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An ab Initio Study of $^{15}N-^{11}B$ Spin−Spin Coupling Constants for Borazine and Selected Derivatives

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Ab initio equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) calculations have been performed to investigate substituent effects on coupling constants for borazine and selected substituted borazines. For molecules in which F atoms are not bonded to adjacent atoms in the ring, F substitution increases the one-bond $^{11}B-^{15}N$ coupling constants involving the atom at which substitution occurs but leaves the remaining one-bond B−N coupling constants essentially unchanged. For these molecules, the magnitudes of one-bond B−N coupling constants are only slightly dependent on the number of F atoms present. Fluorine substitution at adjacent B and N atoms in the borazine ring further increases the one-bond B−N coupling constant involving the substituted atoms and has the same effect on the other one-bond coupling constants as observed for corresponding molecules in which substitution occurs at alternate sites. In contrast to the effect of F substitution, substitution of Li at either N or B decreases one-bond B−N coupling constants relative to borazine. The effects of F and Li substitution on one-bond B−N coupling constants for borazine are similar to F and Li substitution effects on $^{13}C-^{13}C$ coupling constants for benzene.

Introduction

The chemical and physical properties of each element of the periodic table are fascinating, but there are some elements with properties so unusual that even after years of study, they still pose intriguing, unanswered questions. Among the elements with dramatically unusual bonding properties is boron, “a unique and exciting element”.[1] The complexities of its allotropic modifications, the borides, the boranes (boron hydrides), the carboranes (among them the strongest of the superacids),[2] the metallocarboranes, the boron halides, the borates (boron−oxygen compounds), and, finally, the boron−nitrogen compounds, provide a plethora of examples of the great versatility of boron chemistry and the variety of its bonding motifs.

Our fascination with boron has led us to undertake a systematic study of the B−N bond in several series of molecules, investigating geometries, bonding properties, energetics, and the NMR property of nuclear $^{11}B-^{15}N$ spin−spin coupling. For our studies, we have subdivided B−N compounds into several classes: amineboranes $H_3B{\cdot}NH_3$ (the analogue of ethane) and its derivatives; aminoboranes $H_2B{=}NH_2$ (the analogue of ethylene) and its derivatives; iminoboranes $HB{\equiv}NH$ (the analogue of acetylene) and its derivatives; borazine $B_3N_3H_6$ (the analogue of benzene) and its derivatives; boron nitride (hexagonal and cubic, the analogues of graphite and diamond). The structures and bonding properties of borazine have been investigated by many other groups.[3−13] In particular, recent density functional studies of borazine and some of its derivatives have been reported by Miao and co-workers[12] and Rahaman and co-workers,[13] with the aim of quantifying the aromaticity of this molecule. Although these investigators computed chemical shifts for these molecules, they did not compute coupling constants. Given that much of our recent work has focused on the calculation of spin−spin coupling constants and that this NMR property has not been investigated theoretically for molecules such as borazine, we decided to initiate our studies of boron-containing molecules by computing and analyzing $^{11}B-^{15}N$ spin−spin coupling constants for borazine and substituted borazines with one, two, or three F atoms bonded to B and/or N, as well as the two Li-substituted isomers of borazine. Thus, substituent effects on B−N coupling constants may be evaluated by using two substituents which are at opposite ends of the electron-donating/electron-withdrawing spectrum. All of the borazine derivatives included in this study have C_{2v} or higher symmetry, a requirement dictated by the computational demands of EOM-CCSD calculations. For comparative purposes, we have also evaluated F and Li substitution effects on $^{13}C-^{13}C$ spin−spin coupling constants for benzene. The purpose of this paper is to report the results of this investigation.

Methods

The structures of borazine, the mono-, di-, and trifluoro-substituted derivatives, and two Li-borazine isomers were optimized at second-order Møller−Plesset perturbation theory (MP2)[14−17] with the 6-311++G(d,p) basis set.[18−20] Computed vibrational frequencies confirm that the optimized structures of C_{2v} or higher symmetry are equilibrium structures on their potential surfaces, except for the Li-borazine molecule with Li bonded to N, which is a transition structure with 1 imaginary frequency. However, this transition structure has been included in this study for comparison purposes. The structures of benzene, F-benzene, 1,3-diF-benzene, and Li-benzene were optimized at MP2 with the 6-31+G(d,p) basis set.

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TABLE 1: ^1J(B−N) (Hz) for HBNH, H_2BNH_2, and H_3BNH_3 as a Function on the Basis Set on H

basis set	PSO	DSO	FC	SD	^1J(B−N)
			HBNH		
qz2p	−1.9	−0.0	−84.9	−2.7	−89.5
cc-pVDZ	−1.8	−0.0	−85.1	−2.7	−89.6
			H_2BNH_2		
qz2p	3.0	−0.0	−31.4	−0.3	−28.8
cc-pVDZ	3.0	−0.0	−31.4	−0.3	−28.7
			H_3BNH_3		
qz2p	−0.2	−0.1	−0.1	−0.4	−0.8
cc-pVDZ	−0.2	−0.1	0.0	−0.4	−0.7

Equation-of-motion coupled-cluster singles and doubles (EOM-CCSD)[21−24] calculations in the CI (configuration interaction)-like approximation were carried out using the Ahlrichs[25] qzp basis set on B, N, and F atoms and the cc-pVDZ basis set on H atoms.[26,27] Since an Ahlrichs qzp basis is not available for B or Li, a new "hybrid" basis has been constructed for these two atoms. For B, the new basis set was constructed from the boron cc-pV5Z basis for s orbitals, the boron cc-pVQZ basis for p orbitals, and a single set of d polarization functions. The hybrid Li basis set was constructed in a similar manner. These new basis sets have the same number of contracted functions (6s, 4p, 1d) as the Ahlrichs qzp basis used for the second-period elements C, N, and F.

