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Spin−Spin Coupling Constants for Iminoboranes RBNH, HBNR, and RBNR and Comparisons with Corresponding Isoelectronic Acetylenes RCCH and RCCR, for R = H, CH₃, NH₂, OH, and F

Janet E. Del Bene,*,[†] José Elguero,[‡] Ibon Alkorta,[‡] Manuel Yáñez,[§] and Otilia Mó[§]

Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555, Instituto de Química Médica, Consejo Superior de Investigaciones Científicas, Juan de la Cierva, 3, E-28006 Madrid, Spain, and Departamento de Química, C-9, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain

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Abstract: Ab initio equation-of-motion coupled-cluster singles and doubles method calculations have been performed on iminoboranes RBNH, HBNR, and RBNR, for R = H, CH₃, NH₂, OH, and F, to evaluate substituent effects on one- and two-bond $^{15}N-^{11}B$, $^{11}B-^{1}H$, and $^{15}N-^{1}H$ spin−spin coupling constants. For comparison purposes, $^{13}C-^{13}C$ coupling constants were evaluated for corresponding isoelectronic molecules RCCH and RCCR. The absolute values of $^{1}J(N-B)$ and $^{1}J(C-C)$ increase in the series HBNR and RCCH as the σ-electron-withdrawing ability of R increases. In contrast, NH₂ substitution at B leads to a decrease in the absolute value of $^{1}J(N-B)$, but OH and F substitution increase $^{1}J(N-B)$. Disubstitution has dramatically different effects on coupling constants for RCCR and RBNR. In the former, $^{1}J(C-C)$ more than doubles relative to the corresponding RCCH and HCCH; in the latter, disubstitution of OH and F decreases $^{1}J(N-B)$ relative to the corresponding monosubstituted derivatives, while NH₂ substitution increases $^{1}J(N-B)$. Changes in one- and two-bond B−H and N−H coupling constants upon substitution are similar to changes observed for $^{1}J(N-B)$ in the corresponding monosubstituted derivatives RBNH and HBNR.

Introduction

The examination of substituent effects on molecular properties has proven to be a very fruitful approach in a wide range of studies of organic molecules.[1−5] In a previous study,[6] we used this approach to examine the relative stabilities of corresponding isomers in two series of iminoboranes RBNH and HBNR, where R is H, CH₃, NH₂, OH, and F. We investigated ground-state bonding and selected IR spectroscopic properties of these molecules, as well as the bonding characteristics and IR properties of their disubstituted counterparts, RBNR. The present paper reports the results

of an extension of our investigation of iminoboranes to include substituent effects on $^{15}N-^{11}B$ spin−spin coupling constants in molecules RBNH, HBNR, and RBNR, as well as one- and two-bond $^{15}N-^{1}H$ and $^{11}B-^{1}H$ spin−spin coupling constants in the monosubstituted derivatives. We also present $^{13}C-^{13}C$ coupling constants for RCCH and RCCR, molecules that are isoelectronic with corresponding RBNH and HBNR, and RBNR, respectively. In this paper, we compare and contrast substituent effects of one-bond B−N coupling constants in mono- and disubstituted iminoborazines and compare them to substituent effects on C−C coupling constants in the corresponding mono- and disubstituted acetylenes.

The present study is also an extension of our previous investigation of B−N coupling constants in borazine and its fluoro- and lithio-substituted derivatives.[7] In that study, we

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* Corresponding author e-mail: jedelbene@ysu.edu.

† Youngstown State University.

‡ Consejo Superior de Investigaciones Científicas.

§ Universidad Autónoma de Madrid.

examined the sensitivity of ^1J(N–B) to the site of substitution and the number of substituents and also observed the opposing effects of σ-electron-donating and -electron-withdrawing substituents, since F substitution at either B or N increases ^1J(N–B), whereas Li substitution decreases ^1J(N–B). These substituent effects in borazine are similar to those observed for benzene and are consistent with available experimental data.[7] Recently, we have also reported one-bond B–H and B–Li coupling constants for the five-membered boron-containing rings diazaborole and Li-diazaborole, as well as B–N coupling constants for these molecules and the corresponding diazaborole anion,[8] species which served as models for newly synthesized five-membered nucleophilic boron-containing rings.[9] NMR coupling constants and chemical shifts were used experimentally to identify these species. It is anticipated that the newly developed synthetic techniques which produced nucleophilic boron moieties will lead to the synthesis of a new class of molecules containing B–N bonds and that NMR spin–spin coupling constants will be an important tool for the identification and characterization of these molecules. Hence, a systematic study of substituent effects on B–N coupling constants is both warranted and timely.

