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Two-Bond $^{13}C-^{15}N$ Spin−Spin Coupling Constants ($^{2h}J_{C-N}$) Across C−H−N Hydrogen Bonds[†]

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Ab initio EOM-CCSD calculations have been performed to determine $^{13}C-^{15}N$ spin−spin coupling constants ($^{2h}J_{C-N}$) across C−H−N hydrogen bonds in 17 neutral, 3 cationic, and 3 anionic complexes. The contributions of the paramagnetic spin−orbit, diamagnetic spin−orbit, and spin−dipole terms to the total $^{13}C-^{15}N$ spin−spin coupling constants ($^{2h}J_{C-N}$) are negligible, so $^{2h}J_{C-N}$ is determined solely by the Fermi contact term, which is distance-dependent. $^{2h}J_{C-N}$ for complexes stabilized by C−H···N hydrogen bonds exhibits some dependence on the nature of the hybridization and the nature of the bonding at the C atom of the proton-donor C−H group. Nevertheless, a single curve can be constructed from $^{2h}J_{C-N}$ and C−N distances for the equilibrium structures of the entire set of complexes that should be useful for estimating C−N distances from experimental measurements of coupling constants across C−H−N hydrogen bonds. Small deviations from linearity of the C−H−N hydrogen bond lead to only small changes in $^{2h}J_{C-N}$.

Introduction

A relatively recent and exciting development in studies of hydrogen-bonded complexes has been the characterization of two-bond spin−spin coupling constants across X−H−Y hydrogen bonds by NMR techniques. Both experimental and theoretical studies of two-bond spin−spin coupling constants ($^{2h}J_{X-Y}$) have been reported.[1−30] In our previous studies,[19−30] we have applied predictive quantum chemical tools (EOM-CCSD) to investigate spin−spin coupling constants across hydrogen bonds in an effort to understand the factors that are important in determining the values of coupling constants and to lay the foundation for extracting structural information for hydrogen-bonded complexes from NMR spectral data. We have systematically investigated two-bond spin−spin coupling constants in various series of complexes stabilized by N−H−N, N−H−O, O−H−O, and Cl−H−N hydrogen bonds as well as the F−F and F−N coupling constants in FHF^{-1} and FH:collidine, respectively. When comparisons between computed EOM-CCSD and experimental coupling constants could be made, good agreement has been found.[22,28,30] In recent work, we have also investigated the effect of isotopic substitution of D for the hydrogen-bonded H on two-bond coupling constants.[28,31] The complexes that have been investigated include examples of neutral, cationic, and anionic species that are stabilized by traditional, proton-shared, or ion-pair hydrogen bonds.[32] In the present paper, we report an extension of these studies to determine the dependence of two-bond $^{13}C-^{15}N$ coupling constants across C−H−N hydrogen bonds on the C−N distance, the charge on the complex, the hybridization of C and N, and the linearity of the hydrogen bond.

Methods

Two-bond C−N spin−spin coupling constants have been evaluated for neutral, cationic, and anionic complexes stabilized by C−H−N hydrogen bonds. Included among these are 17 neutral and 3 anionic complexes stabilized by C−H···N or C−H···$^-$N hydrogen bonds, 1 cationic complex with a C−H$^+$···N hydrogen bond, and 2 cationic complexes with N−H$^+$···C hydrogen bonds. The structures of these complexes were optimized by second-order many-body perturbation theory [MBPT(2)][33−36] with the 6-31+G(d,p) basis set.[37−40] Electronic binding energies were computed 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.[41] This level of theory has been shown to provide reliable structures and vibrational frequency shifts of X−H stretching bands in complexes with X−H···Y hydrogen bonds (provided that the anharmonicity correction in the complex is not unusually large) and reasonable binding energies.[42]

Harmonic vibrational frequencies were computed to confirm that these complexes are equilibrium structures on their potential surfaces and to evaluate zero-point vibrational energy contributions to binding enthalpies. In addition, searches of the potential surfaces were performed in attempts to find other minima corresponding to the interchange of the proton-donor and proton-acceptor species while maintaining a C−H···N or N−H···C hydrogen bond. In all cases, the new structures converted to the equilibrium structures with no energy barrier. The hydrogen bonds in these complexes have also been characterized in terms

