Systematic ab Initio Study of ^{15}N−^{15}N and ^{15}N−^{1}H Spin−Spin Coupling Constants Across N−H^{+}−N Hydrogen Bonds: Predicting N−N and N−H Coupling Constants and Relating Them to Hydrogen Bond Type

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A systematic ab initio EOM-CCSD study of ^{15}N−^{15}N and ^{15}N−^{1}H spin−spin coupling constants has been carried out for a series of complexes formed from 11 nitrogen bases with experimentally measured proton affinities. When these complexes are arranged in order of increasing proton affinity of the proton-acceptor base and, for each proton acceptor, increasing order of proton affinity of the protonated N−H donor, trends in distances and signs of coupling constants are evident that are indicative of the nature of the hydrogen bond. All two-bond spin−spin coupling constants ($^{2h}J_{N-N}$) are positive and decrease as the N−N distance increases. All one-bond N−H coupling constants ($^{1}J_{N-H}$) are negative ($^{1}K_{N-H}$ are positive). $^{1}J_{N-H}$ is related to the N−H distance and the hybridization of the donor N atom. One-bond H···N coupling constants ($^{1h}J_{H-N}$) are positive ($^{1h}K_{H-N}$ are negative) for traditional hydrogen bonds, but $^{1h}J_{H-N}$ becomes negative when the hydrogen bond acquires sufficient proton-shared character. The N−N and H···N distances at which $^{1h}J_{H-N}$ changes sign are approximately 2.71 and 1.62 Å, respectively. Predictions are made of the values of $^{2h}J_{N-N}$ and $^{1}J_{N-H}$, and the signs of $^{1h}J_{H-N}$, for those complexes that are too large for EOM-CCSD calculations.

Introduction

The first experimental measurement of two-bond spin−spin coupling constants was reported by Dingley and Greziek in 1998,[1] and marked the beginning of both theoretical and experimental studies of two-bond spin−spin coupling constants across hydrogen bonds. Some of these studies are summarized in recent review articles.[2−10] In two early papers,[11,12] we examined spin−spin coupling constants across N−H−N and N−H^{+}−N hydrogen bonds in small neutral and cationic complexes using ab initio equation-of-motion coupled-cluster techniques. In these and subsequent papers, we have demonstrated the ability of such calculations to provide values of coupling constants in agreement with experiment and have used these data to provide insight into the experimental findings.[13−15] Moreover, we have been able to make generalizations about the signs of one- and two-bond reduced coupling constants and relate these to hydrogen bond type.[16−18]

In the present paper we have significantly expanded our study of N−N and N−H coupling constants across N−H^{+}−N hydrogen bonds in cationic complexes. Eleven nitrogen bases with known experimental proton affinities were selected, and using these bases, the 66 possible protonated complexes with N−H^{+}−N hydrogen bonds were formed. It is expected that because these bases hydrogen bond and protonate at the same site, the base with the lower protonation energy will be the proton acceptor in the hydrogen-bonded complex.[19] Therefore, the 66 complexes have been grouped according to increasing protonation energy of the proton-acceptor nitrogen base and, for a given proton acceptor, increasing protonation energy of the proton donor. Using this systematic grouping facilitates examining both one- and two-bond coupling constants as a function of changing hydrogen bond type. In this paper we report computed one-bond ($^{1}J_{N-H}$ and $^{1h}J_{H-N}$) and two-bond ($^{2h}J_{N-N}$) coupling constants, examine them as a function of hydrogen-bond type, develop equations that correlate coupling constants with corresponding distances, and use these to predict coupling constants for larger complexes for which EOM-CCSD calculations are not feasible.

