Borepin and Its Analogues: Planar and Nonplanar Compounds

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Density-functional calculations are used to study methylated borepins and aminoborepins, dibenzoborepins, and tribenzoborepin. Steric hindrance and attenuated aromatic character produce significant nonplanarity of the seven-membered ring in some of these derivatives. Geometries, ^{13}C and ^{11}B chemical shifts, and magnetic susceptibilities are reported for these and for reference compounds. For permethylated 1-aminoborepin, the calculated geometry and chemical shifts are in good agreement with an unpublished experimental study. Tribenzoborepin and two dibenzoborepins are predicted to be nonplanar. One of the latter is studied in detail.

The suggestion of Vol'pin[1] more than forty years ago (1958) that the 6π-electron heterocycle borepin **1a** is a Hückel-type aromatic compound initiated experimental and theoretical studies continuing to the present time. While the following decade saw the preparation of highly substituted borepins such as B-hydroxydibenzoborepin[2] and benzoborepin,[3] there is now a wider variety of borepins,[4] including the parent **1a**[5b] and the 1-methyl,[5a,b] 1-chloro, and 1-amino derivatives **1b**−**d**.[5d]

Borepin is significantly less aromatic than the tropylium ion **2**, on the basis of its thermochemistry, extent of bond alternation, and magnetic properties.[6] Calculations at various levels indicate that the monocyclic borepins **1a**−**d** and all three benzoborepins are planar, despite their angle strain. Experimental confirmation has thus far been limited to an X-ray structure of 1-chloroborepin **1c**.[5c,d] However, the vibrational mode of lowest frequency, leading to out-of-plane distortions, has a much lower frequency in borepin and 1-aminoborepin than in tropylium, and ab initio calculations suggest that 1-(dimethylamino)borepin **3a** has a small energetic preference for a boat-shaped structure, due in part to steric interactions.[6b] We show here that definitively nonplanar structures can be obtained through adverse steric interactions in polymethylated borepins and 1-aminoborepins and in borepins having more than one fused benzene ring. These cases are examined by means of ab initio calculation at the density functional level of geometries, energies, chemical shifts, and, in several instances, magnetic susceptibilities.

Methods

Energies and optimized geometries are reported at the B3LYP/6-311+G** density-functional level.[7,8] Chemical shifts at these geometries were calculated by the GIAO method[9] at HF/6-31G*. Boron chemical shifts are relative to $BF_3{\cdot}OEt_2$. Magnetic susceptibilities were computed by the CSGT method.[10] All calculations were performed with GAUSSIAN 98[11] on Digital Alpha servers.

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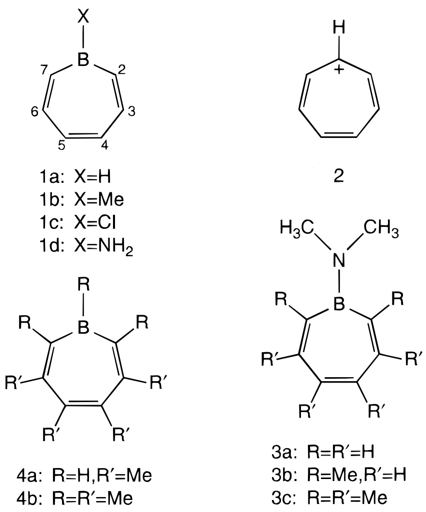
Chart 1



1a: X=H
1b: X=Me
1c: X=Cl
1d: $X=NH_2$

2

3a: R=R′=H
3b: R=Me,R′=H
3c: R=R′=Me

4a: R=H,R′=Me
4b: R=R′=Me

Dimethylaminoborepins

The BN bond and its substituents are in a near planar arrangement in all the aminoborepins discussed here. While aminoborepin itself is planar, MP2/6-31G* calculations show that 1-(dimethylamino)borepin **3a** (Chart 1) adopts a boat conformation of C_s symmetry.[6b] The present density-functional calculations furnish the same result, with boron-prow (α) and ethylene-stern (*β*) elevation angles of 28° and 10°, respectively. The calculated boron and carbon chemical shifts (Table 2) are in good agreement with those of diisopropylaminoborepin, studied by Ashe and co-workers.[5d] The boat structure of **3a** is quite flexible, with distortion into a planar form (having two imaginary vibrational frequencies) costing only ca. 1 kcal/mol.