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of the charge density at the bond critical point using the atoms-in-molecules theory of Bader.[43]

^{13}C−^{15}N spin−spin coupling constants ($^{2h}J_{C-N}$) were obtained from equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) calculations in the CI-like approximation[44−47] using the Ahlrichs (qzp, qz2p)[48] 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 basis set (cc-pVDZ).[49,50] For most of these complexes, all of the terms that contribute to $^{2h}J_{C-N}$ were evaluated to determine the relative importance of the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi contact (FC), and spin−dipole (SD) terms. Structure optimizations were carried out using the Gaussian 98 suite of programs,[51] and coupling constants were evaluated using ACES II.[52] These calculations were carried out on the SV1 computer at the Ohio Supercomputer Center. Charge densities at bond critical points were calculated using the computing facilities at the University of Madrid.

Results and Discussion

Structures and Binding Energies. The symmetries of the optimized complexes, intermolecular C−N distances, C−H or N−H distances, and binding energies and enthalpies for all complexes investigated in this study are reported in Table 1. The neutral complexes include those with sp-hybridized carbons (HCCH, FCCH, ClCCH, and NCH) as proton donors to nitrogen bases in which the N atom is either sp hybridized (NCH and NCLi) or sp^3 hybridized (NH_3). One complex in which an sp^2-hybridized nitrogen is the proton acceptor (NCH$\cdots$pyridine) has also been investigated. To examine the effect of changing the hybridization of the C of the C−H proton-donor group, complexes with an sp^2-hybridized carbon (fluoroformaldehyde, F(O)CH) and an sp^3 carbon (trifluoromethane, F_3CH) as proton donors to NCH and NH_3 have also been included. The cationic complexes are $HNCH^+\cdots NCH$, $C_5H_5N-H^+\cdots CNH$ (pyridinium$\cdots$CNH), and $H_3NH^+\cdots CNH$, whereas the anionic complexes are those with HCCH, FCCH, and NCH as proton donors to NC^-. Within a given group of complexes with the same proton acceptor, the listing in Table 1 is in order of decreasing C−N distance.

In each of the three sets of complexes with a given base (either NCH, NCLi, or NH_3) and HCCH, ClCCH, FCCH, and NCH as proton donors, the complex with HCCH has the longest C−N distance and is the most weakly bound, whereas the complex with NCH has the shortest C−N distance and is the most strongly bound. The binding energies of complexes with FCCH and ClCCH as proton donors to a given base are identical, and the C−N distances in the two complexes differ by no more than 0.004 Å. The binding enthalpies of corresponding complexes with ClCCH are slightly greater than those with FCCH, owing to differences in zero-point energy corrections. For a given proton donor, the binding energies increase with respect to the proton acceptor in the order NCH < NH_3 < NCLi, reflecting the intrinsic basicity of the proton acceptor, and the C−N distances decrease as these binding energies increase. The set of complexes with NCH as the proton donor includes pyridine as a base, and the order of increasing binding energies is NCH < pyridine ≈ NH_3 < NCLi.

Comparing sp, sp^2, and sp^3 C−H proton donors with a given proton acceptor is not as straightforward because unsubstituted C−H donors such as CH_4 and H_2CO are very weak. Nevertheless, in complexes with fluorosubstituted sp, sp^2, and sp^3 C−H donors with either NCH or NH_3 as the acceptor, FCCH, with an sp C, forms the weakest complex but has the shortest C−N distance. The complexes in which the sp^2 and sp^3 carbons of F(O)CH and F_3CH are the C−H proton donors to the same N acceptor have similar binding energies and similar C−N distances.