In the nonrelativistic approximation, the nuclear spin−spin coupling constant is composed of four terms: the paramagnetic spin−orbit (PSO); diamagnetic spin−orbit (DSO); Fermi contact (FC); spin−dipole (SD).[28] All terms have been computed for borazine and the two monofluoro-substituted derivatives. It was observed that for these molecules the contributions of the SD terms to the total one-, two-, and three-bond B−N coupling constants are less than 0.2 Hz. Since the SD term is an extremely expensive term to compute, it was not evaluated for the di- and trifluoro derivatives. Total coupling constants were computed for benzene, but for comparison purposes, only Fermi-contact terms were obtained for the substituted benzenes. No one-bond B−H and N−H coupling constants are reported for borazine and its derivatives since the basis set used on H is not sufficiently large to produce accurate coupling constants involving this atom and using the qz2p basis on H was computationally prohibitive. The effect of using the smaller H basis on B−N coupling constants will be examined by comparing ^1J(B−N) for HBNH, H_2BNH_2, and H_3BNH_3 computed with these two different H atom basis sets. Geometry optimizations were carried out using the Gaussian 03 suite of programs,[29] and coupling constants were evaluated using ACES II.[30] All calculations were performed on the Cray X1 or the Itanium Cluster at the Ohio Supercomputer Center.

Results and Discussion

Sensitivity of ^1J(B−N) to the H Basis Set. To evaluate the sensitivity of ^1J(B−N) to the basis set used for the H atoms bonded to B and N, total B−N coupling constants for HBNH, H_2BNH_2, and H_3BNH_3 were computed with the cc-pVDZ basis set on H atoms and again with the qz2p basis set on H. The computed values of ^1J(B−N) are reported in Table 1. For a given molecule, there is only an 0.1 Hz difference in ^1J(B−N) when these two different H atom basis sets are used. These results justify the use of the cc-pVDZ basis on H when evaluating B−N coupling constants for the borazines.

Substituted Borazines. To carry out a systematic analysis of the effect of fluorine substitution on B−N coupling constants, it is necessary to adopt a consistent numbering system for atoms in the ring. The numbering system employed is illustrated for borazine in Figure 1. In this system, a nitrogen atom is always atom 1. Single substitution always occurs at N1 or at B2. The disubstituted isomers are 1,3-diF-borazine, 2,6-diF-borazine, and 1,4-diF-borazine; the trisubstituted isomers are 1,3,5-, 2,4,6-, 1,2,3-, and 1,2,6-triF-borazine. With this system, the N1−B2 bond always has an F atom bonded to N1 and/or B2 in all of the derivatives. All of the F-substituted borazines are illustrated in Figure 1.

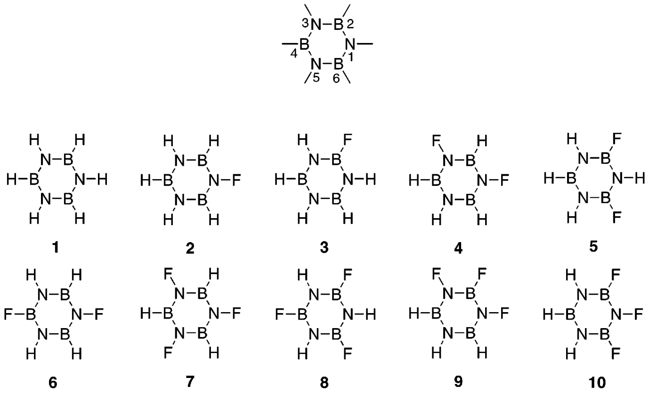

Figure 1. Borazine, illustrating the ring numbering system, and F-substituted borazines investigated in this study.

Borazine, 1,3,5-triF-borazine, and 2,4,6-triF-borazine have only one unique one-bond coupling constant ^1J(N1−B2), two unique two-bond coupling constants ^2J(N1−N3) and ^2J(B2−B4), and one unique three-bond coupling constant ^3J(N1−B4). The situation is quite different for the mono- and disubstituted derivatives, 1,2,3-triF-borazine, and 1,2,6-triF-borazine, which have three unique one-bond coupling constants, four unique two-bond coupling constants, and two unique three-bond coupling constants. The one-bond coupling constants are usually ^1J(N1−B2), ^1J(B2−N3), and ^1J(N3−B4). However, for 2-F-borazine, 1,3-diF-borazine, and 1,2,3-triF-borazine ^1J(N1−B2) and ^1J(B2−N3) are equivalent, and the third unique coupling constant is ^1J(B4−N5). Similarly, the four unique two-bond coupling constants are ^2J(N1−N3), ^2J(N3−N5), ^2J(B2−B4), and ^2J(B4−B6). However, ^2J(B2−B4) and ^2J(B4−B6) are equivalent in 1-F-borazine, 1,4- and 2,6-diF-borazine, and 1,2,6-triF-borazine, and the fourth unique coupling constant for these derivatives is ^2J(B2−B6). Finally, the mono- and disubstituted derivatives and 1,2,3- and 1,2,6-triF-borazine have two unique three-bond coupling constants, ^3J(N1−B4) and ^3J(B2−N5). The two- and three-bond B−N coupling constants are relatively small and will not be discussed in this paper. However, they are reported in Table S1 of the Supporting Information. Fermi-contact terms and total coupling constants for one-bond couplings for borazine and its fluoro-substituted derivatives and Fermi-contact terms for 1,2,6- and 1,2,3-triF-borazine are reported in Table 2.

F Substitution Effects on One-Bond B−N Coupling Constants. *Substitution at Nonadjacent Atoms of the Borazine Ring*. The data for Table 2 show that the FC terms for B−N coupling in all F-substituted borazines differ from total coupling constants by less than 2.5 Hz and are therefore good approximations to ^1J(B−N). Moreover, ^1J(B−N) is always negative, and therefore, the reduced coupling constant [^1K(B−N)] is always positive, since

$$^nK_{\mathrm{B-N}} \propto {}^nJ_{\mathrm{B-N}}/(\gamma_{\mathrm{B}})(\gamma_{\mathrm{N}})$$

where γ_B is the magnetogyric ratio of ^{11}B (positive) and γ_N is the magnetogyric ratio of ^{15}N (negative). A comparison of the one-bond coupling constant ^1J(N1−B2) for 1-F-borazine and

TABLE 2: One-Bond FC Terms and Coupling Constants *J* (Hz) for Borazine and Selected Fluoro-Substituted Derivatives

