# Characterizing Complexes with F−Li···N, H−Li···N, and $CH_3Li$···N Lithium Bonds: Structures, Binding Energies, and Spin−Spin Coupling Constants

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*Received: April 19, 2009; Revised Manuscript Received: August 5, 2009*

Ab initio calculations have been carried out to determine the structures, binding energies, and spin−spin coupling constants of complexes stabilized by X−Li···N bonds with F−Li, H−Li, and $CH_3Li$ as the Lewis acids. Complexes of these acids with the nitrogen bases $N_2$, HCN, 1,3,5-triazine, pyrazine, 1,2,3-triazine, pyridine, and $NH_3$ have linear X−Li···N bonds. Methylamine forms a nonlinear lithium bond only when F−Li is the lithium donor. Two bases, $HN{=}CH_2$ and aziridine, form nonlinear X−Li···N bonds with each acid. Except for complexes with $N_2$, which have small binding energies of about 5 kcal/mol, the binding energies of lithium-bonded complexes are appreciable, varying between 15 and 23 kcal/mol. The one-bond coupling constant $^1J$(F−Li) may increase or decrease upon complexation, but $^1J$(H−Li) and $^1J$(C−Li) decrease significantly. These coupling constants have their smallest values in complexes with nonlinear X−Li···N bonds. No correlations appear to exist between $^1J$(X−Li) and the X−Li distance and $^{1li}J$(Li−N) and the Li−N distance. Values of the two-bond coupling constants $^{2li}J$(X−N) are extremely small. Comparisons of $^{2li}J$(F−N) with $^{2h}J$(F−N) for coupling across a hydrogen bond and $^{2x}J$(F−N) for coupling across a halogen bond suggest that the extremely small values of $^{2li}J$(X−N) are not due to long X−N distances but to the low valence electron density on Li in lithium-bonded complexes.

## Introduction

In a recent study, Legon demonstrated that there is a strong parallelism between experimentally measured properties of halogen-bonded and hydrogen-bonded complexes.[1] This work prompted us to carry out a theoretical study of complexes with F−Cl···N halogen bonds in which we characterized these complexes in terms of structures, binding energies, and spin−spin coupling constants. We then compared the computed properties of the halogen-bonded complexes with those of corresponding complexes stabilized by F−H···N hydrogen-bonds.[2] Such comparisons can serve to enhance our understanding of the nature of intermolecular interactions.

In the present study, we turn our attention to another type of intermolecular interaction, this time for complexes stabilized by lithium bonds. For this study, we have chosen three molecules as the Lewis acids: F−Li, H−Li, and $CH_3Li$. The set of nitrogen Lewis bases consists of two that are sp hybridized ($N_2$ and HCN); five $sp^2$-hybridized bases, four of which are aromatic (1,3,5-triazine, 1,2,3-triazine, pyrazine, and pyridine) and one nonaromatic ($HN{=}CH_2$); and three $sp^3$-hybridized bases ($NH_3$, $NH_2CH_3$, and aziridine). We have characterized the structures, binding energies, and spin−spin coupling constants of these complexes and have compared corresponding complexes with F−Li···N and F−H···N bonds. Because F−Li is significantly more polar than F−H, the relative importance of the electrostatic interaction increases in lithium-bonded complexes. This influences both the structures and the binding energies of these complexes, thereby providing further insight into the nature of intermolecular interactions. Moreover, it is of particular interest to investigate variations in the two-bond coupling constant $^2J$(F−N) across F−H···N, F−Li···N, and F−Cl···N bonds as the intervening atoms (H, Li, Cl) change. In this article we report the results of this study and compare and contrast lithium-bonded, hydrogen-bonded, and halogen-bonded complexes.

## Methods

The structures of the 3 Lewis acids, 10 bases, and 30 complexes stabilized by X−Li···N lithium bonds were fully optimized at second-order Møller−Plesset perturbation theory (MP2)[3−6] with the 6-31+G(d,p)[7−10] basis set. Vibrational frequencies were computed to verify that the optimized structures correspond to minima on their potential energy surfaces. A further geometry optimization was carried out at MP2 with the aug-cc-pVTZ basis set.[11,12] Structures of hydrogen-bonded complexes in which F−H is the acid with the same set of nitrogen bases were also optimized at the same levels of theory for comparison purposes. The optimization and frequency calculations were performed using Gaussian 03.[13]

Spin−spin coupling constants for complexes with lithium bonds were evaluated at the MP2/aug-cc-pVTZ geometries using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the CI (configuration interaction)-like approximation with all electrons correlated.[14,15] For these calculations, the Ahlrichs qzp basis set[16] was placed on $^{19}F$, $^{15}N$, and $^{13}C$ atoms, and the previously developed hybrid basis set was used for $^7Li$.[17] The Dunning cc-pVDZ basis set was placed on all $^1H$ atoms.[11,12] For complexes with F−H···N hydrogen bonds, the Ahlrichs qz2p basis was placed on the hydrogen-bonded $^1H$ atom.

In the Ramsey approximation, the total coupling constant ($J$) consists of four terms: the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi-contact (FC), and spin-

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10.1021/jp9035919 CCC: $40.75

**TABLE 1: MP2/aug-cc-pVTZ X−Li, Li$\cdots$N, and X−N Distances (*R*, angstroms), Li−X−N Angles (<, deg), and Binding Energies (Δ*E*, kilocalories per mole) for Complexes with F−Li$\cdots$N, H−Li$\cdots$N, and $H_3C$−Li$\cdots$N Bonds**