Methods

The structures of all monomers and hydrogen-bonded complexes were optimized at second-order Møller−Plesset perturbation theory (MP2)[20−23] with the 6-31+G(d,p) basis set.[24−27] Vibrational frequencies were computed to verify that each complex is an equilibrium structure on its potential energy surface. Spin−spin coupling constants were computed using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the CI (configuration interaction)-like approximation,[28−31] with the Ahlrichs[32] qzp basis set on C, N, and F atoms, and the qz2p basis set on the hydrogen-bonded hydrogen atom. The Dunning cc-pVDZ basis set[33,34] was placed on all other hydrogens. In the nonrelativistic approximation, the total coupling constant (J) is a sum of four contributions: the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi-contact (FC), and spin-dipole (SD) terms.[35] For some complexes, the calculation of all terms is not feasible, so the FC term has been used to approximate J. Previous studies of N−N and N−H coupling across N−H−N hydrogen bonds provide justification for this approximation.[11,12] Geometry optimizations were carried out using the Gaussian 03 suite of programs,[36] and coupling constants were evaluated using ACES II.[37] All calculations were performed on the Cray X1 or the Itanium Cluster at the Ohio Supercomputer Center.

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TABLE 1: Computed Electronic Protonation Energies and Experimental Proton Affinities (kcal/mol) of Nitrogen Bases[a]

base	$-\Delta H^{298\ b}$	$-\Delta E_e$
1. N_2	118.0	121.6
2. F_3N	132.5[c]	136.3
3. $N\equiv C-C\equiv N$	161.3	160.3
4. $F-C\equiv N$	168.9[d]	167.6
5. $H-C\equiv N$	170.4	178.1
6. $H-C\equiv C-C\equiv N$	179.5	183.4
7. $H_3C-C\equiv N$	186.2	189.8
8. 1,3,5-triazine	202.9	204.9
9. H_3N	204.0	214.7
10. pyrazine	209.6	216.5
11. pyridine	222.	229.6

[a] The electronic protonation energy, like the proton affinity, is defined as the negative of the energy for the reaction $B + H^+ \rightarrow BH^+$. [b] Experimental data from the NIST website, ref 38, except where noted. [c] Reference 39. [d] Reference 40.

Results and Discussion

Proton Affinities of Nitrogen Bases. Table 1 reports the computed MP2/6-31+G(d,p) electronic proton affinities ($-\Delta E_e$) of the 11 bases used to form the hydrogen-bonded complexes, and the corresponding experimental proton affinities ($-\Delta H^{298}$).[38−40] Because a higher level of theory than MP2/6-31+G(d,p) is needed to obtain computed proton affinities which are in better agreement with experimental values, only electronic protonation energies are reported in Table 1. The computed protonation energies are greater than the experimental proton affinities except for NC−CN and F−CN, which are lower by 1 kcal/mol. The computed protonation energies will be lowered when the sum of zero-point and thermal corrections are made to convert $-\Delta E_e$ to $-\Delta H^{298}$. Nevertheless, a linear relationship (with a correlation coefficient of 0.990) exists between the computed electronic protonation energies and the experimental proton affinities.

Structures of Hydrogen-Bonded Complexes. Table 2 provides N−N, N_d−H, and H−N_a distances for the equilibrium structures of the 66 hydrogen-bonded complexes with $N_d-H^+-N_a$ hydrogen bonds that can be formed from the 11 bases listed in Table 1. In this notation, N_d−H is the shorter N−H distance (N_d−H is the proton donor) and N_a is the proton acceptor. In Table 2, nonsymmetric hydrogen bonds are designated $N-H^+\cdots N$, whereas symmetric hydrogen bonds are indicated as $N\cdots H^+\cdots N$. The listing of complexes in Table 2 is in order of increasing computed protonation energy. Thus, the first group of complexes are those formed from the weakest base, N_2. The first complex is the protonated N_2 dimer ($NN\cdots H^+\cdots NN$), which has a symmetric $N\cdots H^+\cdots N$ hydrogen bond. The next 10 complexes have N_2 as the proton acceptor, consistent with the fact that the hydrogen-bonded proton is covalently bonded to the stronger base, and are listed in order of increasing protonation energy of the nitrogen base that acts as the proton donor. The first group of complexes illustrates quite well that as the difference between the protonation energies of the two bases increases, the N−N distance tends to increase while the N_d−H distance decreases. This indicates that, in general, as the difference between the proton affinities of the hydrogen-bonded nitrogen bases increases, the hydrogen bond loses proton-shared character and acquires characteristics typical of a traditional $N-H^+\cdots N$ hydrogen bond. Such structural changes have a significant influence on both one- and two-bond N−N and N−H coupling constants, as will be evident from the discussion below. Following the 11 complexes with N_2 are the 10 complexes with NF_3, followed by the 9 complexes with NCCN, and so on. In all of these complexes, the proton donor (N_d) is the base with the greater computed protonation energy.

