spectrum of IIIb (Nujol): ν_{CO} at 1970 and 2025 cm^{-1}.

Acknowledgments. We wish to thank the National Science Foundation (Grant CHE78-05679) and the Office of Naval Research for their generous support of this work. The authors thank Dr. C. A. O'Con, Dr. D. C. Busby, and Mr. T. B. Marder for assistance in obtaining the ^{11}B, ^{1}H, and ^{31}P FT NMR spectra, Mr. R. E. King for measurement of the crystal density, Dr. Bradley Katz for assistance with the diffractometer, and Miss Susan Heytens for the illustrations. The Syntex $P\bar{1}$ automated diffractometer and the Bruker WP-200 FT NMR spectrometer were purchased with funds from NSF Grants GP2824 and CHE76-05926, respectively, and computer time was furnished by the UCLA Campus Computing Network.

Supplementary Material Available: Root-mean-square amplitudes of vibration and equivalent *B* values (Table IV), structure factor amplitudes (Table V), interatomic distances (Table VI), average bond lengths (Table VII), interatomic angles (Table VIII), and selected least-squares planes and interplanar angles (Table IX) (22 pages). Ordering information is given on any current masthead page.

Tris(amino)boranes: The Effect of Angle Strain on Hybridization

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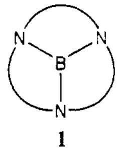
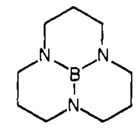
Received January 28, 1980

Abstract: The four tris(amino)boranes represented by structure **1** with ethylene and/or trimethylene bridges have been prepared. Predictions that the smallest member of this series, 10-bora-1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane, would be highly strained were supported by the observation that this compound exists only as a tight dimer. 11-Bora-1,4,7-triazatricyclo[5.3.1.0^{4,11}]undecane is dimeric in solution but monomeric in the gas phase. The X-ray crystal structure and properties of 13-bora-1,5,9-triazatricyclo[7.3.1.0^{5,13}]tridecane show that it has a stable planar BN$_3$ aray.

We report experiments pertaining to the effect of angle strain on the hybridization and reactivity of boron–nitrogen bonds. Our results also apply to isoelectronic carbon–nitrogen systems.[1] We have prepared the series of compounds depicted by structure **1** where the curved lines represent ethylene or trimethylene bridges.



1



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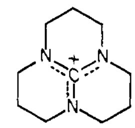
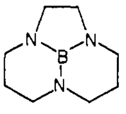


3

The largest member of this series, **2**, is isoelectronic with guanidinium ion **3**. Models indicate that both **2** and **3** are reasonably unstrained when the four atoms of the central array are trigonal coplanar. Since salts of **3** had previously been prepared[2,3] and exhibit normal stability, we expected that **2** would represent an especially stable tris(amino)borane.

Structures **4**–**6** represent three lower homologues of **2** which show increasing strain. Models[4] suggest that **4**, with one less methylene group, is considerably more strained than **2** if the four atoms of the BN$_3$ array remain trigonal and coplanar—a geometry that is impossible for **5** and **6**, assuming normal bond distances. However, if the three nitrogens of **5** and **6** adopt a pyramidal geometry (sp^3 hybridization), then the BN$_3$ nuclei can maintain a semblance of coplanarity.



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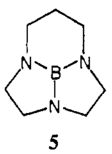

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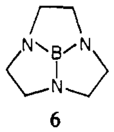
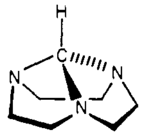


6

Models also show that a conformation for **6** free of angle strain can be achieved if all four atoms of the BN$_3$ array adopt a pyramidal geometry—a conformation quite similar to that expected for **7**, recently reported[3] to be a stable compound. However, this conformation for **6** requires a *trivalent pyramidal* boron atom, an electronic strain that must be very considerable.[1,5] The tendency for trivalent boron to remain planar is similar to the tendency for planarity in isoelectronic carbocations.[5]



7

We report the synthesis of compounds **2**, **4**, and **5** and properties for these compounds that are consistent with the above considerations. Attempts to synthesize **6** have given only a dimer of this structure.

Results and Discussion

Syntheses. The synthesis of the polycyclic aminoboranes, **1**, in each case started with the triaza-monocyclic ring. However, the four compounds described in this paper were best synthesized by three different methods. Compound **2** was prepared in good yield by refluxing 1,5,9-triazacyclododecane[6] with excess methyl

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[1] For a discussion of the analogy between boranes and carbonium ions, see: Davis, R. E.; Ohno, A. *Tetrahedron* **1967**, *23*, 1015–28. Davis, R. E.; Murthy, A. S. N. *Ibid.* **1968**, *24*, 4595–4603.