A substantially more distorted structure is **3b** (Figure 1; H atoms are omitted in Figures 1−3 for clarity), having methyls on the 2,7 carbons. Its elevation angles are $\alpha = 50.8°$, $\beta = 20.8°$. The ^{11}B chemical shift, 38.5 ppm, is downfield from that of **3a**, 33.5 ppm, consistent with a smaller electronic population on boron. Carbons 3 and 6, which are in conjugation with boron, show a deshielding of ca. 14 ppm in **3b** relative to **3a**; however, the α carbons are much less changed. The formal single bonds in **3b** are slightly longer than those of **3a** (Table 1).

Permethylated aminoborepin **3c**, having eight methyls, is even more distorted (Figure 2), with elevation angles $\alpha = 50.6°$, $\beta = 34.8°$. The prow value is close to that of **3b**. The calculated boron chemical shift, 40.2 ppm, is also close to that of **3b**, 38.5, consistent with their nearly identical prow-elevation angles.

Fagan and co-workers have synthesized and studied **3c**.[12] Their X-ray structure shows two molecules per unit cell, each of which is slightly distorted (in a different manner) from C_s symmetry. The bond lengths are in good agreement with our calculated B3LYP/6-311+G** values (Table 1), except for a rather short BN bond. The X-ray structure gives the dihedral angle $C_7BC_2C_3$ as 57.0−60.0°, compared with the calculated value of 60.1°; the (smaller) dihedral angle $C_2C_3C_4C_5$, related to the stern elevation, ranges from 7.5° to 11.1° in the X-ray structure vs 4.1° calculated. The X-ray prow and stern elevation angles are ca. $\alpha = 48°$, $\beta = 40°$. Fagan's carbon and boron chemical shifts of **3c** are in good agreement with our calculated GIAO HF/6-31G*//B3LYP/6-311+G** values (Table 2), particularly for boron, where the difference is only 0.2 ppm.

Borepins

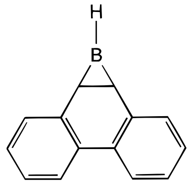
Aminoborepins are probably more susceptible to nonplanar distortion than borepins, since the BN (partial) double bond competes with 6*π*-electron delocalization in the ring by forming a cross-conjugated system. Nonetheless, we have found several nonplanar derivatives of borepin. Stern-substituted 3,4,5,6-tetramethylborepin **4a** has a C_2 structure, since twisting relieves the methyl interactions; the dihedral angle about the C_4C_5 double bond is 16.6°. The boron and C_2 chemical shifts are similar to those of borepin itself. Like dimethylaminoborepin, **4a** is fluxional: its planar form is only ca. 1 kcal/mol higher in energy.

Heptamethylborepin **4b** (Figure 3) is boat-shaped (C_s), having $\alpha = 31.4°$, $\beta = 30.1°$. The stern angle is similar to that calculated for permethylaminoborepin **3c**, 34.8°. The C_3C_4 single bond is 0.038 Å longer than that of (planar) methylborepin **1b**, reflecting steric interactions of the C_3 and C_4 methyls. The barrier for boat-to-boat conversion is ca. 10 kcal/mol.

Benzoborepins

The four dibenzoborepins **5a**−**d** and tribenzoborepin **6** (all as yet unknown) are depicted in Chart 2. The energies of **5b**−**d**, relative to **5a**, are 9.0, 15.0, and 29.0 kcal/mol. **5a** (C_{2v}) and **5c** (C_s) are planar, implying that the B-hydroxyl derivative of **5a** is also planar.[2] Due to interaction between the hydrogen on boron and the nearest H atom of a benzene ring, calculated to be 2.09 Å apart, **5b** is nonplanar; for example, the dihedral angle $C_4C_5C_6C_7$ is 36.5°.

Isomers **5c** and **5d**, 5*H*-dibenzo[*b*,*e*]borepin and 6*H*-dibenzo[*c*,*e*]borepin, respectively, are substantially less stable than **5a**, since ring fusion entails loss of conjugation within one or both benzene rings. **5d** has a C_2 structure (Figure 4), thereby reducing the eclipsing interactions of *ortho* hydrogens (1.977 Å distant). It is only 5.8 kcal/mol lower in energy than its boranorcaradiene isomer **5e**, whereas borepin is 40.0 kcal/mol more stable than boranorcaradiene at the B3LYP 6-311+G** level.



5e

In tribenzo[*b*,*d*,*f*]borepin **6** (Figure 5) the shortest interhydrogen distance is found to be 2.252 Å. Its boat structure has elevation angles $\alpha = 24.0°$, $\beta = 37.2°$. The downfield ^{11}B chemical shift of 60.1 ppm is similar to that of **5a**, 58.7.

