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Two-Bond $^{19}F-^{15}N$ Spin−Spin Coupling Constants ($^{2h}J_{F-N}$) across F−H···N Hydrogen Bonds

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Equation-of-motion coupled cluster calculations (EOM-CCSD) have been performed to determine two-bond $^{19}F-^{15}N$ spin−spin coupling constants ($^{2h}J_{F-N}$) for thirteen neutral complexes stabilized by F−H···N hydrogen bonds. The proton acceptors include nitrogens that are sp (HCN and its derivatives), sp^2 (aromatic azines), and sp^3 (NH_3 and its derivatives) hybridized. $^{2h}J_{F-N}$ is determined by the Fermi-contact term, which is strongly dependent on the intermolecular F−N distance but varies only slightly with small perturbations of the hydrogen bond from linearity. $^{2h}J_{F-N}$ is more sensitive to the hybridization and bonding at the nitrogen in F−H···N hydrogen bonds than is $^{2h}J_{N-N}$ for complexes stabilized by N−H−N and N−H$^+$−N hydrogen bonds. As a result, $^{2h}J_{F-N}$ at the same F−N distance for different complexes can vary by 10−15 Hz, and this reduces the quality of the quadratic curve used to relate $^{2h}J_{F-N}$ to the F−N distance. However, if the complexes are grouped according to the hybridization of the nitrogen, excellent quadratic correlations are found between $^{2h}J_{F-N}$ and the F−N distance. Moreover, if the same groupings are used, $^{2h}J_{F-N}$ also correlates with the charge density at the bond critical point of the hydrogen bond.

Introduction

A new and important area of both experimental and computational research is the investigation of NMR spin−spin coupling constants across hydrogen bonds.[1−30] In our previous studies,[18−30] we have applied predictive quantum chemical tools (EOM-CCSD) to investigate spin−spin coupling constants across N−N−N, N−H−O, O−H−O, C−H−N, and Cl−H−N hydrogen bonds in an effort to understand the factors that are important in determining the magnitudes of coupling constants and to lay the foundation for extracting structural information for hydrogen-bonded complexes from NMR spectral data. For all of these complexes, the two-bond spin−spin coupling constant ($^{2h}J_{X-Y}$) across the X−H−Y hydrogen bond is dominated by the Fermi-contact term, which is distance dependent. Therefore, this term may be used as a good approximation to $^{2h}J_{X-Y}$. In contrast, the F−F coupling constant ($^{2h}J_{F-F}$) in $[F-H-F]^{-1}$ receives non-negligible contributions from other terms and cannot be approximated by the Fermi-contact term.[18,27] Experimental F−N spin−spin coupling constants have been measured by Limbach et al.[15] for the FH:collidine complex as a function of temperature. A complementary theoretical study of model systems for this complex has also been carried out previously in this laboratory.[31]

In the present study we report a systematic investigation of two-bond $^{19}F-^{15}N$ spin−spin coupling constants across F−H···N hydrogen bonds and address the following questions.

1. Can F−N coupling constants be approximated by the Fermi-contact term?

2. How does $^{2h}J_{F-N}$ vary with the F−N hydrogen bond distance and with small perturbations to the linearity of the hydrogen bond?

3. Can a single curve be constructed from coupling constants computed at equilibrium distances for a group of complexes with F−H−N hydrogen bonds, and can that curve be useful for predicting intermolecular distances from experimentally measured F−N coupling constants?

Methods

Two-bond $^{19}F-^{15}N$ spin−spin coupling constants have been evaluated for a set of 13 neutral complexes stabilized by F−H···N hydrogen bonds. The neutral complexes have sp (HCN, LiCN, FCN, and NCCN), sp^2 (pyridine, 4-Li-pyridine, 1,4-diazine, and 1,3,5-triazine), and sp^3 [NH_3, NFH_2, NF_2H, NF_3, and $NH_2(CH_3)$] hybridized nitrogens as proton acceptors. The structures of these complexes were fully optimized at second-order many-body perturbation theory [MBPT(2)][32−35] with the 6-31+G(d,p) basis set[36−39] and are equilibrium structures on their potential surfaces with no imaginary frequencies. Electronic binding energies were computed for these complexes as the difference between the total energy of the complex and the sum of the energies of the isolated monomers. No counterpoise corrections for basis-set superposition errors have been made.[40]