One-Bond Coupling Constants with Substituents on Nonadjacent Atoms

	N1−B2		B2−N3		N3−B4		B4−N5	
compd	FC	J	FC	J	FC	J	FC	J
borazine	−28.7	−26.7	−28.7	−26.7	−28.7	−26.7		
1-F-borazine	−33.4	−31.3	−29.1	−27.2	−28.7	−26.8		
1,3-diF-borazine	−34.5	−32.2	−34.5	−32.2	−33.5	−31.2	−29.5	−27.4
1,4-diF-borazine	−33.8	−31.5	−29.6	−27.6	−36.9	−35.2		
1,3,5-triF-borazine	−35.1	−32.7	−35.1	−32.7	−35.1	−32.7		
2-F-borazine	−36.6	−35.0	−36.6	−35.0	−28.9	−27.0	−28.8	−26.9
2,6-diF-borazine	−37.0	−35.3	−36.7	−35.0	−29.2	−27.1		
1,4-diF-borazine	−33.8	−31.5	−29.6	−27.6	−36.9	−35.2		
2,4,6-triF-borazine	−37.4	−35.7	−37.4	−35.7	−37.4	−35.7		

One-Bond Coupling Constants with Substituents on Adjacent Atoms

compd	N1−B2 FC	B2−N3 FC	N3−B4 FC	B4−N5 FC
1,2,3-triF-borazine	−40.3	−40.3	−33.9	−29.5
1,2,6-triF-borazine	−40.0	−37.2	−28.9	

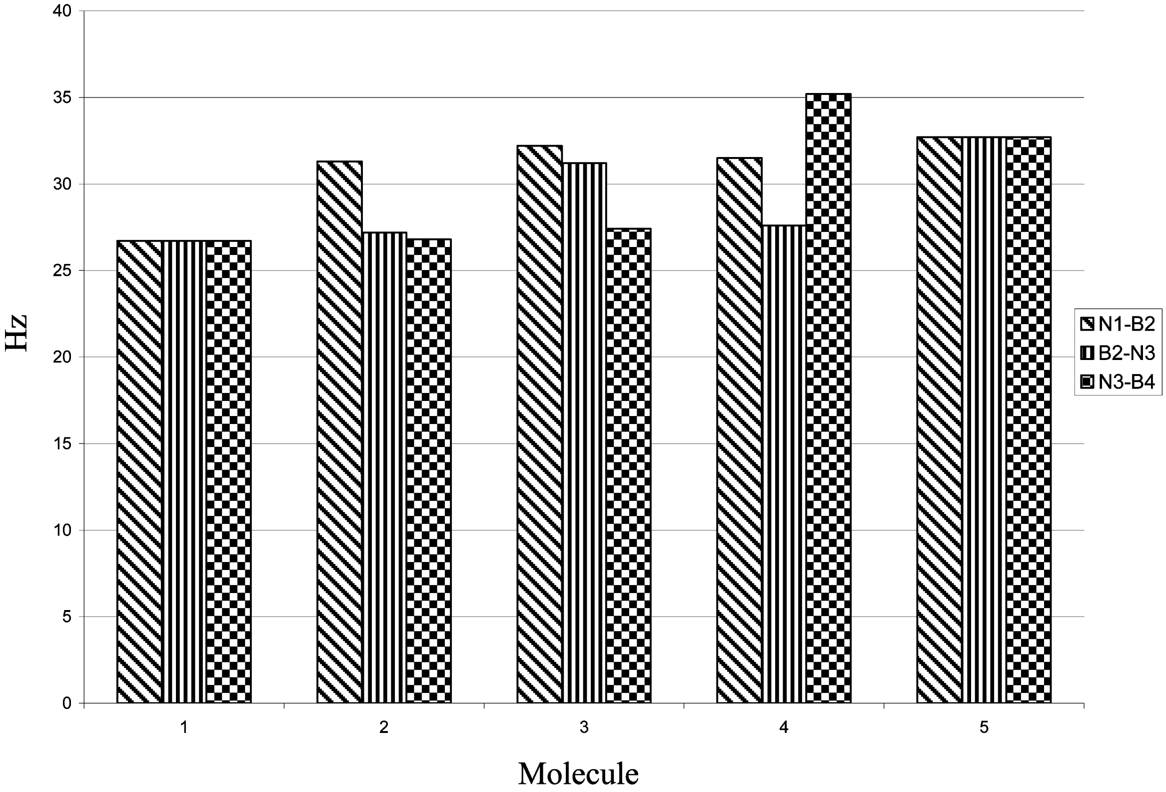

Figure 2. Absolute values of one-bond coupling constants in borazine (1), 1-F-borazine (2), 1,3-diF-borazine (3), 1,4-diF-borazine (4), and 1,3,5-triF-borazine (5). In each derivative, at least one F is bonded to N1. For molecule 3, the columns refer to N1−B2, N3−B4, and B4−N5 coupling.

2-F-borazine indicates that substitution of the strong electron-withdrawing substituent fluorine increases the absolute value of ^1J(N1−B2) relative to borazine, with substitution at B having a greater effect.

An examination of fluorine substitution effects at B and N on one-bond coupling constants is facilitated by Figures 2 and 3, which present bar graphs that illustrate the absolute values of the three unique one-bond B−N coupling constants for these molecules. Figure 2 shows the graph generated for molecules that have at least 1 F atom bonded to N with no F atoms on adjacent atoms of the ring; Figure 3 shows the corresponding graph for molecules having at least 1 F atom bonded to B and no F atoms on adjacent atoms of the ring. From Figure 2 it can be seen that F substitution at N1 in 1-F-borazine (molecule 2) increases (the absolute value of) ^1J(N1−B2) from about 27 Hz in borazine (molecule 1) to 31 Hz but produces only small increases in the remaining one-bond coupling constants ^1J(B2−N3) and ^1J(N3−B4). For the disubstituted molecule 1,3-diF-borazine (molecule 3), the two coupling constants that involve N1 and N3, namely, ^1J(N1−B2) and ^1J(N3−B4), increase relative to borazine and are similar to ^1J(N1−B2) in 1-F-borazine. However, the third one-bond coupling constant ^1J(B4−N5) increases by less than 1 Hz. For 1,4-diF-borazine (molecule 4) in which one F is bonded to N1 and the other to B4, ^1J(N1−B2) and ^1J(N3−B4) increase, but ^1J(B2−N3) increases only slightly by less than 1 Hz. The change in ^1J(N1−B2) is similar to that found for F-substitution in 1-F-borazine. ^1J(N3−B4) is the largest one-bond coupling constant in the set, reinforcing the previous observation that F substitution at B has a slightly larger effect on B−N coupling constants than substitution at N. Finally, the one-bond coupling constants for the trisubstituted molecule 1,3,5-borazine (molecule 5) are 33 Hz, the largest values among derivatives with F substitution at N.

