Evaluation of the Aromaticity of Borepin: Synthesis and Properties of 1-Substituted Borepins

Arthur J. Ashe III,* Wolfram Klein, and Roger Rousseau

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

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The reaction of 1,1-dibutylstannepin with BCl_3 gave 1-chloroborepin, which has been converted to a variety of 1-substituted borepins, C_6H_6BX, where X = OH, $O_{1/2}$, OCH_3, $2,4,6-Me_3C_6H_2$, $CH_2CH_2CH_2NMe_2$, F, NH_2, $N(CH_2)_5$, $N(iPr)_2$, H. 1-Chloroborepin and 1-aminoborepin have been investigated by ab initio methods. All borepins have been studied using ^1H NMR, ^{11}B NMR, and ^{13}C NMR spectroscopy. The X-ray crystal structure of 1-chloroborepin gives evidence of a π-delocalized structure. All properties are discussed in terms of the aromatic character of the borepin ring system.

Introduction

Borepin (1) is a neutral boron-containing heterocycle which is isoelectronic with the tropylium cation (2). In 1958, Vol'pin first suggested that borepin might be a Hückel 6π-aromatic compound.[1] Subsequently a number of ring-fused and other highly substituted borepins,[2-8] e.g. 3[5] and 4,[3] were prepared. Although heavy substitution may have masked the intrinsic properties of the borepin ring, aromatic character has been inferred from studies of the UV and NMR spectra of these derivatives.

Recently Schulman and co-workers have reported their ab initio MO studies on borepins and related molecules.[9] It was concluded that borepin is a planar but only weakly aromatic ring. The synthesis of the minimally substituted 1-methylborepin (5a)[10] has opened the way for an experimental examination of borepin aromaticity uncomplicated by C-ring substitution. We have made preliminary reports of the synthesis of 1H-borepin (1h)[11] and the structure of 1-chloroborepin (5c).[12] We now wish to record in detail our observation on 1-substituted borepins.

Synthesis

Borepins are most conveniently prepared by an exchange reaction of the appropriate stannepin with boron halides.[3,7,8,10] The preparation of 1-substituted borepins 5 requires the availability of 1,1-dialkylstannepin 6. As

Chart I

Chart I
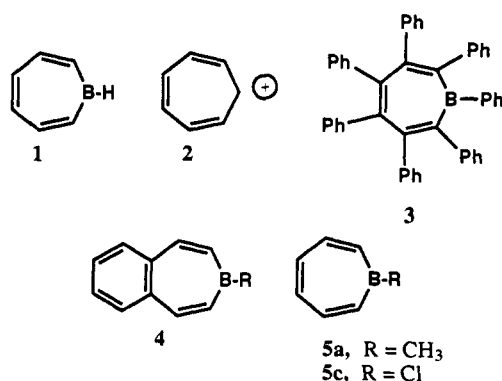
reported by Nakadaira and co-workers, the carbenoid ring expansion of lithium 1,1-dibutylstannacyclohexadienide (7(Li)) with alkyllithium and CH_2Cl_2 gives 1,1-dibutylstannepin (6).[13] We find the stannepin is always formed together with about 25% of its bicyclic isomer 8. Stannepin 6 is thermally labile, forming benzene and presumably dibutylstannylene when heated to 80 °C for 2 h. Heating the mixture of 6 and 8 to 100 °C followed by Kugelrohr distillation affords pure 8, which was identified on the basis of its spectra. It is presumed that isomers 6 and 8 are derived from the common intermediate 9, which either undergoes Sn migration to give 6 or double-bond addition which ultimately results in 8. An analogous mechanism has been proposed for the corresponding silicon compounds.[14]

While pure 6 can be separated by column chromatography, it is most convenient to use the mixed isomers in subsequent reactions with boron halides, since products derived from 8 are not found. The exchange reaction of 6 with methylboron dibromide in pentane gives a mixture of dibutyltin dibromide and 1-methylborepin (5a),[10] which can be separated by distillation. In a similar manner the exchange with phenylboron dibromide in benzene afforded 1-phenylborepin (5b) in 30% yield.[11] Attempted extension of this procedure to more hindered arylborepins was unsuccessful. Mesitylboron dibromide did not react with 6 at 25 °C. Alkyl- or arylborepins are sensitive to oxygen, and brief exposure to air colors them purple. They are

(1) Vol'pin, M. E. *Russ. Chem. Rev. (Engl. Transl.)* 1960, *29*, 129.

(2) van Tamelen, E. E.; Brieger, G.; Untch, K. G. *Tetrahedron Lett.* 1960, *8*, 14.

(3) (a) Leusink, A. J.; Drenth, W.; Noltes, J. G.; van der Kerk, G. J. M. *Tetrahedron Lett.* 1967, 1263. (d) Axelrad, G.; Halpern, D. *J. Chem. Soc. D* 1971, 291. (c) Ashe, A. J., III; Kampf, J. W.; Kausch, C. M.; Konishi, H.; Kristen, M. O.; Kroker, J. *Organometallics* 1990, *9*, 2944.

(4) Jeffries, A. T., III; Gronowitz, S. *Chem. Scr.* 1973, *4*, 183.

(5) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* 1975, *97*, 4436.

(6) Schacht, W.; Kaufmann, D. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 665.

(7) (a) Ashe, A. J., III; Drone, F. J. *J. Am. Chem. Soc.* 1987, *109*, 1879; 1988, *110*, 6599. (b) Ashe, A. J., III; Drone, F. J.; Kausch, C. M.; Kroker, J.; Al-Taweel, S. M. *Pure Appl. Chem.* 1990, 513.

(8) Sugihara, Y.; Yagi, T.; Murata, I.; Imamura, A. *J. Am. Chem. Soc.* 1992, *114*, 1479.

(9) (a) Schulman, J. M.; Disch, R. L.; Sabio, M. L. *J. Am. Chem. Soc.* 1982, *104*, 3785; 1984, *106*, 7696. (b) Disch, R. L.; Sabio, M. L.; Schulman, J. M. *Tetrahedron Lett.* 1983, *24*, 1863. (c) Schulman, J. M.; Disch, R. L. *Organometallics* 1989, *8*, 733.

(10) Nakadaira, Y.; Sato, R.; Sakurai, H. *Chem. Lett.* 1987, 1451.

(11) Ashe, A. J., III; Kampf, J. W.; Nakadaira, Y.; Pace, J. M. *Angew. Chem., Int. Ed. Engl.* 1992, *31*, 1255.

(12) Ashe, A. J., III; Kampf, J. W.; Klein, W.; Rousseau, R. *Angew. Chem., Int. Ed. Engl.*, in press.

