

## N–N Spin–Spin Coupling Constants [ ${}^2hJ(^{15}\text{N}–^{15}\text{N})$ ] Across N–H $\cdots$ N Hydrogen Bonds in Neutral Complexes: To What Extent Does the Bonding at the Nitrogens Influence ${}^2hJ_{\text{N–N}}$ ?

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In recent years there has been significant interest in and excitement about NMR spin–spin coupling constants across X–H–Y hydrogen bonds.<sup>1–14</sup> This interest is related to the potential usefulness of coupling constants for structure determination, particularly in biological systems. Recently, Dingley and Grzesiek obtained a value of about 7 Hz for N–N coupling constants [ ${}^2hJ(^{15}\text{N}–^{15}\text{N})$ ] across N–H $\cdots$ N hydrogen bonds in the adenine–uracil (A–U) and guanine–cytosine (G–C) base pairs.<sup>5</sup> They noted that  ${}^2hJ_{\text{N–N}}$  for A–U was greater than G–C, and that this correlates with the shorter N–N distance in A–U. In a recent paper,<sup>12</sup> we reported N–N, N–O, and O–O coupling constants for a series of model cationic, neutral, and anionic hydrogen-bonded complexes. We observed that total  $J$  is dominated by the Fermi-contact term, and that this term is distance dependent. Using CNH $\cdots$ NCH as a model for an N–H $\cdots$ N hydrogen bond in a neutral complex, we computed a value of 7.2 Hz for  ${}^2hJ_{\text{N–N}}$  at an N–N distance of 2.90 Å, in good agreement with the experimentally measured values in A–U and G–C.<sup>5</sup> This suggests that the N–N coupling constant may not be sensitive to the type of covalent bonding at the nitrogen. It is the purpose of the present paper to examine computed N–N coupling constants in a group of complexes with different N–H donor and N acceptor molecules in which the bonding and therefore the hybridization of the nitrogens varies, and to determine how changes in the nitrogen environment influence coupling constants.

The structures of the complexes CNH $\cdots$ pyridine, CNH $\cdots$ NCLi, CNH $\cdots$ NH<sub>3</sub>, CNH $\cdots$ NCH, and pyrrole:NCH and the corresponding monomers were optimized at second-order many-body perturbation theory [MBPT(2) = MP2]<sup>15–18</sup> with the 6-31+G-

**Table 1.** N–N Equilibrium Distances [ $R_{\text{e}}(\text{N}–\text{N})$ , Å],  ${}^{15}\text{N}–^{15}\text{N}$  Spin–Spin Coupling Constants ( ${}^2hJ_{\text{N–N}}$ , Hz), and Binding Energies ( $\Delta E_{\text{e}}$ , kcal/mol) in Complexes with N–H $\cdots$ N Hydrogen Bonds

complex	symmetry	$R_{\text{e}}(\text{N}–\text{N})$	${}^2hJ_{\text{N–N}}^a$	$\Delta E_{\text{e}}$
pyrrole:NCH	$C_{2v}$	3.16	3.0	–5.3
CNH:NCH	$C_{\infty v}$	3.00	5.5	–7.6
CNH:NH <sub>3</sub>	$C_{3v}$	2.85	8.7	–12.8
CNH:NCLi	$C_{\infty v}$	2.83	9.6	–14.6
CNH:pyridine	$C_{2v}$	2.79	10.7	–25.9

<sup>a</sup>  ${}^2hJ_{\text{N–N}}$  estimated from the Fermi-contact term.

