrared and [11]B and ^{1}H nmr studies it is concluded that although compounds so constructed are more reactive chemically than simple aminoboranes, steric overcrowding is relieved by molecular distortions other than those involving significant B–N bond rotation.

The nature of the B–N bond in simple aminoboranes has attracted considerable attention.[1,2] A principal concern has been the balance between σ and π bonding, represented by eq 1. Double-bond character, as implied in form b, has been

$$\begin{matrix} \backslash & \cdot\cdot / \\ B{\rightarrow}N \\ / & \backslash \end{matrix} \longleftrightarrow \begin{matrix} \backslash \frown\cdot\cdot / \\ B{\rightarrow}N \\ / \delta- & \delta+ \backslash \end{matrix} \qquad (1)$$

$$\quad a \qquad\qquad b$$

observed by many workers[3-5] using nmr to produce a rotational barrier of 17–24 kcal/mol. In spite of significant B–N π bonding, these compounds are not highly polar, as evidenced by a low dipole moment.[6,7] These facts have been reconciled by extended HMO calculations of Hoffmann,[8,9] who noted that σ-electron donation from B to N may exceed π-electron backbonding. Although the B–N infrared stretching frequency is known to vary considerably (1361–1530 cm^{-1}), reliable estimation of the B–N bond order has not been forthcoming. Calculations based on Gordy's rule[10] have yielded bond orders ranging from 1.6[11] to 2[12] for (dimethylamino)dimethylborane. Until recently,[13] more refined estimates of B–N bond order have been hampered by a lack of exact B–N bond length measurements. Moreover, no suitable model compounds are available to provide extrema for the range of theoretically possible B–N bond orders. The purpose of this research was to prepare and examine the physical properties of a series of aminoboranes in which nonbonded steric repulsion between B and N substituents in the planar conformation should lead to severe twisting of the B–N π-interorbital angle, with a concomitant reduction in the B–N π-bond order.

We prepared and studied a series of bridged diarylaminodisubstituted boranes, structures 1–4. Within this series substituents on nitrogen and boron were held nearly constant so as to minimize differences in electronic effects. The bridge between aromatic rings (2–4) made rigid that portion of the molecule, so that ortho aromatic substituents would interact
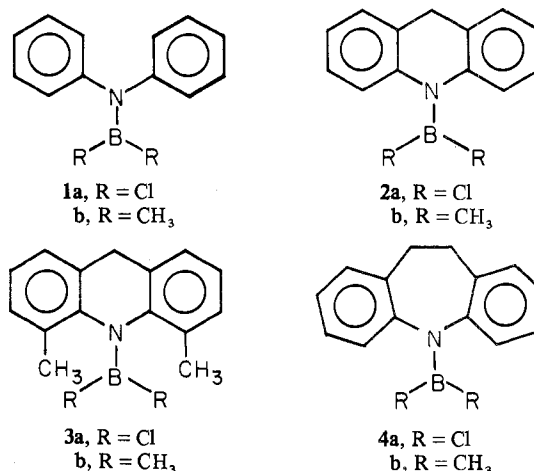

1a, R = Cl
b, R = CH$_3$

2a, R = Cl
b, R = CH$_3$

3a, R = Cl
b, R = CH$_3$

4a, R = Cl
b, R = CH$_3$

Table I

Compd^a	ν_{BN}, cm^{-1}		$\nu_{asym\ BCl_2}$, cm^{-1}
	a	b	a
1	1379	1350	969
2	1361^b	1342	963
3	1363^b	1343	960^c
4	1384	1357	967

^{a} Measured in CCl$_4$ solution. ^{b} This band was unusually sharp, and a second sharp new band at 1200 cm^{-1} was observed but not assigned. ^{c} Two poorly resolved bands of similar intensity are found, instead of the normal single BCl$_2$ band.