(13) (a) Sato, R. Ph.D. Thesis, Tohoku University, 1985. (b) Nakadaira, Y.; Sato, R.; Sakurai, H. *J. Organomet. Chem.* 1992, *441*, 411.

(14) Nakadaira, Y.; Sato, R.; Sakurai, H. *Organometallics* 1991, *10*, 435.
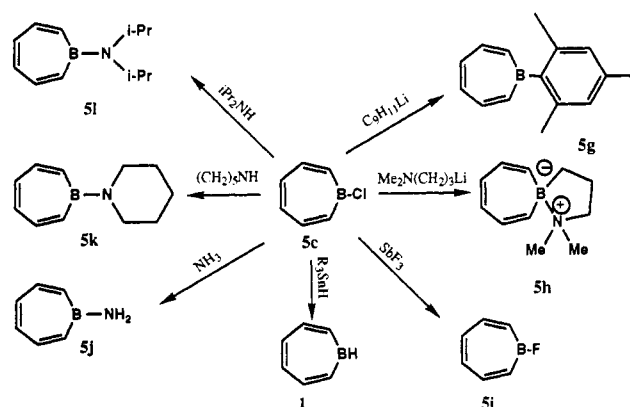
Scheme I
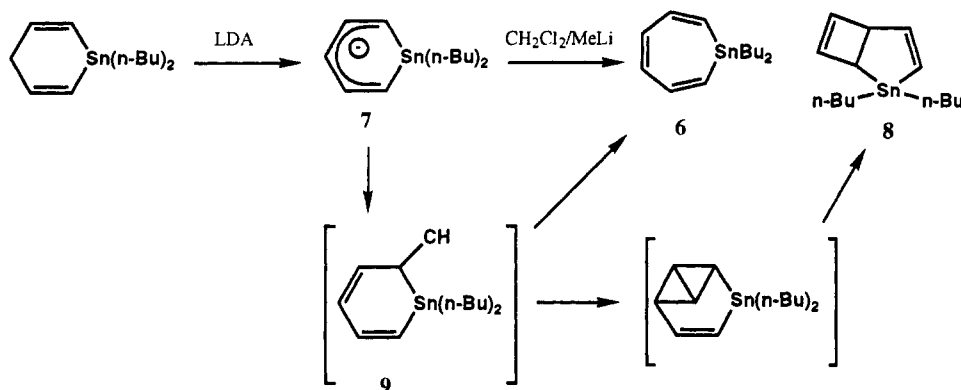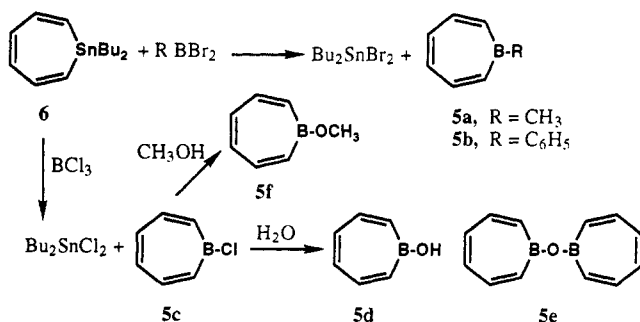
Scheme II

not particularly sensitive to water, and they are thermally stable to at least 150 °C. They are easily handled using ordinary Schlenk techniques, while small pure samples are conveniently obtained using gas chromatography.

The reaction of 1,1-dibutylstannepin with an excess of BCl_3 in hydrocarbon solvents (pentane, butane) at 0 °C affords 67% of 1-chloroborepin (5c).[11] Chloroborepin is a volatile liquid which is easily purified by pot-to-pot distillation. When it is cooled to -37 °C, it freezes to beautifully formed colorless needles. Although chloroborepin is less air-sensitive than 5a and 5b, it is extremely moisture-sensitive. Addition of 1 equiv of water to a solution of 5c in C_6D_6 converted it to a labile product to which we assign the structure 1-hydroxyborepin (5d). This compound slowly forms the B–O–B anhydride 5e on standing. The reaction with 1 equiv of CH_3OH in CH_2Cl_2 gives 1-methoxyborepin (5f) in 73% yield.[11]

1-Chloroborepin may be used to prepare alkyl- and arylborepins which cannot be prepared directly via exchange with 6. The reaction of 5c with mesityllithium in ether gave a 90% yield of 1-mesitylborepin (5g) as a yellow oil. It is interesting to note that, in contrast to 5a and 5b, 5g is moderately stable in air for short periods of time. Clearly the greater steric hindrance of 5g inhibits oxidation. The reaction of 5c with 1-lithio-3-(dimethylamino)propane in hexane gave 65% of the adduct, for which we assign the spiro structure 5h on the basis of spectra as discussed below.

The reaction of 1-chloroborepin with SbF_3 in CH_2Cl_2 gave a modest yield of 1-fluoroborepin (5i). Unfortunately, this compound is difficult to handle. It slowly turns dark on standing at 25 °C and is also extremely moisture-sensitive. Chloroborepin reacts with secondary amines to give good yields of the corresponding aminoborepins. The reaction of 5c with diisopropylamine gives 88% of 1-(diisopropylamino)borepin (5l) as a colorless oil which freezes at -10 °C, while reaction with piperidine gave 1-piperi-

Scheme III

dinoborepin (5k) (mp -45 °C) in 83% yield. In a similar manner the reaction of 5c with anhydrous gaseous ammonia gave 1-aminoborepin 5j.

Finally, it was of interest to prepare the parent 1*H*-borepin (1).[11] Treating a solution of 1-chloroborepin in C_6D_6 or C_6D_{12} with excess Bu_3SnH (or other tin hydrides) gave the very labile 1*H*-borepin, which has been identified largely on the basis of its ^1H, ^{11}B, and ^{13}C NMR spectra as discussed in our preliminary publication.[11] 1*H*-Borepin is extremely moisture-, oxygen-, and heat-sensitive, and we have not been able to isolate it. Addition of CH_3OH to 1 gives 5f. When it stands in dilute solution 1 reacts with adventitious water to give 5d and 5e.

These syntheses have provided us with a series of borepins with a wide range of substituents. It is our hope that a comparative study of their properties will define the extent of aromatic character of the borepin system. The properties of borepins, particularly those properties which bear most closely on the question of aromaticity, are discussed below.

Structure

Structure is a particularly important aspect of aromatic character.[15] The planarity, the lack of appreciable C–C bond alternation, and the multiple-bond character of the ring bonds of heterocycles such as pyridine are associated with their aromaticity.

