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Substituent Effects on B−N Bonding and Coupling Constants in Five-membered Rings $N_3B_2H_4X$ and $N_2B_3H_4X$, for X = H, F, and Li*

Janet E. Del Bene,[a], Otilia Mó,[b] and Manuel Yáñez[b]**

[a]*Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555, USA*
[b]*Departamento de Química, C-9, Universidad Autónoma de Madrid, Cantoblanco, 28094-Madrid, Spain*

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Abstract. Ab initio calculations have been carried out to investigate bonding patterns and B−N coupling constants in five-membered rings $N_3B_2H_4X$ and $N_2B_3H_4X$, for X = H, F, and Li, with substitution occurring only at N. F-substitution results in the formation of a covalent N−F bond, whereas Li-substitution leads to an ion-pair with little covalency. Substitution has a highly localized effect, changing the electron density only at the substituted N. F-substitution also has a very localized effect on coupling constants, at most only changing ^{1}J(B−N) involving the substituted N. Li-substitution has a more delocalized effect. It always decreases ^{1}J(B−N) involving the substituted N, and may also decrease ^{1}J(B−N) of a proximal B−N bond if the B atom is bonded to the substituted N.

Keywords: 5-membered rings, B−N bonding, spin-spin coupling constants

INTRODUCTION

Understanding the structure and properties of a chemical compound requires a fundamental knowledge of its bonding characteristics. For example, it is well established that the basicity of an amine is significantly different from that of an imine, even though in both cases the basic center is a nitrogen atom, but these have quite different connectivities. Zvonko Maksić and his group have very much exploited this idea in their efforts to design superacids and superbases.[1] They have been successful by taking advantage of the cooperativity associated with intramolecular hydrogen bonds,[2,3] inducing significant changes in the aromaticity of a system,[4] enhancing acidity or basicity with a judicious choice of substituents,[5,6] and building supramolecular structures from simpler building blocks.[7–10] Maksić has also explored other interesting aspects of chemical bonding,[11] such as the existence of periodic trends in bond dissociation energies[12] and the existence of covalent bonds between alpha particles and neutral chemical compounds.[13] For the latter, it was possible to demonstrate that alpha particles can produce kinetically stable, long-lived adducts with HCN and HNC.[13] Understanding the electronic structures of these systems was essential for understanding and predicting properties.

Among the properties which are extremely sensitive to the intricacies of electronic structure are magnetic properties, particularly coupling constants. These, being second-order properties, depend on the electronic structure not only of the ground state but also of excited states which couple to the ground state through the coupling operators. Over the past several years we have focused our studies on spin-spin coupling constants for hydrogen-bonded systems[14–16] as well as molecules with normal covalent bonds[17–20] including those with B−N bonds. Among molecules with BN bonds, borazine is undoubtedly among the most studied and the most interesting, due to its aromatic character. In our studies of borazine we investigated the effects of electron-withdrawing (F) and electron-donating (Li) substituents on one-bond ^{11}B−^{15}N coupling constants, and compared them to substituent effects on one-bond ^{13}C−^{13}C coupling constants for benzene.[17] We also examined coupling constants in organoboryl systems which had been recently synthesized, and in which B acts as an electrophilic site. In the present paper, we extend our studies of systems with B−N bonds to examine B−N bonding and coupling constants for a subset of five-membered rings, represented as $N_3B_2H_4X$ and $N_2B_3H_4X$, for X = H (the parent molecule), F, and Li, with substitution occurring only at N.

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* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

** Author to whom correspondence should be addressed. (E-mail: jedelbene@ysu.edu)

METHODS

The molecules $N_3B_2H_4X$ and $N_2B_3H_4X$, for X = H, Li, and F, were optimized at second-order Møller-Plesset perturbation theory (MP2)[21–24] with the 6-311++G(d,p) basis set.[25–27] Vibrational frequencies were computed to establish that each structure is a local minimum on its potential surface. The bonding in these rings has been analyzed by means of the NBO partitioning technique,[28] and the atoms in molecules (AIM) theory.[29] Structure optimizations were done using the Gaussian-03 software package[30] on the Itanium Cluster at the Centro de Computación Científica of the Universidad Autónoma of Madrid.

