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Attacking Boron Nucleophiles: NMR Properties of Five-Membered Diazaborole Rings

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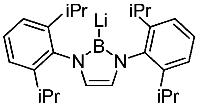
This paper reports computed NMR spectral data for the diazaborole anion ($C_2H_4B_1N_2^-$) and the corresponding neutral five-membered rings with B−H ($C_2H_5B_1N_2$, diazaborole) and B−Li ($C_2H_4B_1Li_1N_2$, Li−diazaborole) bonds, which are the central moieties of newly synthesized nucleophilic organoboryl five-membered rings, recently reported by Segawa et al. (*Science* **2006**, *314*, 113). Both spin−spin coupling constants and chemical shifts were obtained using high-level ab initio calculations. These data are a necessary complement to the very scarce experimental information available.

In a recent article, Segawa, Yamashita, and Nozaki reported the isolation, characterization, and reactivity of a newly synthesized boryllithium five-membered ring.[1a] This landmark paper, introduced by a perspective entitled "Boron Goes on the Attack",[1b] is the first to demonstrate the existence of a nucleophilic, anionic organoboryl species. A key experiment used to confirm the existence of this anion and the corresponding neutral molecules with B−Li (**1**) and B−H (**5**) bonds was the detection of a one-bond NMR $^{11}B-^{1}H$ coupling constant for the neutral five-membered ring $C_2H_3Ar_2B_1N_2$ (**5**), where Ar is a 2,6-diisopropylphenyl group bonded to N. Because the anion produced is a new chemical reagent which may provide a useful synthetic route to new boron-containing compounds, we decided that it would be most appropriate to further characterize the NMR spectra of these species by extending our previous studies of spin−spin coupling constants for borazine and its derivatives[2] to the three novel five-membered boron-containing rings identified in ref 1a. In this paper, we present computed ab initio spin−spin coupling constants for models of the anion with Ar replaced by H giving $C_2H_4B_1N_2^-$ (**2**) (subsequently referred to as the diazaborole anion) and the corresponding neutral five-membered rings with B−Li [$C_2H_4B_1Li_1N_2$ (**3**), Li−diazaborole] and B−H [$C_2H_5B_1N_2$ (**4**), diazaborole] bonds. We compare the computed structures and coupling constants for these five-membered rings with the coupling constants for the corresponding six-membered rings (borazine anion, Li−borazine with Li at B, and borazine) and with the experimental structures and NMR data reported in ref 1a.



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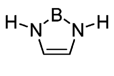

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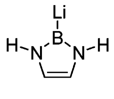

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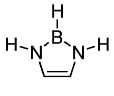

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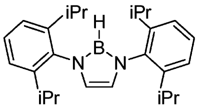

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The structures of the five-membered rings were optimized at second-order Møller−Plesset perturbation theory (MP2), as implemented in Gaussian 03[3] with the 6-311++G(d,p) basis set.[4−6] All of these rings have C_{2v} symmetry and are equilibrium structures with no imaginary frequencies. Spin−spin coupling constants were computed using the equation-of-motion coupled-cluster singles and doubles method (EOM-CCSD) in the configuration interaction (CI)-like approximation with all electrons correlated, as implemented in ACES II.[7] The Ahlrichs[8] qzp basis was placed on N and C atoms and the qz2p basis on the H atom bonded to B, the DDZ basis[9,10] was placed on the remaining H atoms, and the hybrid basis sets used in ref 2 were used for B and Li. Spin−spin coupling constants for the five-membered rings were evaluated as a sum of four terms: paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi contact (FC), and spin dipole (SD). Chemical shifts were computed at MP2 with the same basis sets used to compute coupling constants, employing the GIAO method.[11] All calculations were performed on the Cray X1 or the Itanium cluster at the Ohio Supercomputer Center.