Methods

The geometries of the molecules RBNH, HBNR, and RBNR were optimized at second-order Møller–Plesset theory[10–13] with the 6-311++G(d,p) basis set[14–16] and have been reported previously.[6] Coupling constants were computed for these molecules using the ab initio equation-of-motion coupled-cluster singles and doubles method (EOM-CCSD) in the configuration-interaction- (CI-)like approximation,[17–20] with all electrons correlated. The Ahlrichs qzp basis set[21] was used on C, N, O, and F atoms, and the qz2p basis set was used for H atoms bonded to either B or N. The Dunning cc-pVDZ[22,23] basis set was placed on all other H atoms. Since an Ahlrichs qzp basis is not available for B, a new "hybrid" basis had been constructed for this atom, using the boron cc-pV5Z basis for 1s orbitals, cc-pVQZ for the valence s and p orbitals, and one set of d orbitals. This basis set has the same number of contracted functions (6s, 4p, and 1d) as the Ahlrichs qzp basis used for C, N, O, and F and was used previously in studies of B–N, B–H, and B–Li coupling constants.[7,8]

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), and spin-dipole (SD).[24] All terms have been computed for all molecules. The EOM-CCSD calculations were carried out using the ACES II[25] program on the Itanium Cluster at the Ohio Supercomputer Center.

Results and Discussion

Substitution Effects on ^1J(C–C): RCCH and RCCR. Before analyzing the B–N coupling constants as a function of the substituent, it is advantageous to first examine C–C coupling constants for molecules RCCH, which are isoelectronic with corresponding molecules RBNH and HBNR, and for RCCR, which are isoelectronic with the corresponding

Table 1. C–C Fermi-Contact Terms and Coupling Constants [^1J(C–C), Hz], C–C Distances (Å), and Symmetries for Molecules RCCH and RCCR

	Coupling Constants			
	RCCH		RCCR	
molecule	FC	^1J(C–C)	FC	^1J(C–C)
R = H	178.1	192.3	178.1	192.3
CH$_3$	178.5	192.7	180.9	195.2
NH$_2$	210.8	226.3	253.7	270.1
OH	232.8	250.2	313.6	334.0
F	258.8	278.7	394.1	418.8

C–C Distances and Molecular Symmetry		
molecule	RCCH	RCCR
R = H	1.216 ($C_{\infty v}$)	1.216 ($D_{\infty h}$)
CH$_3$	1.218 (C_{3v})	1.220 (D_{3h})
NH$_2$	1.217 (C_s)	1.217 (C_2)
OH	1.214 (C_s)	1.208 (C_2)
F	1.208 ($C_{\infty v}$)	1.197 ($D_{\infty h}$)

RBNR. The individual contributions of the PSO, DSO, FC, and SD terms to ^1J(C–C) can be found in Table S1 of the Supporting Information. The FC terms, total ^1J(C–C), and C–C distances are reported in Table 1. The Fermi-contact term is the dominant term, although contributions from the PSO terms (ranging from 6 to 15 Hz) and from the SD terms (8 to 10 Hz) cannot be neglected. Moreover, although the data of Table 1 indicate that ^1J(C–C) has its maximum values in the RCCH and RCCR series when R is F and the C–C distances are shortest, ^1J(C–C) does not correlate with this distance. For example, although the C–C distance in H$_2$NCCH is intermediate between that in HCCH and that in H$_3$CCCH, differing from both by only 0.001 Å, ^1J(C–C) for H$_2$NCCH is 34 Hz greater than ^1J(C–C) for HCCH and H$_3$CCCH.

The only experimental coupling constants available for the molecules investigated in this study are for acetylene (170.6 Hz)[26] and methylacetylene (175 Hz).[27] From Table 1, it can be seen that the computed EOM-CCSD values of 192.3 and 192.7 Hz, respectively, overestimate the experimental values by about 10%. This may be due in part to the sensitivity of ^1J(C–C) to the length of the C–C bond, as demonstrated by Wigglesworth et. al,[28] and also to the neglect of zero-point and thermal vibrational effects.[29–32] However, our emphasis in this study is on changes in coupling constants due to the substitution of σ-electron-withdrawing groups, and the results reported below for substituted acetylenes are given only for comparison with substituent effects in iminoboranes. Nevertheless, as will be evident below, our results for substituent effects on ^1J(C–C) are in agreement with results reported by Kamienska-Trela and co-workers, who have carried out extensive studies of substituent effects on C–C coupling constants.[27,33]

What happens to ^1J(C–C) upon the substitution of H by the ground-state σ-electron-withdrawing substituents CH$_3$, NH$_2$, OH, and F? As evident from Table 1, ^1J(C–C) values for HCCH, H$_3$CCCH, and H$_3$CCCCH$_3$ are similar. However, as the σ-electron-withdrawing ability of the substituents