| acid | base | *R*(X−Li) | *R*(Li$\cdots$N) | *R*(X−N) | <Li−X−N | Δ*E* |
|---|---|---|---|---|---|---|
| FLi | $N_2$ | 1.602 | 2.208 | 3.811 | 0 | 5.6 |
| | HCN | 1.616 | 2.074 | 3.690 | 0 | 15.7 |
| | 1,3,5-triazine | 1.614 | 2.096 | 3.710 | 0 | 15.1 |
| | pyrazine | 1.618 | 2.080 | 3.698 | 0 | 17.7 |
| | 1,2,3-triazine | 1.623 | 2.096 | 3.719 | 0 | 19.1 |
| | pyridine | 1.624 | 2.065 | 3.688 | 0 | 20.4 |
| | $H_2C{=}NH$ | 1.638 | 2.029 | 3.048 | 38 | 22.1 |
| | $NH_3$ | 1.620 | 2.080 | 3.700 | 0 | 19.6 |
| | $NH_2CH_3$ | 1.623 | 2.056 | 3.372 | 27 | 20.5 |
| | aziridine | 1.636 | 2.003 | 3.005 | 38 | 23.2 |
| FLi monomer | | 1.595 | | | | |
| HLi | $N_2$ | 1.611 | 2.207 | 3.819 | 0 | 5.5 |
| | HCN | 1.629 | 2.065 | 3.694 | 0 | 15.6 |
| | 1,3,5-triazine | 1.626 | 2.085 | 3.711 | 0 | 15.3 |
| | pyrazine | 1.631 | 2.069 | 3.700 | 0 | 17.8 |
| | 1,2,3-triazine | 1.638 | 2.088 | 3.725 | 0 | 19.1 |
| | pyridine | 1.637 | 2.055 | 3.691 | 0 | 20.5 |
| | $H_2C{=}NH$ | 1.644 | 2.028 | 3.222 | 32 | 20.7 |
| | $NH_3$ | 1.633 | 2.068 | 3.701 | 0 | 19.9 |
| | $NH_2CH_3$ | 1.635 | 2.066 | 3.675 | 8 | 20.6 |
| | aziridine | 1.645 | 2.007 | 3.187 | 33 | 22.1 |
| HLi monomer | | 1.605 | | | | |
| $CH_3Li$ | $N_2$ | 1.993 | 2.215 | 4.208 | 0 | 5.4 |
| | HCN | 2.011 | 2.070 | 4.080 | 0 | 15.2 |
| | 1,3,5-triazine | 2.008 | 2.088 | 4.096 | 0 | 15.0 |
| | pyrazine | 2.014 | 2.075 | 4.089 | 0 | 17.5 |
| | 1,2,3-triazine | 2.019 | 2.093 | 4.113 | 0 | 18.7 |
| | pyridine | 2.019 | 2.061 | 4.080 | 0 | 20.1 |
| | $H_2C{=}NH$ | 2.023 | 2.033 | 3.533 | 29 | 20.4 |
| | $NH_3$ | 2.016 | 2.071 | 4.087 | 0 | 19.4 |
| | $NH_2CH_3$ | 2.017 | 2.079 | 4.050 | 8 | 20.1 |
| | aziridine | 2.023 | 2.013 | 3.517 | 29 | 21.7 |
| $CH_3Li$ monomer | | 1.989 | | | | |

dipole (SD).[18] All terms were computed for the complexes with F−H$\cdots$N hydrogen bonds and the majority of complexes with lithium bonds. Justification for not computing all of the terms for some complexes with aromatic bases will be given below. Consistent with the designations for coupling constants across X−H$\cdots$Y hydrogen bonds and F−Cl$\cdots$N halogen bonds, the coupling constants across these X−Li$\cdots$N lithium bonds are designated $^{1}J$(X−Li), $^{1li}J$(Li−N), and $^{2li}J$(X−N). Coupling constants were evaluated using ACES II[19] on the Itanium cluster or the IBM cluster 1350 (Glenn) at the Ohio Supercomputer Center.

## Results and Discussion

Table 1 presents the X−Li, Li−N, and X−N distances, the Li-X−N angles, and the electronic binding energies of complexes with F−Li, H−Li, and $CH_3Li$ as the Li donors and the nitrogen bases as the acceptors. Complexes with F−Li are listed first, followed by those with H−Li and then $CH_3Li$. For each acid, the complexes are listed in the order of hybridization of the N base: sp, sp$^2$, sp$^3$. Within each group, the listing follows the order of increasing binding energy.

**Structures and Binding Energies.** ***Complexes with $N_2$.*** From Table 1 it can be seen that $N_2$ is a very weak base when interacting with each of the acids, with binding energies near 5.5 kcal/mol compared with binding energies of 15 kcal/mol or greater for the remaining complexes. In all complexes with $N_2$, the X−Li distance lengthens slightly from the monomer distance, and the Li−N and F−N distances are noticeably longer than corresponding distances with the remaining nitrogen bases. Statistical analyses are somewhat skewed by the inclusion of points for these complexes because the data range is significantly expanded. Although it is of interest to have the results for $N_2$ complexes presented, structural and energetic data for these complexes will not be further discussed or included in any of the statistical analyses.

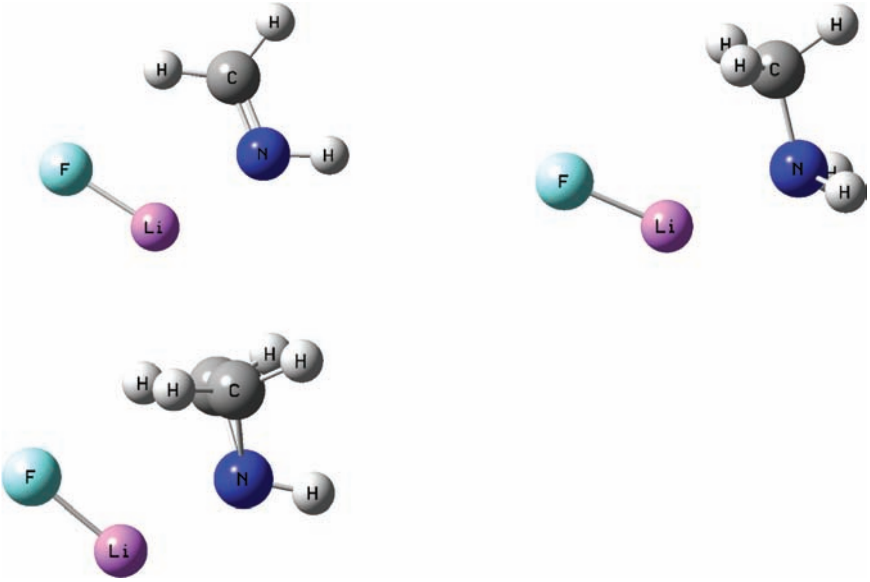
***Complexes with F−Li as the Acid.*** Complexes of F−Li with the bases HCN ($C_{\infty v}$), 1,3,5-triazine ($C_{2v}$), pyrazine ($C_{2v}$), 1,2,3-triazine ($C_{2v}$ with bonding at $N_2$), pyridine ($C_{2v}$), and $NH_3$ ($C_{3v}$) have linear F−Li$\cdots$N lithium bonds. For these, the range of F−Li distances is relatively small, from 1.614 to 1.624 Å, and the Li$\cdots$N and F−N distances also span narrow ranges of 2.074 to 2.096 Å and 3.688 to 3.719 Å, respectively. The long intermolecular distances may be attributed to the large van der Waals radius of Li. In all complexes with linear F−Li$\cdots$N bonds, the lone pair of electrons on N and the dipole moment vector of the base (if there is one) are coincident and are directed toward Li. The binding energies of these complexes vary from 15.5 kcal/mol for FLi:1,3,5-triazine, to 23.2 kcal/mol for FLi:aziridine.