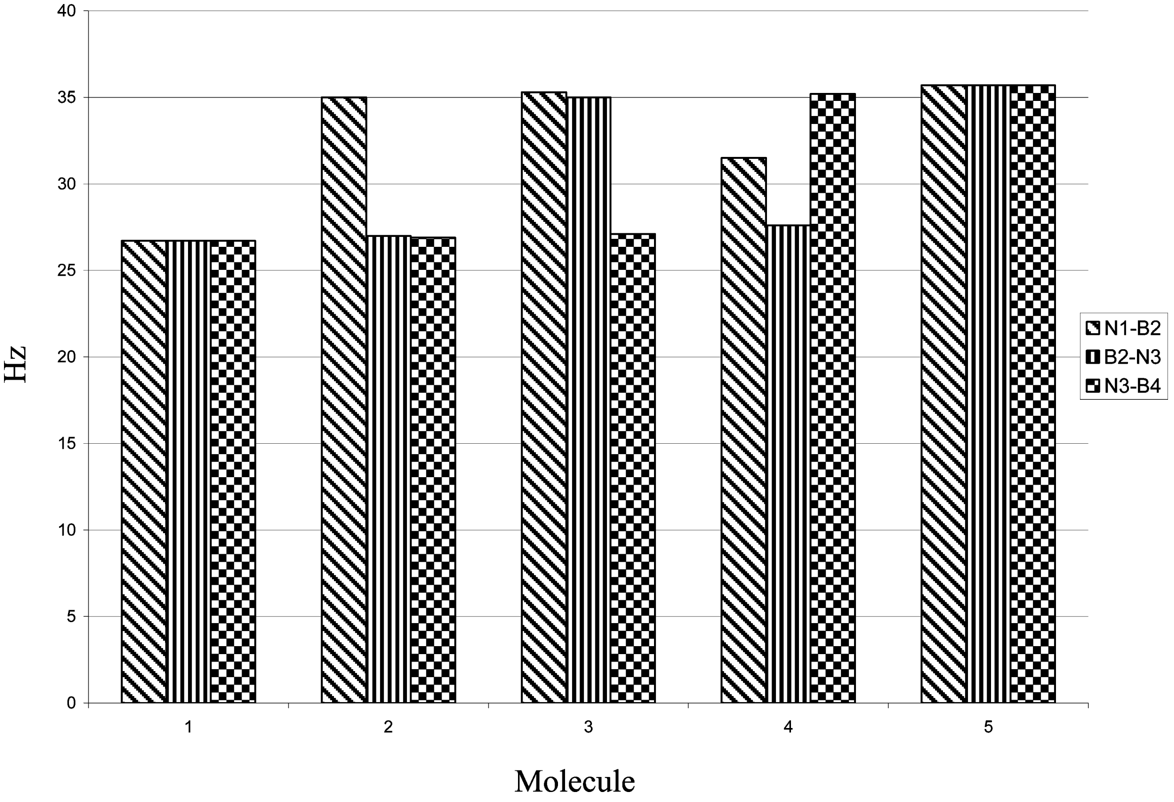

Figure 3. Absolute values of one-bond coupling constants in borazine (1), 2-F-borazine (2), 2,6-diF-borazine (3), 1,4-diF-borazine (4), and 2,4,6-triF-borazine (5). In each derivative, at least 1 F is bonded to B2. For molecule 2, the columns refer to N1−B2, N3−B4, and B4−N5 coupling.

An examination of Figure 3 indicates that similar changes in one-bond B−N coupling constants occur upon substitution at B. Monofluoro substitution at B2 (molecule 2) increases ^1J(N1−B2) relative to borazine but produces only small increases in the remaining one-bond coupling constants. Disubstitution of F at B2 and B6 (molecule 3) increases the two coupling constants involving B2, namely, ^1J(N1−B2) and ^1J(B2−N3) but leaves ^1J(N3−B4) essentially unchanged relative to borazine. Disubstitution at N1 and B4 (molecule 4) increases ^1J(N1−B2) and ^1J(N3−B4). Trisubstitution increases all one-bond B−N coupling constants to 36 Hz.

TABLE 3: Distances (Å) between Adjacent Ring Atoms in Borazine and Its F-Substituted Derivatives

compd	N1−B2	B2−N3	N3−B4	B4−N5
Derivatives with Substituents on Nonadjacent Atoms				
borazine	1.434	1.434	1.434	
1-F-borazine	1.430	1.432	1.434	
1,3-diF-borazine	1.430	1.430	1.431	1.433
1,4-diF-borazine	1.432	1.431	1.430	
1,3,5-triF-borazine	1.430	1.430	1.430	
2-F-borazine	1.429	1.429	1.433	1.435
2,6-diF-borazine	1.429	1.430	1.434	
1,4-diF-borazine	1.432	1.431	1.430	
2,4,6-triF-borazine	1.429	1.429	1.429	
Derivatives with Substituents on Adjacent Atoms				
1,2,6-triF-borazine	1.435	1.428	1.435	
1,2,3-triF-borazine	1.435	1.435	1.430	1.433

The above data indicate that fluorine substitution in borazine always increases the absolute value of the one-bond coupling constant involving the N or B atom at the site of substitution but induces only small changes in the remaining one-bond coupling constants. Thus, these data suggest that the effect of ring substitution on one-bond coupling constants ^1J(N−B) is fairly localized. Moreover, the absolute value of any one-bond coupling constant does not appear to be very sensitive to the number of fluorine substituents present, as evident from Figures 2 and 3. In addition, the increase in ^1J(N−B) upon substitution is slightly greater when substitution occurs at B rather than N. Finally, there is little correlation between the change in one-bond B−N coupling constants upon substitution and the change in B−N distances, as evident from Table 3. The B−N distance, which is 1.434 D in borazine, usually decreases upon substitution, but the change in this distance does not exceed 0.005 Å. The shortest B−N distances of 1.429 Å are found when F substitution occurs at B in 2-F-borazine, 2,6-diF-borazine, and 2,4,6-triF-borazine. However, the difference between the B−N distances in 1,3,5- and 2,4,6-triF-borazine is only 0.001 Å, a difference that is too small to account for the difference of 3.0 Hz (−32.7 vs −35.7 Hz, respectively) between ^1J(N−B) for these isomers.