TABLE 2: N−N and N−H Distances (Å) for Complexes with $N_d-H^+-N_a$ Hydrogen Bonds[a]

complex	N−N	N_d−H	H−N_a
1. $N_2\cdots H^+\cdots N_2$ ($D_{\infty h}$)	2.550	1.275	1.275
2. $F_3N-H^+\cdots N_2$	2.756	1.084	1.672
3. $F-C\equiv N-H^+\cdots N_2$	2.784	1.048	1.736
4. $N\equiv C-C\equiv N-H^+\cdots N_2$	2.776	1.051	1.725
5. $H-C\equiv N-H^+\cdots N_2$	2.815	1.044	1.771
6. $H-C\equiv C-C\equiv N-H^+\cdots N_2$	2.864	1.033	1.831
7. $H_3C-C\equiv N-H^+\cdots N_2$	2.882	1.031	1.851
8. 1,3,5-triazine$-H^+\cdots N_2$	3.081	1.026	2.055
9. $H_3N-H^+\cdots N_2$	3.107	1.029	2.078
10. pyrazine$-H^+\cdots N_2$	3.101	1.025	2.076
11. pyridine$-H^+\cdots N_2$	3.132	1.021	2.111
12. $F_3N-H^+\cdots NF_3$ (C_{3v})	2.691	1.132	1.559
13. $F-C\equiv N-H^+\cdots NF_3$	2.717	1.075	1.642
14. $N\equiv C-C\equiv N-H^+\cdots NF_3$	2.711	1.079	1.632
15. $H-C\equiv N-H^+\cdots NF_3$	2.774	1.061	1.713
16. $H-C\equiv C-C\equiv N-H^+\cdots NF_3$	2.849	1.041	1.808
17. $H_3C-C\equiv N-H^+\cdots NF_3$	2.878	1.038	1.840
18. 1,3,5-triazine$-H^+\cdots NF_3$	3.133	1.027	2.106
19. $H_3N-H^+\cdots NF_3$	3.170	1.031	2.139
20. pyrazine$-H^+\cdots NF_3$	3.156	1.025	2.131
21. pyridine$-H^+\cdots NF_3$	3.190	1.022	2.168
22. $N\equiv C-C\equiv N\cdots H^+\cdots N\equiv C-C\equiv N$ $(\mathrm{D}_{\infty\mathrm{h}})$	2.520	1.260	1.260
23. $F-C\equiv N-H^+\cdots N\equiv C-C\equiv N$	2.536	1.168	1.368
24. $H-C\equiv N-H^+\cdots N\equiv C-C\equiv N$	2.583	1.122	1.461
25. $H-C\equiv C-C\equiv N-H^+\cdots N\equiv C-C\equiv N$	2.632	1.084	1.548
26. $H_3C-C\equiv N-H^+\cdots N\equiv C-C\equiv N$	2.655	1.074	1.581
27. 1,3,5-triazine$-H^+\cdots N\equiv C-C\equiv N$	2.871	1.039	1.832
28. $H_3N-H^+\cdots N\equiv C-C\equiv N$	2.893	1.041	1.852
29. pyrazine$-H^+\cdots N\equiv C-C\equiv N$	2.900	1.035	1.865
30. pyridine$-H^+\cdots N\equiv C-C\equiv N$	2.940	1.030	1.910
31. $F-C\equiv N\cdots H^+\cdots N\equiv C-F$ ($D_{\infty h}$)	2.510	1.255	1.255
32. $H-C\equiv N-H^+\cdots N\equiv C-F$	2.554	1.143	1.411
33. $H-C\equiv C-C\equiv N-H^+\cdots N\equiv C-F$	2.597	1.099	1.498
34. $H_3C-C\equiv N-H^+\cdots N\equiv C-F$	2.620	1.085	1.535
35. 1,3,5-triazine$-H^+\cdots N\equiv C-F$	2.823	1.043	1.780