(d,p) basis set<sup>19–22</sup> under the symmetry constraints indicated in Table 1. Harmonic vibrational frequencies were computed to confirm that each complex is an equilibrium structure (no imaginary frequencies) on the intermolecular surface. The coupling constants  ${}^2hJ_{\text{N–N}}$  were obtained from equation-of-motion coupled cluster singles and doubles (EOM-CCSD) calculations using the configuration interaction (CI-like) approximation,<sup>23–26</sup> a level of theory that produces quantitatively accurate coupling constants (without rescaling) when compared to experimentally measured values. These calculations were carried out using Ahlrichs<sup>27</sup> qzpq basis set on N, C, and O atoms, tzp1 on Li, qz2p on the hydrogen-bonded proton, and Dunning's cc-pVDZ basis set on all other hydrogens.<sup>28,29</sup> For CNH $\cdots$ NCH all terms (paramagnetic spin–orbit, diamagnetic spin–orbit, Fermi contact, and spin dipole) which contribute to  ${}^2hJ_{\text{N–N}}$  were evaluated, and once again it was observed that terms other than the Fermi-contact are negligible,<sup>12,13</sup> with values less than 0.1 Hz at all distances. Therefore, in this study total  $J$  has been estimated solely from the Fermi contact term. The structures of monomers and complexes were optimized using Gaussian 98,<sup>30</sup> and NMR  ${}^{15}\text{N}–^{15}\text{N}$  spin–spin coupling constants were computed using ACES II.<sup>31</sup> All calculations were carried out on the SGI-Origin and Cray SV1 computers at the Ohio Supercomputer Center.

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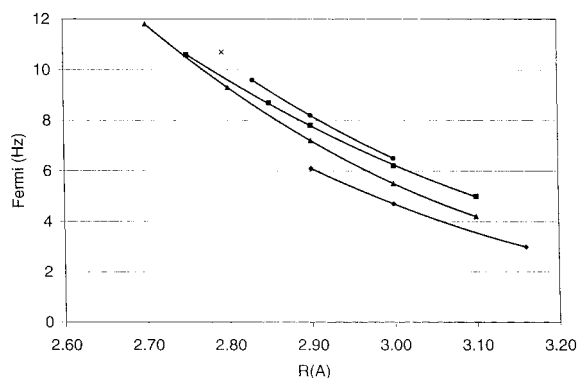
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**Table 2.** N–N Distances [ $R(\text{N–N})$ , Å] and  $^{15}\text{N–}^{15}\text{N}$  Spin–Spin Coupling Constants ( $^2hJ_{\text{N–N}}$ , Hz) in Hydrogen-Bonded Complexes with N–H···N Hydrogen Bonds

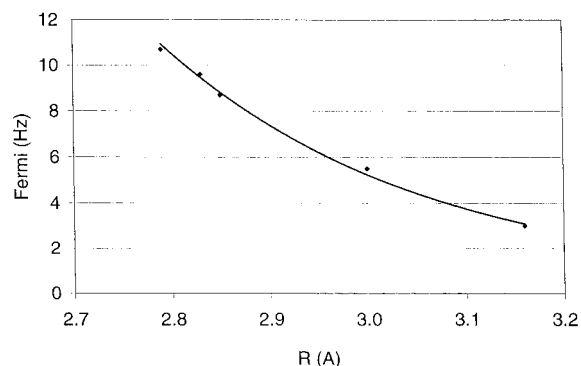
complex	$R(\text{N–N})$	$^2hJ_{\text{N–N}}^a$	complex	$R(\text{N–N})$	$^2hJ_{\text{N–N}}^a$
pyrrole:NCH	2.90	6.1	CNH:NH <sub>3</sub>	2.75	10.6
	3.00	4.7		2.85	8.7
	3.16	3.0		2.90	7.8
CNH:NCH	2.70	11.8	CNH:NCLi	3.00	6.2
	2.80	9.3		3.10	5.0
	2.90	7.2		2.83	9.6
	3.00	5.5		2.90	8.2
	3.10	4.2		3.00	6.5
			CNH:pyridine	2.79	10.7

<sup>a</sup>  $^2hJ_{\text{N–N}}$  estimated from the Fermi-contact term.

**Figure 1.** The Fermi-contact term contribution to  $^2hJ_{\text{N–N}}$  versus the N–N distance. ◆: Pyrrole:NCH; ▲: CNH:NCH; ■: CNH:NH<sub>3</sub>; ●: CNH:NCLi; ×: CNH:pyridine.