TABLE 1: Selected Structural Parameters, Binding Energies, and Enthalpies for Complexes with C−H−N Hydrogen Bonds

neutral complexes	sym	R(C−N), Å	R(C−H), Å[a]	ΔE (kcal/mol)	ΔH° (kcal/mol)
HCCH$\cdots$NCH	$C_{\infty v}$	3.440	1.067	−2.8	−2.0
ClCCH$\cdots$NCH	$C_{\infty v}$	3.413	1.066	−3.1	−2.5
FCCH$\cdots$NCH	$C_{\infty v}$	3.412	1.066	−3.1	−2.3
NCH$\cdots$NCH	$C_{\infty v}$	3.316	1.072	−4.9	−3.8
HCCH$\cdots$NCLi	$C_{\infty v}$	3.303	1.072	−5.2	−4.1
FCCH$\cdots$NCLi	$C_{\infty v}$	3.272	1.071	−5.8	−4.7
ClCCH$\cdots$NCLi	$C_{\infty v}$	3.268	1.072	−5.8	−5.0
NCH$\cdots$NCLi	$C_{\infty v}$	3.160	1.080	−9.7	−8.4
NCH$\cdots$pyridine	C_{2v}	3.163	1.082	−7.6	−6.5
HCCH$\cdots NH_3$	C_{3v}	3.327	1.072	−4.8	−3.1
ClCCH$\cdots NH_3$	C_{3v}	3.303	1.073	−5.2	−3.6
FCCH$\cdots NH_3$	C_{3v}	3.301	1.072	−5.2	−3.5
NCH$\cdots NH_3$	C_{3v}	3.204	1.081	−7.8	−5.9
F(O)CH$\cdots$NCH[b]	C_s	3.466	1.089	−3.6	−3.0
F(O)CH$\cdots NH_3$[b]	C_s	3.340	1.092	−5.7	−4.4
$F_3CH\cdots$NCH	C_{3v}	3.456	1.083	−3.7	−3.2
$F_3CH\cdots NH_3$	C_{3v}	3.341	1.086	−5.8	−4.6

cationic complexes	sym	R(C−N), Å	R(X−H), Å	ΔE (kcal/mol)	ΔH° (kcal/mol)
pyridine−$H^+\cdots$CNH[c]	C_{2v}	2.974	1.042[d]	−18.4	−17.5
$H_3NH^+\cdots$CNH[c]	C_{3v}	2.936	1.057[d]	−22.0	−20.7
$HNCH^+\cdots$NCH	$C_{\infty v}$	2.832	1.129[e]	−21.2	−19.7

anionic complexes	sym	R(C−N), Å	R(C−H), Å	ΔE (kcal/mol)	ΔH° (kcal/mol)
HCCH$\cdots NC^-$	$C_{\infty v}$	3.117	1.088	−10.5	−9.2
FCCH$\cdots NC^-$	$C_{\infty v}$	3.077	1.090	−12.2	−10.9
NCH$\cdots NC^-$	$C_{\infty v}$	2.940	1.110	−21.0	−19.6

[a] Monomer C−H distances (Å): HCCH, 1.064; ClCCH, 1.063; FCCH, 1.061; NCH, 1.067; F(O)CH, 1.089; F_3CH, 1.085; $HNCH^+$, 1.079. Monomer N−H distances (Å): NH_4^+, 1.023; pyridinium, 1.017. [b] The C−H$\cdots$N hydrogen bond is linear in this complex. [c] Complexes with $HNCH^+$ as the proton donor are not equilibrium structures on the potential energy surfaces. [d] Hydrogen-bonded N−H distance. [e] Hydrogen-bonded C−H distance.

Of the three cationic complexes included in this study, only $HNCH^+\cdots$NCH has a C−$H^+\cdots$N hydrogen bond. The complexes $HNCH^+\cdots$pyridine and $HNCH^+\cdots NH_3$ are not equilibrium structures on their potential surfaces but collapse without a barrier to the complexes pyridinium$\cdots$CNH and $H_3NH^+\cdots$CNH that are stabilized by N−$H^+\cdots$C hydrogen bonds. The only anionic complexes investigated are those that have HCCH, FCCH, and NCH as proton donors to NC^-. As expected, binding energies and enthalpies of charged complexes are significantly greater than those of uncharged complexes, and corresponding intermolecular distances are shorter. All of these complexes are stabilized by traditional hydrogen bonds, although the short C−N distance and the long C−H distance in $HNCH^+\cdots$NCH suggest that the hydrogen bond in this complex is approaching proton-shared. The binding energy of this complex is −21.2 kcal/mol, notwithstanding an energy loss of about 1 kcal/mol due to the distortion of the proton donor.