Although it has been stated above that substituent effects on coupling constants are essentially localized at the site of substitution, closer examination of Figures 2 and 3 indicates that there are some relatively small variations in one-bond coupling constants as the number and position of the substituents change. Can these small variations be explained? Table 2 shows that ^1J(N1−B2), ^1J(B2−N3), and ^1J(N3−B4) for 1-F-borazine are greater (in absolute value) by 4.6, 0.5, and 0.1 Hz, respectively, compared to ^1J(B−N) for borazine. When substitution occurs at B in 2-F-borazine, the corresponding increases are 8.3, 0.3, and 0.2 Hz, respectively. These values can be used to understand the small variations observed for coupling constants in the di- and trisubstituted derivatives and to estimate their values. This can be done by determining the additivity factor using the following bond-additivity scheme:

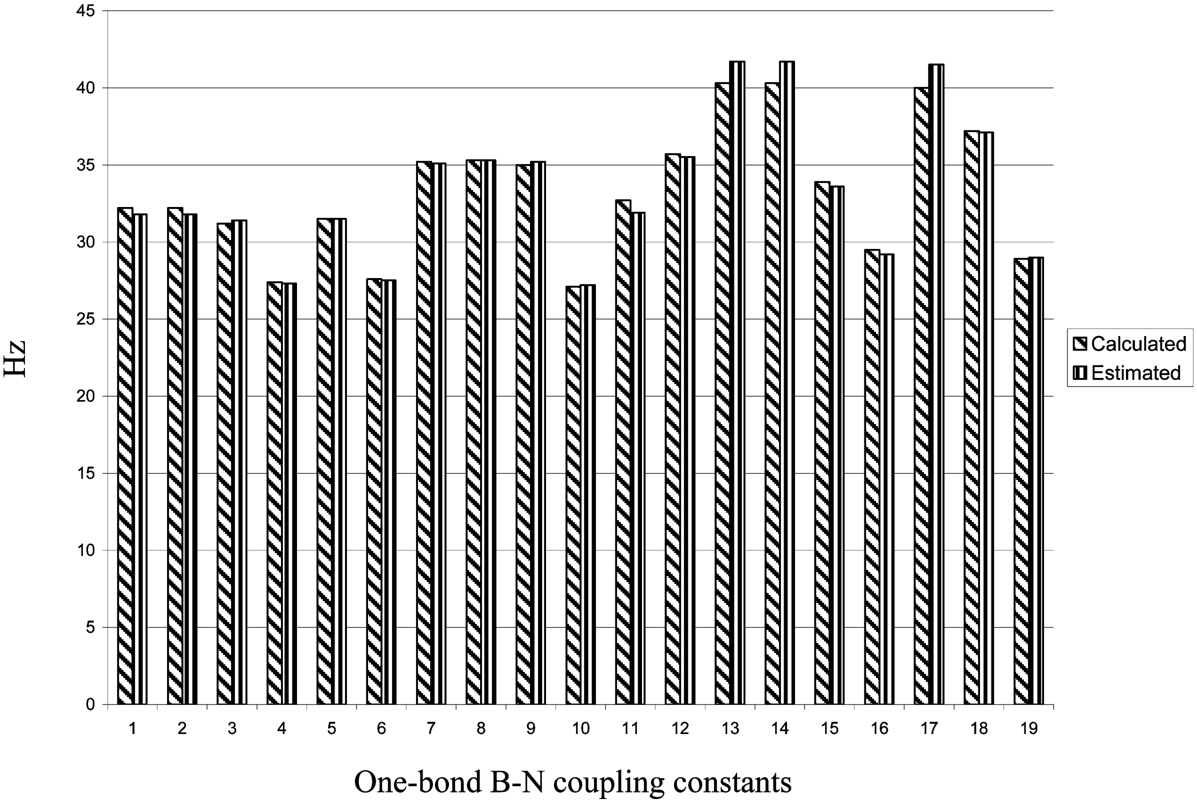

Figure 4. Absolute values of estimated and calculated one-bond coupling constants for fluoroborazines (columns, F-substituted borazine): 1−4, 1,3; 5−7, 1,4; 8−10, 2,6; 11, 1,3,5; 12, 2,4,6; 13−16, 1,2,3; 17−19, 1,2,6. The values for 1,2,3- and 1,2,6-triF-borazine are FC terms. The order of coupling constants is N1−B2, B2−N3, and N3−B4. B4−N5 is also given as the 4th column if it is unique.

(1) For a given bond, if the coupled atoms have an F atom bonded to N, add −4.6 Hz to the additivity factor; if the F atom is bonded to B, add −8.3 Hz.

(2) If for an adjacent bond another F atom is bonded to N, add −0.5 Hz to the additivity factor; if it is bonded to B, add −0.3 Hz.

(3) If a bond which is two bonds away from the bond of interest has an F atom bonded to N, add −0.1 Hz; if the substituent is bonded to B, add −0.2 Hz.

The predicted values of the coupling constants in the higher substituted derivative are equal to ^1J(B−N) for borazine plus the additivity factor. Using 2,6-diF-borazine as an example, the additivity factors for ^1J(N1−B2), ^1J(B2−N3), and ^1J(N3−B4) are [−8.3 + (−0.3)], [−8.3 + (−0.2)], and [−0.3 + (−0.2)] Hz, respectively. Thus, the estimated values of the three one-bond coupling constants ^1J(N1−B2), ^1J(B2−N3), and ^1J(N3−B4) are −35.3, −35.2, and −27.2 Hz, in excellent agreement with the computed EOM-CCSD values of −35.3, −35.0, and −27.1 Hz, respectively. Figure 4 columns 1−12 compare the computed and estimated values of one-bond coupling constants for all of the F-substituted borazines that have substituents on nonadjacent atoms. The agreement is remarkably good.

Substitution on Adjacent Ring Atoms. All of the diF- and triF-borazines considered thus far have F atoms bonded to nonadjacent atoms of the borazine ring. What happens to ^1J(N−B) when the substituents are placed on adjacent atoms? This question has been addressed by computing the Fermi-contact terms only for 1,2,6- and 1,2,3-triF-borazine. Table 2 reports these FC terms, and Figure 5 compares them with Fermi-contact terms for one-bond couplings for borazine (molecule 1), 1,3,5-triF-borazine (molecule 2), and 2,4,6-triF-borazine (molecule 4). Substitution at N1 and B2 in 1,2,3-triF-borazine (molecule 3) further increases the FC term for N1−B2 coupling to 40 Hz, a value larger than all N1−B2 FC terms in the derivatives with F atoms on nonadjacent sites of the ring. The increase in this term relative to borazine is 11 Hz, slightly less than the sum of the increases from single substitution at N1 (5 Hz) and B2 (8 Hz). The FC term for N3−B4 coupling for 1,2,3-triF-borazine (with F at N3 and H at B4) increases relative to borazine and is similar to the N3−B4 FC term for 1,3,5-triF-borazine. Since F atoms are not bonded to B4 or N5, the FC term for B4−N5 coupling is similar to the FC term for N−B coupling in borazine itself.