There are three complexes that are structurally quite different: F−Li$\cdots$NH($CH_2$), F−Li$\cdots$$NH_2CH_3$, and F−Li$\cdots$aziridine, and these are illustrated in Scheme 1. These complexes have very nonlinear lithium bonds, as indicated by Li−F−N angles of 38, 27, and 38°, respectively. Although the F−Li distances are not significantly different from those of complexes with linear lithium bonds, the Li$\cdots$N and F−N distances are noticeably shorter, particularly in the complexes with HN=$CH_2$ and aziridine. What factors influence the structures of these complexes and are responsible for the nonlinearity of the lithium bonds?

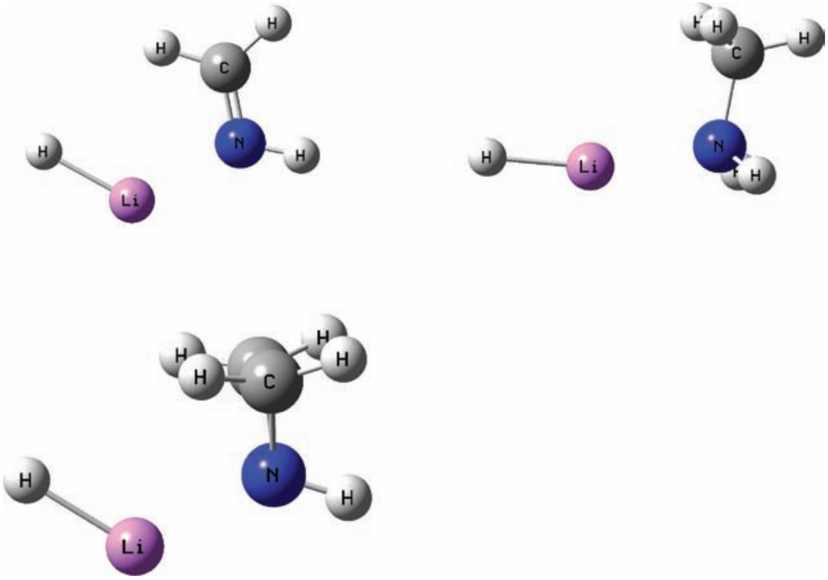
Some insight into the answer to this question can be gained by considering the structures of the corresponding hydrogen-bonded complexes. For these, the hydrogen bonds are linear to within 5°. Moreover, the "tilt" of the base, that is, the angle F−N−C for FH$\cdots$NH($CH_2$) and FH$\cdots$$NH_2CH_3$ and F−N-(bisector of C−N−C) for FH$\cdots$aziridine, are 118, 116, and 116°, respectively. Qualitatively, angles of about 120, 109, and 125°, respectively, are expected because these angles direct a lone pair on N toward H and correspond to the concept of hydrogen bond directionality.[20] In the complexes with FLi (Scheme 1), these angles are quite different at 74, 80, and 78° for FLi$\cdots$NH($CH_2$), FLi$\cdots$$NH_2CH_3$, and F−Li$\cdots$aziridine, respectively, indicating that the bases are "tilted" toward the acid. This tilt is evidence of a stabilizing interaction between one or more H atoms of the base with F, which bears a high negative charge in F−Li. As a result of this tilt, the F−Li−N bond becomes nonlinear, but the Li atom still sits in the region of the negative end of the dipole moment vector of the base, which is also the lone-pair region. It is interesting to note that the Li$\cdots$N distances contract relative to Li$\cdots$N distances in complexes with linear lithium bonds. Moreover, with the Li atom displaced from the F−N axis, the F−N distance decreases dramatically. Using F−Li$\cdots$$NH_3$ and F−Li$\cdots$aziridine as examples, the Li$\cdots$N distances are 2.080 and 2.003 Å, respectively, a difference of 0.077 Å. The F−N distances in these two complexes are 3.700 and 3.005 Å, respectively, which represents a dramatic difference of 0.695 Å.

***Complexes with H−Li as the Acid.*** Complexes of H−Li with the bases HCN, 1,3,5-triazine, pyrazine, 1,2,3-triazine, pyridine, and $NH_3$ also have linear H−Li$\cdots$N lithium bonds. In addition, the complex H−Li$\cdots$$NH_2CH_3$ also has an essentially linear bond with an Li−H−N angle less than 10°. The binding energies of these complexes are within 0.3 kcal/mol of the binding energies of the corresponding complexes with F−Li as the acid,

**SCHEME 1: Structures of Complexes of F−Li with HN═$CH_2$, $NH_2CH_3$, and Aziridine, Which Have Nonlinear F−Li···N Bonds**



**SCHEME 2: Structures of Complexes of H−Li with HN═$CH_2$, $NH_2CH_3$, and Aziridine**



and vary from 15.3 to 20.6 kcal/mol. Once again, the F−Li distances are similar, ranging from 1.626 to 1.645 Å, as are the Li···N and F−N distances, which range from 2.055 to 2.088 Å and 3.675 to 3.725 Å, respectively.