strongly with the boron substituents through nonbonded repulsion. One anticipated result of this destabilizing effect would be to force the B–N π-interorbital angle to a nonzero value by twisting of the B–N bond. A decrease in π bonding should be experimentally observable as a decrease in B–N infrared stretching frequency,[14] as a decrease in the electronic shielding of the boron nucleus, or by the appearance of magnetic nonequivalence of the *B*-methyl groups. The B–N stretching frequency of *N*-phenylaminoboranes is often the strongest absorption bond in the infrared spectrum and can usually be assigned with confidence.[15-17] Table I shows the B–N stretching frequency of compounds 1–4. The most notable fact to be adduced from these data is that the constancy of the B–N stretching frequency within a given substitution pattern was nearly constant. The maximum $\Delta\nu_{BN}$ within the dichloro series (1a–4a) was only 15 cm^{-1}. If indeed the B–N stretching frequency is an indication of B–N bond order, it is apparent from these data that relief of nonbonded repulsive strain in these compounds has occurred by

(1) K. Niedenzu, Ed., *Advan. Chem. Ser.*, No. 42 (1964).
(2) K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Springer-Verlag, New York, N. Y., 1965.
(3) P. A. Barfield, M. F. Lappert, and J. Lee, *Proc. Chem. Soc., London*, 421 (1961).
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(5) D. Imbery, A. Jaesche, and H. Friebolin, *Org. Magn. Resonance*, 2, 271 (1970), and ref 3–8 cited therein.
(6) H. J. Becher, *Z. Anorg. Allg. Chem.*, 270, 273 (1952).
(7) G. E. Coates and J. G. Livingstone, *J. Chem. Soc.*, 1000 (1961).
(8) R. Hoffmann, *J. Chem. Phys.*, 40, 2474 (1964).
(9) R. Hoffmann, *Advan. Chem. Ser.*, No. 42, 78 (1964).
(10) W. Gordy, *J. Chem. Phys.*, 14, 305 (1946).
(11) G. M. Wyman, K. Niedenzu, and J. W. Dawson, *J. Chem. Soc.*, 4068 (1962).
(12) K. Niedenzu and J. W. Dawson, *J. Amer. Chem. Soc.*, 82, 4223 (1960).
(13) G. J. Bullen and N. H. Clark, *J. Chem. Soc. A*, 992 (1970).

(14) Reference 2, p 50.
(15) H. J. Becher, *Z. Anorg. Allg. Chem.*, 289, 262 (1957).
(16) H. J. Becher and H. Diehl, *Chem. Ber.*, 98, 526 (1965).
(17) A. Meller, *Organometal. Chem. Rev.*, 2, 37 (1967).

Table II

Compd[a]	$-\delta_{11B}$, ppm		Compd[a]	$-\delta_{11B}$, ppm	
	a	b		a	b
1[b]	33.5	49.6	3	32.3	50.6
2	33.9	50.0	4	32.9	50.3

[a] Measured in $CDCl_3$ solvent relative to boron trifluoride etherate, external standard. [b] Measured in CCl_4 solvent.
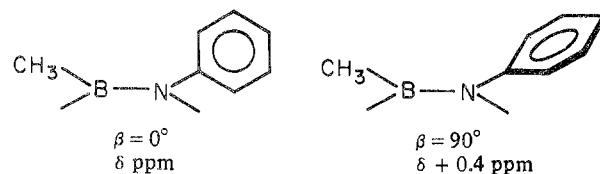
Table III

Compd[a]	Chem shift,[b] ppm			
	B-CH$_3$	C-CH$_3$	-CH$_2$-	Arom
1a				7.21[c,d]
1b	0.39[d,e]			7.07–7.10[f]
2a			3.70[d]	6.9–7.6[f]
2b	0.62[d]		3.59[d]	6.8–7.3[f]
3a		2.48	3.71[d]	7.12[d]
3b	0.34	2.35	3.73[d]	7.01
4a			3.09[g]	7.11[h]
4b	0.34		2.92[g]	6.96[d]

[a] Measured in $CDCl_3$ solution at an ambient temperature unless otherwise stated. [b] δ, in ppm from internal tetramethylsilane. [c] CCl_4 solution. [d] Sharp singlet. [e] H. J. Becher and H. T. Baechle, *Chem. Ber.*, 98, 2159 (1965). [f] Multiplet. [g] Center of an AA'BB' multiplet. [h] Singlet with shoulder.

molecular distortions other than those involving the B–N π-interorbital angle. This thesis is reinforced by the ^{11}B chemical shifts, which are displayed in Table II. A variation of no more than 1.2 ppm within each series suggests a relatively constant shielding of the boron nucleus in each of the compounds within the series. Theoretical calculations[18] suggest that a significant increase in the B–N π-interorbital angle from zero to some higher value should produce a large downfield displacement of the ^{11}B chemical shift. No such shift was observed in this case.