$^{19}F-^{15}N$ spin−spin coupling constants across F−H···N hydrogen bonds ($^{2h}J_{F-N}$) were obtained from equation-of-motion coupled cluster singles and doubles (EOM-CCSD) calculations in the CI-like approximation[41−44] using the Ahlrichs (qzp, qz2p)[45] basis set. For computational efficiency, the qz2p basis set on hydrogen atoms other than the hydrogen-bonded hydrogen was replaced with the Dunning polarized valence double-split

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TABLE 1: F−N and F−H Distances (Å) and Binding Energies (kcal/mol) for Complexes with F−H···N Hydrogen Bonds

complex	sym	F−N	F−H[a]	Δ*E*
$FH:NF_3$	C_{3v}	3.095	0.929	−1.6
FH:NCCN	$C_{\infty v}$	2.895	0.934	−5.3
$FH:NHF_2$[b]	C_s	2.869	0.936	− 5.1
FH:NCF	$C_{\infty v}$	2.847	0.936	− 6.6
FH:NCH	$C_{\infty v}$	2.817	0.938	− 7.5
$FH:NH_2F$[b]	C_s	2.721	0.948	−9.7
FH:1,3,5-triazine	C_{2v}	2.684	0.953	−10.3
FH:NCLi	$C_{\infty v}$	2.660	0.955	−14.1
FH:1,4-diazine	C_{2v}	2.638	0.960	−12.3
$FH:NH_3$	C_{3v}	2.637	0.963	−14.4
FH:pyridine	C_{2v}	2.611	0.967	−14.0
$FH:NH_2(CH_3)$[b]	Cs	2.598	0.973	−15.4
FH:4-Li-pyridine	C_{2v}	2.572	0.979	−17.2

[a] The F−H distance in the monomer is 0.926 Å. [b] This complex was constrained to have a linear F−H···N hydrogen bond. The energy difference between this "linear" structure and the fully optimized structure is less than 0.1 kcal/mol.

basis set (cc-pVDZ).[46,47] For all complexes except those with aromatic azines as proton acceptors and $FH:NF_3$, $^{2h}J_{F-N}$ has been evaluated as the sum of the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi-contact (FC), and spin−dipole (SD) terms. $^{2h}J_{F-N}$ for the FH:azine and $FH:NF_3$ complexes has been approximated by the Fermi-contact term. Structure optimizations were carried out using the Gaussian 98 suite of programs,[48] and coupling constants were evaluated using ACES II.[49] These calculations were carried out on the Cray SV1 computer at the Ohio Supercomputer Center. Electronic features of the hydrogen bonds were analyzed by locating bond critical points using the atoms in molecules (AIM) theory of Bader.[50] The analyses were carried out at MP2/6-31+G(d,p) using the computing facilities at the Universidad Autónoma de Madrid.

Results and Discussion

Symmetries, intermolecular F−N distances, F−H distances, and binding energies for complexes with traditional F−H···N hydrogen bonds are reported in Table 1. The complexes include examples in which the nitrogen base is sp (NCH, NCF, NCLi, NCCN), sp^2 (pyridine, 4-Li-pyridine, 1,4-diazine, 1,3,5 triazine), and sp^3 [NH_3, NH_2F, NHF_2, NF_3, $NH_2(CH_3)$] hybridized. These complexes are listed in Table 1 in order of decreasing F−N distance. It is apparent from these data that while $FH\cdots NF_3$ has the longest F−N distance and the smallest binding energy and FH···4-Li-pyridine has the shortest distance and the largest binding energy, there is not a one-to-one correspondence between these two variables in this series. For example, the F−N distances decrease in the order FH:NCLi > FH:1,4-diazine > $FH:NH_3$ > FH:pyridine, but the binding energies increase in the order FH:1,4-diazine < FH:pyridine < FH:NCLi < $FH:NH_3$. The F−N distances in these four complexes vary by only 0.049 Å, but the binding energies vary by 2.1 kcal/mol. These binding energies are certainly influenced by factors such as the hybridization of the proton-acceptor nitrogen and the nature of the substituent. Within a set of complexes with the same nitrogen hybridization, the order of decreasing F−N distance parallels the order of increasing binding energy. Another factor that influences the relative stabilities of these complexes is the magnitude of the dipole moment of the proton-acceptor molecule. Certainly, the large dipole moment of NCLi (9.6 D) must contribute to the enhanced stability of FH:NCLi.