The computed MP2/6-311++G(d,p) structures of **2**, **3**, and **4** are given in the Supporting Information. The computed N−B bond lengths for the neutral molecules are in agreement with the experimental bond lengths determined from crystallographic data in ref 1a and support the finding that B−N bonds in Li−diazaborole are longer than those in diazaborole. However, the computed B−Li bond length of 2.184 Å for compound **3** is shorter than the experimental bond length of 2.291 Å for compound **1**. This difference most probably arises from the nature of the crystal structure of **1** in which the lithium atom is also coordinated with other atoms that are not present in our calculations. The computed N−**B**−N angles for **3** and **4** agree

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TABLE 1: One- and Two-Bond Spin−Spin Coupling Constants (Hz) for Five-Membered Boron Rings[a]

	diazaborole anion (**2**)		Li−diazaborole (**3**)		diazaborole (**4**)	
	FC	*J*	FC	*J*	FC	*J*
			One-Bond			
N−B	−7.3	−5.2	−17.2	−15.2	−32.4	−30.4
N−C	−9.1	−6.9	−12.6	−10.4	−14.7	−12.7
C−C	95.1	90.6	90.1	85.2	88.6	83.5
B−X			136.8	136.9	145.6	146.1 (154)[b]
			Two-Bond			
B−C	−7.2	−7.6	−2.6	−2.8	2.2	2.1
N−N	−1.1	−1.2	1.1	1.1	2.5	2.4
N−C	−10.2	−11.0	−6.0	−6.5	−3.6	−4.0

[a] The FC terms are dominant, and changes in FC terms parallel changes in total *J*. [b] Experimental value of ^{1}J(B−H) for **5** from ref 1a.

with the experimentally determined values for **1** and **5**, respectively. The computed structure of the anion (**2**) is also in agreement with the computed RHF/6-311+G(d) structure reported by Metzler-Nolte,[12] except for the computed C−C distance (1.338 Å), which is shorter than our value (1.370 Å).

A one-bond coupling constant of 154 Hz was identified in the NMR spectrum of compound **5** in ref 1a and assigned to ^{11}B−^{1}H coupling. The computed value of ^{1}J(B−H) for our model **4** is 146 Hz, in reasonable agreement with the experimental value, given the difference in the substituents (substituted phenyl rings vs H atoms) at the two N atoms. The remaining one-bond couplings involving the ring are reported in Table 1 and can be used for both identification and characterization purposes. The one-bond ^{15}N−^{11}B coupling constant, ^{1}J(N−B), is always negative and has its smallest absolute value of −5.2 Hz in the anion (**2**). ^{1}J(N−B) increases in absolute value to −15.2 Hz when B is bonded to Li in **3** and increases further to −30.4 Hz when B is bonded to H in **4**. This behavior is similar to the increase in the absolute values of the Fermi-contact terms which dominate ^{1}J(N−B) from −9.7 in the borazine anion to −17.4 in Li−borazine to −28.7 Hz in borazine, as reported in the Supporting Information. Thus, it appears that the presence of a lone pair on B in the anion reduces ^{1}J(N−B), but when the lone pair is removed by bond formation, ^{1}J(N−B) increases as the bond acquires increased covalent character. This situation is reminiscent of the changes in ^{1}J(N−C) and ^{1}J(P−C) when the lone pairs on N and P are protonated in going from pyridine to pyridinium (0.5 to −14.6 Hz computed,[13] 0.6 Hz to −12 Hz experimental)[14,15] and from phosphinine to phosphininium (−45.4 to 110.2 Hz).[13] Conversely, if borazine and diazaborole are considered the parent compounds, then substitution of Li decreases ^{1}J(N−B), and removal of the H atom completely to form the anion reduces ^{1}J(N−B) even further. The decrease in ^{1}J(N−B) in going from **4** to **3** is also consistent with Li substitution effects in benzene.[2]

It is interesting to note that the one-bond coupling constants ^{1}J(N−C) increase in absolute value in the same order as ^{1}J(N−B), namely, diazaborole anion < Li−diazaborole < diazaborole. This order is not determined by changes in the corresponding bond distances, as observed previously for borazine and its derivatives.[2] Since the magnetogyric ratio of ^{15}N is negative while those of ^{11}B, ^{13}C, ^{7}Li, and ^{1}H are positive, all of the reduced coupling constants, $^{1}K(X{-}Y)$, are positive, in agreement with the Dirac vector model.[16] Two-bond C−B, N−N, and N−C coupling constants for the diazaborole rings are also reported in Table 1. The B−C and N−C coupling constants have larger absolute values in the diazaborole anion than in the Li−diazaborole and diazaborole molecules. Moreover, all reduced two-bond N−C coupling constants and all reduced two-bond couplings for diazaborole are positive, and therefore in violation of the Dirac vector model.