36. $H_3N-H^+\cdots N\equiv C-F$	2.847	1.045	1.802
37. pyrazine$-H^+\cdots N\equiv C-F$	2.852	1.038	1.814
38. pyridine$-H^+\cdots N\equiv C-F$	2.890	1.033	1.857
39. $H-C\equiv N\cdots H^+\cdots N\equiv C-H$ ($D_{\infty h}$)	2.520	1.260	1.260
40. $H-C\equiv C-C\equiv N-H^+\cdots N\equiv C-H$	2.568	1.126	1.442
41. $H_3C-C\equiv N-H^+\cdots N\equiv C-H$	2.595	1.105	1.490
42. 1,3,5-triazine$-H^+\cdots N\equiv C-H$	2.804	1.047	1.757
43. $H_3N-H^+\cdots N\equiv C-H$	2.829	1.049	1.780
44. pyrazine$-H^+\cdots N\equiv C-H$	2.834	1.042	1.792
45. pyridine$-H^+\cdots N\equiv C-H$	2.872	1.036	1.836
46. $H-C\equiv C-C\equiv N\cdots H^+\cdots N\equiv C-C\equiv C-H$ ($D_{\infty h}$)	2.512	1.256	1.256
47. $H_3C-C\equiv N-H^+\cdots N\equiv C-C\equiv C-H$	2.555	1.136	1.419
48. 1,3,5-triazine$-H^+\cdots N\equiv C-C\equiv C-H$	2.763	1.053	1.710
49. $H_3N-H^+\cdots N\equiv C-C\equiv C-H$	2.793	1.054	1.739
50. pyrazine$-H^+\cdots N\equiv C-C\equiv C-H$	2.796	1.046	1.750
51. pyridine$-H^+\cdots N\equiv C-C\equiv C-H$	2.836	1.038	1.798
52. $H_3C-C\equiv N\cdots H^+\cdots N\equiv C-CH_3$ (D_{3d})	2.514	1.257	1.257
53. 1,3,5-triazine$-H^+\cdots N\equiv C-CH_3$	2.734	1.060	1.674
54. $H_3N-H^+\cdots N\equiv C-CH_3$	2.762	1.059	1.703
55. pyrazine$-H^+\cdots N\equiv C-CH_3$	2.766	1.052	1.714
56. pyridine$-H^+\cdots N\equiv C-CH_3$	2.806	1.043	1.763
57. 1,3,5-triazine$-H^+\cdots$1,3,5-triazine[b]	2.672	1.107	1.565
58. $H_3-N-H^+\cdots$1,3,5-triazine	2.734	1.092	1.642
59. pyrazine$-H^+\cdots$1,3,5-triazine	2.723	1.081	1.642
60. pyridine$-H^+\cdots$1,3,5-triazine	2.771	1.064	1.707
61. $N_3N-H^+\cdots NH_3$(C_{3v})	2.704	1.113	1.591
62. pyrazine$-H^+\cdots NH_3$	2.720	1.093	1.627
63. pyridine$-H^+\cdots NH_3$	2.767	1.073	1.694
64. pyrazine$-H^+\cdots$pyrazine	2.644	1.121	1.523
65. pyridine$-H^+\cdots$pyrazine	2.701	1.085	1.616
66. pyridine$-H^+\cdots$pyridine	2.638	1.119	1.519

[a] The shorter N−H distance is indicated as N−H; the longer as H···N for an $N_d-H\cdots N_a$ hydrogen bond. [b] The equilibrium structures of complexes 57 through 66 have C_{2v} symmetry with the two aromatic rings lying in perpendicular planes.