Spin-spin coupling constants were computed using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the CI(configuration interaction)-like approximation,[31–34] with all electrons correlated. For these calculations the Ahlrichs[35] qzp basis set was placed on ^{15}N and ^{19}F, the hybrid basis sets developed previously were used for ^{7}Li and ^{11}B,[17] and either the Ahlrichs qz2p[35] or Dunning cc-pVDZ basis set[36,37] was placed on ^{1}H. It has been demonstrated that ^{1}J(B−N) is essentially insensitive to these two different H basis sets.[17]

In the Ramsey approximation, the total coupling constant (J) is a sum of four contributions: the paramagnetic spin-orbit (PSO), diamagnetic spin-orbit (DSO), Fermi-contact (FC), and spin-dipole (SD).[38] In the study of borazine,[17] it was demonstrated that the FC term is a reasonable approximation to ^{1}J(B−N), usually underestimating its absolute value by about 2 Hz, which is the contribution from the PSO term. Due to the low computational symmetry of most of the five-membered rings investigated in this study, the FC term will also be used to approximate ^{1}J(B−N). Further justification of this approximation will be given below. The EOM-CCSD calculations were carried out using ACES II[39] on the Itanium Cluster at the Ohio Supercomputer Center.

STRUCTURES AND BONDING

The optimized structures of the substituted 5-membered rings $N_3B_2H_4X$ and $N_2B_3H_4X$, for X = F, Li, are illustrated in Figure 1. Fully-optimized geometries are reported in Table S1 of the supporting information. There are two isomers of $N_3B_2H_5$, designated N3B2_1, the more stable, and N3B2_2. Similarly, the F- and Li-substituted derivatives are designated N3B2_1_X1 and N3B2_1_X2, with the former more stable. A similar scheme has been used to identify isomers of $N_2B_3H_4X$.

Although a detailed description of geometries will not be given here, some unusual structural features deserve comment. The most significant one is that with the single exception of N3B2_1_Li1 due to symmetry, all Li-substituted derivatives have the Li atom in some type of bridging orientation, usually between the N atom to which it is directly bonded and an adjacent boron atom. The bonding responsible for this conformational preference will be discussed below. A particularly interesting derivative is N3B2_2_Li1 in which the Li atom is located above the five-membered ring almost at its center, forming a kind of pyramid with the five-membered ring as the base and the Li atom at the apex.

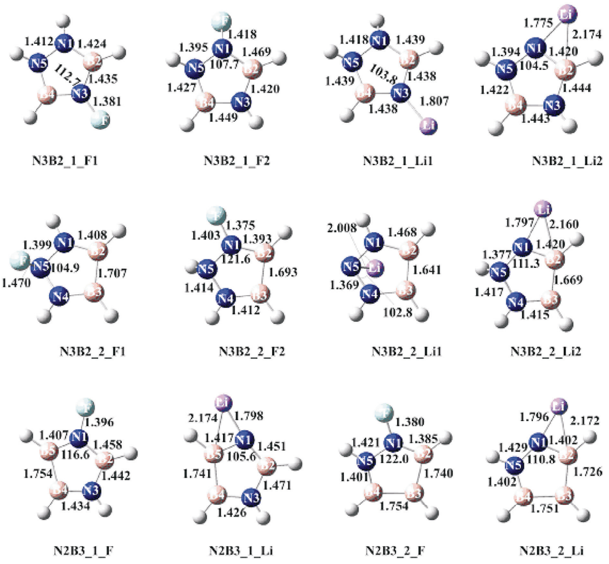

Figure 1. MP2/6-311++G(d,p) optimized geometries. Bond lengths are in Å and bond angles in degrees.

The second interesting geometrical feature is the opposing effects of F- and Li-substitution on the ring bond angle at the substituted nitrogen. This angle is systematically greater for the F-substituted derivative than the corresponding Li derivative. This can be readily seen from N3B2_1_F1 and N3B2_1_Li1 which does not contain a bridging Li. The B2−N3−B4 angles are 112.7 and 103.8°, respectively. This trend may be rationalized by noting that the sp^2 hybridized orbital on N which is involved in the N3−F bond should have increased p character due to the strong electron-withdrawing ability of F. By orthogonality, the other two hybrids which are involved in the N−B bonds should have increased s character leading to a larger B2−N3−B4 angle. In contrast, the Li derivative can be viewed as a complex between Li$^+$ and a five-membered anionic ring, as will be discussed below. As a result, the N3−X bonding orbital becomes essentially a lone-pair orbital on N3 with reduced p character. By orthogonality, the remaining hybrid orbitals on N3 would have greater p character leading to a smaller B2−N3−B4 angle.