Two-Bond ^{13}C−^{15}N Spin−Spin Coupling Constants. Equilibrium C−N distances, total ^{13}C−^{15}N spin−spin coupling

TABLE 2: Equilibrium Distances, the Fermi Contact Term, and Total $^{2h}J_{C-N}$ for Complexes with C−H−N Hydrogen Bonds

neutral complexes	R(C−N), Å	FC (Hz)	$^{2h}J_{C-N}$ (Hz)
HCCH···NCH	3.440	−5.24	−5.26
ClCCH···NCH	3.413	−6.03	−6.06
FCCH···NCH	3.412	−6.33	−6.35
NCH···NCH	3.316	−7.31	−7.34
HCCH···NCLi	3.303	−8.34	−8.37
FCCH···NCLi	3.272	−10.09	−10.09[a]
ClCCH···NCLi	3.268	−9.77	−9.77[a]
NCH···NCLi	3.160	−12.16	−12.21
NCH···pyridine	3.163	−12.66	−12.66[a]
$HCCH\cdots NH_3$	3.327	−8.13	−8.14
$ClCCH\cdots NH_3$	3.303	−9.26	−9.26
$FCCH\cdots NH_3$	3.301	−9.73	−9.73[a]
$NCH\cdots NH_3$	3.204	−10.95	−10.98
F(O)CH···NCH	3.466	−5.19	−5.19[a]
$F(O)CH\cdots NH_3$	3.340	−8.39	−8.39[a]
$F_3CH\cdots NCH$	3.456	−4.68	−4.68[a]
$F_3CH\cdots NH_3$	3.341	−7.30	−7.30[a]
	cationic complexes		
$pyridine-H^+\cdots CNH$	2.974	−22.24	−22.24[a]
$H_3NH^+\cdots CNH$	2.936	−26.40	−26.49
$HNCH^+\cdots NCH$	2.832	−40.03	−40.13
	anionic complexes		
$HCCH\cdots NC^-$	3.117	−16.19	−16.25
$FCCH\cdots NC^-$	3.077	−20.09	−20.09[a]
$NCH\cdots NC^-$	2.940	−24.66	−24.77

[a] Estimated from the Fermi contact term.

TABLE 3: Total $^{2h}J_{C-N}$ and Its Components (Hz) as a Function of C−N Distance (Å) for Complexes with C−H···N Hydrogen Bonds

complex	R(C−N)	PSO	DSO	FC	SD	$^{2h}J_{C-N}$
HCCH···NCH	2.75	0.00	−0.02	−29.50	−0.07	−29.57
	3.00	0.01	−0.02	−16.57	−0.05	−16.63
	3.25	0.02	−0.02	−8.77	−0.03	−8.80
	3.440[a]	0.02	−0.02	−5.24	−0.02	−5.26
NCH···NCH	2.75	0.00	−0.03	−29.67	−0.06	−29.76
	3.00	0.02	−0.03	−16.63	−0.04	−16.68
	3.15	0.02	−0.02	−11.38	−0.04	−11.42
	3.316[a]	0.02	−0.02	−7.31	−0.03	−7.34
$HCCH\cdots NH_3$	2.75	0.05	−0.01	−28.51	−0.06	−28.53
	3.00	0.04	−0.01	−17.01	−0.05	−17.03
	3.327[a]	0.03	−0.01	−8.13	−0.03	−8.14
$HNCH^+\cdots NCH$	2.75	−0.02	−0.03	−46.39	−0.07	−46.51
	2.832[a]	−0.01	−0.03	−40.03	−0.06	−40.13
	3.00	−0.00	−0.03	−28.69	−0.05	−28.77
$NCH\cdots NC^-$	2.80	−0.02	−0.03	−31.84	−0.08	−31.97
	2.940[a]	−0.01	−0.03	−24.66	−0.07	−24.77
	3.10	0.00	−0.02	−17.99	−0.06	−18.07

[a] C−N distance in the equilibrium structure.