In contrast to the complex of F−Li with $NH_2CH_3$, the complex of this base with H−Li has an essentially linear H−Li−N bond. This may be due to the smaller negative charge on H of H−Li, which reduces the interaction between this atom and the methyl group of the base. The fact that this is a weaker interaction is also indicated by the "tilt" angle of the base, which has increased from 80° in the complex with F−Li, to 103° in the complex with H−Li. The complexes H−Li···NH($CH_2$), H−Li···$NH_2CH_3$, and H−Li···aziridine are illustrated in Scheme 2.

The complexes H−Li···NH($CH_2$) and H−Li···aziridine have nonlinear lithium bonds, with the bases titled to allow for interaction between the negatively charge H of H−Li and the positively charged H atoms, which are present as C−H bonds in the base. The fact that this interaction is weaker when H−Li is the acid is indicated by the decrease in the nonlinearity of the lithium bonds from 38 to 32 or 33° and an increase in the "tilt" angle of the base from 74° for F−Li···NH($CH_2$) to 82° for H−Li···NH($CH_2$), and from 78° for F−Li···aziridine to 86° for H−Li···aziridine. It is noteworthy that the H−Li complexes with these two bases have binding energies of 20.7 and 22.1 kcal/mol, respectively, which are reduced relative to the corresponding complexes with F−Li as the acid (22.1 and 23.2 kcal/mol, respectively).

***Complexes with $H_3C$−Li as the Acid.*** The eight complexes that have linear lithium bonds when H−Li is the acid also have linear bonds when $H_3C$−Li is the acid. The C−Li distances are about 0.4 Å longer than the F−Li and H−Li distances, a consequence of the larger van der Waals radius of C. The longer C−Li distances lead to longer C−N distances in these complexes, and the C−Li and Li···N distances become similar. The binding energies of these complexes are 0.3 to 0.5 kcal/mol less than the binding energies of the corresponding complexes with H−Li.

**SCHEME 3: Complexes $H_3C-Li\cdots HN=CH_2$ and $H_3C-Li\cdots$Aziridine**

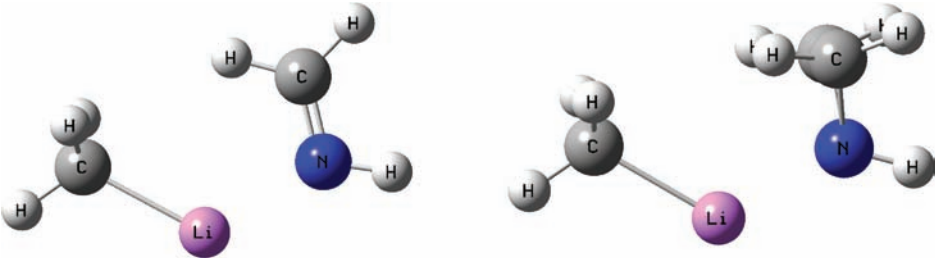


**TABLE 2: Mulliken MP2/aug-cc-pVTZ Charges (*e*) in Monomers and Complexes**

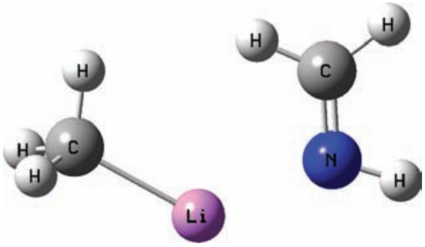
| monomer | charge on X | charge on Li | |
|---|---|---|---|
| FLi | −0.714 | +0.714 | |
| HLi | −0.310 | +0.310 | |
| $CH_3Li$ | −1.006 | +0.255 | |
| **complex** | **charge on X** | **charge on Li** | **charge on N** |
| FLi:aziridine | −0.782 | +0.552 | −0.234 |
| HLi:aziridine | −0.338 | +0.108 | −0.262 |
| $CH_3Li$:aziridine | −1.143 | +0.364 | −0.287 |

For the complexes $H_3C-Li\cdots NH(CH_2)$ and $H_3C-Li\cdots$aziridine, the nonlinearity of the lithium bonds is slightly reduced to 29°. However, the tilt of the base is intermediate between that observed for the corresponding complexes with F−Li and H−Li with tilt angles of 78 and 82°, respectively. The structures of these two complexes, which are illustrated in Scheme 3, suggest that there is a stabilizing interaction now involving the methyl group of the acid and the H atoms of C−H bonds of the base. This interaction may be attributed to the very large negative charge on C, as indicated by Mulliken populations for the acids F−Li, H−Li, and $CH_3Li$ and the complexes of these acids with aziridine, which are reported in Table 2. The charge on C in the monomer is −1.006e, the largest negative charge found among the three acids. This negative charge increases in the complex with aziridine to −1.143e. Therefore, despite the fact that the two H atoms of the C−H bonds of aziridine must be involved in destabilizing interactions with the H atoms of the methyl group, they must also have a very strong attractive electrostatic interaction with the methyl carbon. The $H_3C-Li\cdots NH(CH_2)$ and $H_3C-Li\cdots$aziridine complexes are only 0.3 and 0.4 kcal/mol, respectively, less stable than the corresponding complexes with H−Li as the base. They are, however, 1.7 and 2.5 kcal/mol, respectively, less stable than corresponding complexes with F−Li.

Would these complexes lose stability if the $CH_3$ group of the acid were rotated by 60° so as to place the in-plane C−H "cis" to the base? To examine this possibility, we optimized the structure of $H_3C-Li\cdots NH(CH_2)$ with this conformation of the methyl group, illustrated in Scheme 4. This conformational change has anticipated effects on the structure and binding energy of this complex. The C−N distance across the lithium bond increases from 3.533 Å in the "trans" structure to 3.643 Å in the "cis"; the nonlinearity of the lithium bond decreases slightly from 29 to 26°; the "tilt" of the base increases from 78 to 83°. However, the overall structures are quite similar and again suggest a stabilizing interaction between the adjacent C−H hydrogen of the base and the methyl C. The binding energy of the "cis" structure is reduced by only 0.4 kcal/mol relative to the "trans".