The ^{1}H chemical shifts of B-methyl groups provide insight into the conformation of these compounds, and their temperature dependence suggests conformational mobility. The ^{1}H chemical shifts for compounds 1–4 are shown in Table III. The B-methyl chemical shifts of 1b, 3b, and 4b are nearly identical and are approximately 0.3 ppm to higher field than that of 2b. Becher and Baechle[19] have calculated the relative ^{1}H chemical shift of methyl groups in various phenyl-substituted aminoboranes as a function of the twist angle (β) of the phenyl group with respect to the plane containing the B–N group and its immediate neighbors. Variation of β from 0 to 90° was calculated to produce a change in ring current effect at a cis B-methyl group of ~0.4 ppm. Examination of a scale molecular model of 4b suggests that $\beta \cong 35°$, a value similar to that deduced by Becher and Baechle for compound 1b, and the B-methyl chemical shift is found to be the same in both cases. Molecular overcrowding in the planar or nearly planar molecule of 3b would be expected to produce an out-of-plane deformation of the B-dimethyl group. This would result in positioning of these groups similar to those in 1b and 3b, relative to the aromatic rings. Indeed, the chemical shift is also the same. However, if 2b is nearly planar in the ground state ($\beta \cong 0°$) the B-methyl groups in this compound should be deshielded with respect to other members of the series. A significant difference in chemical shift suggests that this is the case.
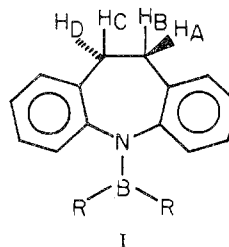
(18) N. Noth and H. Vahrenkemp, *Chem. Ber.*, 99, 1049 (1966).
(19) H. J. Becher and H. T. Baechle, *Chem. Ber.*, 98, 2159 (1965).

$\beta = 0°$
δ ppm

$\beta = 90°$
$\delta + 0.4$ ppm

An observation which suggests that the orientation of the –BR$_2$ group relative to the phenyl rings is different in compounds 2 from other compounds in the series comes from a comparison of ν_{BN} for the B-dichloro and B-dimethyl compounds. Aryl substitution at nitrogen in aminoboranes lowers the infrared frequency of the B–N stretch.[2] Such a lowering of bond order has been attributed[20] to mesomeric competition by the phenyl group for the available lone-pair electrons on nitrogen. The difference between the B–N stretching frequency of 1a and 1b, $\Delta\nu_{BN}(1)$, and of 4a and 4b, $\Delta\nu_{BN}(4)$, are nearly identical but are larger than the same quantity for compounds 2. The orientation of the phenyl rings in 1 and 4 may be similar to each other but different from the orientation in 2.

The temperature-dependent ^{1}H resonance signal of the methylene group of 2b was examined from +35 to –90°. If the chemical shift difference between H$_A$ and H$_B$ (Figure 1) is large, then two signals should be observed if the energy barrier to ring inversion is large. Although the methylene signal broadens slightly as the temperature is lowered, there is no increase in the multiplicity of the signal, even at –90°. Compare this result to the result of Holubec and Jonas[21] for ring inversion of 9-(dichloromethylene)-10,10-dimethyl-9,10-dihydroanthracene (5). Compound 5 should be a good

5
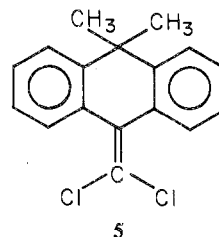
model for 2a. These workers found an nmr barrier to ring inversion of 20.3 kcal/mol for compound 5. Because of the similarity in size between chlorine and methyl, it is suggested that 2b is not fully planar. The central ring of 2b may exist in a shallow boat conformation in which $\delta_{H_A} \approx \delta_{H_B}$. The possibility that strong nonbonded repulsion in 2b can be relieved by in-plane distortion of the C–B–C angle[21] coupled to a small increase in the B–N π interorbital angle cannot be discounted.

