

An evaluation of the rotational barrier about the B–N bond of 1-aminoborepins

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(Received June 15, 1993; in revised form August 2, 1993)

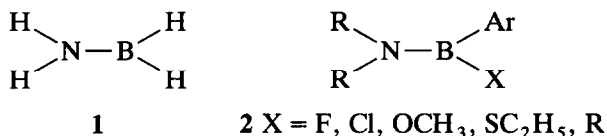
Abstract

^{13}C NMR spectroscopy has been used to determine the barriers to rotation about the B–N bonds of 1-(*N*-benzyl-*N*-methylamino)borepin and 1-(*N*-benzyl-*N*-methylamino)-4,5-dihydroborepin as 18 and 19.8 kcal mol $^{-1}$, respectively. The corresponding rotational barriers of a variety of aminoboranes have been calculated using the semi-empirical AM1 method.

Key words: Boron; Nitrogen; Aminoborane; Borepin; AM1 calculations; Nuclear magnetic resonance

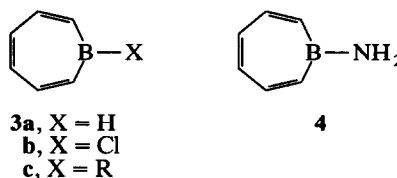
1. Introduction

There has been considerable interest in the nature of the bonding in aminoborane (1) [1–6]. Calculations indicate that the B–N bond should have substantial π -bond character with a large barrier to rotation about that bond [4–6]. NMR spectroscopic investigations on *N,N*-dialkylaminoboranes (2) give ΔG^* values in the range of 17–24 kcal mol $^{-1}$ for rotation about the B–N bonds [2,3,7–10]. These barrier heights depend upon both steric and electronic effects. In particular π -donor substituents at boron lower the barrier, apparently by weakening the B–N π -bond [8–10].

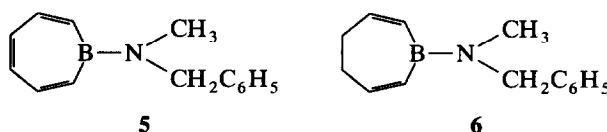


We have been interested in the heterocycle borepin (3) for some time [11–15]. π -Donation from C to B should give borepins a Hückel 6π -aromatic character. Spectroscopic and structural studies of borepins (3, where X = H, Cl, R) are consistent with this aromaticity [13–15]. However in 1-aminoborepin (4) ring π -donation from C to B must compete with the exocyclic

B–N π -bonding [15]. Thus one expects that the barrier to B–N rotation to be lower than normal.



In order to evaluate experimentally the balance between B–C and B–N π -bonding in aminoborepins, we have undertaken a study of the barrier to B–N rotation in 5 and 6. The steric demands of borepin and 4,5-dihydroborepin should be similar, therefore it can be anticipated that the difference in the rotational barriers will reflect only electronic differences between the two systems. Since π -donation from C to B should be more important for the aromatic borepin than the non-aromatic dihydroborepin, we expect that 5 should have a lower B–N barrier than 6.



The aminoboranes 5 and 6 were easily prepared by treating the corresponding chlorides with an excess of *N*-benzyl-*N*-methylamine in pentane. After separation

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of the insoluble hydrochloride of the base, the aminoboranes were isolated as moisture and air sensitive oils.

At 25°C the ^1H NMR spectrum of 1-(*N*-benzyl-*N*-methylamino)borepin (**5**) in C_6D_6 shows a multiplet at δ 6.45 for the γ -protons of the ring. The signal for the β -protons at δ 7.10 is rather broad due to strong quadrupolar interaction with the trans ^{11}B . However the signals from each of the non-equivalent α -protons are doublets of doublets (δ 6.75, 6.67). Thus rotation about the B–N bond must be slow on the NMR time scale.





The ^{13}C NMR spectrum of **5** in C_6D_6 at 25°C shows a broad signal for the α -carbon atoms. However both the signals for the C_β at (δ 142.09, 141.90) and C_γ at (δ 131.68, 131.75) indicate non-equivalence. Because the spectra are simple we have chosen to evaluate the B–N rotational barrier using ^{13}C NMR spectroscopy. On warming to 62°C the signals for C_γ coalesce to a singlet, while the C_β -signals coalesce at 73°C. The ΔG^\ddagger values are 18.1 and 17.8 kcal mol $^{-1}$, respectively. The mean value of ΔG^\ddagger is 18.0 ± 0.5 kcal mol $^{-1}$.