In contrast to the Li derivatives, the F derivatives always have the F atom bonded to a single N atom, although the N−F distance is relatively long compared to a normal covalent N−F distance such as that computed for NF_3 (1.369 Å) at the same level of theory. The longest N−F distance (1.470 Å) is found for N3B2_2_F1, in which case the fluorine atom is attached to N5, the central atom of an N−N−N linkage. The calculated Wiberg bond order for the N5−F bond is only 0.80. The small bond order is most likely a reflection of the enhanced electronegativity of N5 resulting from its bonding to two nitrogen atoms. Hence, as is usually the case when two very electronegative atoms are bonded as in F_2, the bond is weak because electron density accumulates preferentially in the vicinity of both atoms rather than in the internuclear region.[40] This is indeed the case for the N5−F bond of N3B2_2_F1, where the electron density at the bcp (0.240 a.u.) is much smaller than that of the N−F bonds of NF_3 (0.327 a.u.), but similar to that of the F−F bond in F_2 (0.261 a.u.). For the F_2 molecule, the Laplacian at the bond critical point is positive.[40] Although the Laplacian of the electron density (−0.024 a.u.) for the N5−F bond remains negative, it is very small in absolute value, clearly indicating the diffuseness of the electron density.

An NBO analysis shows that in the Li derivatives, the net atomic charge on the Li atom approaches +1.0 *e*. Thus, the NBO description suggests that the bonding in these molecules results primarily from an electrostatic interaction between a Li^+ cation and a five-membered ring with a net charge of −1.0 *e*, with little covalency. This description is also consistent with the bonding picture obtained from AIM theory, which indicates the existence of one bond critical point between the Li atom and the substituted N of the ring. The reduced value of the electron density at this bcp (typically 0.04−0.05 a.u.) and the positive value of the Laplacian are similar to the values obtained for typical interactions between Li^+ and neutral molecules.[41,42] This is the basis leading to bridged Li structures. Such bridged structures are rather common for Li^+ complexes with bases that present two neighboring negatively-charged basic sites, and leads to the enhanced Li^+ basicities of triazoles, tetrazoles,[41] azines,[43] some nitrogen containing three-membered rings,[44] and P_4.[45] Bridging structures are a consequence of the ability of Li^+ to polarize the electron density distribution around two basic sites, favoring dicoordination.[46]

For the five-membered BN rings, charge transfer from Li to the ring leads to a strong interaction of Li^+ not only with the N atom to which it is formally bonded, but also with the H atom of an adjacent B−H bond where negative charge accumulates on the hydrogen. A NBO second-order perturbation analysis shows charge donation from the σ_{BH} bonding orbital of this BH group to the almost empty s orbital of the Li atom. The depopulation of this σ_{BH} bonding orbital is reflected in a lengthening of the B−H bond to 1.23−1.24 Å, relative to the other B−H bonds of the ring which have lengths typically around 1.19 Å. In the particular case of the N3B2_1_Li1 derivative, this interaction is weaker because the Li atom is equidistant and far-removed from the two adjacent B−H bonds. For N3B2_2_Li1, interaction with the two B−H bonds forces the Li atom to sit above the ring. In this position this interaction is again weaker, although a significant charge donation from the σ_{B2B3} bonding orbital to the almost empty s orbital of Li does occur.

The most striking observation concerning the effect of F- and Li-substitution on the electron density distribution in the rings is its highly localized nature. That is, substitution significantly alters the net charge of the substituted nitrogen, and has only a minor effect on the charges of the other atoms of the ring, as clearly illustrated in Table 1 for three derivatives, taken as suitable examples. As expected, F substitution at N significantly decreases the net negative charge on N, while Li substitution increases the net negative charge on the substituted N.

COUPLING CONSTANTS

In a previous study we observed that the FC term is a reasonable approximation to ${}^1J$(B−N), underestimating its absolute value by approximately 2 Hz, the contribution of the PSO term.[17] That this is also the case for the B−N coupling constants of the five-membered rings is illustrated in Table 2, which reports ${}^1J$(B−N) and components of ${}^1J$(B−N) for N3B2_1_F1 and N2B3_1. In this paper, the FC terms are used to approximate ${}^1J$(B−N).