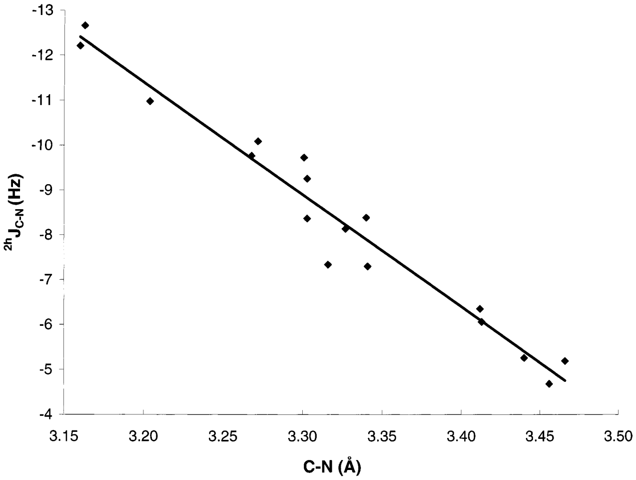

Figure 1. $^{2h}J_{C-N}$ versus the C−N distance for neutral complexes with C−H···N hydrogen bonds.

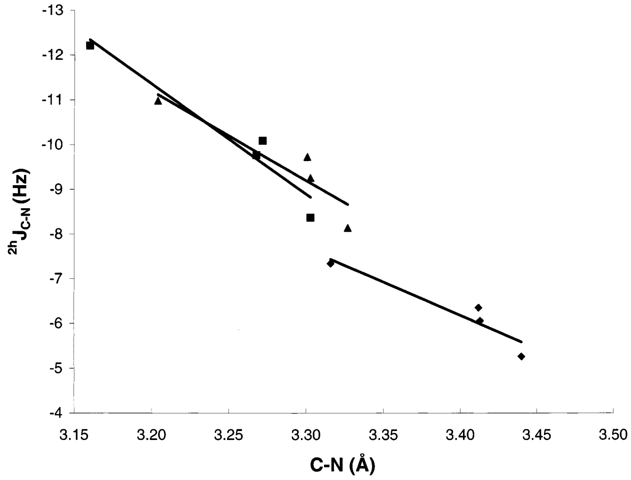

Figure 2. $^{2h}J_{C-N}$ versus the C−N distance for complexes with different C−H donors but the same N acceptor. ◆ NCH; ■ NCLi; ▲ NH_3.

constants ($^{2h}J_{C-N}$), and values of the Fermi contact terms for the complexes investigated in this study are reported in Table 2. For most of these complexes, all of the terms (PSO, DSO, FC, and SD) that contribute to the total coupling constant have been evaluated. However, as can be seen from Table 2, the difference between the Fermi contact term and total J does not exceed 0.1 Hz. That the Fermi contact term approximates $^{2h}J_{C-N}$ so well is not due to a cancellation of the remaining terms but arises from their small absolute values, which are less than 0.1 Hz, as seen from Table 3. Moreover, Table 3 also shows that approximating $^{2h}J_{C-N}$ by the Fermi contact term is valid over a range of intermolecular distances. In the following discussion, values quoted for the coupling constant will be $^{2h}J_{C-N}$ values when they are available. For some complexes, only the Fermi contact term has been computed, and it will be used to approximate $^{2h}J_{C-N}$. All of the C−N coupling constants have negative values, but changes in these will be discussed below in terms of absolute values.

Table 2 lists $^{2h}J_{C-N}$ values for the equilibrium structures of all complexes investigated in this study. The coupling constants for the 17 neutral complexes are plotted as a function of the C−N distance in Figure 1. The trend line shown for reference is linear and quite different from corresponding plots for complexes with N−H−N hydrogen bonds.[22,27] Why is this?

There are three sets of neutral complexes (identified by the proton acceptors NCH, NCLi, and NH_3) that have the same four proton donors, namely, HCCH, ClCCH, FCCH, and NCH. Within each set, the C−N coupling constant is smallest when HCCH is the proton donor and largest when NCH is the proton donor. This difference is a direct consequence of the longer C−N distances in complexes with HCCH and the shorter distances in complexes with NCH as the proton donor. However, with a given proton acceptor, $^{2h}J_{C-N}$ is greater by 0.3−0.5 Hz for FCCH compared to the value for ClCCH, even though the C−N distances in the complexes with these two donors are nearly identical. The dependence of $^{2h}J_{C-N}$ on the nature of the proton donor in these three sets of complexes is evident from Figure 2, which shows $^{2h}J_{C-N}$ plotted against the C−N distance. Since the number of data points is small, first-order plots that give the best fit to the data are shown for reference. These should not be interpreted as suggesting that there is a linear relationship between the C−N distance and $^{2h}J_{C-N}$, as will be shown below.