The ^{1}H resonance pattern of the ethano bridge of 4a and 4b provides an interesting magnetic probe into the ring conformation for these compounds. The situation is illustrated in structure I. In the completely rigid molecule all four

I

(20) J. J. Kaufman and J. R. Hamann, *Advan. Chem. Ser.*, No. 42, 97 (1964).
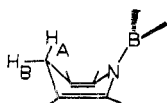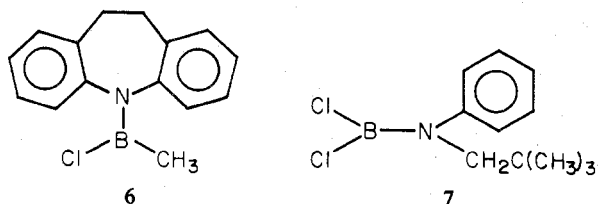(21) Z. M. Holubec and J. Jonas, *J. Amer. Chem. Soc.*, 90, 5986 (1968).

Figure 1.

bridge hydrogens would experience a different magnetic environment giving rise to an ABCD spectrum. Ring inversion or pseudorotation about the $-CH_2-CH_2-$ bond will reduce the spectrum to an AA'BB' pattern. If both processes occur rapidly, the methylene signal should become a singlet. At room temperature the ^1H spectra of both **4a** and **4b** show a simple AA'BB' pattern for the ethano protons. Temperature variation of +50 to −70° for compound **4a** failed to alter the pattern significantly. This suggests a large difference in the energy barrier between the two processes. Pseudorotation, which involves only the eclipsing of two C–H bonds, is not a reasonable candidate for the higher energy process. The higher energy process appears to be ring inversion, perhaps coupled with a rotation about the B–N bond. Studies suggest that processes involving coupled rotation-inversion may possess only a single common transition state for both processes.[22] If the upper limit for the inversion barrier is taken to be equal to the B–N rotational barrier (15–20 kcal/mol),[5] then the coalescence temperature for inversion could easily be beyond the maximum temperature employed in this study. The chemical shifts and coupling constants for the ethano protons of **4a** were calculated so as to fit the AA'BB' portion of the spectrum. The calculated[23] values and a drawing of the central azepine ring of **4a** are given in Figure 2 and its caption. The chemical shift difference $\nu_A - \nu_B$ was confirmed by spin decoupling. When the Karplus relationship[24] for vicinal proton coupling is applied to these values, the resulting HCCH angles are completely consistent with the structures shown in Figure 2.

The boat conformation of the azepine ring (Figure 3) with slow ring inversion also would produce a temperature-invariant AA'BB' spectrum. However, a large increase in torsional strain and in H–H nonbonded repulsion in the boat suggests that this may be the transition state between the two conformations shown in Figure 2, rather than an energy minimum. The preceding rationale is given further support by the fact that the parent amine, iminodibenzyl, shows a sharp singlet at δ 2.92 ppm, due to rapid pseudorotation *and* rapid ring inversion. Since the barrier to pseudorotation should remain largely unaffected by a change in substitution at the remote nitrogen atom, the fact that increasing the size of the substituent at nitrogen leads to the more complex AA'BB' spectrum suggests that *inversion* rather than *rotation* is the higher energy process.

The chloromethylborane **6** was prepared by the addition of

6   **7**

exactly 1 equiv of CH_3Li to the dichloroborane. The ethano ^1H resonance pattern of this compound was a complex ABCD
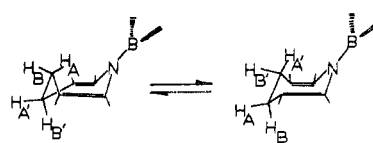
Figure 2. Rotation-inversion of the central azepine ring of **4a**. $\nu_A - \nu_B = 60$ Hz (measured at 100 MHz). $J_{AB} = -14.95$ Hz $= J_{A'B'}$; $J_{AB'} = +2.45$ Hz $= J_{A'B}$; $J_{AA'} = +8$ Hz $= J_{BB'}$ (this value could not be accurately calculated from the spectrum and is therefore estimated).

Figure 3.

spectrum at 2.4–3.6 ppm, consistent with the picture of fast pseudorotation and slow ring inversion. The appearance of a single *B*-methyl resonance signal at 0.63 ppm for **6**, together with the ABCD pattern for the bridge protons, constitutes additional evidence that atoms immediately attached to the B–N bond lie in a plane, or nearly so, and that the B–N bond rotation is slow at room temperature.

