

^{15}N , ^{15}N spin–spin coupling constants across $\text{N}—\text{H}—\text{N}$ and $\text{N}—\text{H}^+—\text{N}$ hydrogen bonds: can coupling constants provide reliable estimates of $\text{N}—\text{N}$ distances in biomolecules?

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Predictive quantum chemical methods based upon coupled cluster theory of spin–spin coupling constants offer a direct tool to explore a variety of questions concerning the relationship between coupling constants and intermolecular distances, molecular orientation, changes in hybridization and related issues. Of particular interest are $^{2h}J(^{15}\text{N},^{15}\text{N})$ couplings across hydrogen bonds. In this work we present EOM–CCSD coupling constants [$^{2h}J(^{15}\text{N},^{15}\text{N})$] for a series of cationic complexes stabilized by either traditional or proton-shared $\text{N}—\text{H}^+—\text{N}$ hydrogen bonds, and relate these to $^{15}\text{N},^{15}\text{N}$ coupling constants in neutral complexes with $\text{N}—\text{H}—\text{N}$ hydrogen bonds. The computed $^{15}\text{N},^{15}\text{N}$ coupling constants in these complexes vary smoothly with $\text{N}—\text{N}$ distance, regardless of the charge or the particular binding at the N atoms. We propose that the curves which show this dependence have sufficient generality that they should be useful for determining $\text{N}—\text{N}$ distances from experimentally measured coupling constants. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{15}N NMR; $^{15}\text{N},^{15}\text{N}$ spin–spin coupling constants; hydrogen bonds; $\text{N}—\text{N}$ distances

INTRODUCTION

This special issue on NMR and Hydrogen Bonds testifies to the excitement that this topic has generated and the promise that NMR holds for studies of hydrogen-bonded complexes, especially in biological systems. If current work on coupling constants can provide structural information, then we have a complement to x-ray diffraction measurements. To explore this prospect, we have applied predictive quantum chemical tools (EOM–CCSD) to obtain coupling constants across hydrogen bonds as a function of the nature of the bonded atoms, the bonding (hybridization) of these atoms, hydrogen bond type, orientation of the hydrogen-bonded species and charge distributions.

Our initial report on this work was at a meeting in Slovakia in 1998,¹ where we proposed that coupling constants could be a probe of ‘low-barrier’ hydrogen bonds. Our first paper reported $^{19}\text{F},^{19}\text{F}$ coupling constants in complexes $[\text{F}(\text{HF})_n]^{-1}$, for $n = 1–4$.² Shenderovich *et al.* had reported experimental $^{19}\text{F},^{19}\text{F}$ coupling constants for complexes with $n = 2, 3$ and 4 , and had also carried out DFT

calculations on these systems.³ Our paper demonstrated that unlike the DFT results, computed $^{19}\text{F},^{19}\text{F}$ coupling constants obtained from coupled-cluster theory are in agreement with experimental data without any rescaling of the computed values. However, to obtain this agreement it is necessary to evaluate all terms (paramagnetic spin orbit, diamagnetic spin orbit, Fermi contact and spin dipole) which may contribute to the $^{19}\text{F},^{19}\text{F}$ coupling constant. Our second paper reported results for prototypical cationic, neutral and anionic complexes with $\text{N}—\text{H}—\text{N}$, $\text{N}—\text{H}—\text{O}$ and $\text{O}—\text{H}—\text{O}$ hydrogen bonds. In that study we demonstrated the dominance of the Fermi contact term for determining J , and the distance dependence of this term.⁴ A third study focused on the $\text{ClH}:\text{NH}_3$ complex, and related Cl, N spin–spin coupling constants and anharmonic proton stretching frequencies to intermolecular distances in equilibrium structures as a function of the strength of an external electric field.⁵ Our fourth paper investigated four-bond P, P spin–spin coupling constants [$^{4h}J(^{31}\text{P},^{31}\text{P})$] across an $\text{N}—\text{H}^+—\text{N}$ hydrogen bond in the complex $[\text{H}_3\text{P}—(\text{H})\text{N}—\text{H}^+—\text{N}(\text{H})—\text{PH}_3]$,⁶ which was designed to model three experimental systems for which $^{4h}J(^{31}\text{P},^{31}\text{P})$ had been measured.⁷ The agreement between computed and experimental values was gratifying. Next, we examined N, N and O, O spin–spin coupling constants in protonated dimers stabilized by $\text{N}—\text{H}^+—\text{N}$ and $\text{O}—\text{H}^+—\text{O}$ hydrogen