In our previous study, we examined the effects of F and Li substitution on ${}^1J$(B−N) for the six-membered ring borazine.[17] Relative to borazine, F-substitution at N was found to increase the absolute value of ${}^1J$(B−N) involving the substituted N, while Li-substitution at N decreased the same ${}^1J$(B−N). Moreover, F-substitution was observed to have a very localized effect, while Li-substitution changed not only the B−N coupling constant involving the substituted N, but also had an effect on a proximal B−N coupling constant involving the B atom bonded to the substituted N. What effects do F- and Li-substitution have on ${}^1J$(B−N) for the five-membered BN rings investigated in this study?

Table 3 present the computed one-bond B−N coupling constants ${}^1J$(B−N). Figures 2 through 5 present bar graphs illustrating changes in B−N coupling con-

Table 1. Natural net atomic charges for selected derivatives[(a)]

N2B3_1_X			N2B3_2_X			N3B2_1_X1		
atom	X = F	X = Li	atom	X = F	X = Li	atom	X = F	X = Li
N1	**−0.481**	**−1.357**	**N1**	**−0.051**	**−0.848**	N1	−0.636	−0.656
B2	0.798	0.818	B2	0.200	0.085	B2	0.606	0.616
N3	−1.084	−1.095	B3	0.208	0.189	**N3**	**−0.408**	**−1.410**
B4	0.454	0.411	B4	0.297	0.274	B4	0.606	0.616
B5	0.360	0.330	N5	−0.636	−0.638	N5	−0.636	−0.656

[(a)] The substituted position is indicated in bold.

Table 2. Total J and components of J for N3B2_1_F1 and N2B3_1

Molecule	Coupled atoms	PSO / Hz	DOS / Hz	FC / Hz	SD / Hz	J / Hz
N3B2_1_F1	N1−B2	2.5	−0.1	−33.2	−0.3	−31.2
	B2−N3	2.2	−0.1	−34.2	−0.2	−32.3
N2B3_1	N1−B2	1.8	−0.1	−29.6	−0.1	−28.0
	N3−B4	2.8	−0.1	−20.5	−0.1	−17.9

Table 3. ^1J(N−B) for $N_3B_2H_4X$ and $N_2B_3H_4X$, for X = H, F, and Li[(a)]

Molecule	$^1J(\text{N1-B2})$ / Hz	$^1J(\text{B2-N3})$ / Hz	$^1J(\text{N3-B4})$ / Hz	$^1J(\text{B4-N5})$ / Hz	Molecule	$^1J(\text{N1-B2})$ / Hz	$^1J(\text{B3-N4})$ / Hz
N3B2_1	−32.7	−28.7	−28.7	−32.7	N3B2_2	−25.9	−25.9
N3B2_1_F1 F at N3	−33.2	−34.2	−34.2	−33.2	N3B2_2_F1 F at N5	−25.8	−25.8
N3B2_1_F2 F at N1	−23.1	−28.9	−26.8	−30.6	N3B2_2_F2 F at N1	−25.3	−24.6
N3B2_1_Li1 Li at N3	−27.6	−19.3	−19.3	−27.6	N3B2_2_Li1 Li over ring	−14.9	−14.9
N3B2_1_Li2 Li bridging N1−B2	−18.2	−29.8	−30.0	−35.7	N3B2_2_Li2 Li bridging N1−B2	−14.9	−27.0

Molecule	$^1J(\text{N1-B2})$ / Hz	$^1J(\text{B2-N3})$ / Hz	$^1J(\text{N3-B4})$ / Hz	$^1J(\text{N1-B5})$ / Hz	Molecule	$^1J(\text{N1-B2})$ / Hz	$^1J(\text{B4-N5})$ / Hz
N2B3_1	−29.6	−29.6	−20.5	−20.5	N2B3_2	−29.7	−29.7
N2B3_1_F F at N1	−34.8	−30.2	−20.2	−21.4	N2B3_2_F F at N1	−28.8	−28.5
N2B3_1_Li Li bridging N1−B5	−21.6	−24.8	−22.3	−12.1	N2B3_2_Li Li bridging N1−B2	−18.8	−29.6

[(a)] ^1J(N−B) approximated from the FC term.

stants in the derivatives relative to the parent molecules N3B2_1, N3B2_2, N2B3_1, and N2B3_2, respectively. In these graphs, the middle bar always refers to the parent compound (PC). The peaks are ordered from left to right as F1, F2 (if it exists), PC, Li1, Li2 (if it exists).