An additional stereochemical complication in all cases discussed here is raised by the possibility of a pyramidal rather than planar configuration at the nitrogen atom. Dewar and Rona[25] have pointed out the interesting fact that pyramidal nitrogen can conjugate very effectively with an adjacent unoccupied 2p orbital. No evidence in the present study bears directly on that question. However, Imbery and coworkers[5] were unable to detect magnetic nonequivalence of the methylene protons in several *N*-benzylaminoboranes, even at −90°. Slow inversion of pyramidal nitrogen should have produced an AB pattern in that case. An examination of the methylene ^1H singlet of phenylneopentylaminodichloroborane (7)[26] showed no change in appearance of this peak, even to −110°, further corroborating the report of Imbery and coworkers.

In the course of this work, an interesting point of theory has emerged which has heretofore not received attention. It is evident from the work of Imbery and coworkers[5] that increasing the size of B and N substituents while holding electronic effects approximately constant has the effect of lowering the energy barrier for rotation about the B–N bond. This effect operates so as to destabilize by the largest amount the conformation in which the B–N π-interorbital angle is zero. The result is qualitatively illustrated in Figure 4, which shows that the overall rotational barrier will be lowered by this effect. Very large substituents on boron and nitrogen could render the steric repulsion component of the total potential energy a very sensitive function of interorbital angle. This has two possible results: the planar conformation could become less stable than the conformation with the B–N π angle 90°, and, if the two energy components are of approximately the same slope at intermediate B–N π angles, a second potential energy minimum at some B–N π angle between 0 and 90° can appear. The electronic *vs.* steric competition here is not unlike the situation with biphenyls.

The destabilizing effect of steric overcrowding became apparent in the preparation and chemical behavior of these compounds. The most hindered compounds from this study (*i.e.*, **2** and **3**) were more reactive than acyclic analogs and required extraordinary precautions to exclude air and moisture during handling. In our usual preparative procedure

(22) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *J. Amer. Chem. Soc.*, **92**, 6349 (1970).

(23) The computer program and calculations were kindly provided by Dennis Marynick, formerly of the Department of Chemistry, California State University, Los Angeles, Calif.

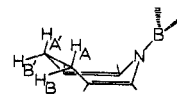(24) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(25) M. J. S. Dewar and P. Rona, *J. Amer. Chem. Soc.*, **91**, 2259 (1969).
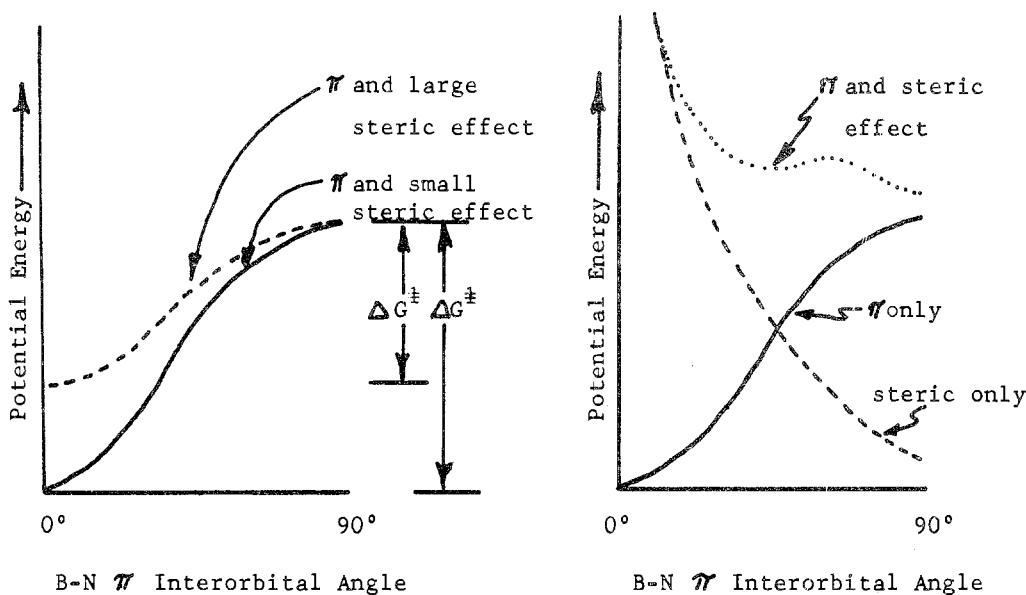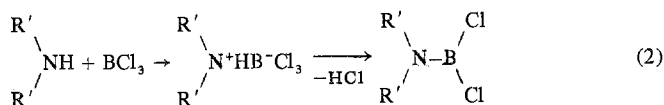
(26) J. Casanova and M. Thomas, unpublished result, 1965.