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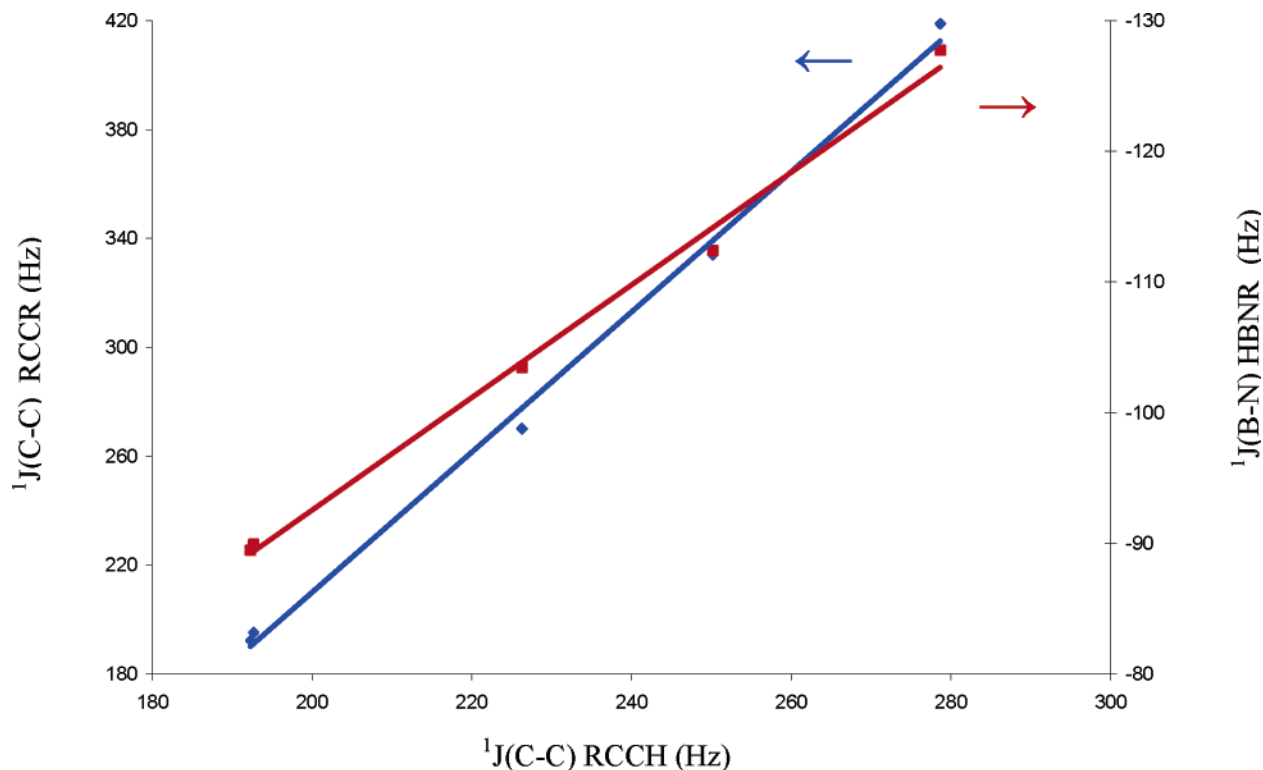
Figure 1. $^1J(C-C)$ for RCCR (blue ◆, left y axis) and $^1J(B-N)$ for HBNR (red ■, right y axis) vs $^1J(C-C)$ for RCCH.

increases in the order CH_3 < NH_2 < OH < F, $^1J(C-C)$ increases in the same order in both the mono- and disubstituted derivatives. Figure 1 graphically illustrates the linear correlation between $^1J(C-C)$ for RCCR and $^1J(C-C)$ for RCCH. As the σ-electron-withdrawing ability of the substituent increases, $^1J(C-C)$ increases, primarily because of an increase in the FC term. A second very interesting observation is the slope of 2.6 for the trend line shown in Figure 1, which indicates that disubstitution is nonadditive in a positive sense, insofar as it more than doubles $^1J(C-C)$ in RCCR relative to the corresponding RCCH and HCCH. These observations indicate that $^1J(C-C)$ increases systematically as the σ-electron-withdrawing ability of the R group increases.

How can these results be explained? Because $^1J(C-C)$ is dominated by the FC term, some insights can be obtained by considering the nature of this term and the nature of the excited triplet-state wavefunctions which couple to the ground state through the FC operator. First, it should be recalled that the FC operator does not contain a specific distance-dependent term. Second, if the function of the R groups is to withdraw σ-electron density from the C−C bond in the ground state, then the increase in $^1J(C-C)$ as the σ-electron-withdrawing ability of the substituent increases suggests that the excited states which dominate must have increased σ-electron densities on the two carbon atoms. Alternatively, in going from NH_2 to OH to F, the number of nonbonding pairs of electrons on the substituent increases. These lone pairs can interact with the C−C π bonds and, from a sum-over-states perspective, influence both the sign and magnitude of the contributions to $^1J(C-C)$ from the various excited states that couple to the ground state. Since the FC term dominates and the sign of $^1J(C-C)$ is positive,

triplet excited states with an odd number of nodes intersecting the C−C bond assume increased importance.[34] The effect of σ-electron-withdrawing substituents on $^1J(C-C)$ in the substituted acetylenes is consistent with the effect of F substitution on one-bond C−C coupling constants in fluorobenzene, which also increase when coupling involves the fluoro-substituted C atom.[7]