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bonds,⁸ again noting the dominance of the Fermi contact term, the distance dependence of this term and the lack of correlation between the magnitude of J and the binding energy of the complex. In that study it was also noted that the nature of the bonding at the hydrogen-bonded atoms influences the value of J for the equilibrium structure of a complex by determining the intermolecular distance. In two recent studies we investigated for the first time in hydrogen-bonded complexes the effects of zero-point motion and thermal vibrational averaging on the $^{15}\text{N},^{15}\text{N}$ spin-spin coupling constant and the chemical shift of the hydrogen-bonded proton in the complex $\text{CNH}:\text{NCH}$,⁹ and on the $^{19}\text{F},^{19}\text{F}$ coupling constant in FHF^{-1} .¹⁰

In this paper, we first summarize the results of our recent study of $^{15}\text{N},^{15}\text{N}$ coupling constants across $\text{N}-\text{H}-\text{N}$ hydrogen bonds in neutral complexes,¹¹ and present new results on the variation of ${}^2hJ(^{15}\text{N},^{15}\text{N})$ as the hydrogen bond becomes non-linear or the lone pair of electrons is removed from the hydrogen bond. Finally, we will examine the distance dependence of ${}^2hJ(^{15}\text{N},^{15}\text{N})$ in cationic complexes stabilized by $\text{N}-\text{H}^+-\text{N}$ hydrogen bonds. Several other groups have investigated $^{15}\text{N},^{15}\text{N}$ spin-spin coupling constants across hydrogen bonds.¹²⁻¹⁶ Their studies were carried out using DFT or restricted MCSCF approaches, and examined $^{15}\text{N},^{15}\text{N}$ coupling constants in specific complexes, often designed to model base pairs. All of these studies agree that $^{15}\text{N},^{15}\text{N}$ couplings are strongly distance dependent. It is the application of a more sophisticated level of theory (EOM-CCSD) and the systematic examination of a wide variety of hydrogen-bonded complexes that distinguishes our work in this area.

CALCULATIONS

We evaluated $^{15}\text{N},^{15}\text{N}$ spin-spin coupling constants in a series of complexes stabilized by $\text{N}-\text{H}^+-\text{N}$ hydrogen bonds. These complexes include protonated 1,4-diazine with NCLi ($1,4\text{-diazine-H}^+:\text{NCLi}$), $\text{NH}_4^+:\text{NCLi}$, pyridine- $\text{H}^+:\text{NCLi}$, $\text{NH}_4^+:\text{NH}_3$, $\text{NH}_4^+:\text{NCH}$, $1,4\text{-diazine-H}^+:\text{NCH}$, pyridine- $\text{H}^+:\text{NCH}$ and $\text{NH}_4^+:\text{N}_2$. The structures of these complexes were optimized at second-order many-body perturbation theory [MBPT(2)]¹⁷⁻²⁰ with the $6-31+G(\text{d,p})$ basis set.²¹⁻²⁴ All of the complexes were found to be equilibrium structures on their respective potential surfaces. In addition, searches of the potential surfaces were performed in an attempt to find other minima corresponding to interchange of the proton-donor and proton-acceptor species. In all cases, the new structures converted to the equilibrium structures with no energy barrier.

Spin-spin coupling constants ${}^2hJ(^{15}\text{N},^{15}\text{N})$ were obtained from equation-of-motion coupled cluster singles and doubles (EOM-CCSD) calculations using the CI-like approximation,²⁵⁻²⁸ with the Ahlrichs (qz2p, qz2p)²⁹ basis set. This level of theory has been shown previously to produce coupling constants in excellent agreement with experimental values.²⁶ 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).^{30,31} For several complexes, all of

the terms which contribute to ${}^2hJ(^{15}\text{N},^{15}\text{N})$ were evaluated, but once again, ${}^2hJ(^{15}\text{N},^{15}\text{N})$ was found to be dominated by the Fermi-contact term, which is more than an order of magnitude greater than any other term. Therefore, in this study, ${}^2hJ(^{15}\text{N},^{15}\text{N})$ will be approximated by the Fermi contact term. Structure optimizations were carried out using the Gaussian 98 suite of programs,³² and coupling constants were evaluated using ACES II.³³ The calculations were carried out on the Cray T94 and SV1 computers at the Ohio Supercomputer Center.