**Coupling Constants.** Spin−spin coupling constants $^1J$(X−Li), $^{1li}J$(Li−N), and $^{2li}J$(X−N) for complexes with $F-Li\cdots N$, $H-Li\cdots N$, and $CH_3Li\cdots N$ bonds are reported in Table 3. Table S1 in the Supporting Information provides values of the terms that contribute to *J*. All terms were computed for complexes of all three acids with the bases $N_2$, NCH, $HN=CH_2$, $NH_3$, $NH_2CH_3$, and aziridine. All terms were also computed for $F-Li\cdots$1,3,5-triazine and $F-Li\cdots$1,2,3-triazine. From these data, it can be seen that evaluation of the PSO term for $^1J$(F−Li) is essential, so the PSO and DSO terms were evaluated for $F-Li\cdots$pyrazine and $F-Li\cdots$pyridine. The SD term, computationally the most expensive term, was set to 0.0 Hz. This approximation can be justified by the data of Table S1 in the Supporting Information.

**SCHEME 4: Complex $H_3C-Li\cdots HN=CH_2$ with the $CH_3$ Group Rotated to Place the In-Plane C−H "Cis" to the Base**



From the data in Table S1, it can be seen that only the FC term makes a significant contribution to *J* in complexes with H−Li as the acid and $N_2$, NCH, $H_2CNH$, $NH_3$, $NH_2CH_3$, and aziridine as bases. The FC term is also the only significant contributor to *J* for the complex $H-Li\cdots$1,2,3-triazine, so only this term was evaluated for the complexes of H−Li with 1,3,5-triazine, pyrazine, and pyridine. Table S1 in the Supporting Information also shows that for complexes with $CH_3Li$ as the acid and $N_2$, NCH, $H_2CNH$, $NH_3$, $NH_2CH_3$, and aziridine as the nitrogen bases, the PSO, DSO, and SD terms are negligible, so only the FC term was evaluated for complexes of $CH_3Li$ with the azabenzenes. All terms were evaluated for the hydrogen-bonded complexes of F−H with the entire set of nitrogen bases.

***Coupling Constants $^1J$(X−Li) for Complexes with $X-Li\cdots N$ Bonds.*** Values of the one-bond X−Li coupling constants for monomers F−Li, H−Li, and $H_3C-Li$ and the complexes of these acids with the 10 nitrogen bases are reported in Table 3. $^1J$(F−Li) is 166.8 Hz in the monomer, and increases in complexes with linear $F-Li\cdots N$ bonds to a maximum of 171.5 Hz for $F-Li\cdots$1,3,5-triazine. It decreases in complexes $FLi\cdots NHCH_2$, $FLi\cdots NH_2CH_3$, and $FLi\cdots$aziridine, which have nonlinear bonds, and has its smallest value in $F-Li\cdots$aziridine. In contrast, $^1J$(H−Li) and $^1J$(C−Li) decrease significantly in complexes with $H-Li\cdots N$ and $C-Li\cdots N$ lithium bonds. For complexes with $F-Li\cdots N$ bonds, there is no correlation between $^1J$(F−Li) and the F−Li distance independent of the inclusion or omission of points for complexes with nonlinear

**TABLE 3: $^1J$(X−Li), $^{1li}J$(Li−N), and $^{2li}J$(X−N) (Hz) for Complexes with F−Li···N H−Li··· N, and $H_3C$−Li··· N Bonds**

| donor | acceptor | $^1J$(X−Li) | $^{1li}J$(Li−N) | $^{2li}J$(X−N) |
|---|---|---|---|---|
| FLi[a] | $N_2$ | 169.6 | −9.4 | 0.1 |
| | HCN | 169.5 | −16.2 | 0.2 |
| | 1,3,5-triazine | 171.5 | −15.5 | 0.3 |
| | pyrazine | 170.7 | −16.4 | 0.2 |
| | 1,2,3-triazine | 168.1 | −18.0 | 0.2 |
| | pyridine | 169.5 | −17.4 | 0.3 |
| | $H_2C{=}NH$ | 153.6 | −15.1 | 1.3 |
| | $NH_3$ | 170.0 | −15.1 | 0.2 |
| | $NH_2CH_3$ | 163.6 | −14.6 | 0.4 |
| | aziridine | 152.7 | −17.2 | −0.1 |
| FLi monomer | | 166.8 | | |
| HLi[b] | $N_2$ | 118.5 | −6.1 | −2.3 |
| | HCN | 99.1 | −12.5 | −2.5 |
| | 1,3,5-triazine | 102.7 | −12.2 | −1.9 |
| | pyrazine | 100.2 | −13.1 | −1.9 |
| | 1,2,3-triazine | 97.2 | −14.8 | −1.4 |
| | pyridine | 95.8 | −14.1 | −1.7 |
| | $H_2C{=}NH$ | 87.3 | −12.7 | −2.7 |
| | $NH_3$ | 96.7 | −10.7 | −4.0 |
| | $NH_2CH_3$ | 95.7 | −11.7 | −2.7 |
| | aziridine | 87.3 | −14.5 | −2.9 |
| HLi monomer | | 159.2 | | |
| $CH_3Li$[c] | $N_2$ | 80.6 | −5.7 | −0.9 |
| | HCN | 73.8 | −12.1 | −0.9 |
| | 1,3,5-triazine | 75.1 | −11.9 | −0.7 |
| | pyrazine | 74.2 | −12.7 | −0.7 |
| | 1,2,3-triazine | 73.8 | −14.4 | −0.5 |
| | pyridine | 72.8 | −13.8 | −0.6 |
| | $H_2C{=}NH$ | 69.2 | −11.7 | −1.3 |
| | $NH_3$ | 72.4 | −10.2 | −1.6 |
| | $NH_2CH_3$ | 72.3 | −11.3 | −1.1 |
| | aziridine | 69.6 | −13.4 | −1.4 |
| $CH_3Li$ monomer | | 95.5 | | |

[a] For complexes with F−Li as the donor and 1,3,5-triazine, pyrazine, and pyridine as the acceptors, the value of *J* is the sum of the PSO, DSO, and SD terms. See Table S1 in the Supporting Information for a justification of this approximation. [b] For complexes with H−Li as the donor and 1,3,5-triazine, pyrazine, and pyridine as the acceptors, the value of *J* has been approximated by the FC term. See Table S1 in the Supporting Information for a justification of this approximation. [c] For complexes with $CH_3$−Li as the donor and the azabenzenes as the acceptors, the value of *J* has been approximated by the FC term. See Table S1 in the Supporting Information for a justification of this approximation.