(15) The aromaticity problem has been discussed many times. For particularly critical discussions see: (a) Badger, G. M. *Aromatic Character and Aromaticity*; Cambridge University Press: New York, 1969. (b) Garratt, P. J. *Aromaticity*; Wiley-Interscience: New York, 1986. (c) *Aromaticity, Pseudoaromaticity Antiaromaticity*; Jerusalem Symposia on Quantum Chemistry and Biochemistry 3; Israel Academy of Science and Humanities: Jerusalem, 1971.
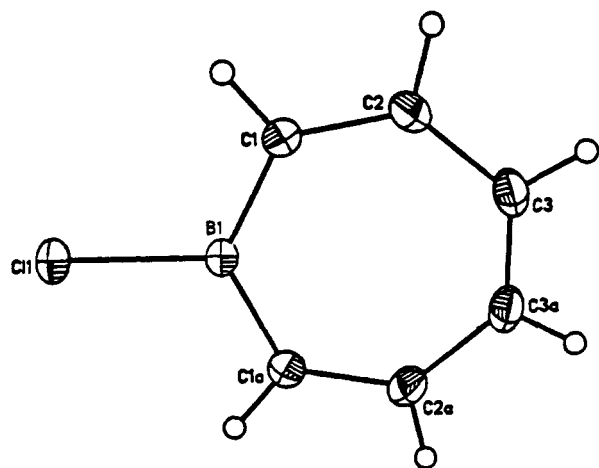
Figure 1. ORTEP view of 1-chloroborepin (5c), showing the atom-numbering scheme.

Table I. Comparison of the Calculated (6-31G*) Bond Distances (Å) for Selected Borepins (C₆H₆BX) with the Experimental Distances (X-ray) Found for C₆H₆BCl

bond[a]	1 (X = H)[b]	5j (X = NH₂)[c,d]	5c (X = Cl)[d]	5c (X-ray)[e]
B–X	1.197	1.411	1.804	1.802(2)
B–C(1)	1.537	1.558	1.531	1.514(1)
C(1)–C(2)	1.351	1.340	1.349	1.369(2)
C(2)–C(3)	1.438	1.453	1.440	1.424(1)
C(3)–C(3a)	1.349	1.340	1.347	1.366(1)
C–C range	±0.089	±0.113	±0.093	±0.058
calcd μ (D)[f]	+2.0	−0.58	+4.03	

[a] Numbering scheme used in Figure 1. [b] Reference 9. [c] N–H = 1.00. [d] C–H = 1.08. [e] Reference 11. [f] The negative end of the dipole moment points toward the B substituent for a positive μ and away from the B substituent for a negative μ.

While borepins **5a–l** are liquids at room temperature, the observation that 1-chloroborepin formed nice-looking crystals at low temperature encouraged us to attempt an X-ray crystal study of **5c**. Liquid **5c** was sealed in capillaries and cooled on the diffractometer until crystals formed at −37 °C. The molecular structure determined for 1-chloroborepin is illustrated in Figure 1, while bond distances are listed in Table I.[12,16]

The structure of 1-chloroborepin shows a completely planar ring, the largest deviation from the average ring plane being only ±0.01 Å. The C–C bond distances range from 1.37 to 1.42 Å, with the formal double bonds (C(1)–C(2) and C(3)–C(3a)) shorter than the formal single bonds (C(2)–C(3)). However, the range of C–C distances of ±0.058 Å is considerably less than that found in cycloheptatrienes (1.33–1.46 Å)[17] and other polyolefinic rings.[18] Indeed, this range is smaller than that found for naphthalene (1.36–1.42 Å)[19,20] and anthracene (1.37–1.44 Å).[19] The B–C(1) distance of 1.51 Å is considerably shorter than

the usual B–C single bonds (1.55–1.59 Å)[21] and must be ascribed to multiple bonding between boron and carbon. On this empirical basis it must be concluded that 1-chloroborepin meets the structural criteria for aromaticity.

MO Calculations

The planarity of 1-chloroborepin had been anticipated in analogy to the calculated structure for 1*H*-borepin.[9] However, these calculations had also indicated a greater alternation of C–C bond lengths than we have found for **5c**. In order to obtain an estimate of the structural consequences of changing substituents of borepins, we have performed MO calculations on **5c** and **5j**.

These Hartree–Fock-level ab initio MO calculations were run using the 6-31G* basis set (GAUSSIAN 90).[22] The geometrical parameters were optimized within the constraint of planar C_{2v} symmetry for **5c** but in C_s symmetry for **5j**. Subsequent vibrational analysis indicated that the planar structures were minima, since all of the calculated frequencies were positive. None of the computations included corrections for the effects of electron correlation.

The optimized bond lengths and dipole moments for **5c** and **5j** are compared in Table I. Also included are the published values for **1** calculated at the same level. The calculated bond distances for **1** and **5c** are not significantly different for the ring atoms. The average difference is only ±0.003 Å. Thus, no structural differences are predicted for substitution of 1-Cl for 1-H in borepin. The calculated and experimental structures for **5c** are in reasonable agreement with the corresponding bond lengths (±0.02 Å). However, the larger range of C–C distances (±0.093 Å) of the calculated structure overestimates the degree of bond alternation in chloroborepin. It might be noted that a similar situation is found for the closely related molecule tropone (**10**). The 6-31G* calculation gives a bond alternation of ±0.114 Å for **10**,[23] while the X-ray diffraction study showed the C–C bond alternation to be only ±0.077 Å.[24]

In contrast to the results of **5c**, calculations on the donor-substituted 1-aminoborepin (**5j**) show shorter formal double bonds and longer formal single bonds. The B–C bond is calculated to be 1.56 Å, while the range of C–C bonds is ±0.113 Å. In addition the exocyclic B–N bond of 1.41 Å is an appropriate distance for an aminoborane which has multiple B–N bonding.[25]

These changes are readily explained. The π-delocalization of borepins should increase with the Lewis acidity of the boryl group (BX). Electron withdrawal by the chlorine atom of **5c** should allow the boron atom to accept substantial electron density from the carbon atoms, thereby maximizing π-delocalization. However, π-donation from nitrogen to boron of **5j** should saturate the boron and greatly attenuate the CB delocalization. We have

(16) **5c**: monoclinic, C2/c (No. 15), with a = 11.338(0) Å, b = 8.597(5) Å, c = 7.493(4) Å, β = 121.61(4)°, V = 622.1(6) Å³, and Z = 4 (ρ_{calcd} = 1.328 g cm⁻³); μ(Mo Kα) = 4.88 cm⁻¹; 1133 unique reflections, 1094 with $F_o \geq 0.6\sigma(F)$ were used in refinement; R = 3.65%, R_w = 6.62%, GOF = 1.20. Details of the crystal structure determination are available from the Director of the Cambridge Crystallographic Data Centre.