RESULTS AND DISCUSSION

Coupling constants across neutral $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds

Previously we noted⁴ that the value of the $^{15}\text{N},^{15}\text{N}$ spin-spin coupling constant in $\text{CNH}:\text{NCH}$ at an $\text{N}-\text{N}$ distance of 2.90 Å is in agreement with the coupling constant measured experimentally at this distance in $\text{A}-\text{U}$ and $\text{G}-\text{C}$ base pairs.³⁴ This suggests that the $^{15}\text{N},^{15}\text{N}$ coupling constant might be independent of the bonding at the nitrogens, so we assessed this possibility by studying a series of complexes which display different nitrogen bonding. Previously we reported¹¹ the distance dependence of ${}^2hJ(^{15}\text{N},^{15}\text{N})$ for four complexes, pyrrole: NCH (C_{2v}), $\text{CNH}:\text{NCH}$ (C_{00v}), $\text{CNH}:\text{NH}_3$ (C_{3v}), and $\text{CNH}:\text{NCLi}$ (C_{00v}), and the value of ${}^2hJ(^{15}\text{N},^{15}\text{N})$ for the equilibrium structure of $\text{CNH}:\text{pyridine}$. These complexes have sp and sp^2 nitrogens as proton donors, and sp , sp^2 and sp^3 nitrogens as proton acceptors. Each complex is stabilized by a traditional $\text{N}-\text{H}\cdots\text{N}$ hydrogen bond³⁵ and the hydrogen-bonding $\text{N}-\text{N}$ axis is a symmetry axis for the complex. Figure 1 shows the distance dependence of ${}^2hJ(^{15}\text{N},^{15}\text{N})$ for the four complexes, and the value of ${}^2hJ(^{15}\text{N},^{15}\text{N})$ for $\text{CNH}:\text{pyridine}$ at its equilibrium geometry. It is apparent from Fig. 1 that these curves are similar, and only slightly displaced from one another, even though the values of ${}^2hJ(^{15}\text{N},^{15}\text{N})$ for the equilibrium structures of these complexes differ significantly. Creating a new plot of coupling constants for only the equilibrium $\text{N}-\text{N}$ distances (reported in Table 1, and plotted in Fig. 2) in these complexes allows for the separation of the indirect effect of the type of bonding at the nitrogen from the distance dependence of the coupling constant.

The striking feature about Fig. 2 is the smooth variation of ${}^2hJ(^{15}\text{N},^{15}\text{N})$ with $\text{N}-\text{N}$ distance. The value of ${}^2hJ(^{15}\text{N},^{15}\text{N})$ obtained from this curve at a distance of 2.90 Å is 7.4 Hz, in good agreement with the value obtained from the model

Table 1. $\text{N}-\text{N}$ distances and $^{15}\text{N},^{15}\text{N}$ spin-spin coupling constants [${}^2hJ(^{15}\text{N},^{15}\text{N})$] in equilibrium structures of neutral complexes stabilized by traditional $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds^a

Complex	Symmetry	$\text{N}-\text{N}$ (Å)	${}^2hJ(^{15}\text{N},^{15}\text{N})$ (Hz)
$\text{CNH}:\text{pyridine}$	C_{2v}	2.79	10.7
$\text{CNH}:\text{NCLi}$	C_{00v}	2.83	9.6
$\text{CNH}:\text{NH}_3$	C_{3v}	2.85	8.7
$\text{CNH}:\text{NCH}$	C_{00v}	3.00	5.5
$\text{Pyrrole}:\text{NCH}$	C_{2v}	3.16	3.0

^a Data taken from Ref. 11.