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(12) Dr. Paul J. Fagan, Central Research and Development Department, Experimental Station, the DuPont Company, Wilmington, DE 19880-0328, private communication.

Table 1. B3LYP/6-311+G Bond Lengths (Å) of Borepins**[a]

molecule	BC_2	C_2C_3	C_3C_4	C_4C_5	BX
		Borepins			
borepin (**1a**)	1.524	1.374	1.421	1.374	1.197
1-methylborepin (**1b**)	1.534	1.371	1.421	1.374	1.587
1-chloroborepin (**1c**)	1.520 (1.514)[b]	1.370 (1.369)	1.425 (1.424)	1.371 (1.366)	1.809 (1.802)
1-aminoborepin (**1d**)	1.544	1.361	1.437	1.364	1.420
3,4,5,6-tetramethylborepin (**4a**)	1.512	1.376	1.453	1.396	1.198
heptamethylborepin (**4b**)	1.545	1.375	1.459	1.377	1.591
		1-(Dimethylamino)borepins			
1-(dimethylamino)borepin (**3a**)	1.553	1.362	1.436	1.362	1.427
2,7-dimethyl- (**3b**)	1.569	1.361	1.442	1.364	1.407
2,3,4,5,6,7-hexamethyl- (**3c**)	1.567 (1.567)[c]	1.360 (1.331)	1.474 (1.487)	1.369 (1.348)	1.408 (1.365)
		Model Compounds			
9a	1.542	1.356	1.449	1.492	1.198
9b	1.555	1.349	1.454	1.492	1.413
9c	1.564	1.351	1.451	1.487	1.427

[a] Bond lengths of benzoborepins are in Chart 2. [b] Experimental values in parentheses are from Ashe et al., ref 5c. [c] Experimental values in parentheses are from Fagan, ref 12.

Table 2. HF/6-31G*//B3LYP/6-311+G Chemical Shifts (ppm)**[a]

molecule	C_2, C_7	C_3, C_6	C_4, C_5	B
		Borepins		
borepin (**1a**)	149.6 (152)[b]	148.5 (149)	134.1 (136.4)	44.6 (48.0)
1-methylborepin (**1b**)	149.3 (151)	146.7 (146.3)	133.2 (134.7)	49.2 (54.8)
1-chloroborepin (**1c**)	146.2 (150)	148.3 (148.3)	133.8 (135.4)	47.8 (47.9)
1-aminoborepin (**1d**)	140.3 (142)	143.6 (143.4)	130.2 (131.6)	33.2 (36.6)
3,4,5,6-tetramethylborepin (**4a**, C_2)	148.5	158.9	144.0	42.2
heptamethylborepin (**4b**)	144.8	149.6	134.0	57.4
		Benzoborepins		
dibenzoborepin (**5a**, C_{2v})	138.0	146.8	131.9	58.7
dibenzoborepin (**5b**, C_1)	131.0, 141.6	154.5, 148.2	135.1, 141.2	54.7
dibenzoborepin (**5c**, C_s)	149.2, 142.0	142.1, 154.1	149.3, 132.5	46.6
dibenzoborepin (**5d**, C_2)	180.0	145.2	142.4	30.6
tribenzoborepin (**6**, C_s)	141.2	148.5	139.0	60.1
		1-(Dimethylamino)borepins		
1-(dimethylamino)borepin (**3a**, C_s)	136.5 (138)	141.6 (138.7)	130.2 (130.9)	33.5 (34.0)
2,7-dimethyl- (**3b**, C_s)	135.3	128.0	126.4	38.5
2,3,4,5,6,7-hexamethyl- (**3c**, C_s)	133.9 (136)[c]	136.5 (135.6)	134.2 (133.4)	40.2 (40.4)
		Model Compounds		
(**9a**, C_{2v})	127.3	149.7	144.9	52.7
(**9b**, C_{2v})	126.8	143.6	144.5	32.7
(**9c**, C_s)	126.4	143.9	145.2	33.2

[a] Numbers identifying carbon atoms of the seven-membered ring are those of Chart 1; ^{13}C shifts are relative to TMS, ^{11}B to $BF_3{\cdot}OEt_2$. [b] Values in parentheses are from Ashe et al., ref 5d; the values for **3a** are those of dialkylaminoborepins. [c] Experimental values for **3c** are from Fagan, ref 12.