[2] Richman, J. E., presented at the Gordon Heterocycles Conference, New Hampton, NH, June 1974.

[3] Atkins, T. J. "Abstracts of Papers", ACS/CJS Chemical Congress, Honolulu, HI, April 1979; American Chemical Society: Washington, D.C.; ORGN 106.

[4] Dreiding and Framework Molecular Models were used.

[5] Jemmis, E. D.; Buss, V.; Schleyer, P. v. R.; Allen, L. C. *J. Am. Chem. Soc.* **1976**, *98*, 6483–9.

[6] (a) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268–70; (b) Koyama, H.; Yoshino, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 481–4.

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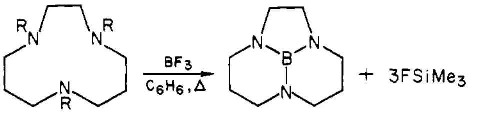
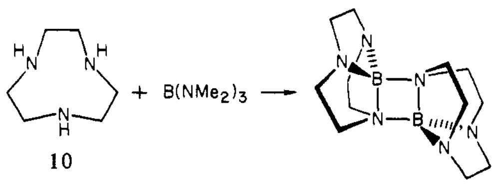
orthoborate.[7] Crystals of **2** that are only slightly hygroscopic spontaneously separate from the mixture. The next lower homologue, **4**, was prepared by the reaction of BF_3 with the silylated amine **9**.[8] Compound **4** is a moderately hygroscopic, distillable liquid.



8, R = H
9, R = $SiMe_3$
4

Compound **5** was prepared by transamination,[9] refluxing 1,4,7-triazacyclododecane[6] and tris(dimethylamino)borane in benzene. Compound **5** is a sublimable white solid that is *extremely* hygroscopic.

When the preparation of **6** was attempted by the analogous reaction of 1,4,7-triazacyclononane (**10**)[6] with tris(dimethylamino)borane, the reaction proceeded even more rapidly, and again



10
11

an extremely hygroscopic white solid was obtained. However, the mass spectrum of this solid is consistent with a *dimer of* **6**. Spectroscopic evidence (vide infra) supports structure **11** for this dimer.

The three different synthetic methods described above afford the cleanest syntheses of compounds **2**, **4**, **5**, and **11**. The transamination method which succeeds for the syntheses of **5** and **11** fails completely for the syntheses of **2** and **4**. In both of these cases, the transamination is extremely slow and proceeds only to partial completion even in higher boiling solvents. Amination with methyl orthoborate, which proceeds cleanly for the synthesis of **2**, also applies to the synthesis of **4** (an unstable crystalline solvate of **4** and methyl orthoborate forms in low yield) but does not apply to the syntheses of **5** and **11**. The silylamine/BF_3 route used for **4** also applies to the other members of this series but is considerably more difficult and appears to be optimal only for the synthesis of **4**.

Structural Data. The structure and chemical properties of compounds **2**, **4**, **5**, and **11** are consistent with the principles set forth in the introduction. The X-ray crystal structure[10] of **2** shows that the BN_3 atoms are very nearly trigonal and coplanar, and the two methylene carbons attached to each nitrogen also deviate only slightly (0.14–0.20 Å) from the N_3 plane. The central methylene carbons in the three bridges are displaced considerably from the N_3 plane, all on the same side of this plane. The crystal structure of **2** closely resembles that of its bicyclic analogue, the triazaboradecalin derivative (1-bora-2,6,10-triazabicyclo[4.4.0]-decane).[11]

The structure of **4** appears to be only slightly distorted from the trigonal-planar BN_3 array in **2**. Both **2** and **4** show intense infrared absorbances in the region 1500–1600 cm^{-1}. In fact, these bands appear at higher energy in **4** (1510, 1545, and 1580 cm^{-1}) than in **2** (1510 cm^{-1}, br). This suggests that the unique B-N bond in **4** has more double-bond character than the average B-N bonds in the symmetrical molecule **2**. This effect might be complicated by the absence of the symmetrical BN_3 stretching-mode absorbance in **2** due to the symmetry of this molecule.