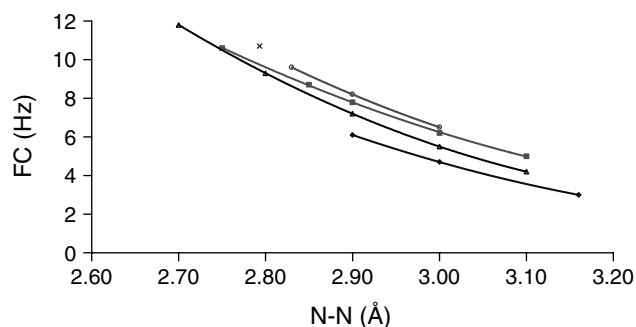


Figure 1. The Fermi-contact term (FC, Hz) versus the N—N distance (Å) in complexes stabilized by traditional N—H···N hydrogen bonds, taken from Ref. 11. To generate these curves, all intramolecular coordinates were held fixed at their optimized values, and only the N—N distance was varied. ◆ Pyrrole : NCH; ▲ CNH : NCH; ■ CNH : NH₃; ● CNH : NCLi; ×, CNH : pyridine.

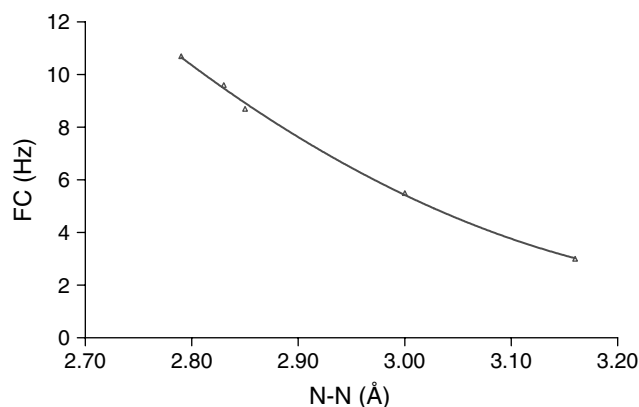


Figure 2. Fermi-contact term (FC, Hz) versus the N—N distance (Å) in complexes with traditional N—H···N hydrogen bonds. The points represent the value of the Fermi contact term at the equilibrium geometry of each complex listed in Table 1. Data taken from Ref. 11.

CNH:NCH complex, and with the experimental value measured for A–U and G–C. Figure 1 suggests that $^{15}\text{N}, ^{15}\text{N}$ coupling constants are not very sensitive to the hybridization of the nitrogens, but Fig. 2 indicates that the bonding at the nitrogen has an indirect effect since it determines the equilibrium intermolecular N—N distance, and $^2hJ(^{15}\text{N}, ^{15}\text{N})$ is very dependent on this distance. Therefore, we present Fig. 2 as a first approximation for obtaining intermolecular N—N distances in complexes with neutral N—H···N hydrogen bonds from experimentally measured coupling constants, and propose that tests be conducted.

In each of the complexes listed in Table 1, the hydrogen bond is linear and the lone pair of electrons on the proton-acceptor N lies along the N—N axis and is directed toward the proton donor NH (the 'directed' lone pair). This raises the question of how sensitive the coupling constant might be to structural changes which distort the hydrogen bond from linearity, or remove the directed lone pair. We address these questions in the model complex CNH:NCH. Non-linearity of the hydrogen bond is introduced through a rotation of the proton-donor CNH molecule about an axis through

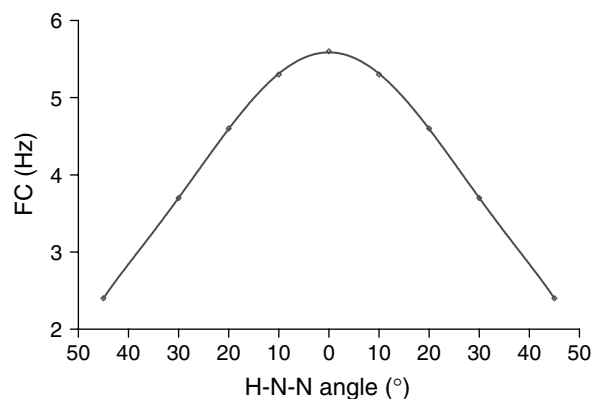


Figure 3. Variation of $^2hJ(^{15}\text{N}, ^{15}\text{N})$ in CNH : NCH as a function of the linearity of the hydrogen bond. An angle of 0° corresponds to a linear N—H···N hydrogen bond.