Figure 4.

the appropriate amine–borane was dehydrochlorinated by refluxing in benzene[27] (eq 2). However, compound **3a** was

$$\underset{R'}{\overset{R'}{\diagdown}}NH + BCl_3 \rightarrow \underset{R'}{\overset{R'}{\diagdown}}N^+HB^-Cl_3 \xrightarrow[-HCl]{} \underset{R'}{\overset{R'}{\diagdown}}N-B\underset{Cl}{\overset{Cl}{\diagup}} \qquad (2)$$

not formed at all by this procedure when **8** was heated and required an alternative procedure. This suggests that in the dehydrochlorination of **3a**, a large destabilizing effect was introduced.
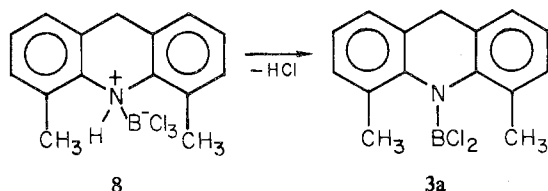
The present results suggest that the initial goal of this research may be more difficult to attain than originally supposed. Of the cases so far examined, relief of steric overcrowding appears to arise by molecular deformations other than those involving significant rotation of the B–N bond. Moreover, as more steric overcrowding is introduced in an effort to produce B–N interorbital deformation, the compounds under study will become increasingly more difficult to prepare and manipulate.

Experimental Part

Diphenylaminodichloroborane[27] and diphenylaminodimethylborane[16] were prepared by published procedures. All manipulations were carried out by using standard high-vacuum or Schlenk[28] procedures or by using a controlled-atmosphere glove box with purified argon. Samples for nmr were prepared and sealed on a high-vacuum line. Infrared spectra were determined using Beckman IR-5 and IR-12 instrumentation. Nuclear magnetic resonance measurements were carried out with Varian A-60 and HA-100 spectrometers. All solvents were predried.

Dichloro(10-acridanyl)borane (2a).[15,29] Five grams (27.6 mmol) of acridane (Aldrich 13,089-3), recrystallized from methanol, was dissolved in 100 ml of dry CH_2Cl_2 and added under stirring during 1 hr to a solution of 4.7 g (40 mmol) of BCl_3 in 60 ml of dry CH_2Cl_2

(27) H. J. Becher, *Z. Anorg. Allg. Chem.*, **289**, 262 (1957).
(28) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969 pp 141–159.
(29) See W. Gerrard and E. P. Mooney, *J. Chem. Soc.*, 4028 (1960), for a model procedure.

at $-80°$. After addition was complete, the cooling bath was removed. When the mixture reached room temperature, a red-brown, clear solution was formed. The solvent and excess BCl_3 were removed by distillation at normal pressure. The yellow crystalline residue was suspended in 100 ml of dry benzene, and the mixture was refluxed with stirring for about 4 hr. The evolved HCl was removed by passing a slow stream of dry nitrogen through the benzene solution. The benzene was removed at normal pressure and the concentrated solution transferred by syringe to a sublimation apparatus attached to the vacuum line. After removal of benzene, the residue sublimed at 90–110° (0.1 Torr); 4.71 g (73%). *Anal.* Calcd for $Cl_2BNC_{13}H_{10}$: B, 4.13. Found: B, 4.17.

Dimethyl(10-acridanyl)borane (2b). Compound **2a**, freshly prepared from 2 g (11.0 mmol) of acridane by the preceding procedure, was dissolved in 40 ml of dry ether. To this was added with stirring 480 mg (21.8 mmol) of CH_3Li dissolved in 30 ml of dry ether at $-80°$ during about 10 min. After addition, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred at room temperature overnight and then filtered in a Schlenk apparatus. The filtered solution was light yellow with a green fluorescence. Most of the ether was removed at normal pressure. The concentrated solution (*ca.* 6 ml) was transferred by syringe into a small distillation apparatus, attached to the vacuum line. After removing the ether, a very viscous, colorless, clear liquid distilled at about 110° (0.1 Torr). It solidified after standing for a short while; 800 mg (33%).