Table I. ^{13}C NMR Chemical Shifts

compd	N-CH_2[a]	N-CH_2[b]	CH_2-CH_2-CH_2
2[c]		+47.7	27.0
4[d]	49.6[e]	46.3,[e] 45.2	27.6
5[c]	54.9, 52.3	49.3	21.8
11[c]	53.0, 52.6, 52.3		

[a] Ethylene bridge. [b] Trimethylene bridge. [c] In C_6D_6 solution. [d] In $CDCl_3$ solution. [e] These assignments may be reversed.

The mass spectrum of the aminoborane prepared from the smallest cyclic amine that we studied (1,4,7-triazacyclononane) shows a molecular ion for the dimer of **6**. At 15 eV, the molecular ion is the base peak in the spectrum, and the fragment ion at half the mass of the molecular ion (corresponding to the mass of **6**) represents one fourth of the intensity of the molecular ion. Other major fragments appear at M – 1, M – C_2H_4N, M – C_2H_4NH, M – $C_2H_4NH_2$, M – C_3H_6N, and M/2 + 1. The pattern and intensities of the ions in this mass spectrum strongly support a tight polycyclic structure for this dimer of **6**. The ^{13}C NMR spectrum (Table I) indicates structure **11** for this compound. Whereas structure **6** should exhibit only a single chemically distinct carbon, the dimeric structure **11** has a center of inversion and a mirror plane of symmetry and should show three chemically similar but spectroscopically distinct carbon types. Three singlets were observed in the proton-decoupled ^{13}C spectrum at 52.3, 52.6, and 53.0 ppm. The infrared spectrum shows no strong bands in the region 1330–1530 cm^{-1} where trigonal aminoboranes (e.g., **2** and **4**) absorb.[12]

This preservation of the triazacyclononane ring in **11** was confirmed by hydrolysis and recovery of triazacyclononane (as the tris-benzoyl derivative). We feel that our structural data are uniquely satisfied by structure **11** for the dimer of **6**.[13]

In the series of compounds **2**, **4**, and **5**, and **11**, the first two clearly are monomeric whereas **11** is a tight dimer of **6**. Our results suggest that **5** represents the crossover point between monomeric and dimeric structures. The mass spectrum of **5** shows no ions above the molecular ion peaks for the monomeric form. This and the comparable volatility of **5** with **2** and **4** suggest that **5** is freely monomeric in the gas phase.

However, in benzene solution, **5** is predominantly dimeric, but rapidly exchanges; i.e., **5** exists as a weakly bonded dimeric complex. This structure for **5** is indicated by the ^{13}C NMR data in Table I. The observation of only four signals in the ^{13}C spectrum is consistent with the monomeric structure or a dimeric structure that is rapidly exchanging through the monomer. The chemical shifts of the ethylene bridge carbons in **5** coincide with the similar carbons in the dimeric molecule **11** and differ greatly from ethylene carbon chemical shifts in the monomeric compound **4**. The multiplicity and shifts considered together are only consistent with a dimeric structure that is rapidly exchanging so that the symmetry of the monomer is rapidly attained. Although other exchange mechanisms are possible, we suggest that the rapid equilibrium $5_2 \rightleftharpoons$ two **5** is the most likely explanation of these results.

That **5** is indeed dimeric in benzene solution was confirmed by solution osmometric molecular weight determination.[14] The

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(7) Mezey, E. J.; Girardot, P. R.; Bissinger, W. E. *Adv. Chem. Ser.* **1964**, *No. 42*, Chapter 19.

(8) Burg, A. B.; Kuljian, E. S. *J. Am. Chem. Soc.* **1950**, *72*, 3103–7. Ebsworth, E. A. V.; Emeleus, H. J. *J. Chem. Soc.* **1958**, 2150. For a related reaction of silylated cyclic amines with PF_5, see: Richman, J. E. *Tetrahedron Lett.* **1977**, *559*–62.

(9) English, W. D.; McCloskey, A. L.; Steinberg, H. *J. Am. Chem. Soc.* **1961**, *83*, 2122–4.

(10) Bullen, G. J. *J. Chem. Soc., Dalton Trans.*, in press.

(11) Bullen, G. J.; Clark, N. H. *J. Chem. Soc. A* **1969**, 404–10.

(12) Cf. structure **2** which shows a strong band at 1510 cm^{-1}. See also: (a) Coates, G. E.; Livingstone, J. G. *J. Chem. Soc.* **1961**, 1000–8; (b) Niedenzu, K.; Dawson, J. W. *J. Am. Chem. Soc.* **1959**, *81*, 5553–5. Niedenzu, K.; Dawson, J. W.; Fritz, P.; Jenne, H. *Chem. Ber.* **1965**, *98*, 3050–2. (d) Lappert, M. F.; Majumdar, M. K.; Tilley, B. P. *J. Chem. Soc. A* **1966**, 1590–5.