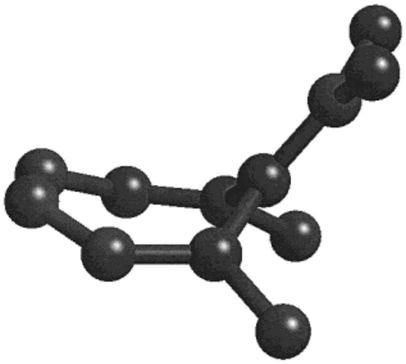

Figure 1. Dimethylamino-2,7-dimethylborepin, **3b**.

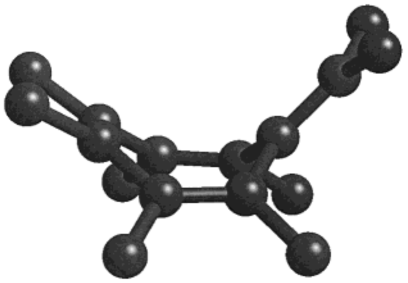

Figure 2. Permethylated 1-aminoborepin, **3c**.

Discussion

Dibenzoborepin **5d** merits further comment because its uncharged valence-bond structure has two quinoidal benzene rings, but its magnetic properties show it to be perhaps the most aromatic isomer. The magnetic susceptibilities of **5a**−**d** (in ppm cgs) are −111.9, −108.5, −115.7, and −123.3, respectively. NICS(0)[13] values of the borepin and benzene rings of **5d** are −7.3 and −10.6 ppm, the former value being more negative than in the other isomers and in borepin itself, −3.7.[6a] This result is consistent with the 14π-electron periphery of **5d**. Similarly, there is a 10π-electron cycle in **5c**, which has NICS(0) values in its borepin and benzene rings of −5.3, −12.0 (*b*), and −4.5 (*e*), respectively.

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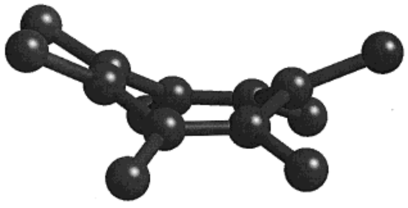
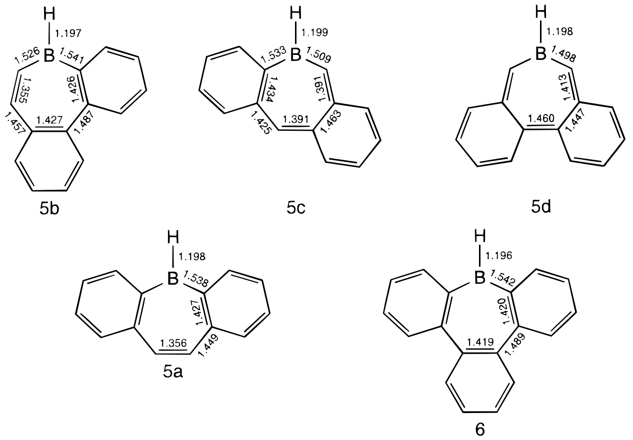


Figure 3. Heptamethylborepin, **4b**.

Chart 2



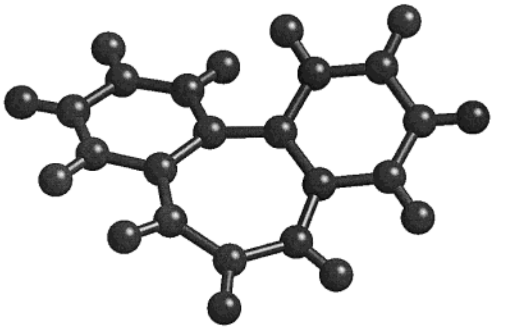
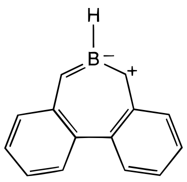


Figure 4. 6*H*-Dibenzo[*c*,*e*]borepin, **5d**.