In ref 1a, the authors reported a broad singlet peak with a half-width of 36 Hz in the ^{7}Li NMR spectrum of **1**. They attributed this broadening to the interaction of Li with the quadruple boron nucleus. Our computed values of ^{1}J(B−Li) are 136.9 and 140.4 Hz for Li−diazaborole and Li−borazine, respectively. Our computed value of 136.9 for ^{1}J(B−Li) suggests that it is unlikely that the 36 Hz broadening is due to B−Li coupling. However, B−Li coupling constants computed for BH_2-Li and $BH_2Li{\cdot}2H_2O$ indicate that coordination of Li with O reduces ^{1}J(B−Li), which suggests that Li coordination with the oxygens of THF may also lower ^{1}J(B−Li) in **1**.

A few chemical shifts (δ) were reported in ref 1a for compounds **1** [$^{6(7)}$Li, 0.46 ppm; ^{11}B, 45.4 ppm] and **5** (^{11}B, 22.9 ppm). In addition, the ^{11}B chemical shift of borazine has been reported as 30.7 ppm.[17] We have computed ^{11}B shieldings (σ, ppm) for borazine, BH_4^-, and $B(CH_3)_3$, for which the chemical shifts have been determined experimentally,[18] and have found a linear relationship between the experimental chemical shifts and the computed shieldings, given by the equation

$$\delta(^{11}\mathrm{B}) = 106.5 - 0.90\sigma(^{11}\mathrm{B}), \quad r^2 = 1.00$$

From this equation, the chemical shifts are predicted to be 43.7 for **2**, 31.0 for **3**, 22.8 for **4**, 68.2 for borazine anion, and 48.6 ppm for Li−borazine. The predicted value for **4** which is our model for **5** is in excellent agreement with the experimental value for **5** (22.9 ppm).[1a] However, although the predicted chemical shift increases by 8.1 ppm in **3** relative to **4**, the predicted chemical shift for **3** significantly underestimates the experimental value for **1** (45.4 ppm). This underestimation may be attributed, at least in part, to the solution environment in which Li is also coordinated with the oxygens of THF,[1a] and possibly to the presence of the two 2,6-diisopropylphenyl groups in **1**.

It should be noted that the computed value for the B chemical shift for **2** (43.7 ppm) is much closer to the experimental value for **1** (45.4 ppm) than the computed value for **3** (the model for **1**, 31.0 ppm). This again indicates that our gas-phase molecule **3** does not have enough ion-pair character. It may well be that Li coordination with the O atoms of DME in the solid state and with those of THF in solution[1a] makes the system more closely resemble a separated ion pair. On the other hand, Li chemical shifts are rather insensitive to the environment. The reference, LiCl, has $\delta^{6(7)}$Li = 0.00 ppm and $\sigma^{6(7)}$Li = 89.3 ppm. The Li shielding, $\sigma^{6(7)}$Li, computed for **3**, which is our model of **1**, is 90.9 ppm, while that for Li−borazine is 92.4 ppm. Thus, it should be expected that the $\delta^{6(7)}$Li value for **1** should be close to 0 ppm. The experimental value is 0.46 ppm.[1a]

In summary, since NMR coupling constants and chemical shifts will be used to identify newly synthesized boron-containing compounds produced from nucleophilic boryl rings, the computed NMR data presented in this work should provide insight into these NMR properties, and assist in the identification and characterization of these nucleophiles and the compounds produced from them.

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Supporting Information Available: Geometries of **2**, **3**, and **4**, coupling constants for borazine and its derivatives, and full references for the Gaussian 03 and ACES II programs. This material is available free of charge via the Internet at http://pubs.acs.org.

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