(17) (a) Traetteberg, M. *J. Am. Chem. Soc.* **1964**, *86*, 4265. (b) Butcher, S. S. *J. Chem. Phys.* **1965**, *42*, 1833. (c) Davis, R. E.; Tulinsky, A. *J. Am. Chem. Soc.* **1966**, *88*, 4583.

(18) Bastiansen, O.; Hedberg, L.; Hedberg, K. *J. Chem. Phys.* **1957**, *27*, 1311.

(19) Cruickshank, D. W. J.; Sparks, R. A. *Proc. R. Soc. London, Ser. A* **1960**, *258*, 270.

(20) Almenningen, A.; Bastiansen, O.; Dyvik, F. *Acta Crystallogr.* **1961**, *14*, 1056.

(21) For example, Me₃B is 1.58 Å: Bartell, L. S.; Caroll, B. L. *J. Chem. Phys.* **1965**, *42*, 3076.

(22) (a) Gaussian 90, Revision I: Frisch, M. J.; Head-Gordon, M.; Tucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Fox, D. J.; Whiteside, R. A.; Seager, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Topiol, S.; Pople, J. A. Gaussian Inc. Pittsburgh, PA, 1990. (b) 6-31G* basis set: Hariharar, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Francil, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DiFries, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(23) Redington, R. L.; Latimer, S. A.; Bock, C. W. *J. Phys. Chem.* **1990**, *94*, 163.

(24) Barrow, M. J.; Mills, O. S.; Filippini, G. *J. Chem. Soc., Chem. Commun.* **1973**, 66.

(25) Thorne, L. R.; Gwinn, W. D. *J. Am. Chem. Soc.* **1982**, *104*, 3822.

Table II. ¹H NMR Parameters of Borepins (C₆H₆BX)ᵃ

X (compd)	δ (Δ)			$^3J_{H_\alpha H_\beta}$	$^3J_{H_\beta H_\gamma}$	X δ (Δ)
	H_α	H_β	H_γ			
H (1)ᵇ	8.06(−0.03)	7.93(0.33)	7.31(0.42)	12.4	8.3	n.o.ᶜ
CH₃ (5a)	7.66(0.02)	7.73(0.31)	7.18(0.39)	12.3	8.0	1.02 (−0.16)
C₆H₅ (5b)	8.14(0.04)	8.03(0.41)	7.35(0.50)	12.9	8.0	7.51 (−0.16) m, p; 8.09 (−0.03) o
Cl (5c)	7.63(0.03)	7.85(0.60)	7.31(0.74)	12.4	8.3	
HO (5d)	6.85(−0.01)	7.54(0.31)	6.90(0.40)	13.4	7.8	1.55
O₁/₂ (5e)	7.03(−0.07)	7.66(0.33)	6.98(0.37)	13.4	7.8	
OCH₃ (5f)	6.96(−0.03)	7.57(0.27)	6.89(0.33)	13.1	8.0	3.80 (0.50)
2,4,6-Me₃C₆H₂ (5g)	7.86(0.03)	7.97(0.35)	7.39(0.54)	12.9	8.2	2.09 (−0.07) Me$_o$, 2.38 (0.10) Me$_p$, 6.90 (−0.02) CH
CH₂CH₂CH₂NMe₂ (5h)	5.85(−0.18)	6.69(−0.23)	6.22(−0.15)	13.6	6.6	2.69 (0.45) NCH₂, 2.18 (0.56) Me, 1.90 (0.30) CH₂, 0.79 (−0.21) BCH₂
F (5i)ᵈ	7.12(0.07)	7.84(0.52)	7.17(0.59)	13.1	8.0	
NH₂ (5j)	6.62(0.11)	7.19(0.13)	6.58(0.19)	12.6	7.6	3.45(0.60)
N(CH₂)₅ (5k)	6.67(−0.03)	7.10(0.02)	6.55(0.08)	13.7	7.3	1.52 (0.27), 1.69 (0.31), 3.40 (0.22)
N(iPr)₂ (5l)	6.73(−0.04)	7.06(0.00)	6.57(0.08)	13.3	7.3	1.25 (0.2) 3.82 (0.2)

ᵃ All δ(CDCl₃) values in ppm; Δ = δ(CDCl₃) − δ(C₆D₆). $^3J_{H_\alpha H_\beta}$ and $^3J_{H_\beta H_\gamma}$ values are in Hz. ᵇ In c-C₆D₁₂ instead of CDCl₃. ᶜ n.o. = not observed. ᵈ $^3J_{H_\alpha F}$ = 2.8 Hz.
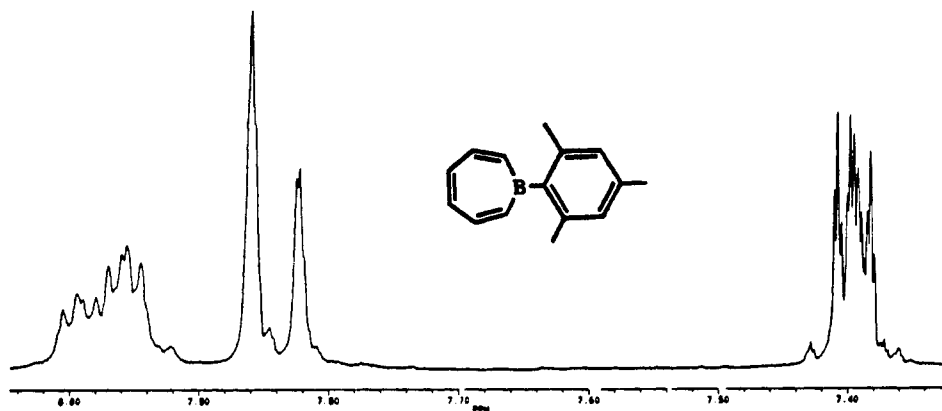

Figure 2. Low-field portion of the 360-MHz proton NMR spectrum of 1-mesitylborepin (5g), showing the signals for the borepin ring protons H_β (δ 7.97), H_α (δ 7.86), and H_γ (δ 7.39). The higher field signals due to the mesityl group have been omitted. The spectrum was recorded in CDCl₃.

not performed calculations on the oxygen-substituted borepins (5d–f), but we presume them to be intermediate between 5c and 5j in delocalization.

Although several of the aminoborepins are crystalline at low temperature, we have not been able to obtain crystals suitable for an X-ray diffraction study. Therefore, there is no direct structural information on aminoborepins.