One- and Two-Bond Spin−Spin Coupling Constants. Computed one- ($^{1}J_{N-H}$ and $^{1h}J_{H-N}$) and two- ($^{2h}J_{N-N}$) bond spin−spin coupling constants and Fermi-contact terms are reported in Table 3. Total coupling constants or Fermi-contact

TABLE 3: Fermi Contact Terms and Total Coupling Constants (Hz) for One-Bond ($^{1}J_{N-H}$ and $^{1h}J_{H-N}$) and Two-Bond ($^{2h}J_{N-N}$) Couplings Across $N-H^+-N$ Hydrogen Bonds[a]

complex	FC	$^{2h}J_{N-N}$	FC	$^{1}J_{N-H}$	FC	$^{1h}J_{H-N}$
1. $N_2\cdots H^+\cdots N_2$	28.5	28.6	−57.0	−57.5	−57.0	−57.5
2. $F_3N-H^+ ...N_2$	15.0	15.1	−120.1	−121.6	1.9	1.4
3. $F-C\equiv N-H^+\cdots N_2$	14.6	14.6	−149.5	−149.6	0.6	0.2
4. $N\equiv C-C\equiv N-H^+\cdots N_2$	14.1	14.1	−140.7	−140.6	0.5	0.1
5. $H-C\equiv N-H^+\cdots N_2$	12.1	12.1	−138.1	−138.3	1.5	1.1
6. $H-C\equiv C-C\equiv N-H^+\cdots N_2$	10.4	10.5	−145.0	−144.9	2.1	1.7
7. $H_3C-C\equiv N-H^+\cdots N_2$	9.6		−141.2		2.3	
8. 1,3,5-triazine$-H^+\cdots N_2$	3.6		−94.9		3.0	
9. $H_3N-H^+\cdots N_2$	3.2	3.2	−74.2	−75.6	3.0	2.6
10. pyrazine-$-H^+\cdots N_2$	3.4		−92.9		3.0	
11. pyridine$-H^+\cdots N_2$	3.0		−92.5		2.7	
12. $F_3N\cdots H^+\cdots NF_3$	25.9		−103.0		−6.0	
13. $F-C\equiv N-H^+\cdots NF_3$	24.0		−136.3		−4.3	
14. $N\equiv C-C\equiv N-H^+\cdots NF_3$	22.9		−127.6		−4.6	
15. $H-C\equiv N-H^+\cdots NF_3$	18.4		−130.7		−1.0	
16. $H-C\equiv C-C\equiv N-H^+\cdots NF_3$	14.9		−141.1		1.2	
17. $H_3C-C\equiv N-H^+\cdots NF_3$	13.3		−138.2		1.7	
19. $H_3N-H^+\cdots NF_3$	3.8		−73.6		3.0	
22. $N\equiv C-C\equiv N\cdots H^+\cdots N\equiv C-C\equiv N$	34.3	34.4	−58.8	−58.9	−58.8	−58.9
23. $F-C\equiv N-H^+\cdots N\equiv C-C\equiv N$	34.4	34.5	−95.3	−95.3	−30.9	−31.1
24. $H-C\equiv N-H^+\cdots N\equiv C-C\equiv N$	27.2	27.3	−106.4	−106.7	−14.8	−15.1
25. $H-C\equiv C-C\equiv N-H^+\cdots N\equiv C-C\equiv N$	23.7		−123.8		−5.9	
26. $H_3C-C\equiv N-H^+\cdots N\equiv C-C\equiv N$	21.5		−124.3		−3.3	
28. $H_3N-H^+\cdots N\equiv C-C\equiv N$	7.6		−73.5		5.0	
31. $F-C\equiv N\cdots H^+\cdots N\equiv C-F$	39.6	39.6	−62.7	−62.7	−62.7	−62.7
32. $H-C\equiv N-H^+\cdots N\equiv C-F$	31.5	31.5	−97.9	−98.1	−22.6	−22.6
33. $H-C\equiv C-C\equiv N-H^+\cdots N\equiv C-F$	27.9		−117.5		−10.2	
34. $H_3C-C\equiv N-H^+\cdots N\equiv C-F$	25.2		−119.5		−6.3	
35. 1,3,5-triazine$-H^+\cdots N\equiv C-F$	10.3		−93.3		5.4	
36. $H_3N-H^+\cdots N\equiv C-F$	9.2		−73.1		5.5	
39. $H-C\equiv N\cdots H^+\cdots N\equiv C-H$	32.5	32.5	−56.6	−56.9	−56.6	−56.9
40. $H-C\equiv C-C\equiv N-H^+\cdots N\equiv C-H$	28.4	28.4	−105.5	−105.4	−16.9	−17.2
41. $H_3C-C\equiv N-H^+\cdots N\equiv C-H$	25.4	25.5	−111.4	−111.5	−10.6	−10.9
42. 1,3,5-triazine$-H^+\cdots N\equiv C-H$	10.3		−92.6		4.7	
43. $H_3N-H^+\cdots N\equiv C-H$	9.3	9.3	−72.7	−73.8	4.9	4.6
44. pyrazine$-H^+\cdots N\equiv C-H$	9.4		−91.6		5.0	
45. pyridine$-H^+\cdots N\equiv C-H$	8.2		−92.0		5.1	
46. $H-C\equiv C-C\equiv N\cdots H^+\cdots N\equiv C-C\equiv C-H$	34.5		−57.9		−57.9	
47. $H_3C-C\equiv N-H^+\cdots N\equiv C-C\equiv C-H$	29.3		−98.8		−19.6	
49. $H_3N-H^+\cdots N\equiv C-C\equiv C-H$	10.6		−72.0		5.0	
52. $H_3C-C\equiv N\cdots H^+\cdots N\equiv C-CH_3$	33.0		−56.0		−56.0	
54. $H_3N-H^+\cdots N\equiv C-CH_3$	11.6		−71.1		4.5	
58. $H_3N-H^+\cdots$1,3,5-triazine	12.5		−64.6		0.9	
61. $N_3N-H^+\cdots NH_3$	12.9	12.9	−60.5	−61.1	−0.1	−0.3
62. pyrazine$-H^+\cdots NH_3$	12.6		−80.3		1.2	