Figure 5 illustrates that a similar effect on one-bond coupling constants occurs when the F atoms are placed on N1, B2, and B6 (molecule 5). The FC term for N1−B2 coupling in 1,2,6-triF-borazine is 40 Hz, the same as in 1,2,3-triF-borazine. The FC term for B2−N3 coupling in the 1,2,6 molecule is similar to the FC term for B2−N3 coupling in 2,4,6-triF-borazine. Finally, the FC term for N3−B4 coupling for 1,2,6-triF-borazine is similar to the value for borazine. Thus, these data reinforce the observation that, in the borazines, substitution effects appear to be quite local. They also demonstrate that substitution on adjacent coupled atoms increases the coupling constant relative to its value when only one of the two atoms is bonded to a substituent.

The additivity scheme proposed above can be used to estimate the Fermi-contact terms for one-bond couplings in 1,2,3- and 1,2,6-triF-borazine using data derived from the FC terms for 1-F- and 2-F-borazine. It should not be surprising that this scheme does not estimate ^1J(N1−B2) as well for these two molecules, since the increase in these coupling constants relative to borazine is less than the sum of the increases observed for 1-F- and 2-F-borazine, as noted above. As a result, the additivity scheme underestimates ^1J(N1−B2) by about 1.5 Hz, although the estimates for the two remaining one-bond couplings are quite

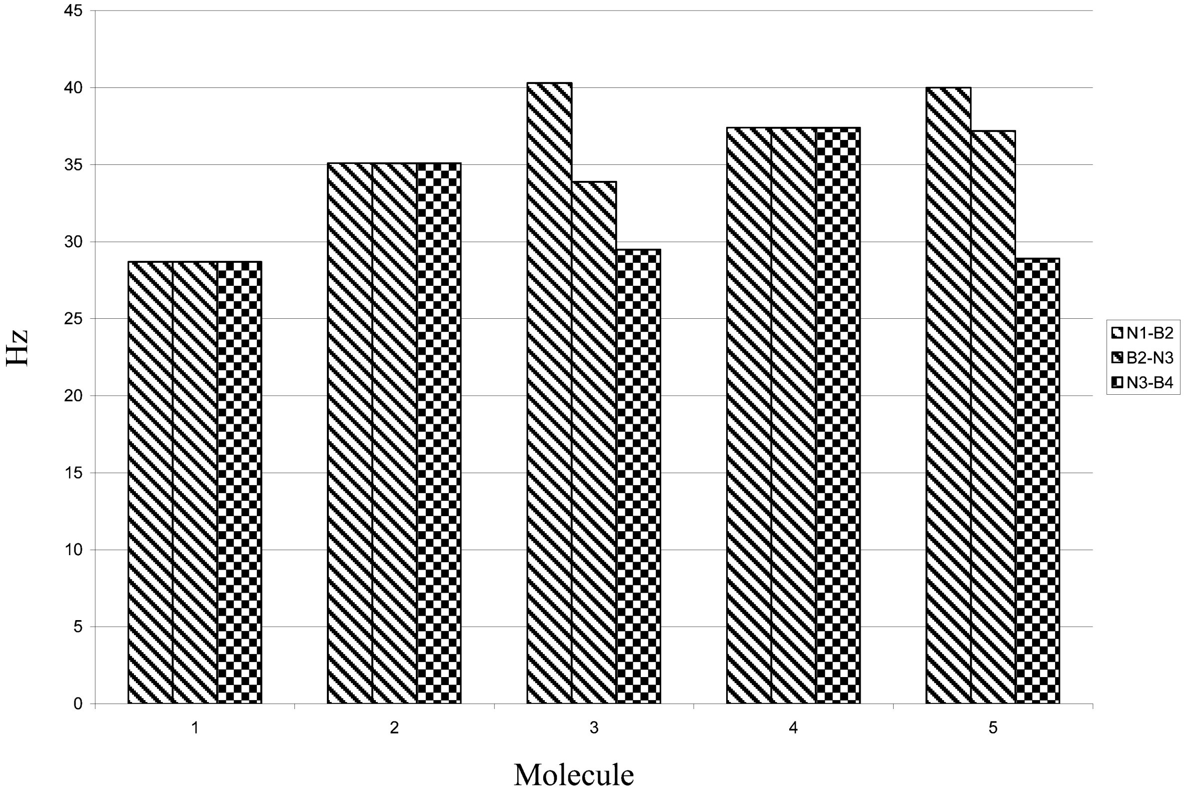

Figure 5. Absolute values of one-bond FC terms for borazine (1), 1,3,5-triF-borazine (2), 1,2,3-triF-borazine (3), 2,4,6-triF-borazine (4), and 1,2,6-triF-borazine (5). For molecule 3, the columns refer to N1−B2, N3−B4, and B4−N5.

TABLE 4: Fermi-Contact Terms (Hz) for One-Bond Couplings in Borazine, 1-Li-Borazine, and 2-Li-Borazine

compd	N1−B2	B2−N3	N3−B4	B4−N5
borazine	−28.7	−28.7	−28.7	
1-Li-borazine	−22.3	−25.2	−29.1	
2-Li-borazine	−17.4	−17.4	−27.9	−28.4

good. The comparisons are shown in Figure 4, columns 13−19.

The magnitude of the FC terms for coupling in 1,2,3- and 1,2,6-tri-F-borazine further strengths the argument that coupling constants in these molecules do not correlate with interatomic distances. As can be seen from Table 3, the N1−B2 distances in these two isomers are 1.435 Å, which are the longest B−N bonds in the entire series of F-substituted borazines. Yet, the FC terms for N1−B2 couplings in these two isomers are the largest among all F-substituted borazines.