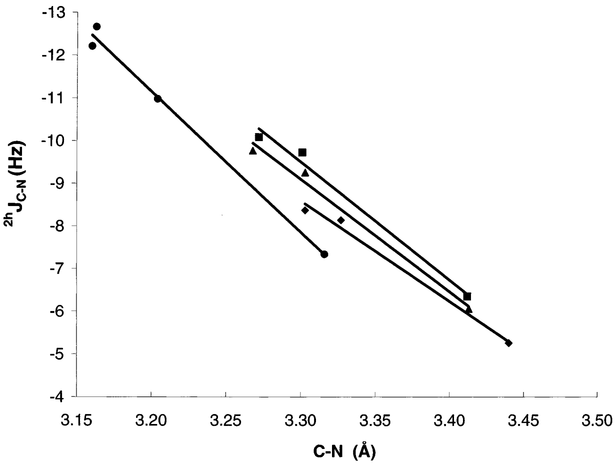

Figure 3. $^{2h}J_{C-N}$ versus the C−N distance for complexes with the same C−H donor but different N acceptors. ◆ HCCH; ■ FCCH; ▲ ClCCH; ● NCH.

The dependence of the coupling constant on the nature of the proton donor is also apparent when complexes F(O)CH··· NCH and F_3CH···NCH are compared. The intermolecular C−N distance is longer by 0.010 Å in the complex with F(O)CH, yet $^{2h}J_{C-N}$ is 0.5 Hz greater for this complex. Even more dramatic is the difference between $^{2h}J_{C-N}$ in F(O)CH···NH_3 and F_3CH···NH_3. Whereas the C−N distances in these complexes differ by only 0.001 Å, $^{2h}J_{C-N}$ is 1.1 Hz greater in the complex with F(O)CH.

That the variation in $^{2h}J_{C-N}$ is not due primarily to the nature of the N acceptor in these complexes can be seen from Figure 3, in which $^{2h}J_{C-N}$ has been plotted as a function of distance for complexes in which HCCH, FCCH, ClCCH, and NCH are proton donors to different nitrogen bases. Once again, the best-fit first-order curves are shown for reference. These data reinforce our previous observation that the hybridization of the proton-acceptor nitrogen does not directly determine the coupling constant.[27] Its influence is an indirect one, insofar as it is important in determining the equilibrium distance in the complex, which in turn determines the coupling constant for the equilibrium structure.

$^{2h}J_{C-N}$ for cationic complexes pyridinium···CNH, $HNCH^+$··· NCH, and H_3NH^+···CNH and for anionic complexes HCCH···$^-$NC, FCCH···$^-$NC, and NCH···$^-$NC are also reported in Table 2. Only one cationic complex, $HNCH^+$···NCH, has a C−H^+···N hydrogen bond, whereas the other two have N−H^+··· C hydrogen bonds. The intermolecular distances in these complexes are short relative to the distances in the neutral complexes, ranging from 2.974 to 2.832 Å. Values of $^{2h}J_{C-N}$ are correspondingly much greater at −22.2 and −26.5 Hz in the complexes with N−H^+···C hydrogen bonds and −40.13 Hz in HNC−H^+···NCH, which has the shortest C−N distance. The anionic complexes also have short C−N distances that range from 3.117 to 2.940 Å. C−N coupling constants for these complexes are also large, varying from −16.3 to −24.8 Hz. Figure 4 shows a plot of $^{2h}J_{C-N}$ versus the C−N distance for the six charged complexes. The trend line is quadratic, with a correlation coefficient of 0.98.

Values of $^{2h}J_{C-N}$ for the entire set of 23 complexes investigated in this work have been plotted in Figure 5 as a function of the C−N distance. Once again, the scatter in the data is evident, although a quadratic fit that has a correlation coefficient of 0.97 can be made. The variation observed is due primarily to the dependence of $^{2h}J_{C-N}$ on the bonding at the proton-donor C−H group. Nevertheless, this curve should be useful for providing estimates of C−N distances from experimentally measured C−N coupling constants.