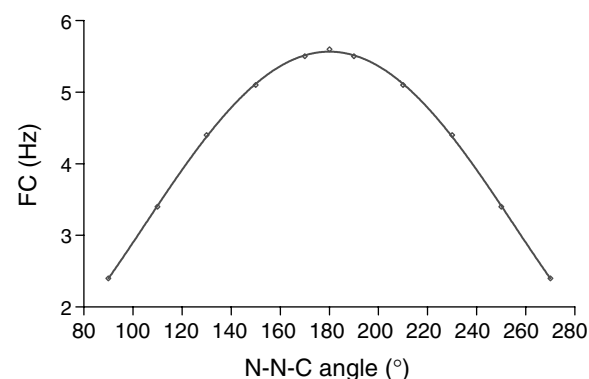


Figure 4. Variation of $^2hJ(^{15}\text{N}, ^{15}\text{N})$ with the directionality of the lone pair of electrons on the proton-acceptor N. An angle of 180° corresponds to a linear N—H···NCH arrangement.

the proton-donor N and perpendicular to the N—N line. Changing the directionality of the lone pair is achieved by rotating the proton-acceptor molecule about an axis through the proton-acceptor N and perpendicular to the N—N line. Except for the intermolecular rotational angles, all other distances and angles are held constant at their equilibrium values. Figures 3 and 4 show the changes in $^2hJ(^{15}\text{N}, ^{15}\text{N})$ as a function of these intermolecular rotations. It is apparent from these figures that small deviations from linearity of the hydrogen bond, or from directionality of the lone pair, lead to only small changes in the $^{15}\text{N}, ^{15}\text{N}$ coupling constant. Larger deviations, which would result in significant destabilization of the hydrogen-bonded complex, also lead to significant decreases in $^2hJ(^{15}\text{N}, ^{15}\text{N})$. These results are consistent with the findings for $[\text{CN} \cdots \text{H} \cdots \text{NC}]^{-1}$ reported in Ref. 14.

Coupling constants across N—H⁺—N hydrogen bonds

The complexes investigated in this study, namely 1,4-diazine-H⁺:NCLi, NH₄⁺:NCLi, pyridine-H⁺:NCLi, NH₄⁺:NH₃, NH₄⁺:NCH, 1,4-diazine-H⁺:NCH, pyridine-H⁺:NCH and NH₄⁺:N₂, are stabilized by N—H⁺—N hydrogen bonds. Four of these complexes have sp²-hybridized nitrogens as proton donors, and four have sp³-hybridized nitrogens. The proton-acceptor nitrogens in seven of these complexes are sp

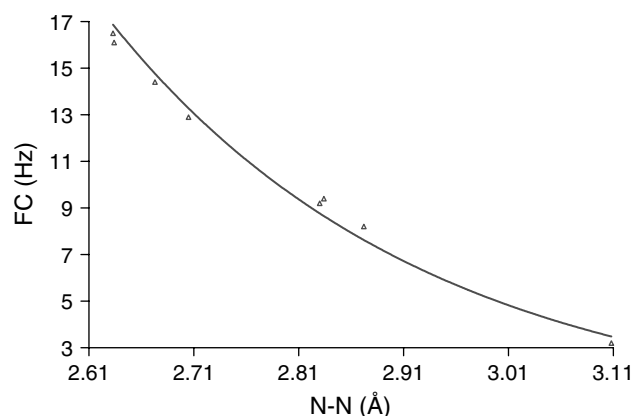
Table 2. N—N and N—H distances and $^{15}\text{N},^{15}\text{N}$ spin–spin coupling constants [$^2hJ(^{15}\text{N},^{15}\text{N})$] in equilibrium structures of cationic complexes stabilized by N—H⁺—N hydrogen bonds