Dichloro(4,5-dimethylacridan-10-yl)borane (3a). BCl_3 (1.12 g, 9.6 mmol) was condensed in an empty 100-ml three-necked flask at $-80°$; then 10 ml of dry benzene was added. After the solution warmed to $+5°$, 0.5 g (2.4 mmol) of 4,5-dimethylacridane[30] was dissolved in 10 ml of dry benzene under stirring for 30 min. The cooling bath was removed and when the solution warmed to 20°, 0.55 ml (5.5 mmol) of 2,6-lutidine (dried over molecular sieve) was added to the suspension in benzene all at once. At first the solution became homogeneous (clear yellow); then an oil separated. After stirring for 1.5 hr at room temperature, the upper (benzene) phase was transferred by syringe into a flask attached to the vacuum line and the benzene was removed. The residue was treated with CCl_4, and the CCl_4 solution was transferred into a sublimation apparatus. After removal of the CCl_4, the residue was sublimed at 100–110° (0.1 Torr); 0.645 g (92%) of white crystals. *Anal.* Calcd for $Cl_2BNC_{15}H_{14}$: B, 3.73. Found: B, 3.74.

Dimethyl(4,5-dimethylacridan-10-yl)borane (3b). Dichloride **3a** (500 mg, 1.72 mmol) was dissolved in 200 ml of dry ether in a 50-ml three-necked flask. After cooling of the flask to $-80°$, 3.44 mmol (1.57 ml) of a 2.2 M solution of CH_3Li in ether was added by syringe while stirring. The cooling was then removed and the mixture was allowed to come to room temperature. After *ca.* 30 min of stirring, the other solution was transferred in a sublimation apparatus and the ether was removed under vacuum. The residue

(30) A. Albert and J. P. Willis, *J. Soc. Chem. Ind., London, Trans. Commun.*, **65**, 26 (1946).

sublimed at 100–110° (0.1 Torr) to give a white crystalline solid.

Dichloro(10,11-dihydro-5H-dibenz[b,f]azepin-5-yl)borane (4a). Dry benzene (50 ml) was placed in a 200-ml three-necked flask equipped with a dropping funnel, reflux condenser (acetone–Dry Ice type), gas inlet tube, and magnetic stirrer. Under stirring and cooling at *ca.* 6°, 50 mmol of BCl₃ was added. A light yellow, clear solution of 5 g (25.6 mmol) of iminodibenzyl (Aldrich, sublimed at 110° (0.1 Torr) before use) in 30 ml of dry benzene was added dropwise over 45 min, under stirring and cooling. A blue-green solid was formed. The acetone–Dry Ice condenser was replaced by ordinary reflux condenser and the reaction mixture was refluxed for 3 hr under a slow stream of dry nitrogen. The solid went in solution with HCl evolution. After the reflux period, most of the benzene was removed under normal pressure. The residue was transferred into a sublimation apparatus by syringe. After removal of the benzene, the light pink solid residue was sublimed at 100° (0.1 Torr) to give white crystals, 5.4 g (77%). *Anal.* Calcd for Cl₂BNC₁₄H₁₂: B, 3.92. Found: B, 3.79.

Dimethyl(10,11-dihydro-5H-dibenz[b,f]azepin-5-yl)borane (4b). Aminodichloroborane 4a, prepared from 2 g (10 mmol) of iminodibenzyl by the preceding procedure, was dissolved in 40 ml of dry ether. To this was added under stirring a solution of 21 mmol of CH₃Li in 29 ml of ether at −80° over about 10 min. The cool bath was removed and after 3 hr of stirring the white precipitate was removed by filtration in a Schlenk apparatus. The filtered solution was yellow and clear. Most of the ether was removed by distillation

at normal pressure, and the concentrated solution was transferred into a small distillation apparatus by syringe. After removing the ether in the vacuum line, the residue was distilled at 110–120° (0.1 Torr), to give a clear colorless liquid, 1.5 g (55%).