[a] The numbering of complexes refers to Table 2.

terms have been computed for 45 of the 66 complexes listed in Table 3. Although some of the 45 complexes listed in Table 2 contain one aromatic ring, the 21 complexes not listed are those with one aromatic ring and either C_s symmetry or more than two nonhydrogen atoms in the proton-acceptor molecule, or complexes with two aromatic rings. Computing EOM-CCSD coupling constants for these complexes is either not feasible or too expensive. One-bond N−H and two-bond N−N coupling constants will subsequently be predicted for these complexes.

Before analyzing the data of Table 3, three important generalizations made previously concerning the signs of reduced one- and two-bond spin−spin coupling constants across X−H−Y hydrogen bonds (for X, Y = ^{13}C, ^{15}N, ^{17}O, and ^{19}F) should be recalled and applied to the complexes investigated in this study.

(1) All reduced two-bond coupling constants ($^{2h}K_{X-Y}$) are positive, except for $^{2h}J_{F-F}$ for the equilibrium structure of $(HF)_2$.[16] Thus, all $^{2h}J_{N-N}$ listed in Table 3 are positive.

(2) All reduced one-bond coupling constants ($^{1}K_{X-H}$) are positive.[17] Because the magnetogyric ratio of ^{15}N is negative and that of ^{1}H is positive, all $^{1}J_{N-H}$ are negative.

(3) All reduced one-bond coupling constants ($^{1h}K_{H-Y}$) are negative for traditional hydrogen bonds but positive for hydrogen bonds with sufficient proton-shared character.[18] Thus, positive $^{1h}J_{H-N}$ is indicative of a traditional hydrogen bond, whereas negative $^{1h}J_{H-N}$ indicates some degree of proton-shared character.