TABLE 2: $^{2h}J_{F-N}$ and Its Components[a] (Hz) as a Function of the N−F Distance (Å) for Complexes with F−H···N Hydrogen Bonds

complex	F−N	PSO	DSO	FC	SD	$^{2h}J_{F-N}$
FH:NCH	2.51	−0.4	0.0	−60.4	−1.0	−61.8
	2.61	0.0	0.0	−43.5	−0.8	−44.3
	2.71	0.2	0.0	−31.0	−0.7	−31.5
	2.817	0.3	0.0	−21.2	−0.6	−21.5
	2.91	0.3	0.0	−15.1	−0.5	−15.3
FH:NCLi	2.44	0.0	0.0	−88.2	−1.2	−89.4
	2.55	0.4	0.0	−65.2	−1.1	−65.9
	2.660	0.6	0.0	−47.5	−0.9	−47.8
	2.77	0.6	0.0	−34.3	−0.8	−34.5
	2.88	0.6	0.0	−24.5	−0.7	−24.6
$FH:NH_3$	2.44	3.8	0.0	−74.5	−1.4	−72.1
	2.54	3.3	0.0	−58.0	−1.4	−56.1
	2.637	2.8	0.0	−45.2	−1.3	−43.7
	2.74	2.3	0.0	−34.5	−1.3	−33.5
	2.84	1.9	0.0	−26.5	−1.2	−25.8
FH:pyridine	2.44			−87.0		−87.0[a]
	2.611			−57.0		−57.0[a]
	2.78			−36.8		−36.8[a]

[a] Estimated from the Fermi-contact term.

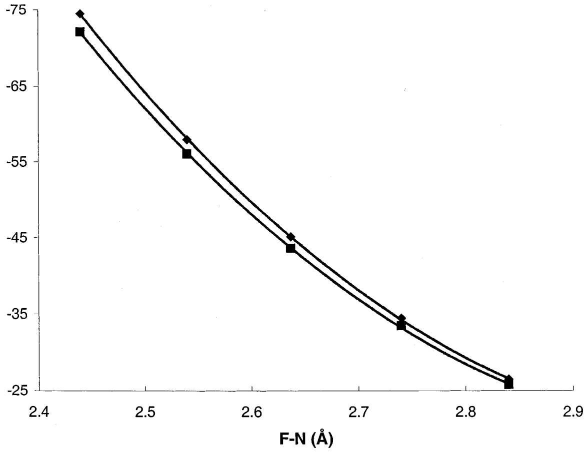

Figure 1. $^{2h}J_{F-N}$ and the Fermi-contact term versus the F−N distance for $FH:NH_3$: ◆, Fermi-contact term; ■, $^{2h}J_{F-N}$.

Table 2 presents the distance dependence of $^{2h}J_{F-N}$ and its components for the complexes FH:NCH, FH:NCLi, and $FH:NH_3$ and the variation of the Fermi-contact term with distance for FH:pyridine. It is apparent from this table that, over a wide range of F−N distances, the Fermi-contact term is dominant and is a good approximation to the total coupling constant $^{2h}J_{F-N}$. The error in this approximation is greatest at short F−N distances, but at the equilibrium distances, the error is 1.5 Hz in the worst case, $FH:NH_3$. Figure 1 presents a plot of the Fermi-contact term and $^{2h}J_{F-N}$ versus distance for this complex. Unfortunately, the FC term can either underestimate (FH:NCH and FH:NCLi) or overestimate ($FH:NH_3$) the absolute value of $^{2h}J_{F-N}$. This limits to some extent the reliability of the Fermi-contact term as a predictor of $^{2h}J_{F-N}$ for those complexes for which calculation of all terms is not feasible, as is the case for the complexes of FH with the azines and $FH:NF_3$.