$^1J(N-B)$ **and B−N Distances.** Molecular symmetries, B−N distances, Fermi-contact terms, and one-bond B−N coupling constants [$^1J(N-B)$] for the entire set of molecules RBNH, HBNR, and RBNR are reported in Table 2. The individual contributions of PSO, DSO, FC, and SD terms can be found in Table S2 of the Supporting Information. As observed previously for borazine,[7] the FC term dominates $^1J(N-B)$, accounting for more than 90% of the total coupling constant in all cases. The data of Table 2 also indicate that there is little correlation between one-bond B−N coupling constants and B−N distances. For example, among the disubstituted iminoboranes, the B−N distances are shortest in HBNH and H_3CBNCH_3, but these two molecules have the smallest B−N coupling constants. Thus, it can be concluded that, in general, changes in B−N coupling constants in substituted iminoboranes do not depend simply on changes in B−N distances. This observation is consistent with previous theoretical and experimental data on coupling constants and distances for molecules[35,36] and is really not surprising in view of the absence of a distance-dependent term in the Fermi-contact operator.

Substituent Effects on $^1J(N-B)$**.** Having examined $^1J(C-C)$ as a function of the substituent for RCCH and RCCR, it is appropriate to now return to $^1J(N-B)$ for RBNH, HBNR, and RBNR. The B−N coupling constants for these molecules are reported in Table 2. As observed for CH_3 substitution

Table 2. B−N Fermi-Contact Terms and Coupling Constants [^1J(N−B), Hz]; B−N Distances (Å); and Symmetries for Molecules RBNH, HBNR, and RBNR

	Coupling Constants					
	RBNH		HBNR		RBNR	
molecule	FC	^1J(N−B)	FC	^1J(N−B)	FC	^1J(N−B)
R = H	−84.9	−89.4	−84.9	−89.4	−84.9	−89.4
CH_3	−84.1	−88.2	−84.9	−89.9	−84.3	−89.0
NH_2	−83.4	−86.4	−96.9	−103.4	−110.1	−115.6
OH	−108.5	−112.6	−104.5	−112.4	−91.0	−96.1
F	−118.3	−123.1	−118.1	−127.7	−99.5	−106.6

	B−N Distances and Molecular Symmetry		
molecule	RBNH	HBNR	RBNR
R = H	1.247 ($C_{\infty v}$)	1.247 ($C_{\infty v}$)	1.247 ($C_{\infty v}$)
CH_3	1.250 (C_{3v})	1.250 (C_{3v})	1.252 (C_{3v})
NH_2	1.264 (C_s)	1.248 (C_s)	1.254 (C_1)
OH	1.250 (C_s)	1.246 (C_s)	1.268 (C_1)
F	1.245 ($C_{\infty v}$)	1.241 ($C_{\infty v}$)	1.260 (C_s)

on ^1J(C−C), substitution of one CH_3 group at either B or N, or two CH_3 groups, one at B and one at N, has little effect on ^1J(N−B). Moreover, in the series HBNR, substitution of the stronger σ-electron-withdrawing substituents NH_2, OH, and F increases the absolute value of ^1J(N−B) in the order CH_3 < NH_2 < OH < F, consistent with the RCCH series. The correlation between substituent effects on ^1J(N−B) in the series HBNR and ^1J(C−C) for RCCH is also illustrated in Figure 1. [It should be noted that, since the magnetogyric ratio of ^{15}N is negative, while that of ^{11}B is positive, the one-bond B−N coupling constant ^1J(N−B) is negative, but the reduced one-bond coupling constant ^1K(N−B) is positive, as is ^1K(C−C).]

In contrast, a correlation between ^1J(C−C) and ^1J(N−B) is not observed for substitution at B in the series RBNH. In particular, NH_2 substitution at B leads to a decrease of ^1J(N−B) relative to HBNH, while OH and F substitution increase ^1J(N−B). [Changes in ^1J(N−B) will be discussed in terms of absolute values.] Thus, ^1J(N−B) is extremely sensitive to the site of substitution when the substituent is NH_2 but is relatively insensitive to which site is substituted when R is OH or F. This is illustrated graphically in Figure 2, a plot of ^1J(N−B) for HBNR versus ^1J(N−B) for RBNH. The reference line shown passes through the origin and has a slope of 1. Relative to the other molecules in the two series of monosubstituted derivatives, ^1J(N−B) for H_2NBNH appears to be too small; that is, NH_2 bonded to B acts more like H and CH_3 rather than the stronger σ-electron-withdrawing substituents OH and F. Since ^1J(N−B) for HBNR is linearly correlated with ^1J(C−C), it is apparent that no such correlation exists for coupling constants between RBNH and RCCH.