Complex	Symmetry	N—N (Å)	N—H (Å)	$^2hJ(^{15}\text{N},^{15}\text{N})$ (Hz)
1,4-Diazine-H ⁺ :NCLi	C _{2v}	2.633	1.095	16.5
NH ₄ ⁺ :NCLi	C _{3v}	2.634	1.107	16.1
Pyridine-H ⁺ :NCLi	C _{2v}	2.673	1.075	14.4
NH ₄ ⁺ :NH ₃	C _{3v}	2.705	1.113	12.9
NH ₄ ⁺ :NCH	C _{3v}	2.830	1.049	9.2
1,4-Diazine-H ⁺ :NCH	C _{2v}	2.834	1.042	9.4
Pyridine-H ⁺ :NCH	C _{2v}	2.872	1.036	8.2
NH ₄ ⁺ :N ₂	C _{3v}	3.108	1.029	3.2

hybridized, and one complex has an sp³-hybridized nitrogen. The N—N and N—H distances in the equilibrium structures are reported in Table 2, which lists the complexes in order of increasing N—N distance. The N—N distances cover a wide range, from 2.633 to 3.108 Å, while the hydrogen-bond N—H distances also vary significantly from 1.029 to 1.113 Å. Based on the N—N and N—H distances, the hydrogen bond in N₂H₇⁺ can be classified as proton-shared, but it is not symmetric.³⁵ The hydrogen bonds in 1,4-diazine-H⁺:NCLi, NH₄⁺:NCLi and pyridine-H⁺:NCLi also exhibit proton-shared character with short N—N distances and longer N—H distances relative to the proton-donor cation. The remaining complexes are stabilized by traditional hydrogen bonds, with longer N—N distances and N—H distances only slightly elongated relative to the isolated proton donor. Table 2 lists the computed $^{15}\text{N},^{15}\text{N}$ spin–spin coupling constants for these complexes, which range from 3.2 to 16.5 Hz.

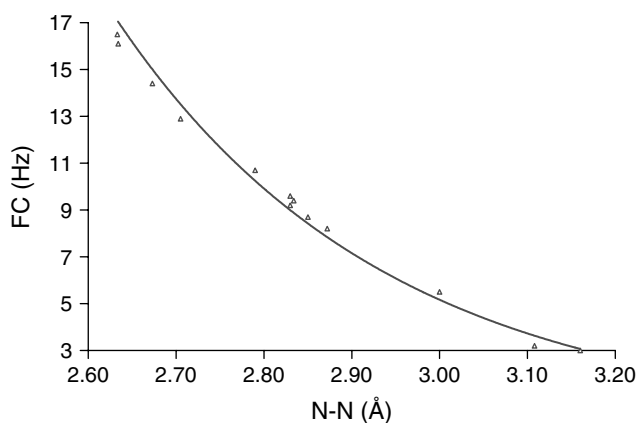
Can we anticipate a correlation between $^{15}\text{N},^{15}\text{N}$ spin–spin coupling constants across N—H⁺—N hydrogen bonds and N—N distances, as in the neutral species? Analogous to Fig. 2, Fig. 5 shows the computed $^{15}\text{N},^{15}\text{N}$ spin–spin coupling constants, estimated from the Fermi contact term, for the equilibrium structures of the cationic complexes plotted against the equilibrium N—N distances. It is apparent from Fig. 5 that $^2hJ(^{15}\text{N},^{15}\text{N})$ varies smoothly with the N—N distance over a range of 0.5 Å. Given the variation in the nature of the proton-donor ions and proton-acceptor molecules, and that proton-shared as well as traditional N—H⁺—N hydrogen bonds have been included, the correlation is good.

It is apparent from Tables 1 and 2 that the equilibrium distances in neutral and cationic complexes with traditional hydrogen bonds extend over the same range, from about 2.8 to 3.2 Å. The shorter N—N distances between 2.6 and 2.7 Å are found in the cationic complexes in which the hydrogen bonds have proton-shared character. Do the coupling constants in the neutral and cationic complexes exhibit a similar distance dependence? Figure 6 shows $^2hJ(^{15}\text{N},^{15}\text{N})$ plotted against the N—N distance for the set of 13 neutral and cationic complexes. This plot suggests that the variation of $^2hJ(^{15}\text{N},^{15}\text{N})$ with N—N distance is essentially independent of the charge on the complex. The $^{15}\text{N},^{15}\text{N}$ spin–spin coupling constant obtained from this curve at an N—N distance of 2.90 Å is about 7.3 Hz, in remarkably good agreement with the value from Fig. 2 for the