¹H NMR Spectra

The ¹H NMR spectra of the borepins have been recorded in both C₆D₆ and CDCl₃, since they are subject to rather large solvent shifts. The spectra consist of an [AA′BB′CC′] pattern due to signals of the six ring protons. In all cases the signals due to the γ-protons occur as sharp symmetrical multiplets at highest field. The signals for the β-protons are broad doublets because of strong quadrupolar interaction with the trans ¹¹B, while the signals for the α-protons are an only slightly broadened doublets. The relative chemical shift values of the α- and β-signals vary with the B substituent and in some cases with solvent. The spectra are readily analyzed by computer simulation (Bruker PANIC or RACCOON). The chemical shift values and coupling constants are listed in Table II, while a typical spectrum, that of 1-mesitylborepin, is illustrated in Figure 2.

While the chemical shift values vary with both substituents and solvents, the coupling constants of the borepins (1, 5a–g, and 5i) are all virtually identical. Analysis of the spectra allows further discussion of the conformations of the borepins. It has been shown that
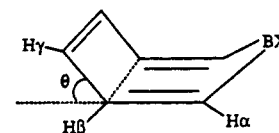

Figure 3. Illustration of the angle θ, the amount of folding of the ring C₆H₆BX. The angle θ is equal to the dihedral angle between planes $H_\gamma C_\gamma C_\beta$ and $C_\gamma C_\beta H_\beta$.

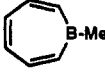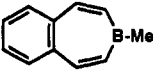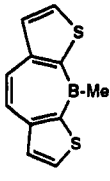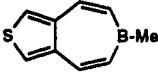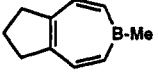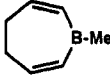the Karplus relationship[26] between the magnitude of the vicinal coupling constants $^3J_{H_\beta H_\gamma}$ and the torsional angle $H_\beta C_\beta C_\gamma - C_\beta C_\gamma H_\gamma$ applies to cycloheptatrienes[27] and various heterocycloheptatrienes[13,14] (see Figure 3 for illustration). Since the torsional angle corresponds to the degree of folding of the seven-membered ring, the ^3J values are direct measures of the planarity of the rings. The observed value of 8.3 Hz for $^3J_{H_\beta H_\gamma}$ of 1-chloroborepin is very close to that calculated for a torsional angle of 0° in the planar crystallographic conformation. Since borepins 1, 5a, 5b, 5d–g, and 5i also have $^3J_{H_\beta H_\gamma}$ values which are very close to 8.3 Hz, they must also adopt planar conformations.

The observed values for $^3J_{H_\beta H_\gamma}$ of the aminoborepins 5j–l are slightly smaller (7.3–7.6 Hz). If this decrease is significant, it suggests a conformation with a small deviation from planarity. The $^3J_{H_\beta H_\gamma}$ value of 5h is appreciably smaller (6.6 Hz). This value indicates a folding of 25° for 5h. It seems likely that the boron atom of 5h

(26) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

(27) Günther, H.; Görlitz, M.; Meisenheimer, H. *Org. Magn. Reson.* **1974**, *6*, 388.

Chart II

5a	**4**[3c]	**12**[4]
^{11}B NMR δ: 54.8	56.7	52.6

13[8]	**14**[7]	**15**[35]
^{11}B NMR δ: 50.8	53.6	64.1

Table III. ^{11}B NMR Chemical Shift Values (ppm) of Borepins (C_6H_6BX) and Dimethylboranes (Me_2BX)[a]

X	C_6H_6BX (compd)[b]	Me_2BX[c]
CH_3	54.8 (**5a**)	86.2
2,4,6-$Me_3C_6H_2$	54.1 (**5g**)	
C_6H_5	48.8 (**5b**)	77.6
H	48.0, J_{BH} = 99 Hz (**1**)	
Cl	47.9 (**5c**)	77.2
F	42.1, J_{BF} = 92 Hz (**5i**)	59.0, J_{BF} = 119 Hz
OH	40.3 (**5d**)	54.6
$O_{1/2}$	40.3 (**5e**)	52.0
OMe	40.0 (**5f**)	53.0
NH_2	36.6 (**5j**)	47.1
$N(iPr)_2$	34.0 (**5l**)	45.0[d]
$N(CH_2)_5$	34.0 (**5k**)	45.0[d]
$CH_2CH_2CH_2NMe_2$	0.8 (**5h**)	

[a] Data in ppm from external $BF_3\cdot OEt_2$. [b] C_6D_6 solution. [c] Reference 36. [d] Data for Me_2BNMe_2.

is four-coordinated, due to association with the pendant $-N(CH_3)_2$ group.[28] Since the boron atom is thereby removed from conjugation, the conformation of **5h** is more likely to be similar to a boatlike cycloheptatriene[17] than to the planar borepins.

One of the most widely used criteria of aromaticity relies on the magnetic properties of conjugated molecules.[15,29] The exterior protons of planar aromatic molecules exhibit low-field chemical shift values (in comparison to an appropriate model) which are indicative of a diamagnetic ring current.

While the chemical shift values for H_α and H_β of many borepins are in the nominal aromatic region (e.g. Figure 2 for 1-mesitylborepin), using these values to evaluate ring current effects seems problematical. The α- and β-protons experience large local magnetic effects due to proximity to the boron atoms and to the different boron substituents. Rather, it seems more appropriate to examine the chemical shift values of the remote γ-protons as measured in $CDCl_3$. These values differ by 0.8 ppm, from δ 7.39 for **5g** to δ 6.55 for **5k**. It is rather striking that the borepins with donor substituents (OR, NR_2) show rather high field signals, while 1H-, alkyl-, aryl-, and haloborepins show low-field signals. Since the aminoborepins in particular show chemical shifts which are very close to those of the nonaromatic cycloheptatriene (δ 6.42),[30] only a very modest ring current is indicated. On the other hand, the borepins with substituents which enhance the acceptor properties of boron seem to show appreciable ring currents.

As had been noted previously, the ^{1}H NMR chemical shifts of borepin rings show rather large aromatic solvent-induced shifts (ASIS)[31] between C_6D_6 and $CDCl_3$. The upfield shifts in benzene are largest for H_γ and decline in the order $H_\gamma > H_\beta > H_\alpha$. The largest effects are for 1-chloroborepin, where $\Delta(H_\gamma)$ = 0.74, $\Delta(H_\beta)$ = 0.60, and $\Delta(H_\alpha)$ = 0.03 ppm (Δ = δ($CDCl_3$) − δ(C_6D_6)). The smallest shifts are observed for the aminoborepins; e.g., for **5k** $\Delta(H_\gamma)$ = 0.08, $\Delta(H_\beta)$ = 0.02, and $\Delta(H_\alpha)$ = −0.03 ppm.