Chloromethyl(10,11-dihydro-5H-dibenz[b,f]azepin-5-yl)borane (6). To 1.00 g (3.62 mmol) of 4a dissolved in 30 ml of dry ether was added a solution of 3.64 mmol of CH₃Li dissolved in 6.5 ml of ether. The solution was cooled at −20° and stirred during the addition, which required 5 min. After 1 hr of stirring at −20°, the white precipitate was removed by filtration in a Schlenk apparatus. Most of the ether was distilled under normal pressure and the residue was transferred in a small distillation apparatus attached to the vacuum line by syringe, while nitrogen gas was blowing through the apparatus. Ether was then removed completely. The residue, a very viscous, colorless liquid, was distilled into an nmr tube at 120–150° (0.1 Torr). The yield was about 500 mg (54%).

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Microwave Spectrum, Structure, and Dipole Moment of Aminodiborane

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The microwave spectra of ten isotopic species of $H_2NB_2H_5$ have been assigned. The following substitution values for the structural parameters were determined: $r(B-B) = 1.916 \pm 0.002$ Å, $r(B-N) = 1.558 \pm 0.001$ Å, $r(B-H_{br}) = 1.355 \pm 0.005$ Å, $r(B-H_t) = 1.193 \pm 0.001$ Å, $\angle BNB = 75.9 \pm 0.1°$, $\angle BH_{br}B = 90.0 \pm 0.6°$, $\angle H_t BH_t = 121.0 \pm 0.3°$, $\epsilon = 16.8 \pm 0.1°$. From the center of mass equations, the amino hydrogen parameters were calculated to be $r(N-H) = 1.005 \pm 0.006$ Å and $\angle HNH = 111.0 \pm 1.2°$. The dipole moment was measured to be 2.67 ± 0.03 D. Also the ^{14}N nuclear quadrupole coupling constants were found to be $\chi_{aa} = -2.71 \pm 0.03$ MHz, $\chi_{bb} = 0.84 \pm 0.05$ MHz, and $\chi_{cc} = 1.87 \pm 0.08$ MHz.

Introduction

For the last few years, the molecular structures and properties of small carboranes have been the subjects of investigation in this laboratory. In the course of these studies, it became apparent that the structure of aminodiborane (ADB), a small, common cyclic diborane derivative, was never properly determined, probably because ADB is unstable and decomposes gradually at ambient temperatures. In an early electron diffraction study on ADB, the difficulties in discriminating closely spaced, nonequivalent internuclear distances led to large uncertainties in the structure.[1] Also, the present log sector method of electron diffraction was not used, and the experimental results might include effects from some decomposition products. An attempt was made in this laboratory to determine the structure of the more stable *N,N*-dimethyl derivative of this compound.[2] However, because the heavy methyl groups shifted the center of mass close to the nitrogen atom, an accurate structure determination was not possible. Accordingly, we have studied the rotational spectrum of the parent ADB.

The microwave spectra of ten isotopic species of ADB

have been obtained. From these data, an accurate molecular structure was determined. Since the spectra of both singly isotopically substituted and doubly isotopically substituted species were assigned, all ambiguities in the signs of the center of mass coordinates were resolved and the internal consistency afforded a check on the precision of the results. The final structure is given in Figure 1. We refer to the terminal and bridge hydrogen atoms as H_t and H_{br}, respectively. The nuclear quadrupole coupling constants of the nitrogen were determined. Also, the dipole moment was measured by determining the Stark effect for selected transitions.

Experimental Section

Various isotopic species of ADB were made by the original procedure,[3] slightly modified to employ smaller quantities of the available rare isotopic reagents. The "diammoniate of diborane," $(NH_3)_2$-$BH_2{}^+BH_4{}^-$, was formed in a small U tube in a high-vacuum system. It was treated repeatedly with diborane in excess, with brief exposure to temperatures as high as 90° and immediate removal of hydrogen and other volatiles, from which small yields of the desired ADB were isolated and accumulated. Finally, the accumulated product was purified very carefully by high-vacuum fractional condensation. The ^{15}N species were made from 99.9% enriched $^{15}NH_3$, obtained as a gas from Stohler Chemical Co., Azusa, Calif.

Due to the rather large dipole moment of ADB, lines were ex-

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