It is also the case that **5d** has conjugated benzenes in its forms **5d′**, which are therefore more important than in other borepins.[4h−j] The contribution of **5d′** can be gauged by geometric and electronic effects. It is found that the BC bonds of **5d** are even shorter (1.498 Å) than those of **5c**. Similarly, the stern double bond, C_4C_5, is quite long in **5d**, 1.460 Å. The zwitterionic resonance forms are reflected in the electric dipole moment of **5d**, $\mu = 3.27$ D, which exceeds the values $\mu = 1.06$ and 1.89 in **5a** and **5b**. The negative charge on B attending *c*-ring-fusion is also reflected in the more upfield ^{11}B chemical shifts in **5c** (46.6 ppm) and **5d** (30.6, the most shielded boron in this study) vs 58.7 ppm found in **5a**. Conversely, the ^{13}C shifts of the flanking carbons, C_2 and C_7, in **5d** are downfield from TMS by 180.0 ppm, their hydrogens by 10.2 ppm. Similar, but less dramatic, effects are found in **5c** and in the (10π-electron) *c*-fused benzoborepin studied computationally by Subramanian et al.[6a]



5d′

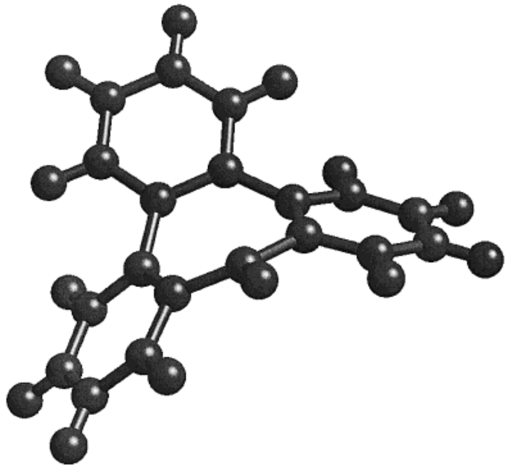
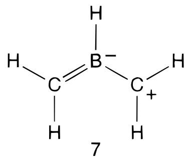


Figure 5. Tribenzo[*b*,*d*,*f*]borepin, **6**.

The resonance structure **5d′** (C_{2v}) can be likened to **7**, a transition state possibly related to ring opening of boracyclopropane.[14] **7** is calculated to have 1.489 Å BC bonds, a boron chemical shift of 29.5 ppm, a carbon chemical shift of δ 237.5, and an electric dipole moment of 1.53 D.



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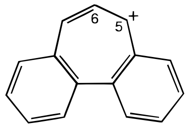
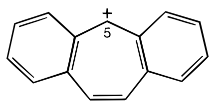
Cation **8a**, the analogue of **5d**, also has a C_2 structure. This species, the dibenzo[*a*,*c*]cycloheptenylium ion, is less stable than **8b**, the **5a** analogue, dibenzo[*a*,*d*]-cycloheptenylium ion, by 7.2 kcal/mol. The calculated ^{13}C chemical shifts on carbon 5 are δ 174 and 178 in **8a** and **8b**, respectively, and δ 120 for carbon 6 of **8a**. These shifts parallel those of **5d** and **5a**.

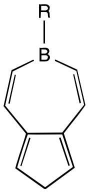


8a



8b

The geometries and chemical shifts of the borepins and aminoborepins can be compared with those of the nonaromatic model systems **9**. **9a** and **9b** are planar, while **9c** has elevation angles α = 9.8°, $\beta = 5.0°$. The



9a: R=H
9b: R=NH_2
9c: R=$N(Me)_2$

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(14) Taylor, C. A.; Zerner, M. C.; Ramsey, B. *J. Organomet. Chem.* **1986**, *317*, 1.

BC_2 bond lengths of **9a**−**c**, 1.542, 1.555, and 1.564 Å, are greater than their counterparts in **1a** and **1d** and similar to the value in **3a**. Conversely, the lengths of double bonds C_2C_3 in **9a**−**c**, 1.356, 1.349, and 1.351 Å, are less than those of their borepin counterparts.

The boron chemical shifts in the amino and dimethylamino model compounds **9b** and **9c**, δ 32.7 and 33.2, are nearly identical to the values in **1d** and **3a**, indicating the similarity of the BN bonds in aminoborepins and their nonaromatic models. Carbons C_2 of **9a**−**c** resonate farther upfield than C_3 by 12−17 ppm (e.g., C_2 δ 127.3 vs C_3 149.7 in **9a**), in contrast to their values in **1** and **3**. From the valence-bond viewpoint, aromatic borepins have zwitterionic resonance structures in which positive charge can reside on a carbon either α or β to boron, whereas positive charge in dibutadienylboranes such as **9** resides only on a β carbon. Near equality of the chemical shifts of C_2 and C_3 is yet another measure of aromatic character in borepins.

Finally, we note that calculations show heptaphenylborepin[4c] to be boat-shaped. This compound has been inferred to be a reaction intermediate in the thermal rearrangement of heptaphenyl-7-borabicyclo[2.2.1]heptadiene.[15]

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