These ASIS effects can be plausibly explained in the usual manner.[31] Benzene must preferentially orient itself relative to the heterocycle so that protons near the positive end of the molecular dipole moment are in the shielding cone of benzene and thus experience a strong upfield shift.

Protons near the negative end of the molecular dipole moment experience little or sometimes downfield shifts. In this manner, ASIS has been used to assign the direction of the dipole moment of a number of heteroaromatic compounds (pyridine, pyrrole, thiophene, etc.).[32–34] The observed shifts for 1-chloroborepin experimentally establish that the negative end of its dipole moment points away from carbon toward boron and chlorine, as has been predicted by our MO treatment. The same direction of the dipole moment is indicated for 1H-borepin when the ASIS effects are compared between benzene and the less anisotropic solvent cyclohexane. Again, this conforms to the MO prediction. The ASIS data also establish that the borepins **5a**, **5b**, **5g**, and **5i** are similar. However, the lack of any sizable ASIS effects for **5j** is consistent with our calculations of a small dipole moment which is inverted in direction; i.e., the ring is negative and the $B-NH_2$ group positive.

^{11}B NMR Data

The ^{11}B NMR chemical shift for 1-methylborepin (**5b**) of δ 54.8, which had not previously been reported, is very close to the values for the more highly substituted methyl borepins which are listed in Chart II. The upfield shift of the methylborepins relative to the non fully conjugated 1-methyl-4,5-dihydroborepin (**15**)[35] is consistent with an increase in the electron donation to boron in the borepins.

The ^{11}B NMR chemical shift values of the 1-substituted borepins are collected in Table III. The substituent effects on the chemical shifts are not exceptional. In fact, the borepin chemical shift values (δ(C_6H_6BX)) show a good linear correlation in the chemical shift of the correspondingly substituted dimethylboranes (δ(Me_2BX)). Thus, δ-(C_6H_6BX) = 0.427[δ(Me_2BX)] + 16.6 ppm with R = 0.982.

However, the chemical shift value of 1-(3-(dimethylamino)propyl)borepin is far upfield (δ 0.8). This value is typically found for four-coordinated boron.[36] It provides strong evidence that **5h** has the assigned spiro structure.

^{13}C NMR Spectra

The ^{13}C NMR chemical shift values of the 1-substituted borepins are collected in Table IV. In all cases the signals

(28) Pelter, A.; Smith, K. Boron Nitrogen Compounds. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon: Oxford, U.K., 1979; Vol. 3, p 925.

(29) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722.

(30) Wehner, R.; Günther, H. *Chem. Ber.* **1974**, *107*, 3152.

(31) Laszlo, P. *Prog. NMR Spectrosc.* **1967**, *3*, 231.

(32) Marino, G. *J. Heterocycl. Chem.* **1972**, *9*, 817.

(33) Barton, T. J.; Roth, R. W.; Verkade, J. G. *J. Am. Chem. Soc.* **1972**, *94*, 8854.

(34) Fringuelli, F.; Gronowitz, S.; Hörnfeldt, A.-B.; Taticchi, A. *J. Heterocycl. Chem.* **1974**, *11*, 827.

(35) Kausch, C. M. Ph.D. Thesis, The University of Michigan, 1989.

(36) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61.

Table IV. ^{13}C NMR Chemical Shift Values (δ) for Borepins (C_6H_6BX)[a]

X (compd)	C_α	C_β	C_γ	X
H (1)	152 (br)[b]	149.2	136.4	
CH$_3$ (5a)	151 (br)	146.3	134.7	n.o.[c]
C$_6$H$_5$ (5b)	149.5 (br)	148.2	135.4	133.9 (C$_o$), 129.6 (C$_p$), 128.0 (C$_m$), C$_i$ (n.o.)
Cl (5c)	150 (br)	148.3	135.4	
OH (5d)	n.o.	146.3	132.6	
O$_{1/2}$ (5e)	n.o.	147.0	133.3	
OMe (5f)	140 (br)	146.2	132.7	n.o.
2,4,6-Me$_3$C$_6$H$_2$ (5g)	152 (br)	148.1	135.7	147.7 (C$_i$), 137.8 (C$_o$), 136.5 (C$_\beta$); 127.2 (C$_m$)
(CH$_2$)$_3$NMe$_2$ (5h)	147.0 (br)	135.0	130.0	44.2 (Me), 60.8, 21.3 (CH$_2$), CH$_2$B (n.o.)
F (5i)	149.0 (br)	149.5 (d), J_{CF} = 17.0 Hz	134.0	
NH$_2$ (5j)	142 (br)	143.4	131.6	
N(CH$_2$)$_5$ (5k)	138 (br)	141.2	131.5	48.0, 28.3, 25.9 (CH$_2$)
N(iPr)$_2$ (5l)	138 (br)	138.7	130.9	46.6 (CH), 22.9 (CH$_3$)

[a] Solvent C$_6$D$_6$. [b] br = broad. [c] n.o. = not observed.

due to the α-carbons are broad due to ^{11}B coupling, while the other ring signals are sharp. It is interesting that for all the borepins measured, including 4, 13, and 14, the α- and β-positions are almost equivalently deshielded. In contrast, the ^{13}C NMR spectra of most simple vinylboranes, such as 15, show the β-carbon signals substantially downfield.[37,38] This has frequently been ascribed to a preferential π-donation from the β-carbon to boron. If the π-charge densities are important in determining the chemical shift values of borepins, the data suggest equivalent electron donation from both α- and β-carbons to boron. The 6-31G* calculations on 1, 5c, and 5j give pπ orbital populations which are nearly identical for the α- and β-carbons. There is rather little variation in the chemical shift values of the γ-carbon atoms with B substituents (δ 131-136). Thus, little change in charge density at the γ-carbon is indicated.

UV Spectra

The UV spectrum of 1-methylborepin (5a) consists of bands centered at 218 nm (log ϵ = 4.24) and 283 nm (log ϵ = 3.72). The lower energy band has marked vibrational fine structure (λ_{max} 315, 306, 300, 295, 288, 283 nm), as had been observed for the corresponding band of 14. These bands are red-shifted from those of cycloheptatriene (λ_{max} 199, 261 nm),[39] which is consistent with conjugation between the MeB and hexatrienyl moiety of 5a. The UV spectra of 5c, 5h, and 5j are similar with bands at 224, 294 nm for 5c, 211, 277 nm for 5h, and 222, 299 nm for 5j. The fact that the UV spectrum of the spiro compound 5h more clearly resembles that of 5a than that of cycloheptatriene is surprising on the basis of the structural assignment for 5h.