**Figure 5.** Fermi-contact term (FC, Hz) versus the N—N distance (Å) for complexes with N—H⁺—N hydrogen bonds. The points represent the value of the Fermi contact term at the equilibrium geometry of each complex listed in Table 2.

neutral complexes, and with the experimentally measured value for A—U and G—C. It is proposed that the curve in Fig. 6 will be useful for determining N—N distances from coupling constants measured in hydrogen-bonded complexes stabilized by either N—H—N or N—H⁺—N hydrogen bonds.

Having emphasized the generality of the correlation between $^{15}\text{N},^{15}\text{N}$ spin–spin coupling constants and N—N

**Figure 6.** Fermi-contact term (FC, Hz) versus the N—N distance (Å) for the two sets of complexes with N—H—N and N—H⁺—N hydrogen bonds.

distances for a number of situations, we must note that an entire set of complexes has been omitted from these plots. All of the complexes listed in Table 2 have proton-donor nitrogens which are sp^2 or sp^3 hybridized. All complexes satisfy the condition that the hydrogen-bonding N—N axis is a local rotational axis for the proton-donor ion and the proton-acceptor molecule. This constraint insures that the hydrogen bond is linear, and that the lone pair of electrons on the proton-acceptor molecule lies along the N—N axis. However, no complexes with sp hybridized nitrogens as proton donors in $\text{N—H}^+—\text{N}$ hydrogen bonds were included in this study even though they would satisfy this constraint. Why have these been omitted? First, the equilibrium structures of some of these ($\text{HCNH}^+ : \text{NCH}$ and $\text{NNH}^+ : \text{NN}$) have symmetric hydrogen bonds, and consequently very large ^{15}N , ^{15}N spin-spin coupling constants. At a given distance, coupling constants across symmetric hydrogen bonds tend to be larger than coupling constants across non-symmetric hydrogen bonds. If complexes with sp -hybridized nitrogens as proton donors had been included, the correlation between ${}^{2h}J(^{15}\text{N}, ^{15}\text{N})$ and N—N distance would not be as good as shown in Figs 5 and 6. Finally, our intent is to provide data which may be useful for correlating experimental values of ${}^{2h}J(^{15}\text{N}, ^{15}\text{N})$ with N—N distances in biological systems, and sp -hybridized nitrogens are not generally important in such systems.

CONCLUSIONS

EOM-CCSD calculations were performed to determine spin-spin coupling constants [${}^{2h}J(^{15}\text{N}, ^{15}\text{N})$] across N—H—N and $\text{N—H}^+—\text{N}$ hydrogen bonds in a series of neutral and cationic complexes as a function of the distance between the nitrogens. All of these complexes are stabilized by linear hydrogen bonds formed with a directed lone pair of electrons on the proton-acceptor nitrogen. The neutral complexes are stabilized by traditional hydrogen bonds, while the cationic complexes are stabilized by either traditional or proton-shared hydrogen bonds. The computed coupling constants in these complexes are dependent upon, and vary smoothly with, N—N distance. This suggests that the curve for the distance dependence of ${}^{2h}J(^{15}\text{N}, ^{15}\text{N})$ should be useful for extracting N—N distances to an accuracy of about 0.05 Å, from experimental ^{15}N , ^{15}N coupling constants. Small deviations of the hydrogen bond from linearity, or perturbations which remove the directed lone pair, result in small changes in ${}^{2h}J(^{15}\text{N}, ^{15}\text{N})$. These small changes could be estimated from the orientation dependence shown in Figs 3 and 4, perhaps further improving estimates of distances. We do not claim that a single J versus distance curve will be valid for all X—H—Y hydrogen bonds, but for $\text{X}, \text{Y} = \text{N}$, the curves are insensitive to most bonding patterns. Other X—H—Y systems are currently being investigated. Having first-principle predictive theoretical tools for coupling constants makes it possible to provide reliable information in the absence of controlled experiments.

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