(13) The B_2N_2 ring in **11** is not expected to be square. Extensive lengthening of the horizontal B–N bonds would imply a weak dimer of **6**—inconsistent with the mass spectrum. Extensive lengthening of the vertical bonds should allow a nearly trigonal B═N bond—inconsistent with the absence of a strong B═N band in the infrared spectrum.

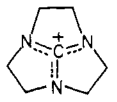
(14) Performed by Galbraith Labs, Knoxville, TN.

extreme hygroscopic nature of this compound made this determination very difficult and introduced a considerable error, but the observed molecular weight of 354 ± 90 is clearly consistent with the dimer (282 g/mol) and not the monomer (141 g/mol).

The infrared spectrum of **5** in the solid state also suggests the dimeric structure. As in **11**, but in contrast to **2** and **4**, there are no strong absorbances in the region 1500–1600 cm^{-1}. There are, however, weak bands between 1300 and 1410 cm^{-1} that could indicate a weak B–N double-bond character in this compound.

Our results are consistent with the strain considerations described in the introduction. Although **2**, **4**, and under certain conditions **5** are monomeric compounds, the most highly strained member of this series, **6**, has not been identified in solution or in the gas phase. Indeed, this molecule apparently exists only in dimeric form, **11**, with tetrahedral *tetravalent* boron atoms.

These results also bear on the question of the existence and stability of guanidinium ion, **12**. Previous attempts to prepare this cation have not succeeded.[2] Since **12** is isoelectronic with **6**, our results suggest that if **12** is prepared in the absence of nucleophiles it will probably dimerize to a dication with a structure that is analogous to **11**.



12

Experimental Section

^{13}C NMR data reported in Table I were recorded on a Bruker WH90 FT NMR spectrometer at 22.63 MHz. Mass spectra were recorded on a Perkin-Elmer Hitachi RMU-6E mass spectrometer at 15-eV ionizing potential unless otherwise indicated. For extremely hygroscopic compounds (**5** and **11**), this instrument was equipped with an argon glovebag enclosing the solid sample injection probe.

13-Bora-1,5,9-triazatricyclo[7.3.1.0^{5,13}]tridecane (2). In a small flask under nitrogen, 0.46 g (2.7 mmol) of 1,5,9-triazacyclododecane[6] and 5 mL of methyl orthoborate [$B(OMe)_3$] were refluxed 6 days and cooled, and the excess methyl orthoborate was evaporated from crystals of **2**. These crystals can be purified by recrystallization from methyl orthoborate or benzene and can be sublimed at 45–47 °C (0.01 kPa): ^{1}H NMR ($CDCl_3$) δ 1.70–2.25 (m, 6), 2.55–2.85 (t, 12); IR (KBr) 2940–2600, 1510 (b), 1440 (b), 1355, 1315, 1215, 1130, 1110, 1065, 650, 630, 407 cm^{-1}; mass spectrum (MS), *m/z* (rel intensity) 179 (90), 178 (100), 177 (27), 164 (6), 163 (2), 150 (3). Anal. ($C_9H_{18}BN_3$) C, H, N.

12-Bora-1,5,9-triazatricyclo[7.2.1.0^{5,12}]dodecane (4). 1,5,9-Triazacycloundecane[6] (**8**, 1.0 g, 6.4 mmol) was lithiated by stirring under nitrogen in 50 mL of anhydrous tetrahydrofuran at −78 °C and adding 12.6 mL of 1.6 M *n*-butyllithium. The resulting slurry was warmed to 20 °C and stirred 15 min and then was cooled to −78 °C and treated with 2.6 mL (20.5 mmol) of trimethylchlorosilane. After the mixture was stirred for 30 min at 20 °C, the solvent was exchanged to cyclohexane by distillation. This slurry was filtered, and the filtrate was concentrated and distilled bulb-to-bulb at 110 °C (7 Pa), giving 2.35 g (99%) of **9**, mp 50 °C. In a 200-mL flask, 1.39 g of **9** (3.7 mmol) dissolved in 20 mL of benzene was frozen and evacuated. Boron trifluoride gas (100 mL) was introduced, and the contents were warmed and stirred at 40–50 °C before introducing nitrogen to the flask. This mixture was then refluxed 24 h and concentrated, and the residue was distilled bulb-to-bulb at 80 °C (0.01 kPa), giving 0.48 g (78%) of **4**: ^{1}H NMR ($CDCl_3$) δ 3.13 (s, 4), 2.89 (q, $J = 6$ Hz, 8), 1.95 (m, 4); IR (neat) 2945, 2920, 2870–2800 (b), 1580 (sh), 1547 (b), 1510, 1472 (sh), 1447, 1434 (sh), 1347, 1325, 1294, 1223, 1182, 1125 (w), 1045 (w), 971 (w), 637 cm^{-1}; MS, *m/z* (rel intensity) 165 (100), 164 (100), 163 (28), 150 (3), 137 (5), 136 (5), 135 (3), 122 (2), 111–115 (m* 165, 164 → 137, 136). Anal. ($C_8H_{16}N_3B$) C, H, B.