bonds. Figure 1 presents a plot of $^1J$(H−Li) versus the H−Li distance. The correlation coefficient for the trendline is 0.983. Note however, that the point for the monomer is far removed from the points for the complexes, and its inclusion significantly extends the range of values of $^1J$(H−Li). When the monomer is omitted, the curvature of the trendline changes, as illustrated in Figure 2, and the correlation coefficient decreases to 0.928. Corresponding plots for $^1J$(C−Li) versus the C−Li distance behave similarly, although the correlation coefficients are even lower. The lack of correlation between $^1J$(X−Li) and the X−Li distance is most probably due to the relatively small changes that occur in these distances and coupling constants in the lithium complexes.

It is also interesting to note that the smallest values of $^1J$(X−Li) are found in the complexes in which $HN{=}CH_2$ and aziridine are the nitrogen bases, and the lithium bonds are nonlinear. These complexes have the longest X−Li distances and the shortest Li−N distances as Li approaches a bridging position between X and N.

***Coupling Constants $^{1li}J$(Li−N) for Complexes with X−Li···N Bonds.*** Coupling constants $^{1li}J$(Li−N) are reported in Table 3. Complexes with linear X−Li···N bonds (excluding those with $N_2$ as the base) have similar values of $^{1li}J$(Li−N) that vary between −10.2 Hz for $CH_3Li$···$NH_3$ to −18.0 Hz for FLi···1,2,3-triazine. $^{1li}J$(Li−N) values for corresponding complexes with FLi as the acid are about 3 to 4 Hz greater in absolute value compared with those having HLi as the acid, even though the Li−N distances are shorter in the latter complexes. The values of $^{1li}J$(Li−N) for corresponding complexes with H−Li as the acid are similar to but slightly greater than those having $CH_3$−Li as the acid, with differences of only 0.3 to 0.5 Hz.

When nonlinear lithium bonds are formed with the bases $HN{=}CH_2$ and aziridine, the absolute values of $^{1li}J$(Li−N) decrease in the same order with respect to the acid as observed for the complexes with linear lithium bonds: F−Li > H−Li > $CH_3Li$. $^{1li}J$(Li−N) values for F−Li complexes with $HN{=}CH_2$ and aziridine are about 2.5 Hz greater in absolute value compared with those having H−Li as the acid, which in turn, are about 1 Hz greater than those with $CH_3Li$. No relationship between $^{1li}J$(Li−N) and the Li−N distance was observed for any of the three acids.

***Coupling Constants $^{2li}J$(X−N) for Complexes with X−Li···N Bonds.*** For complexes with F−Li as the acid, $^{2li}J$(F−N) values are extremely small, varying between −0.1 and 0.4 Hz,, except for F−Li···$NHCH_2$, in which case $^{2li}J$(F−N) is 1.3 Hz. The F−N distances are remarkably similar, varying from 3.688 to 3.719 Å in complexes with linear lithium bonds. The distances are much shorter when the bonds are nonlinear. However, values of $^{2li}J$(F−N) do not appear to be a function of the F−N distance.

When H−Li is the acid, $^{2li}J$(H−N) increases in absolute value but is still relatively small, varying from −1.4 Hz for H−Li···1,2,3-triazine to −4.0 Hz for H−Li···$NH_3$. The values for the two complexes with nonlinear lithium bonds are within this range. When $CH_3Li$ is the acid, $^{2li}J$(C−N) is also very small, varying between −0.5 and −1.6 Hz.

Why are the absolute values of two-bond coupling constants across lithium bonds so small? Is this simply a consequence of the long X−N distances in these complexes? To investigate this possibility, we have compared two-bond F−N coupling constants across the F−Li···N lithium bond [$^{2li}J$(F−N)], F−Cl···N halogen bond [$^{2x}J$(F−N)], and F−H···N hydrogen bond [$^{2h}J$(F−N)] in equilibrium complexes with a single base, $NH_3$. In addition, for comparison purposes, we have set the F−N distance in FH:$NH_3$ to the F−N distance in the lithium-bonded complex. The F−H distance was set equal to the F−Li distance for one calculation and equal to the F−H distance in equilibrium FH:$NH_3$ for another. These comparisons are summarized in Table 4.

Some very interesting and enlightening observations can be made from the data of Table 4. The first is the very large absolute value of −48.6 Hz for F−N coupling in the halogen-bonded complex compared with −43.5 Hz for the hydrogen-bonded complex, despite the much longer F−N distance in F−Cl···$NH_3$ (3.949 Å) compared with that in F−H···$NH_3$ (2.636 Å). This makes the extremely small value of +0.1 Hz for $^{2li}J$(F−N) at an F−N distance of 3.700 Å in F−Li···$NH_3$ even more curious. Moreover, when the F−N distance in F−H···$NH_3$ is set to the distance in F−Li···$NH_3$ (3.700 Å), $^{2h}J$(F−N) has a greater absolute value than $^{2li}J$(F−N) has in F−Li···$NH_3$. At this F−N distance, when the F−H distance is set equal to the F−H distance in equilibrium F−H···$NH_3$, $^{2h}J$(F−N) is small at −2.4 Hz, but when it is set equal to the