Why does the substitution of NH_2 at B fail to produce the expected increase in ^1J(N−B)? Some insight into the answer to this question can be gained by considering the nature of the BN bond in H_2NBNH. At the outset, it must be stated that coupling constants are second-order properties that depend on electron densities in both the ground state and the excited states to which they couple, and any explanation

of changes in coupling constants based on ground-state properties must be incomplete. However, it is not unreasonable to suggest that, in a series of related molecules, differences in ground-state bonding characteristics may be manifested by differences in coupling constants. In our previous study of the ground-state bonding characteristics of substituted iminoboranes,[6] we concluded that, while substitution at N only slightly perturbs the BN triple bond, NH_2 substitution at B has a rather dramatic effect on this bond. In H_2N−BNH, there is a strong contribution to the BN bond from a canonical form of the type H_2N=B=N− H, which indicates that the BN bond loses triple bond character. This is associated with a significant increase in the B−N distance relative to all other monosubstituted derivatives and a value of ^1J(N−B) that is much less than expected, as clearly illustrated in Figure 2.

The effect of disubstitution of NH_2, OH, and F on ^1J(N−B) is dramatically different from the effect of monosubstitution. In particular, disubstitution of NH_2 increases ^1J(N−B) relative to both H_2NBNH and HBNNH₂, but disubstitution of OH or F decreases ^1J(N−B) relative to the corresponding monosubstituted derivatives RBNH and HBNR. Specifically, ^1J(N−B) decreases from −112 Hz in HOBNH and HBNOH to −96 Hz in HOBNOH, and from −123 and −128 Hz in FBNH and HBNF, respectively, to −107 Hz in FBNF, while ^1J(N−B) increases from −86 and −103 Hz in H_2NBNH and HBNNH₂, respectively, to −116 Hz in H_2NBNNH₂. These differences are also shown graphically in Figure 2, where ^1J(N−B) for RBNR is plotted against ^1J(N−B) for RBNH. Once again, the reference line passes through the origin and has a slope of 1. The corresponding plot for RBNR versus HBNR has a similar appearance. It is apparent that disubstitution of NH_2 leads to a dramatic increase in ^1J(N−B) relative to HBNNH₂ and H_2NBNH, whereas disubstitution of OH or F actually decreases ^1J(N−B) relative to the corresponding monosubstituted derivatives.