The variation of $^{2h}J_{F-N}$ with the F−N distance for FH:NCH, FH:NCLi, $FH:NH_3$, and FH:pyridine (approximated by the FC term) is shown graphically in Figure 2. While these curves share some features with those in refs 21 and 26 for complexes with N−H−N hydrogen bonds, values of $^{2h}J_{F-N}$ are much larger (in an absolute sense) than $^{2h}J_{N-N}$ values, reflecting the large coupling associated with the F nucleus. (Of course, when comparing coupling constants involving different atoms, it is the reduced coupling constant $^{2h}K_{X-Y}$ which should be used.) We make this observation to emphasize that $^{2h}J_{F-N}$ for two complexes can vary by 10−15 Hz at the same F−N distance.

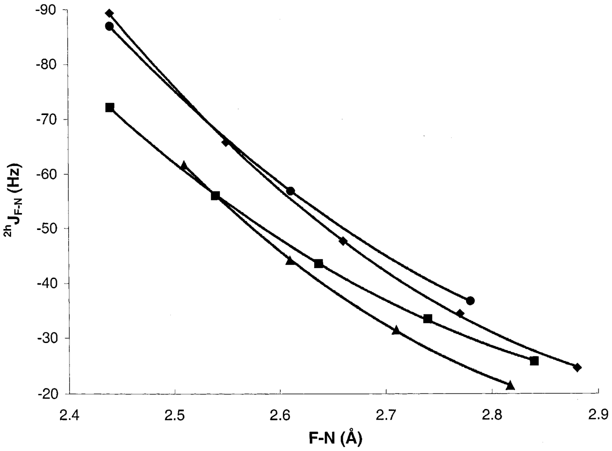

Figure 2. Distance dependence of $^{2h}J_{F-N}$ for complexes with F−H···N hydrogen bonds: ▲, FH:NCH; ◆, FH:NCLi; ●, FH:pyridine; ■, FH:NH$_3$.

TABLE 3: Equilibrium Distances (Å) and Two-Bond Spin−Spin Coupling Constants ($^{2h}J_{F-N}$) and Components[a] of $^{2h}J_{F-N}$ (Hz) for Complexes with F−H···N Hydrogen Bonds

complex	F−N	PSO	DSO	FC	SD	$^{2h}J_{F-N}$
FH:NF$_3$	3.095			−4.2		−4.2[b]
FH:NCCN	2.895	0.2	0.0	−13.1	−0.5	−13.4
FH:NHF$_2$	2.869	−0.5	−0.1	−16.1	−1.2	−17.9
FH:NCF	2.846	0.4	0.0	−18.1	−0.4	−18.1
FH:NCH	2.817	0.3	0.0	−21.2	−0.6	−21.5
FH:NH$_2$F	2.721	0.3	0.0	−32.4	−1.6	−33.7
FH:1,3,5-triazine	2.684			−40.3		−40.3[b]
FH:NCLi	2.660	0.6	0.0	−47.5	−0.9	−47.8
FH:1,4-diazine	2.638			−49.1		−49.1[b]
FH:NH$_3$	2.637	2.8	0.0	−45.2	−1.3	−43.7
FH:pyridine	2.611			−57.0		−57.0[b]
FH:NH$_2$(CH$_3$)	2.598	2.9	0.0	−53.3	−1.7	−52.1
FH:4-Li-pyridine	2.572			−70.5		−70.5[b]

[a] PSO = paramagnetic spin−orbit; DSO = diamagnetic spin−orbit; FC = Fermi-contact; SD = spin−dipole. [b] Estimated from the Fermi-contact term.