Summary

Our discussion has emphasized that borepins have aromatic character. It is well to remember that aromaticity is not a precisely defined quality. Aromaticity is derived empirically from the particular properties, aromatic character, of benzene-like molecules. We have argued that the borepins meet the structural and spectroscopic criteria for aromaticity. As yet we have no evidence that borepins meet the thermodynamic criteria (resonance energy). This remains a goal for further research.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of nitrogen or argon. Solvents were dried by using standard procedures. The mass spectra were determined by using a VG-70-S spectrometer, while the NMR spectra were obtained by using either a Bruker WM-360 or WM-300 spectrometer, on solutions in CDCl$_3$, C$_6$D$_6$, or C$_6$D$_{12}$ as noted. The ^{1}H NMR and ^{13}C NMR spectra were calibrated using signals from the solvents referenced to Me$_4$Si, while external BF$_3$·OEt$_2$ and CCl$_3$F were used to calibrate the ^{11}B NMR and ^{19}F NMR spectra, respectively. The UV spectra were run using a Shimadzu UV-2101 PC UV/vis scanning spectrometer Experimental procedures have been previously reported for 1, 5b, 5c, and 5f.[11] Mesityllithium,[40] (3-(dimethylamino)propyl)lithium,[41] and 1,1-dibutylstannacyclohexa-2,5-diene[42] were prepared by literature procedures. All other compounds are commercially available.

1,1-Dibutylstannepin (6) and 2,2-Dibutyl-2-stannabicyclo-[3.2.0]hepta-3,6-diene (8). This procedure has been adapted from an original by Nakadaira and co-workers.[13] A solution of lithium diisopropylamide was prepared from 5 g (50 mmol) of diisopropylamine in 90 mL of ether and 18 mL (44 mmol) of 2.5 N butyllithium in hexane. After this solution was cooled to -78 °C, 1,1-dibutyl-1-stannacyclohexa-2,5-diene (10.0 g, 33.4 mmol) was added dropwise with stirring over 5 min. The reaction mixture was warmed to 25 °C with stirring over 2 h, during which time the color changed from yellow to red-green. Then the reaction mixture was cooled to -78 °C and a solution of methyllithium (68.5 mmol) in ether was added slowly. This mixture was added over 30 min to a solution of 10 mL of CH$_2$Cl$_2$ in 50 mL of ether at -78 °C. Afterwards, the reaction mixture was added to water and the organic layer was separated, washed sucessively with 10% aqueous HCl and excess H$_2$O, and dried over anhydrous MgSO$_4$. Removal of the solvent left 8.3 g of an air-sensitive orange liquid, the ^{1}H NMR spectrum of which showed it to be 40% 6, 12% 8, and 48% tetrabutyltin and other uninvestigated butyltin derivatives. This material was used in subsequent reactions. However, small quantities of pure 6 and 8 could be obtained as follows.

(a) 1,1-Dibutylstannepin (6). A sample of the above mixture (0.46 g) was subject to column chromatography over silica gel using hexane elution, giving 0.16 g of 6, which showed spectra identical with those reported.[13] ^{1}H NMR (CDCl$_3$): δ 0.9-1.6 (Bu), 6.08 (d, J = 13.4 Hz, J_{SnH} = 81 Hz, 2H), 6.21 (m, 2H), 7.07 (dm, J = 13.4 Hz, J_{SnH} = 145 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 10.1, 13.6, 27.2, 29.1 (Bu), 132.6, 133.4, 142.2 (CH).

(b) 2,2-Dibutyl-2-stannabicyclo[3.2.0]hepta-3,6-diene (8). A 50-mg sample of the mixture of 6 and 8 was dissolved in 1.0 mL of CDCl$_3$ and the solution sealed in an NMR tube. The mixture was heated to 100 °C for 21 h. The ^{1}H NMR spectrum

(37) Yamamoto, Y.; Moritani, I. *J. Org. Chem.* **1975**, *40*, 3434.

(38) Zweifel, G.; Clark, G. M.; Leung, T.; Whitney, C. C. *J. Organomet. Chem.* **1976**, *117*, 303.

(39) *DMS UV Atlas of Organic Compounds*; Perkampus, H. H., Sandeman, J., Timmons, C. J., Eds.; Butterworths: London, 1966; p A 15/4.

(40) Gillette, G. R.; Yokelson, H. B.; West, R. *Organomet. Synth.* **1988**, *4*, 529.

(41) Thiele, K.-H.; Langguth, T. E.; Müller, G. E. *Z. Anorg. Allg. Chem.* **1980**, *462*, 152.

(42) Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804. Ashe, A. J., III; Chan, W.-T. *J. Org. Chem.* **1979**, *44*, 1409.

showed the presence of benzene, 8, and an unidentified butyltin product(s). Removal of solvent left an oil which on Kugelrohr distillation (120 °C, 0.05 Torr) gave 10 mg of pale yellow oil which rapidly turned dark on exposure to air. MS(EI): m/z (relative intensity) 312 (2, M^+ for $C_{14}H_{24}^{120}Sn$), 121 (100). MS (EI, exact mass): calcd for $C_{14}H_{24}^{120}Sn$ 312.0900, found 312.0901. ^1H NMR (CDCl$_3$): δ 7.03 (dd, J = 10.2, 3.3 Hz, H$_4$), 6.33 (dd, J = 10.2, 2.0 Hz, H$_3$), 6.30 m, 6.08 m (H$_6$H$_7$), 4.05 (tq, J = 3.4, 1 Hz, H$_5$), 2.86 (d, J = 3.4 Hz, H$_1$) 1.5–0.8 (Bu). ^{13}C NMR (C$_6$D$_6$): δ 150.1, 141.1, 137.2, 129.5, (CH=CH) 58.8, 34.0 (CH), 29.5, 29.3, 27.0, 26.9, 17.6, 13.64, 13.58, 11.5 (Bu).

1-Methylborepin (5b). 1,1-Dibutylstannepin (6.5 g of mixed isomers 6 and 8, 8.4 mmol) was added dropwise with stirring to methylboron dibromide (2.66 g, 14 mmol) in 3 mL of pentane at –78 °C over 15 min. The mixture was warmed slowly to 25 °C and then stirred at 25 °C for 12 h. The solvent was removed under vacuum at –5 °C, and the residue was subjected to pot-to-pot distillation (50 °C, 0.05 Torr), affording 650 mg (74%) of **5b** as a yellow oil. A very pure sample was obtained by GLPC using a 1.5 m × ¹/₄ in. column packed with 20% Apiezon L on Chromosorb W. **5b** had a retention time of 10 min at 120 °C using He elution. ^1H NMR, ^{13}C NMR, and MS data were consistent with those reported by Nakadaira et al.[10] UV (cyclohexane): λ$_{max}$ (log ε) 218 nm (4.24), 283 (3.72).