The NMR spectra of **6** are quite analogous. Although the room temperature ^1H NMR spectrum shows that the α -protons are non-equivalent (doublets at δ 6.18 and 6.21), we have again chosen to use the simpler ^{13}C NMR spectra to evaluate the B–N rotational barrier. At 25°C the ^{13}C NMR spectrum shows two signals each for the non-equivalent C_γ atoms at (δ 29.74, 29.80) and the non-equivalent C_β atoms (δ 147.33, 147.40). On warming both signals coalesce at 97°C given a ΔG^\ddagger value of 19.8 ± 0.5 kcal mol $^{-1}$.

In order to obtain a better understanding of this process we have calculated the rotation barriers for model compounds **4** and **7** and related aminoboranes **1**, **8**, and **9** using the semi-empirical AM1 method [16,17*] (see Table 1). The equilibrium geometry of **7** has C_2 -symmetry, although the B, N and the four attached atoms are close to coplanar. *Ab initio* (6-31G* basis set) calculations of 4,5-dihydroborepin yielded a similar geometry [18]. All other aminoboranes have C_{2v} symmetry. Upon rotation about the B–N bond the nitrogen atoms assume a pyramidal configuration as had previously been found for *ab initio* calculations on **1** [5,19]. In all cases the B–N bond length elongates by about 0.09 Å as the π bond is broken [20].

The B–N rotational barrier for H_2NBH_2 (**1**) has previously been calculated as 29.4 kcal mol $^{-1}$ by *ab initio* (6-31G*) [5] and 23.8 kcal mol $^{-1}$ by semiempirical (MNDO) [19] methods. Agreement with our AM1 barrier of 25.8 kcal mol $^{-1}$ seems acceptable. Both *ab*

TABLE 1. The AM1 rotation barriers about the B–N bonds

Compound	Barrier (kcal mol $^{-1}$)	$\Delta(\text{B–N})^a$ (Å)
H_2BNH_2 (1)	25.8	0.090
 B–NH $_2$ (4)	15.5	0.087
 B–NH $_2$ (7)	19.0	0.086
 B–N(CH $_3$) $_2$ (8)	12.2	0.080
 B–NH $_2$ (9)	22.4	0.083

^a The bond length increase on going from the most stable conformation to the transition state for B–N rotation. The other bond lengths do not change significantly.

initio and semiempirical methods give a B–N bond distance of 1.37 Å, while the experimental distance determined from microwave spectra is 1.391(2) Å [21].

The barrier heights calculated for **4** and **7** seem fortuitously close to the experimental values found for **5** and **6**. Changing the substituents on nitrogen from H to CH_3 (**4** \rightarrow **8**) makes the absolute agreement poorer. However the difference between the calculated barrier height of borepin **4** and dihydroborepin **7** ($\Delta = 3.5$ kcal mol $^{-1}$) and the observed difference between **5** and **6** ($\Delta = 1.8$ kcal mol $^{-1}$) are in reasonable agreement. As had been anticipated from qualitative arguments, the aminoborepin systems have lower B–N rotational barriers than the aminodihydroborepins. However the differences between the two systems are rather small. Apparently the C–B π -bonding of the aromatic borepin is only slightly more effective than that of the non-aromatic dihydroborepin in weakening the exocyclic B–N π -bond. It may be that the resonance stabilization of borepin is only slightly greater than that of dihydroborepin as had been suggested from *ab initio* calculations [18].

In order to find larger electronic effects we have compared aminoborepin **4** with aminoborole **9**. π -Donation from C to B should give boroles a Hückel 4π -antiaromatic character [22–24]. Aminoboroles are highly labile but form stable transition metal complexes [22,25]. The B–N rotational barriers of bis(dialkylaminoborole) nickel are high on the NMR time scale [25]. The calculated B–N barrier of **9** (22.5 kcal mol $^{-1}$) is 7 kcal mol $^{-1}$ higher than the barrier of **4**. Therefore C to B π -donation in the borepin is significantly greater than in the borole.