Similar to the effect of F-substitution on ^1J(B−N) for borazine, F-substitution in these five-membered B−N rings has a very localized effect, altering at most only ^1J(B−N) involving the substituted N atom. However, in contrast to its effect in borazine, F-substitution has a variable effect on this coupling constant, since it may increase, decrease, and leave its absolute value essentially unchanged. Thus, for N3B2_1_F1 with F-substitution at N3, ^1J(B2−N3) and ^1J(N3−B4) increase in absolute value. Similarly, F-substitution at N1 in N2B3_1_F also leads to an increase in ^1J(N1−B2). It

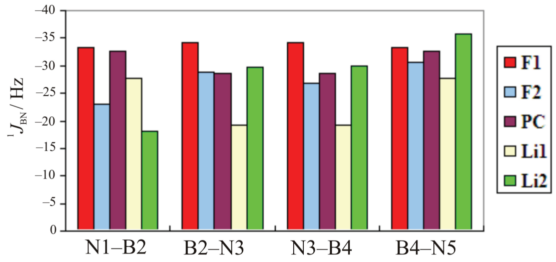

Figure 2. Bar graph for N3B2_1 and its derivatives, illustrating substituent effects on ^1J(B–N)

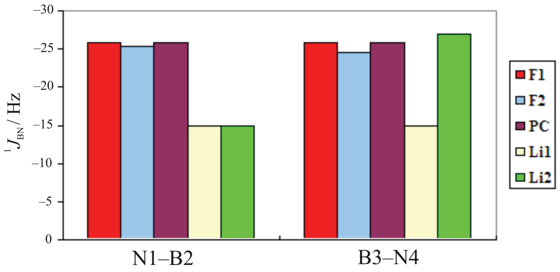

Figure 3. Bar graph for N3B2_2 and its derivatives, illustrating substituent effects on ^1J(B–N)

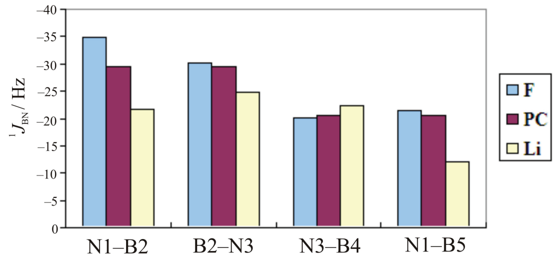

Figure 4. Bar graph for N2B3_1 and its derivatives, illustrating substituent effects on ^1J(B–N)

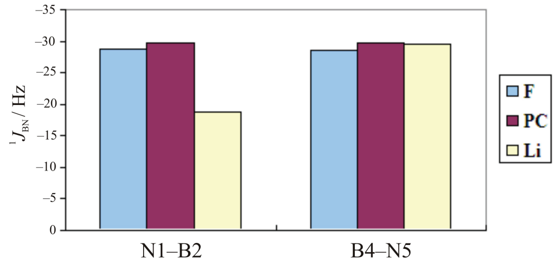

Figure 5. Bar graph for N2B3_2 and its derivatives, illustrating substituent effects on ^1J(B–N)

should be noted that in these two molecules, the substituted N atom is bonded to two B atoms, as it is in borazine. In contrast, F-substitution at N1 in N3B2_1_F2 decreases ^1J(N1−B2). ^1J(N1−B2), which couples the substituted N1 to B2 in N3B2_2_F2 and N2B3_2_F, are unchanged by substitution. In these molecules, the coupled N is bonded to one N and one B atom. This indicates that the bonding environment of the coupled N atom influences the change in the coupling constant. The localized effect of F-substitution on coupling constants may reflect to some extent the localized effect of F-substitution on the ground-state electron densities. However, it must be noted once again that coupling constants are second-order properties which depend on both ground- and excited-state electron densities.