Some insight into at least one factor which influences this rather strange behavior can be obtained by comparing ^1J(N−B) for RBNR and ^1J(C−C) for RCCR. Figure 3 indicates
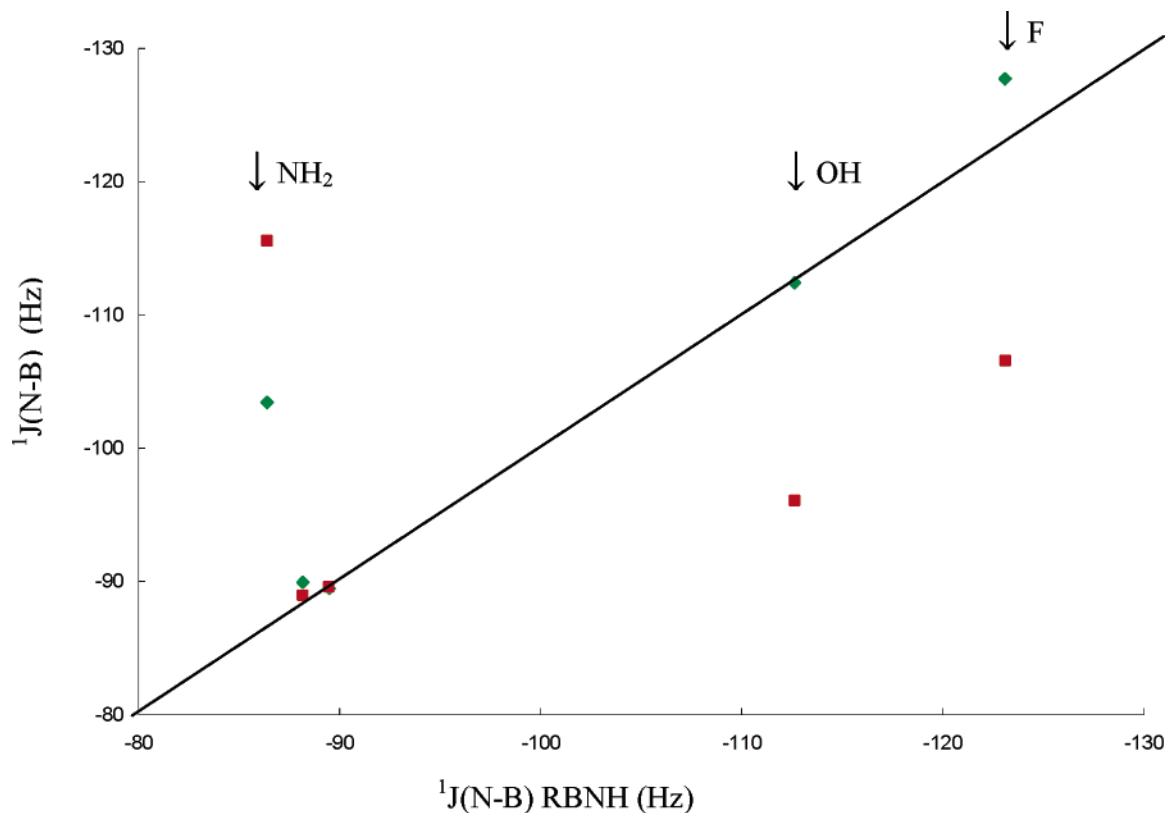
Figure 2. $^1J(N-B)$ for HBNR (green ◆) and $^1J(N-B)$ for RBNR (red ■) vs $^1J(N-B)$ for RBNH. The reference line has a slope of 1 and passes through the origin. The points corresponding to NH_2, OH, and F as substituents are marked by arrows. The points for H and CH_3 are at the bottom left of the graph.
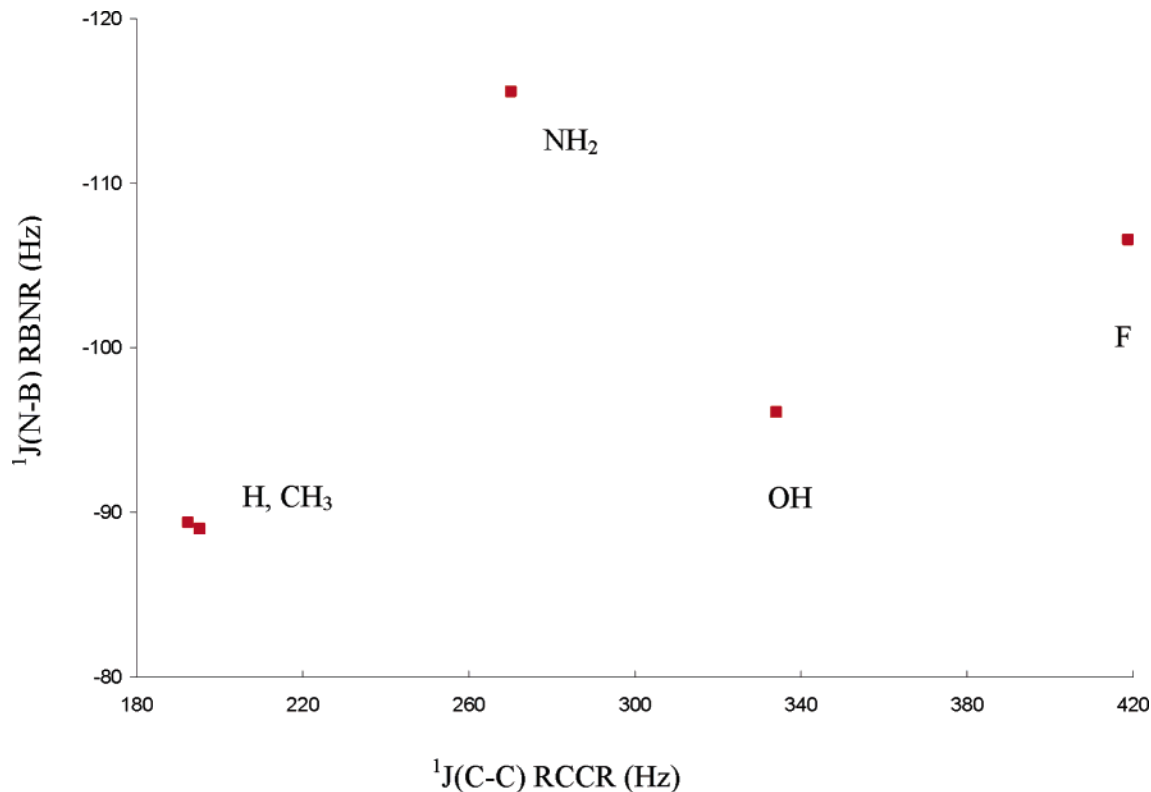
Figure 3. $^1J(N-B)$ for RBNR vs $^1J(C-C)$ for RCCR.

that, while disubstitution of CH_3 has very little effect on these two one-bond coupling constants, there is no correlation between $^1J(N-B)$ for RBNR and $^1J(C-C)$ for RCCR when

R is NH_2, OH, and F. From Figure 1, it is apparent that disubstitution of OH and F in the acetylenes significantly increases $^1J(C-C)$ for HOCCOH and FCCF relative to

Table 3. One- and Two-Bond B−H and N−H Coupling Constants and Fermi-Contact Terms (Hz) and B−H and N−H Distances (Å) for Molecules RBNH and HBNR