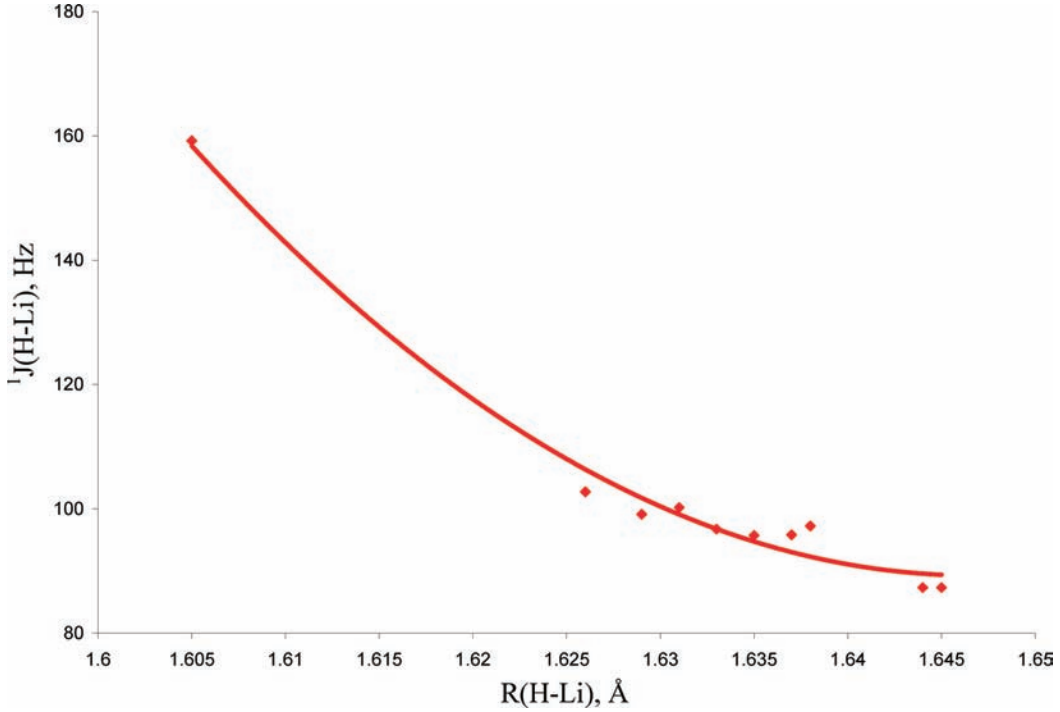


**Figure 1.** $^{1}J$(H−Li) versus the H−Li distance.

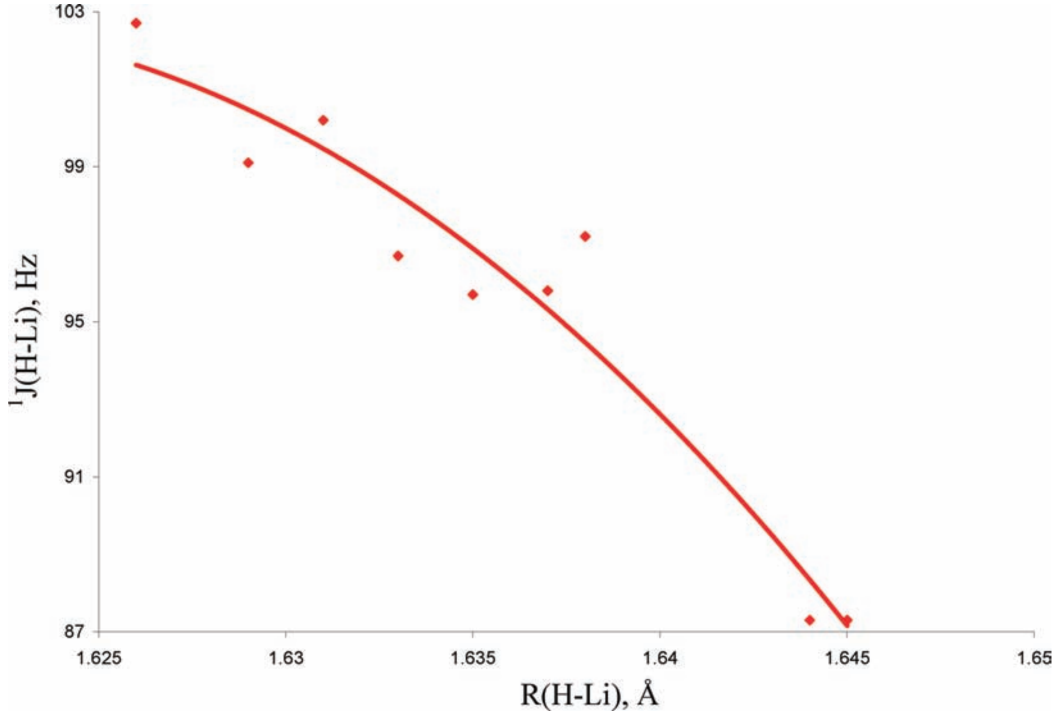


**Figure 2.** $^{1}J$(H−Li) versus the H−Li distance with the point for the H−Li monomer omitted.

F−Li distance in F−Li···$NH_3$, $^{2h}J$(F−N) increases in absolute value to −11.6 Hz, a reflection of the increased proton-shared character of this bond.[21] These comparisons indicate that the F−N distance is not the primary factor leading to reduced F−N coupling constants in complexes with F−Li···N lithium bonds. Rather, the very large positive charge on Li (+0.792*e*) in F−Li···$NH_3$ relative to H (+0.261*e*) and Cl (+0.254*e*) in F−H···$NH_3$ and F−Cl···$NH_3$, respectively, may be responsible, at least in part. Two-bond F−N coupling in F−H···$NH_3$ and F−Cl···$NH_3$ is dominated by the Fermi-contact term, but this term in all of the lithium-bonded complexes is very small, as evident from Table S1 in the Supporting Information. It may well be that the very low valence "s" electron density of Li in F−Li···$NH_3$ prevents effective coupling between the ground-

**TABLE 4: Two-Bond F−N Coupling Constants (Hz) Across F−Li···$NH_3$, F−Cl···$NH_3$, and F−H···$NH_3$ Bonds**

| complex | F−N distance | F−X distance | F−N coupling constant |
|---|---|---|---|
| F−H···$NH_3$ | 2.636 | 0.957 | −43.5 |
| F−Li···$NH_3$ | 3.700 | 1.620 | +0.1 |
| F−Cl···$NH_3$ | 3.949 | 1.714 | −48.6 |
| F−H···$NH_3$ | 3.700 | 1.620[a] | −11.6 |
|  | 3.700 | 0.957[b] | −2.4 |

[a] F−Li distance in F−Li···$NH_3$. [b] F−H distance in F−H···$NH_3$.