The symmetries, equilibrium intermolecular N–N distances, binding energies, and  $^{15}\text{N–}^{15}\text{N}$  spin–spin coupling constants estimated from the Fermi-contact term for the complexes pyrrole:NCH, CNH:NCH, CNH:NH<sub>3</sub>, CNH:NCLi, and CNH:pyridine are reported in Table 1. The nitrogen proton-donor molecules include an  $\text{sp}^2$  hybridized nitrogen (pyrrole) and an  $\text{sp}$  hybridized nitrogen (HNC). The proton-acceptor molecules include nitrogens which are  $\text{sp}^3$  hybridized (NH<sub>3</sub>),  $\text{sp}^2$  hybridized (pyridine), and  $\text{sp}$  hybridized (HCN and LiCN). The equilibrium structures of all complexes are stabilized by traditional<sup>32</sup> N–H···N hydrogen bonds which are linear, and the intermolecular N–N axis coincides with the principal rotational axes of the proton-donor and proton-acceptor molecules. This implies that the proton-donor and proton-acceptor nitrogens are symmetrically bonded with respect to the intermolecular hydrogen-bonding axis. Table 2 presents values of the Fermi contact term for these complexes as a function of the N–N distance. These data are shown graphically in Figure 1.

It is apparent from Table 2 and Figure 1 that the Fermi contact term is dependent on the intermolecular N–N distance and that the curves for each complex in Figure 1 are similar. Because of the computational demands of computing the Fermi-contact term for CNH:pyridine, only a single point corresponding to the equilibrium N–N distance was obtained. Although the curves in Figure 1 are not superimposable, they are only slightly displaced from one another. That is, there is only a small variation in the value of  $^2hJ_{\text{N–N}}$  for a given N–N distance among these complexes. For example, at a distance of 2.90 Å, the Fermi-contact term is 6.1, 7.2, and 8.2 Hz in pyrrole:NCH, CNH:NCH, and CNH:NCLi, respectively. The four curves in Figure 1 are ordered such that

**Figure 2.** The Fermi-contact term versus the N–N distance. The points represent the value of the Fermi-contact term at the equilibrium geometry of each complex.

the curve corresponding to the complex with the longest equilibrium N–N distance (pyrrole:NCH) is at the bottom. The higher curves are in the order CNH:NCH, CNH:NH<sub>3</sub>, and CNH:NCLi, which is the order of decreasing N–N distance in the equilibrium structures.

Since the distance dependence of  $J$  is not very sensitive to the bonding at the nitrogen, using CNH:NCH as a model for computing  $^2hJ_{\text{N–N}}$  for A–U and G–C at the N–N distance in the base pairs yielded coupling constants in agreement with experimental values.<sup>12</sup> However, it is apparent from Table 1 that the bonding at the nitrogens is important in determining the binding energy of the complex, the equilibrium intermolecular N–N distance, and therefore the  $^{15}\text{N–}^{15}\text{N}$  spin–spin coupling constant for that complex. As the binding energy increases, the intermolecular distance decreases, and the spin–spin coupling constant increases. Figure 2 shows a plot of the  $^{15}\text{N–}^{15}\text{N}$  Fermi-contact term versus the N–N distance. The points are the equilibrium values for each complex. Two observations can be made from this curve.

(1) The relationship between the  $^{15}\text{N–}^{15}\text{N}$  spin–spin coupling constant across the hydrogen bond and the equilibrium intermolecular N–N distance holds for all complexes, irrespective of the hybridization of the nitrogen in the proton-donor and proton-acceptor molecules, that is, irrespective of the bonding at the nitrogens. The points for the five complexes can be fitted by the same curve. The N–N spin–spin coupling constant obtained from this curve at a distance of 2.90 Å is 7.4 Hz, in agreement with the experimental value for the A–U and G–C base pairs, and with the value previously predicted from the model complex CNH···NCH.

(2) The hybridization and nature of the covalent bonding at the nitrogens determine the proton-donating and proton-accepting abilities of the hydrogen-bonded molecules, which in turn, determine binding energies and intermolecular distances for these complexes. As a result,  $^{15}\text{N–}^{15}\text{N}$  spin–spin coupling constants across hydrogen bonds can be used to determine equilibrium intermolecular distances and relative binding energies for neutral complexes with traditional N–H···N hydrogen bonds.

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