This variation implies that there is some dependence of the F−N coupling constant on the nature of the bonding at the nitrogen, certainly a much greater dependence than that observed for N−N coupling constants in both neutral and cationic complexes stabilized by N−H−N hydrogen bonds. In these latter complexes, the value of the coupling constant depends on the nature of the bonding at the nitrogen only indirectly, insofar as this bonding determines the equilibrium intermolecular distance.

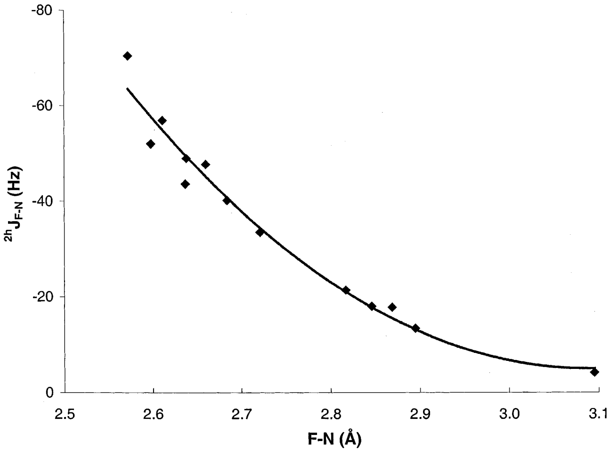

Figure 3. $^{2h}J_{F-N}$ versus the F−N distance for the equilibrium structures of complexes stabilized by F−H···N hydrogen bonds.

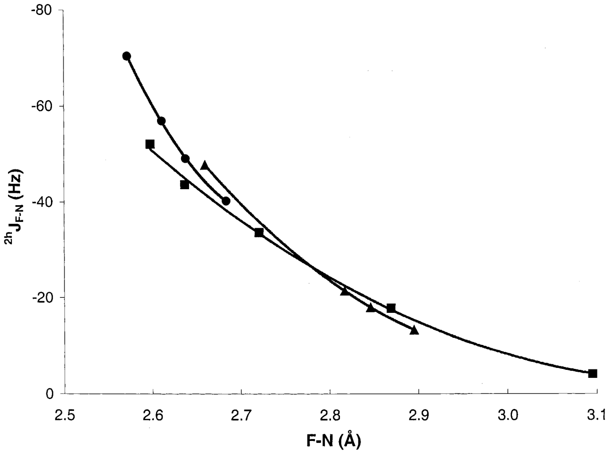

Figure 4. $^{2h}J_{F-N}$ versus the F−N distance for the equilibrium structures of complexes stabilized by F−H···N hydrogen bonds, grouped according to the hybridization of the nitrogen: ▲, sp; ●, sp^2; ■, sp^3.

Table 3 reports $^{19}F-^{15}N$ spin−spin coupling constants ($^{2h}J_{F-N}$) for the entire set of neutral complexes investigated in this work. As noted above, the large variation in F−N coupling constants at a given F−N distance makes it more difficult to extract F−N distances from experimentally measured coupling constants. This is apparent from Figure 3, in which two-bond F−N spin−spin coupling constants for the equilibrium structures of the 13 neutral complexes stabilized by traditional, linear F−H···N hydrogen bonds are plotted against the F−N distance. The curve shown is quadratic, with a correlation coefficient of 0.971. The scatter in the data points is the result of the sensitivity of $^{2h}J_{F-N}$ to the hybridization of the nitrogen. This is apparent from Figure 4, in which trend lines that relate $^{2h}J_{F-N}$ to the F−N distance have been drawn for complexes grouped according to the hybridization of the nitrogen. For each line, the correlation coefficient is 1.00. Hence, these curves are better suited for predicting F−N distances from experimentally measured coupling constants than the single curve shown in Figure 3. We have used the curve for the complexes with sp hybridized nitrogens as acceptors to predict the F−N distance from the computed $^{19}F-^{15}N$ coupling constant (−99.1 Hz) for FH···$^-$NC, an anionic complex stabilized by a traditional hydrogen bond. The predicted F−N distance is 2.465 Å, within 0.05 Å of its optimized F−N distance of 2.511 Å.