Coupling Constants				
RBNH	FC	^1J(N−H)	FC	^2J(B−H)
R = H	110.3	−111.9	54.8	57.6
CH$_3$	−110.3	−112.1	54.5	57.2
NH$_2$	−102.1	−104.4	46.0	47.6
OH	−116.9	−119.1	66.0	68.5
F	−119.8	−121.8	70.9	73.6
HBNR	FC	^1J(B−H)	FC	^2J(N−H)
R = H	230.7	231.0	−13.9	−15.5
CH$_3$	229.2	229.5	−13.2	−15.0
NH$_2$	239.4	239.6	−14.4	−16.3
OH	249.8	249.9	−15.2	−17.2
F	265.0	265.1	−16.9	−18.9

Distances				
	RBNH		HBNR	
molecule	N−H	B−H	B−H	N−H
R = H	0.996	2.243	1.168	2.415
CH$_3$	0.995	2.245	1.169	2.418
NH$_2$	0.997	2.195	1.168	2.415
OH	0.993	2.244	1.167	2.412
F	0.993	2.239	1.166	2.407

HOCCH and FCCH, respectively. In contrast, disubstitution of OH and F in the iminoboranes actually decreases ^1J(N−B) relative to either of the corresponding monosubstituted derivatives. The opposite effects of these two substituents on ^1J(N−B) and ^1J(C−C) are consistent with our earlier

observations that disubstitution of OH and F have opposite effects on C−C and B−N bonds.[6] Disubstitution of these two groups appears to strengthen and shorten the C−C bond relative to the corresponding monosubstituted derivatives but lengthen the B−N bond relative to either of the corresponding monosubstituted derivatives, as evident from Tables 1 and 2, respectively. What remains unclear is why substitution of two NH$_2$ groups in iminoborane should increase ^1J(N−B) relative to either monosubstituted derivative, thereby having a similar effect to mono- and disubstitution of NH$_2$ in acetylene.

Substitution Effects on B−H and N−H Coupling Constants. Table 3 presents one- and two-bond B−H and N−H Fermi-contact terms and coupling constants and corresponding distances for the monosubstituted derivatives RBNH and HBNR. The contributions of all terms to these coupling constants are reported in Table S2 of the Supporting Information. Once again, the FC term dominates, contributing more than 90% of the coupling constant except for two-bond N−H coupling in HBNR molecules, in which case ^2J(N−H) is relatively small, ranging from −15 to −19 Hz. One-bond N−H distances in RBNH and B−H distances in HBNR show little sensitivity to substitution, varying by only 0.004 and 0.003 Å, respectively, in these two series. Despite the small variation in N−H and B−H distances, ^1J(N−H) varies from −104 to −122 Hz in the series RBNH, while ^1J(B−H) varies from 230 to 265 Hz in the series HBNR.

Patterns similar to those observed for B−N coupling constants in the two series RBNH and HBNR are also observed for one- and two-bond B−H and N−H coupling constants. Both B−H and N−H coupling constants are relatively insensitive to the replacement of H by CH$_3$. With
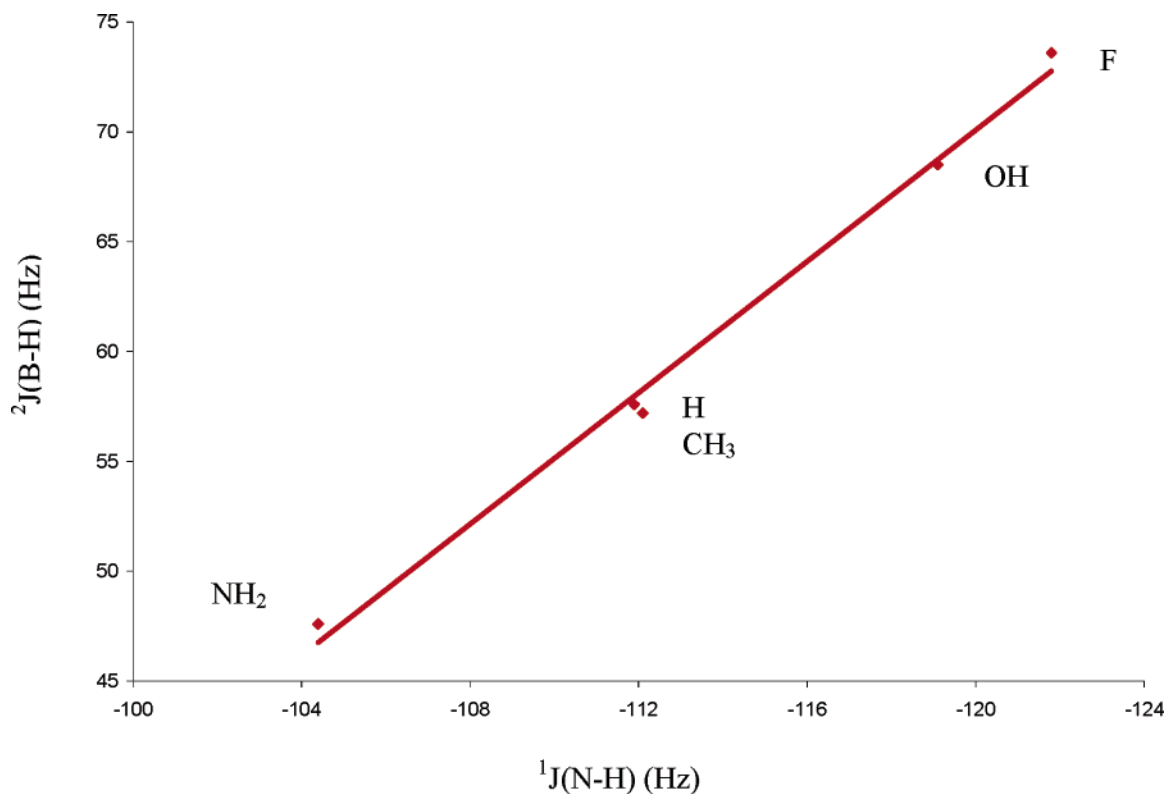
Figure 4. ^2J(B−H) vs ^1J(N−H) for molecules RBNH.