1-Hydroxyborepin (5d) and 1,1-Bis(borepin) Oxide (5e). In an NMR tube, 2 μL of H$_2$O was added to 10 μL (0.1 mmol) of 1-chloroborepin in 400 μL of C$_6$D$_6$. **5d** formed immediately and was characterized by ^1H, ^{11}B, and ^{13}C NMR. This solution was treated with 10 mg of anhydrous MgSO$_4$ for 14 h. **5e** formed and was characterized by NMR.

1-Mesitylborepin (5g). To a solution of 1-chloroborepin (171 mg, 1.38 mmol) in 4 mL of ether at –78 °C was added with stirring a suspension of mesityllithium (164 mg, 1.30 mmol) in 5 mL of ether. After it was warmed to 25 °C, the mixture was stirred for 14 h. The solvent was then removed under vaccum, and the residue was extracted with pentane. Removal of the solvent left a yellow oil which was subject to pot-to-pot distillation (80–90 °C, 0.1 Torr), giving 258 mg (1.24 mmol, 90%) of a yellow oil, which is air-stable for a short period of time. MS: m/z (relative intensity) 208 (93, M^+), 102 (100). High-resolution MS: calcd for $C_{15}H_{17}^{11}B$ 208.1423, found 208.1423.

1-(3-(Dimethylamino)propyl)borepin (5h). A solution of 1-lithio-3-(dimethylamino)propane (7.0 mL of a 0.16 M solution in hexane, 1.12 mmol) was added dropwise with stirring at –60 °C to a solution of 1-chloroborepin (100 μL, 1.05 mmol) in 8 mL of hexane. The stirring was continued for 4 h after warming to 25 °C. The mixture was then filtered, and the solvent was removed under vacuum, leaving a semisolid residue which still contained traces of the lithium reagent. This material was taken up in 5 mL of pentane, and the resulting solution was cooled to –40 °C. Dropwise addition of 1,2-dibromoethane resulted in the formation of a white precipitate, which was filtered off. Removal of the solvent left a colorless, air-sensitive oil (119 mg, 0.08 mmol, 65%). Attempted distillation led to decomposition. MS: m/z (relative intensity) 174 (100, M^+). High-resolution MS: calcd for $C_{11}H_{17}^{11}BN$ 174.1454, found 174.1458. UV (cyclohexane): λ$_{max}$ (log ε) 211 nm (4.04), 277 (3.67).

1-Fluoroborepin (5i). 1-Chloroborepin (335 mg, 2.7 mmol) was added with stirring at 25 °C to a suspension of freshly sublimed SbF$_3$ (580 mg, 3.2 mmol) in 3 mL of CH$_2$Cl$_2$. After the

brown reaction mixture had stirred for 90 min, it was concentrated at 0 °C under vacuum. The residue was pot-to-pot distilled (25 °C, 0.05 Torr), yielding 30 mg of an extremely air- and moisture-sensitive colorless liquid, which became dark on standing at 25 °C. MS: m/z (relative intensity) 108 (31, M^+). High-resolution MS: calcd for $C_6H_6^{11}BF$ 108.0547, found 108.0545. ^{19}F NMR (C$_6$D$_6$): δ –86.2 (br q, J_{BF} = 86 Hz).

1-Aminoborepin (5j). Dry gaseous ammonia was bubbled through a stirred solution of 1-chloroborepin (260 mg, 200 μL, 2.1 mmol) in 12 mL of pentane at –40 °C at the rate of ca. 3 bubbles/s. A white precipitate formed immediately. After the mixture was warmed to 25 °C, the stirring was continued for 12 h. The mixture was then filtered, and the residue was concentrated under vacuum to a yellow oil which was pot-to-pot distilled (25 °C, 0.05 Torr), giving 120 mg (1.1 mmol, 54%) of an extremely air- and moisture-sensitive colorless liquid, mp –25 °C. MS: m/z (relative intensity) 105 (35, M^+), 104 (100). High-resolution MS: calcd for $C_6H_8^{11}BN$ 105.0750, found 105.0744. UV (cyclohexane): λ$_{max}$ (log ε) 212 nm (4.14), 299 (3.60).

1-(Diisopropylamino)borepin (5l). Diisopropylamine (650 μL, 469 mg, 4.6 mmol) was added dropwise with stirring to a solution of 1-chloroborepin (150 μL, 195 mg, 1.6 mmol) in 6 mL of pentane at 25 °C. A white precipitate formed immediately. After the reaction mixture had been stirred at 25 °C for 3 h, the suspension was filtered, affording a clear filtrate. The solvent was removed under vacuum, and the residue was subjected to a pot-to-pot distillation (50 °C, 0.05 Torr), affording 265 mg (1.41 mmol, 88%) of a colorless, air-sensitive liquid, mp –10 °C. MS: m/z (relative intensity) 189 (19, M^+), 174 (100). High-resolution MS: calcd for $C_{12}H_{20}^{11}BN$ 189.1689, found 189.1676.

1-Piperidinoborepin (5k). Piperidine (316 μL, 270 mg, 3.2 mmol) was added with stirring to a solution of 1-chloroborepin (100 μL, 130 mg, 1.05 mmol) in 10 mL of pentane at 25 °C. Further workup as described for **5l** above yielded 150 mg (0.87 mmol, 83%) of a colorless, air-sensitive liquid: bp 80 °C, 0.05 Torr; mp –45 °C. MS: m/z (relative intensity) 173 (87, M^+), 172 (100). High-resolution MS: calcd for $C_{11}H_{16}^{11}BN$ 173.1376, found 173.1371.

Computer-Simulated H NMR Spectra. The ^1H NMR spectra were simulated using the RACCOON program. All peaks in the simulated spectra matched the experimental spectra within 1 Hz. The values for δ(H$_α$,H$_β$,H$_γ$), $J_{H_αH_β}$, and $J_{H_βH_γ}$ are listed in Table II. The following values for ^1H–^1H coupling constants were used in all cases: $J_{H_αH_γ}$ = 1.0, $J_{H_αH_γ'}$ = 0.7, $J_{H_αH_β'}$ = 0, $J_{H_αH_α'}$ = 3.2, $J_{H_βH_γ'}$ = 1.0, $J_{H_βH_β'}$ = $J_{H_βH_α'}$ = 0, $J_{H_γH_γ'}$ = 11.1 Hz.

Supplementary Material Available: Listings giving complete specifications of the 6-31G* geometries for **5c** and **5j** (Z matrices and coordinates) (2 pages). Ordering information is given on any current masthead page.