Li-Substituted Borazines. Table 4 presents one-bond Fermi-contact terms for borazine, 1-Li-borazine, and 2-Li-borazine. Substitution of Li reduces the N1−B2 FC terms for N1−B2 coupling from −29 Hz in borazine to −22 Hz for 1-Li-borazine and −17 Hz for 2-Li-borazine. Thus, F and Li substitution have opposite effects on N1−B2 coupling constants, with F substitution increasing (the absolute value of) ^1J(N1−B2) relative to borazine, while Li substitution decreases it. Using two substituents with very different electronic effects, one electron-withdrawing and the other electron-donating, provides reference points on opposite ends of the spectrum for changes in ^1J(N1−B2) resulting from substitution of electron-donating or electron-withdrawing groups. Substitution of Li at B has little effect on the remaining one-bond coupling constants ^1J(N3−B4) and ^1J(B4−N5), again suggesting that substitution effects are dramatic only for coupling constants involving the atom at the site of substitution. However, when substitution of Li occurs at N, the coupling constant for the adjacent bond, ^1J(B2−N3), is also slightly reduced by 3.5 Hz to −25 Hz. The third coupling constant ^1J(N3−B4) is essentially unchanged. Using an additivity scheme similar to that derived above for F-substitution in borazine makes possible the prediction of coupling constants for the di-Li- and tri-Li-substituted derivatives, based on the FC terms. For example, the predicted values of ^1J(N1−B2), ^1J(B2−N3), and ^1J(N3−B4) for 2,6-diLi-borazine are −16.6, −17.1, and −27.6 Hz, respectively; the computed EOM-CCSD FC terms are −17.4, −18.1, and −27.6 Hz, respectively.

Unfortunately, experimental values of coupling constants for borazine and substituted borazines are scarce. A one-bond B−N coupling constant has been measured for ^{11}B−^{14}N coupling in 1,3,5-trimethylsilylborazine. When converted to ^{11}B−^{15}N, its value is 32 Hz.[31] According to Wrackmeyer, the sign of the corresponding reduced coupling constant ^1K(^{15}B−^{11}N) is positive, which means that ^1J(^{15}B−^{11}N) is negative. Although these data refer to three trimethylsilyl groups as substituents, the sign of the coupling constant is consistent with the computed signs, and the magnitude is not unreasonable.

Substituent Effects on One-Bond Coupling in Borazine vs Benzene. Substituent effects in borazine may also be compared to those in benzene using the data for Table 5, which provide one-, two-, and three-bond PSO, DSO, FC, and SD terms and total *J* for benzene, as well as FC terms for F-benzene, 1,3-diF-benzene, and Li-benzene. The data for benzene show that ^{13}C−^{13}C coupling constants are dominated by the Fermi-contact terms, although the contribution of the PSO term to ^1J(C−C) is significant. The experimental values of ^1J(C−C), ^2J(C−C), and ^3J(C−C) for benzene are 56.0, −2.5, and 10.1 Hz, respectively,[32,33] in excellent agreement with the computed values of 59.8, −2.8, and 10.1 Hz, respectively.[34]

Since the FC term is the dominant term for C−C coupling in benzene, the discussion of the effect of F and Li substitution on one-bond C−C coupling constants will be based on this term. F substitution at C1 increases ^1J(C1−C2) from 65 to 80 Hz but

TABLE 5: C−C Coupling Constants for Benzene and Fermi-Contact Terms (Hz) for F-Benzene, 1,3-diF-Benzene, and Li-Benzene

benzene	PSO	DSO	FC	SD	J
C1−C2	−6.3	0.2	64.9	1.0	59.8
C1−C3	0.0	0.0	−2.2	−0.6	−2.8
C1−C4	0.4	0.0	8.3	1.4	10.1

compd	C1−C2	C2−C3	C3−C4	C4−C5
benzene	64.9	64.9	64.9	
F-benzene	79.8	65.6	65.4	
1,3-diF-benzene	81.4	81.4	80.1	66.5
Li-benzene	44.5	60.5	64.8	

leaves the remaining one-bond coupling constants ^1J(C2−C3) and ^1J(C3−C4) only slightly changed relative to benzene. Substitution of 2 F atoms in 1,3-diF-benzene increases the two one-bond coupling constants involving the atoms bonded to F. Thus, ^1J(C1−C2) and ^1J(C3−C4) increase to 81 and 80 Hz, respectively. The remaining one-bond coupling constant ^1J(C4−C5) increases to 67 Hz. Thus, the effects of mono- and difluorine substitution in benzene are similar to those observed for F substitution in borazine. The experimentally determined value of ^1J(C1−C2) for F-benzene is 70.8 Hz.[35] Thus, the experimentally observed increase in the C1−C2 coupling constant upon fluorine substitution is reproduced by the calculations, although the computed EOM-CCSD coupling constant overestimates the increase by about 10 Hz.

Li substitution in benzene decreases the FC term for C1−C2 coupling from 65 to 45 Hz. Moreover, analogous to 1-Li-borazine, the FC term for C2−C3 coupling for the adjacent bond is also slightly reduced to 61 Hz, while the C3−C4 FC term remains essentially unchanged. Thus, the pattern of changes in FC terms upon Li substitution in benzene is very similar to that observed for Li substitution in borazine. Experimentally, substitution of the electron-donating group SiH_3 reduces ^1J(C1−C2) from 56.0 to 49.5 Hz,[35] consistent with the computed results for Li substitution in benzene. If corresponding reduced one-bond coupling constants for F- and Li-substituted benzenes and borazines are compared, it appears that benzene substitution and substitution at B in borazine induces similar changes in reduced coupling constants. However, relative to benzene substitution, the effects of substitution at N in borazine are clearly attenuated.

How can the changes in B−N coupling constants upon substitution in these aromatic rings be explained? There are two plausible approaches. Both arise from the fact that the coupling constants in benzene and borazine are dominated by the Fermi-contact term and that the operator for this term connects the ground-state wave function to excited triplet-state wave functions of σ symmetry. F is a ground-state electron-withdrawing substituent that leads to an increase in ^1J(B−N) in the substituted molecules relative to the parent; Li is a ground-state electron-donating substituent which leads to a decrease in ^1J(B−N). Thus, it may be that, in the excited σ states that dominate the FC term, the F atom loses electron density, thereby increasing the s electron density of the atom to which it is bonded and increasing the one-bond coupling constant involving that atom and its neighbor. On the other hand, since Li is electron-donating in the ground state, it may gain electron density in the dominant excited triplet states, decreasing the s electron density of the atom to which it is bonded and decreasing ^1J(B−N) relative to the parent molecule. Unfortunately, EOM-CCSD excited-state wave functions are not available. However, electron populations computed for the lowest energy $^3A_1$ states of F-benzene and Li-benzene indicate that F loses electron density while Li gains electron density in the triplet state relative to the ground state.