respect to the substituents, changes in ^1J(N−H) and ^2J(B−H) in the series RBNH, and ^1J(B−H) and ^2J(N−H) in the series HBNR, are similar to changes in ^1J(N−B) in the corresponding series. Figure 4 shows a linear correlation between ^2J(B−H) and ^1J(N−H) for iminoboranes RBNH. Just as NH_2 substitution at B decreases ^1J(N−B) relative to its value for HBNH, NH_2 substitution also decreases ^1J(N−H) and ^2J(B−H) relative to HBNH. OH and F substitution increases ^1J(N−H), ^2J(B−H), and ^1J(N−B) relative to the corresponding coupling constants for the parent molecule HBNH. B−H and N−H coupling constants in molecules HBNR are also linearly correlated.

All of the reduced one-bond B−N, B−H, and N−H coupling constants are positive in RBNH, HBNR, and RBNR, in agreement with the Dirac vector model,[37] which states that reduced one-bond coupling constants are positive, two-bond negative, three-bond positive, and so on. However, ^2J(N−H) values are negative for HBNR, and ^2J(B−H) values are positive for RBNH. Thus, the reduced two-bond coupling constants ^2K(N−H) and ^2K(B−H) in these series of molecules are both positive and, as such, are exceptions to this generalization.

Conclusions

In this study, ab initio EOM-CCSD calculations were carried out on iminoboranes RBNH, HBNR, and RBNR, for R = H, CH_3, NH_2, OH, and F, to evaluate substituent effects on one- and two-bond $^{15}N−^{11}B$, $^{11}B−^1H$, and $^{15}N−^1H$ coupling constants. For comparison purposes, calculations were also performed on corresponding isoelectronic acetylene derivatives RCCH and RCCR. The following statements are supported by the results of these calculations:

1. Mono- or disubstitution of CH_3 in iminoborane or acetylene has little effect on B−N or C−C coupling constants.

2. As the σ-electron-withdrawing ability of the substituent increases in the order CH_3 < NH_2 < OH < F, ^1J(C−C) increases in both series RCCH and RCCR. The increase in ^1J(C−C) upon disubstitution is more than double the increase upon monosubstitution.

3. For the monosubstituted iminoborane derivatives HBNR, ^1J(N−B) also increases as the σ-electron-withdrawing ability of the substituent increases in the order CH_3 < NH_2 < OH < F, as observed for ^1J(C−C) in the corresponding isoelectronic series RCCH.

4. ^1J(N−B) does not vary systematically with the σ-electron-withdrawing ability of the substituent in the series RBNH. NH_2 substitution decreases ^1J(N−B) relative to HBNH, while substitution of OH or F leads to similar increases for ^1J(N−B) in RBNH and HBNR. The sensitivity of ^1J(N−B) to the site of NH_2 substitution may be related to the significant loss of BN triple-bond character in H_2NBNH.

5. The effect of disubstitution in the series RBNR is dramatically different from the effect of monosubstitution. Disubstitution of NH_2 increases ^1J(N−B) relative to either monosubstituted derivative, while disubstitution of OH or F decreases ^1J(N−B) relative to the corresponding monosubstituted derivatives. Disubstitution of OH or F has the opposite effect on coupling constants in RBNR and RCCR.

6. Changes in B−N coupling constants in iminoboranes do not correlate with changes in B−N distances.

7. Changes in ^1J(N−H) and ^2J(B−H) for molecules RBNH, and ^2J(N−H) and ^1J(B−H) for HBNR, are similar to changes in ^1J(N−B) for RBNH and HBNR, respectively. Changes in N−H and B−H coupling constants in each series are linearly correlated.

Supporting Information Available: Tables reporting the PSO, DSO, FC, and SD components of one- and two-bond coupling constants for acetylenes and iminoboranes and the complete author list for ref 25, are included as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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