Similar to the effect of Li-substitution at N in borazine, Li-substitution always decreases ^1J(B−N) involving the substituted nitrogen, irrespective of whether this nitrogen has the bonding pattern found in borazine. Moreover, Li-substitution has a somewhat more delocalized effect on coupling constants insofar as coupling constants involving the B atom bonded to the substituted N may also decrease. For example, for N3B2_1_Li1 in which Li is bonded to N3 and is not in a bridging position, substitution decreases ^1J(B2−N3) and ^1J(N3−B4) as expected, but also decreases to a lesser extent the two coupling constants ^1J(N1−B2) and ^1J(B4−N5) with the B atoms bonded to N3. On the other hand, in N3B2_1_Li2 Li bridges N1 and B2, and only ^1J(N1−B2) is markedly changed by substitution. Li sits over the ring in N3B2_2_Li1, and both ^1J(N1−B2) and ^1J(B3−N4) are decreased by substitution, while for N3B2_2_Li2 in which Li bridges N1−B2, only ^1J(N1−B2) decreases relative to the parent molecule.

For the N2B3 derivatives, Li bridges N1−B5 in N2B3_1_Li, and the two coupling constants involving N1, ^1J(N1−B2) and ^1J(N1−B5), decrease. In addition, since B2 is bonded to N1, ^1J(B2−N3) also decreases but to a lesser extent. Only ^1J(N3−B4) is unchanged by substitution. For N2B3_2_Li with Li bridging N1−B2, only ^1J(N1−B2) decreases relative to N2B3_2.

CONCLUSIONS

Ab initio calculations have been carried out to investigate bonding and B−N spin-spin coupling constants in five-membered rings $B_3N_2H_4X$ and $B_2N_3H_4X$, for X = H, F, and Li, with substitution occurring at N. The following statements are supported by the results of these calculations.

1. There are two notable effects of substitution on the structures of these rings. First, with only one exception, all Li-substituted derivatives have the Li atom in some type of bridging orientation. Second, the bond angle at the substituted N is always greater for the F-substituted than the corresponding Li-substituted derivative.

2. F-substitution in these rings results in the formation of a covalent N−F bond. However, Li-substitution leads to the creation of an ion pair with Li^+ and an anionic ring, with little covalency.

3. The effect of F- and Li-substitution on the electron density of the ring is highly localized at the site of substitution.

4. F-substitution has a very localized effect on B−N coupling constants, influencing only ^1J(B−N) involving the substituted nitrogen. If the substituted N is bonded to two B atoms as in borazine, then F-substitution increases ^1J(B−N). If the substituted N is bonded to one N and one B, then substitution may either decrease or leave ^1J(B−N) unchanged relative to the parent molecule. This indicates that the bonding environment of the coupled N influences the change in the coupling constant.

5. Similar to the effect of Li-substitution in borazine, Li-substitution in these five-membered rings has a more delocalized effect. Li-substitution always decreases ^1J(B−N) involving the substituted N, and may also decrease proximal B−N coupling constants involving the B atom which is bonded to the substituted N.

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SAŽETAK

Supstitucijski efekti na B−N vezu i konstante sprege u peteročlanim prstenovima $N_3B_2H_4X$ i $N_2B_3H_4X$, za X = H, F i Li

Janet E. Del Bene,[a] Otilia Mó[b] i Manuel Yáñez[b]

[a]*Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555, USA*
[b]*Departamento de Química, C-9, Universidad Autónoma de Madrid, Cantoblanco, 28094-Madrid, Spain*

Provedeni su *ab initio* računi radi istraživanja veznih svojstava i B–N konstante sprege u peteročlanim prstenovima $N_3B_2H_4X$ i $N_2B_3H_4X$, za X = H, F, i Li, sa supstitucijom jedino na N atomu. F-supstitucija uzrokuje stvaranje kovalentne N–F veze, dok Li-supstitucija dovodi do ionskog para s malo kovalentnog karaktera. Supstitucija ima vrlo lokalizirani efekt, mijenjajući elektronsku gustoću samo na supstituiranom N atomu. F-supstitucija također ima vrlo lokalni efekt na konstante sprege, najviše mijenjajući samo ^1J(B–N) u kojoj sudjeluje supstituirani N atom. Li-supstitucija ima više delokalizirani efekt. Ona uvijek smanjuje ^1J(B–N) u kojoj sudjeluje supstituirani N, te može smanjiti i ^1J(B–N) proksimalne B–N veze ukoliko je B atom povezan sa supstituiranim N atomom.