Since Figure 4 indicates the sensitivity of $^{2h}J_{F-N}$ to the details of bonding at the nitrogen, it is reasonable to ask whether this sensitivity correlates with charge densities at bond critical points of the hydrogen bonds. The bond critical point is that point along the hydrogen-bonding axis at which the electron density is a minimum. Such a correlation was observed previously between $^1H-^1H$ coupling constants and charge densities for complexes with dihydrogen bonds.[51] Figure 5 presents plots of $^{2h}J_{F-N}$ versus the charge density at the hydrogen bond critical point for the 13 complexes. The scatter in the data for the entire set is removed when the complexes are again grouped according to the hybridization of the nitrogen. The correlation coefficient for each trend line is 1.00. This is a very interesting correlation, since it relates an NMR property to electronic characteristics of the hydrogen bond. However, it should be emphasized that Figure 5 also shows that this correlation holds only within a very closely related series of complexes.

We have also investigated the variation of $^{2h}J_{F-N}$ with small perturbations that cause the hydrogen bond to deviate from linearity. This has been done for the FH:NH$_3$ complex by

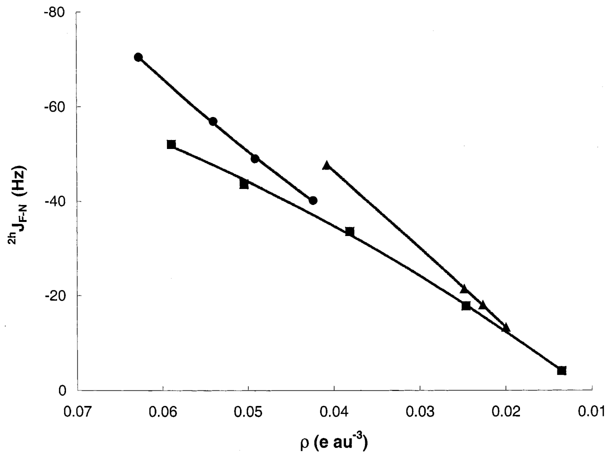

Figure 5. $^{2h}J_{F-N}$ versus the charge density at the bond critical point for complexes with F−H···N hydrogen bonds, grouped according to the hybridization of the nitrogen: ▲, sp; ●, sp^2; ■, sp^3.

rotating the FH molecule about an axis through F, perpendicular to the F−N line. A 10° distortion from linearity reduces $^{2h}J_{F-N}$ by only 0.2 Hz. However, larger perturbations may have different effects. A detailed analysis of the orientation dependence of spin−spin coupling constants will be the subject of a future paper.

Conclusions

The EOM-CCSD calculations carried out to determine ^{19}F−^{15}N spin−spin coupling constants ($^{2h}J_{F-N}$) for neutral complexes stabilized by traditional F−H···N hydrogen bonds are the basis for proposing the following answers to the questions raised in the Introduction.

1. ^{19}F−^{15}N spin−spin coupling constants in complexes stabilized by traditional F−H···N hydrogen bonds can be approximated by the Fermi-contact term.

2. The Fermi-contact term, and therefore the total $^{2h}J_{F-N}$, is strongly dependent on the F−N distance but only slightly dependent on small perturbations of the hydrogen bond from linearity.

3. $^{2h}J_{F-N}$ for complexes with F−H···N hydrogen bonds is much more sensitive to the bonding at the nitrogen than $^{2h}J_{N-N}$ for complexes with N−H−N hydrogen bonds, since $^{2h}J_{F-N}$ for different complexes at the same F−N distance can vary by 10−15 Hz. However, if these complexes are grouped according to the hybridization of the nitrogen, excellent correlations exist between $^{2h}J_{F-N}$ and the F−N distance. These curves individually should be useful for predicting F−N distances from experimentally measured coupling constants. Similarly, with the same groupings, good correlations also exist between $^{2h}J_{F-N}$ and the charge density at the hydrogen bond critical point.

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