**TABLE 5: Electron Densities (ρ, au) and the Laplacians of the Charge Densities [$\nabla^2(\rho)$, au] for F−X and X−N Bonds in Complexes F−H···$NH_3$ and F−Li···$NH_3$**[a]

| F−X bcp's | | | |
|---|---|---|---|
| complex | F−X distance | ρ | $\nabla^2(\rho)$ |
| F−H···$NH_3$ | 0.957 | 0.3270 | −2.1778 |
| F−H···$NH_3$ | 1.620 | 0.0643 | −0.0247 |
| F−Li···$NH_3$ | 1.620 | 0.0650 | +0.5835 |

| X···N bcp's | | | |
|---|---|---|---|
| complex | X−N distance | ρ | $\nabla^2(\rho)$ |
| F−H···$NH_3$ | 2.743 | 0.0055 | +0.0159 |
| F−H···$NH_3$ | 2.080 | 0.0257 | +0.0180 |
| F−Li···$NH_3$ | 2.080 | 0.0253 | +0.1522 |

[a] F−N distance is 3.700 Å, the distance in equilibrium F−Li···$NH_3$.

state wave function and the excited-state wave functions via the Fermi-contact operator.

Further insight into the relatively small coupling constants for the complexes with F−Li···N lithium bonds can be gained by characterizing the F−X and X−N bond critical points (bcp's) for the equilibrium F−Li···$NH_3$ complex, and for two F−H···$NH_3$ complexes both having an F−N distance of 3.700 Å, the distance in F−Li···$NH_3$. In one complex, the F−H distance is 0.957 Å, the distance in the equilibrium F−H···$NH_3$ complex, whereas in the other, it is 1.620 Å, the F−Li distance in F−Li···$NH_3$. Table 5 reports the electron densities (ρ) and the Laplacians of the charge densities [$\nabla^2(\rho)$] at the bcp's. The Laplacians of the F−Li and Li−N bonds in F−Li···$NH_3$ are positive, indicating that electron densities in these two regions have been depleted. Both F−H and F−Li densities (ρ) at distances of 1.620 Å are significantly less than the F−H density at 0.957 Å. At the longer H−N and Li−N distances of 2.080 Å, the H−N and Li−N densities are similar and greater than the H−N density at the longer H−N distance, although all are relatively small. These data lend further support to the suggestion given above that low valence electron densities on Li inhibit effective F−N coupling across the lithium bond.

We have also computed the F−N coupling constant for a structure derived from the equilibrium F−Li···$NH_3$ complex but with Li removed from the bond. This was accomplished by rotating the F−Li molecule by 180° about an axis through F and perpendicular to the symmetry plane of the complex, keeping the F−N and F−Li distances fixed at their equilibrium values. This complex has an Li−F···N arrangement of atoms and is unbound relative to the F−Li and $NH_3$ monomers. Nevertheless, the F−N coupling constant in this nonbonded complex is −2.8 Hz, which means that it has a greater absolute value than $^{2li}J$(F−N) for equilibrium F−Li···$NH_3$. This phenomenon is not new and has been discussed previously in studies of the orientation dependence of coupling in $(FH)_2$[22] and coupling with and without the proton in hydrogen-bonded complexes.[23]

## Conclusions

Ab initio calculations have been carried out to determine the structures, binding energies, and spin−spin coupling constants of complexes stabilized by X−Li···N bonds with F−Li, H−Li, and $CH_3Li$ as the Lewis acids. The following statements are supported by the results of these calculations: (1) Complexes formed with F−Li, H−Li, and $CH_3Li$ as the Lewis acids and the nitrogen bases $N_2$, HCN, 1,3,5-triazine, pyrazine, 1,2,3-triazine, pyridine, and $NH_3$ have linear X−Li···N bonds. Methylamine ($NH_2CH_3$) forms a nonlinear lithium bond only when F−Li is the lithium donor. Two bases, HN═$CH_2$ and aziridine, form nonlinear X−Li···N bonds with each acid. The nonlinearity of these bonds arises from strong electrostatic interactions between the negatively charged X atom of the acid and adjacent acidic H atoms of the base. (2) $N_2$ is a very weak base, and the binding energies of its complexes with the three acids are about 5.5 kcal/mol. The binding energies of the remaining complexes are much greater, varying from 15.0 kcal/mol for $CH_3Li$···1,3,5-triazine to 23.2 kcal/mol for F−Li···aziridine. For a given base, the order of decreasing binding energies with respect to the acid is F−Li > H−Li > $CH_3Li$. (3) Although $^1J$(F−Li) may increase or decrease upon formation of an F−Li···N bond, $^1J$(H−Li) and $^1J$(C−Li) decrease significantly when H−Li···N and $H_3C$−Li···N bonds are formed. For a given acid, complexes with HN═$CH_2$ and aziridine, which have nonlinear X−Li···N bonds, have the smallest values of $^1J$(X−Li). For a given base, $^{1li}J$(Li−N) decreases with respect to the acid in the order F−Li > H−Li > $CH_3Li$. No correlations are found between $^1J$(X−Li) and $^{1li}J$(Li−N) and X−Li and Li−N distances, respectively. (4) $^{2li}J$(X−N) values are extremely small, with the largest absolute value of −4.0 Hz found for H−Li···$NH_3$. Comparisons with $^{2h}J$(F−N) and $^{2x}J$(F−N) for coupling across F−H···N hydrogen bonds and F−Cl···N halogen bonds suggest that the small values of $^{2li}J$(X−N) are not a consequence of long X−N distances. Rather, the very low valence electron density on Li in X−Li···N bonds may hinder effective coupling between X and N.

**Acknowledgment.** The authors thank the Ohio Supercomputer Center for continuing computational support and CTI (CSIC) for an allocation of computer time. This work was carried out with financial support from the Ministerio de Educación y Ciencia (project no. CTQ2007-61901/BQU) and Comunidad Autónoma de Madrid (project MADRISOLAR, ref S-0505/PPQ/0225).

**Supporting Information Available:** EOM-CCSD PSO, DSO, FC, and SD components of J for the complexes investigated in this study. Also included are the full refs 13 and 19. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP9035919