* Reference number with an asterisk indicates a note in the list of references.

2. Experimental details

General remarks: all reactions were carried out under an atmosphere of nitrogen. Solvents were dried using standard procedures. The mass spectra were determined by using a VG-70-S spectrometer, while the NMR spectra were obtained using either a Bruker WH-360 or AM-300 spectrometer. The ^1H NMR and ^{13}C NMR spectra were calibrated using signals from solvents referenced to Me_4Si while external $\text{BF}_3 \cdot \text{OEt}_2$ was used to calibrate the ^{11}B NMR spectra. 1-Chloroborepin [13] and 1-chloro-4,5-dihydroborepin [26] were prepared by literature procedures while all other compounds were commercially available.

2.1. 1-(*N*-Benzyl-*N*-methylamino)borepin (5)

N-Benzyl *N*-methylamine (300 μl , 279 mg, 2.3 mmol) was added dropwise with stirring to a solution of 1-chloroborepin (100 μl , 130 mg, 1.05 mmol) in 15 ml of pentane at 25°C. A white precipitate formed immediately. After the reaction mixture had stirred at 25°C for 3 h, the suspension was filtered affording a clear filtrate. The solvent was removed under vacuum affording 211 mg (1.01 mmol, 96%) of a clear, air-sensitive oil. Attempted distillation led to extensive decomposition. ^1H NMR (C_6D_6): δ 2.56 (s, 3H, *Me*); 4.15 (s, 2H, CH_2); 6.49 (m, 2H, *H α*); 6.73, 6.67 (dd, dd, $J = 13.7, 2.9$ Hz, 2H, *H α*); 7.06 (s, 5H, C_6H_5); 7.10 (br, 2H, *H β*). ^1H NMR (CDCl_3): δ 2.78 (s, 3H, *Me*); 4.15 (s, 2H, CH_2); 6.55 (m, 2H, *H γ*); 6.75, 6.68 (dd, dd, $J = 13.7, 2.9$ Hz, 2H, *H α*); 7.10 (br, 2H, *H β*); 7.20 (s, 5H, C_6H_5). ^{11}B NMR (C_6D_6): δ 35.5. ^{13}C NMR (C_6D_6): δ 36.5 (*Me*); 55.2 (CH_2); 127, 127.3, 128.7, 139.9 (C_6H_5); 131.68, 131.75 (*C γ*); 139 br (*C α*); 142.09, 141.90 (*CB*). EI-MS: m/z (rel. intensity): 209 (28, M^+ for $\text{C}_{14}\text{H}_{16}^{11}\text{BN}$); 130 (43, $\text{M}^+ - \text{C}_6\text{H}_5$); 91 (100). MS exact mass (EI): found 209.1371. $\text{C}_{14}\text{H}_{16}^{11}\text{BN}$ calc: 209.1376.

2.2. 1-(*N*-Benzyl-*N*-methylamino)-4,5-dihydroborepin (6)

In the same manner as above addition of *N*-benzyl-*N*-methylamine (0.4 ml, 3.1 mmol) to 1-chloro-4,5-dihydroborepin (135 mg, 1.05 mmol) in 10 ml pentane gave product which was purified by Kugelrohr distillation at 65°C (0.05 torr) affording 200 mg (88%) of a colorless oil. ^1H NMR (C_6H_6): δ 2.25 (m, 4H, *H γ*); 2.57 (s, 3H, *Me*); 4.12 (s, 2H, CH_2N); 6.18, 6.21 (d, $J = 12.4$ Hz, 2H, *H α*); 6.66 (m, 2H, *H β*); 7.10 (m, 5H, C_6H_5). ^{11}B NMR (C_6D_6): δ 37.0. ^{13}C NMR (C_6D_6): δ 29.74, 29.80 (*C γ*); 36.7 (*Me*); 55.7 (*NCH}_2*); 127.1, 127.5, 128.7, 139.8 (C_6H_5); 147.33, 147.40 (*CB*). MS exact mass (EI): found 211.1538 $\text{C}_{14}\text{H}_{18}^{11}\text{BN}$ calc: 211.1532.

Acknowledgments

We are grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this work. W.K. thanks the Deutsche Forschungsgemeinschaft for a post-doctoral fellowship.

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