11-Bora-1,4,7-triaza[5.3.1.0^{4,11}]undecane (5). A solution of 0.22 g (1.7 mmol) of 1,4,7-triazacyclodecane and 0.24 g (1.7 mmol) of tris(dimethylamino)borane[15] in 5 mL of anhydrous benzene was refluxed under nitrogen sweep with continuous trapping of the evolved base (dimethylamine). After 2 days of refluxing, the titer indicated greater than 95% completion (5 mmol of base). Benzene was removed by freezing and vacuum evaporation, leaving 0.21 g (92%) of **5**, mp 105–108 °C. This compound can be purified by sublimation [83 °C (0.02 kPa)] and is *extremely hygroscopic*: ^{1}H NMR ($CDCl_3$ + Me_2SO-d_6) δ 2.3–3.7 (m); IR (Nujol) 1356, 1341, 1311, 1276, 1256, 1231, 1196, 1176, 1146, 1126, 1056, 1036, 1001, 956, 916, 876, 836, 796, 766 cm^{-1}; MS, *m/z* (rel intensity, 70 eV) 151 (100), 150 (78), 123 (44), 122 (22), 100 (26), 99 (57), 87 (48). Because of the difficulty in handling this compound, elemental analyses were not attempted.

The Dimer 11 of 6. A solution of 0.15 g (1.2 mmol) of 1,4,7-triazacyclononane and 0.17 g (1.2 mmol) of tris(dimethylamino)borane in 5 mL of anhydrous benzene was refluxed 12 h until titration of the evolved base indicated greater than 95% completion. Benzene was removed by freezing and vacuum evaporation, leaving **11** as a white, *extremely hygroscopic* solid: mp 157–163 °C; ^{1}H NMR ($CDCl_3$ + Me_2SO-d_6) δ 2.5–3.9 (m); IR (Nujol) 1260, 1150, 1100, 1070, 1050, 995 (w), 800 cm^{-1}: MS, *m/z* (rel intensity) 274 (100), 273 (52), 272 (10), 259 (8), 246 (11), 245 (13), 244 (9), 243 (5), 233 (13), 232 (64), 231 (52), 230 (40), 229 (16), 219 (8), 218 (34), 217 (22), 216 (17), 215 (7), 204 (12), 203 (10), 202 (6), 189 (5), 188 (4), 163 (6), 152 (10), 151 (6), 150 (8), 138 (26), 137 (25), 136 (16), 135 (5), 124 (12), 123 (6), 122 (16), 121 (5), 78 (9), 45 (7), 44 (7). Because of the difficulty in handling this compound, elemental analyses were not attempted.

Identification of the Hydrolysis Product of 11. A mixture of 0.06 g of **11**, 0.18 g of benzoyl chloride, 0.05 g of sodium hydroxide, and 10 mL of water was refluxed 2 days, concentrated, and compared by TLC on silica gel plates to an authentic sample of the tris-benzoyl derivative of 1,4,7-triazacyclononane prepared by a similar procedure. These two benzoyl derivatives show identical behavior on elution with methanol/ethyl acetate. The benzoyl derivative from **11** is different from the hexabenzoyl derivative of 1,4,7,10,13,16-hexaazacyclooctadecane.

Acknowledgments. Support for this research was provided in part by an M. J. Murdock Trust Grant of Research Corporation. We thank Professor G. J. Bullen for X-ray crystallography on **2**.

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(15) Purchased from Aldrich Chemical Company or prepared by the method of Niedenzu, K.; Dawson, J. W. *Inorg. Synth.* **1967**, *10*, 135–6.