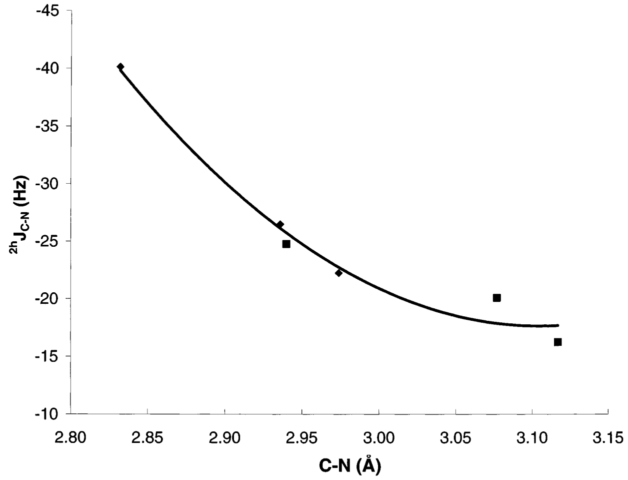

Figure 4. $^{2h}J_{C-N}$ versus the C−N distance for complexes with cations as proton donors and anions as proton acceptors. The cationic complexes include one C−H^+···N and two N−H^+···C hydrogen bonds. ◆ Cationic complexes; ■ anionic complexes.

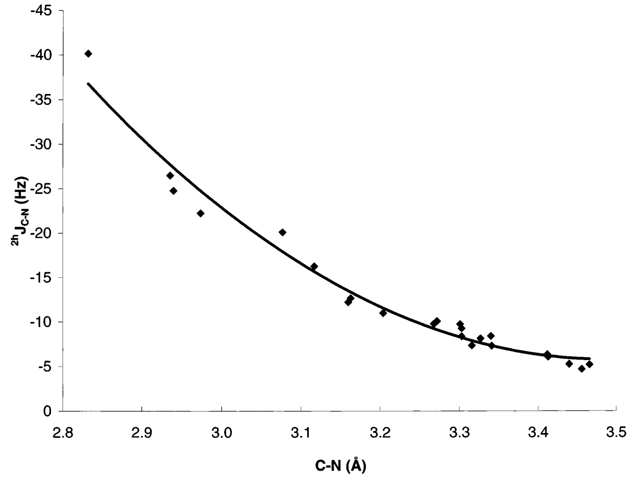

Figure 5. $^{2h}J_{C-N}$ versus the C−N distance for the entire set of neutral, cationic, and anionic complexes with C−H−N hydrogen bonds.

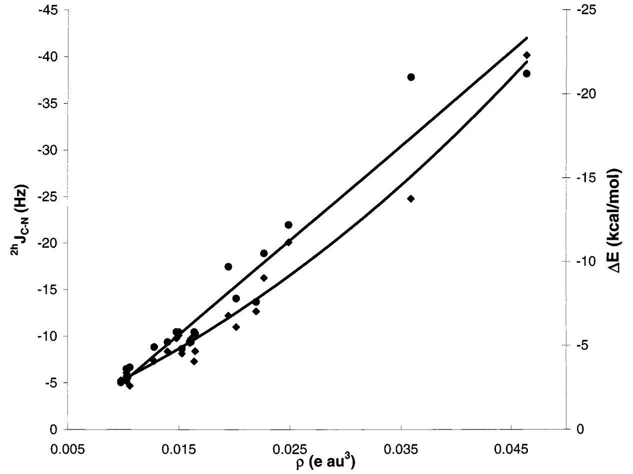

Figure 6. $^{2h}J_{C-N}$ and binding energy versus the charge density at the bond critical point for complexes stabilized by C−H···N hydrogen bonds. ◆ $^{2h}J_{C-N}$; ● binding energy.