A second explanation derives from the nuclear magnetic resonance triplet wave function model (NMRTWM).[36] This model states that the sign and magnitude of J are determined by a competition of contributions from the entire spectrum of excited σ states, with some states making positive contributions and others negative. Using ^1J(C1−C2) for benzene as an example, if a particular excited state of benzene has one or an odd numbers of nodes intersecting the C1−C2 bond, then the orientation of the C1 and C2 nuclear magnetic dipoles is antiparallel, and this state makes a positive contribution to ^1J(C1−C2). On the other hand, if there are an even number of nodes between C1 and C2 in a particular excited state, then the contribution to ^1J(C1−C2) from this state is negative. For the F-substituted benzenes, the states with positive contributions are more heavily weighted than the corresponding states in benzene, thus increasing ^1J(C1−C2). For the Li-substituted benzenes, the states with negative contributions to ^1J(C1−C2) are more heavily weighted than in benzene. Undoubtedly, this question of substituent effects on coupling constants deserves further investigation.

Conclusions. Ab initio EOM-CCSD calculations have been carried out on borazine and selected F- and Li-substituted derivatives. The results of these calculations support the following statements:

(1) Relative to borazine, substitution of the electron-withdrawing substituent F increases the one-bond coupling constants involving atoms at the substitution sites, while Li substitution decreases the corresponding coupling constants. The remaining unique one-bond coupling constants increase or decrease only slightly. The effects of these substitutents on borazine coupling constants are similar to those observed for benzene.

(2) For di- and trisubstituted F-borazines with the substituents on nonadjacent sites, the values of coupling constants involving the atom at which substitution occurs (N1 or B2) are very similar to the values in the corresponding monosubstituted derivatives, suggesting that the effect of substitution has local character. The magnitudes of one-bond B−N coupling constants show only a relatively small dependence on the number of substituents present. Nevertheless, the changes in all of the unique coupling constants for these molecules can be estimated using a bond additivity scheme which takes into account changes in all one-bond coupling constants.

(3) When F substitution occurs at adjacent N and B atoms (1,2,3- and 1,2,6-triF-borazine), the N1−B2 coupling constant increases relative to N1−B2 coupling constants for molecules with only one F atom bonded to either N1 or B2, although the increase is less than the sum of the increases in the corresponding monosubstituted derivatives.

(4) Substitution effects on one-bond coupling constants for borazine are similar to substitution effects on one-bond coupling constants for benzene.

(5) Changes in one-bond coupling constants do not correlate with changes in B−N distances.

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Supporting Information Available: Two- and three-bond coupling constants. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, U.K., 1984; Chapter 6, pp 155−242.

(2) Stoyanov, E. S.; Hoffmann, S. P.; Juhasz, M.; Reed, C. A. *J. Am. Chem. Soc.* **2006**, *128*, 3160.

(3) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.

(4) Kiran, B.; Phukan, A. K.; Jemmis, E. D. *Inorg. Chem.* **2001**, *40*, 3615.

(5) Doerksen, R. J.; Thakkar, A. J. *Int. J. Quantum Chem.* **2002**, *90*, 534.

(6) Loh, K. P.; Yang, S. W.; Soon, J. M.; Zhang, H.; Wu, P. *J. Phys. Chem A* **2003**, *107*, 5555.

(7) Kawahara, S.; Tzuzuki, S.; Uchimaru, T. *J. Chem. Phys*. **2003**, *111*, 10081.

(8) Phukan A. K.; Kalagi, R. P.; Gadre, S. R.; Jemmis, E. F. *Inorg. Chem.* **2004**, *43*, 5824.

(9) Kato, T.; Yamabe, T. *Chem. Phys.* **2005**, *315*, 109.

(10) Benker, D.; Klapötke, T. M.; Kuhn, G.; Li, J.; Miller, C. *Heteroat. Chem.* **2005**, *16*, 311.

(11) Buck, H. *Int. J. Quantum Chem.* **2005**, *101*, 73.

(12) Miao, R.; Yang, G.; Zhao, C.; Hong, J.; Zhu, L. *THEOCHEM* **2005**, *715*, 91, *728*, 197.

(13) Rahaman, A.; Datta, A.; Mallajosyula, S. S.; Pati, S. K. *J. Chem. Theory Comput.* **2006**, *2*, 30.

(14) Pople, J. A.; Binkley J. S.; Seeger, R. *Int. J. Quantum Chem. Quantum Chem. Symp.* **1976**, *10*, 1.

(15) Krishnan, R.; Pople J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(16) Bartlett, R. J.; Silver. D. M. *J. Chem. Phys.* **1975**, *62*, 3258.

(17) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561.

(18) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(19) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer P. v. R. *J. Comput. Chem.* **1982**, *3*, 3633.

(20) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(21) Perera, S. A.; Sekino, H.; Bartlett, R. J. *J. Chem. Phys.* **1994**, *101*, 2186.

(22) Perera, S. A.; Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1996**, *104*, 3290.

(23) Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 8476.

(24) Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 7849.

(25) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(26) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(27) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572.

(28) Kirpekar, S.; Jensen, H. J. Aa.; Oddershede, J. *Chem. Phys.* **1994**, *188*, 171.

(29) Frisch, M. J.; et al. *Gaussian 03*; Gaussian, Inc.: Pittsburgh, PA, 2005.

(30) Stanton, J. F.; et al. *ACES II a program product of the Quantum Theory Project*; University of Florida: Gainesville, FL.

(31) Wrackmeyer, B.; Schwarze, B.; Durran, D. M.; Webb, G. A. *Magn. Reson. Chem.* **1995**, *33*, 557.

(32) Kashi, J.; Vaara, J.; Jokisari, J. *J. Am. Chem. Soc.* **1996**, *118*, 8879.

(33) Ruden, T. A.; Lutnaes, O. B.; Helgaker, T.; Ruud, K. *J. Chem. Phys.* **2003**, *118*, 9572.

(34) Del Bene, J. E.; Elguero, J. *Magn. Reson. Chem.* **2006**, *44*, 784.

(35) Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; John Wiley & Sons: Chichester, U.K., 1997; p 554.

(36) Del Bene, J. E.; Elguero, J. *Chem. Phys. Lett.* **2003**, *382*, 100.