Figure 6 shows plots of $^{2h}J_{C-N}$ and binding energy versus the charge density at the bond critical point (ρ) for the equilibrium structures of the 17 neutral complexes, 3 anionic

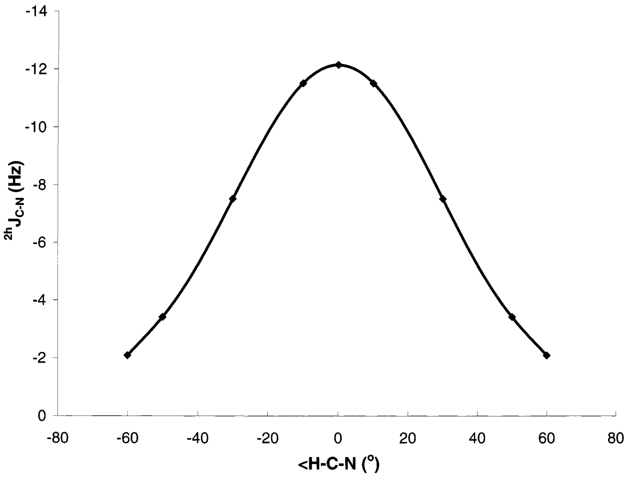

Figure 7. $^{2h}J_{C-N}$ as a function of the linearity of the hydrogen bond in the complex NCH···NCLi. An angle of 0° corresponds to a linear C−H···N bond.

complexes, and 1 cationic complex stabilized by C−H···N hydrogen bonds. Although there is scatter in the data points in both sets, the data suggest that the greater the charge density at the bond critical point, the greater the binding energy and $^{2h}J_{C-N}$. The curve shown relating binding energy to ρ is linear, with a correlation coefficient of 0.94. (The best-fit quadratic curve also has a correlation coefficient of 0.94, but the curvature is incorrect.) The curve relating $^{2h}J_{C-N}$ to ρ is quadratic, with a correlation coefficient of 0.97.

All of the complexes investigated in this study have linear C−H−N hydrogen bonds. To what extent does $^{2h}J_{C-N}$ change as the hydrogen bond becomes nonlinear? This has been investigated in the NCH···NCLi complex by removing the hydrogen-bonded H through rotation of the proton-donor NCH molecule about an axis through C and perpendicular to the C−N intermolecular line. The variation of $^{2h}J_{C-N}$ as a function of the rotational angle is plotted in Figure 7. As has been observed previously in complexes with N−H−N hydrogen bonds, small deviations of the hydrogen bond from linearity lead to relatively small decreases in $^{2h}J_{C-N}$. In this complex, a deviation of 10° reduces $^{2h}J_{C-N}$ by only 0.7 Hz. However, as evident from Figure 7, $^{2h}J_{C-N}$ decreases rapidly as the linearity of the hydrogen bond is further destroyed.

Conclusions

Ab initio EOM-CCSD calculations have been performed to determine $^{13}C-^{15}N$ spin−spin coupling constants ($^{2h}J_{C-N}$) across C−H−N hydrogen bonds in 17 neutral, 3 cationic, and 3 anionic complexes. The results of these calculations support the following statements.

(1) The contributions of the paramagnetic spin−orbit, diamagnetic spin−orbit, and spin−dipole terms to the total $^{13}C-^{15}N$ spin−spin coupling constants ($^{2h}J_{C-N}$) are negligible. $^{2h}J_{C-N}$ is determined solely by the Fermi contact term, which is distance-dependent.

(2) $^{2h}J_{C-N}$ for complexes stabilized by traditional C−H···N hydrogen bonds exhibits some dependence on the nature of the hybridization and bonding at the C of the proton-donor C−H group. Thus, the correlation between $^{2h}J_{C-N}$ and the C−N distance is not as good as that observed between $^{2h}J_{N-N}$ and the N−N distance for complexes stabilized by N−H−N hydrogen bonds.

(3) Complexes with C−H^{+}···N, N−H^{+}···C, and C−H···N^{-} hydrogen bonds have shorter C−N distances and greater C−N spin−spin coupling constants than neutral complexes stabilized by C−H···N hydrogen bonds.

(4) It is possible to construct a single curve relating $^{2h}J_{C-N}$ and C−N distances for the equilibrium structures of all of the neutral, cationic, and anionic complexes stabilized by linear C−H−N hydrogen bonds. Even though $^{2h}J_{C-N}$ shows some dependence on the type of C−H donor group, this curve should be useful for estimating C−N distances from experimental measurements of coupling constants across C−H−N hydrogen bonds.

(5) Small deviations from linearity of the C−H−N hydrogen bond lead to only small changes in $^{2h}J_{C-N}$. $^{2h}J_{C-N}$ decreases rapidly as the H−C−N angle increases.

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