The first set of complexes in Table 3 are the 11 complexes formed with the weakest base, N_2. The coupling constants computed for these complexes illustrate some important features that are evident throughout other series as well. The first observation is that the Fermi-contact term is an excellent approximation to $^{2h}J_{N-N}$, because the difference between FC and $^{2h}J_{N-N}$ does not exceed 0.1 Hz. (In the remainder of this paper, FC and $^{2h}J_{N-N}$ will be used interchangeably.) Moreover, the FC term is also a very good approximation to $^{1}J_{N-H}$, because the largest difference between these two terms is 1.4 Hz for $H_3N-H^+\cdots N_2$ when $^{1}J_{N-H}$ is −75.6 Hz. Finally, the FC term and $^{1h}J_{H-N}$ pass through zero and thus change sign as the difference between the proton affinities of the two nitrogen bases increases going down the series. This sign change is indicative of a change in hydrogen-bond type from proton-shared to traditional.

The first complex in each series is the protonated dimer and always has the largest N−N coupling constant because its hydrogen bond has the greatest degree of proton-shared character. Thus, $^{2h}J_{N-N}$ for the protonated N_2 dimer is 28.6 Hz, compared to 15.1 Hz for $F_3N-H^+\cdots N_2$, the next member of the series. As the proton-shared character of the hydrogen bond tends to decrease and the N−N distance increases in this series, $^{2h}J_{N-N}$ decreases, as observed previously. The last member of the series, pyridine-$H^+\cdots N_2$ has $^{2h}J_{N-N}$ equal to only 3.0 Hz.

For the protonated N_2 dimer, there is no distinction between $^{1}J_{N-H}$ and $^{1h}J_{H-N}$ because the hydrogen bond is symmetric. The value of these two terms is −57.5 Hz, much less than −150.1 Hz, the value of $^{1}J_{N-H}$ for N_2-H^+. The remaining complexes with N_2 as the proton acceptor have much larger values of $^{1}J_{N-H}$, which range from −150 to −76 Hz. The large range reflects the dependence of $^{1}J_{N-H}$ on the nature of the proton donor molecule. For example, $^{1}J_{N-H}$ is −149.3 Hz for protonated HCN, −91.6 Hz for pyridinium (FC term) and −75.1 Hz for ammonium. Except for the protonated N_2 dimer, $^{1h}J_{H-N}$ is small (less than 3.0 Hz) and positive for all other complexes, indicating that these are stabilized by traditional $N-H^+\cdots N$ hydrogen bonds.

Following the series of complexes with NF_3 as the proton acceptor are those with NCCN. This series illustrates quite nicely a gradual change in hydrogen bond type, as evidenced by changes in coupling constants. The first complex in this series, $NCCN\cdots H^+\cdots NCCN$ has a symmetric, proton-shared hydrogen bond. This is evident from $^{2h}J_{N-N}$ which has a value of 34.4 Hz, and from the values of $^{1}J_{N-H}$ and $^{1h}J_{H-N}$ which are both negative and equal (−58.9 Hz), and much less in absolute value than $^{1}J_{N-H}$ for $NCCNH^+$ (−154.5 Hz). The next two complexes, $F-CN-H^+\cdots NC-CN$ and $H-CN-H^+\cdots NC-CN$ are stabilized by hydrogen bonds that have significant proton-shared character. $^{2h}J_{N-N}$ is large for both complexes (34.5 and 27.3 Hz, respectively), and both $^{1}J_{N-H}$ and $^{1h}J_{H-N}$ are large and negative. However, $^{1}J_{N-H}$ is significantly greater than $^{1h}J_{H-N}$ in each complex. The hydrogen bonds in the next two complexes, $H-CC-CN-H^+\cdots NC-CN$ and $H_3C-CN-H^+\cdots NC-CN$ have significantly less proton-shared character. Thus, $^{2h}J_{N-N}$ decreases to 23.7 and 21.5 Hz, respectively, $^{1}J_{N-H}$ increases and approaches the value for the proton donor monomers, whereas $^{1h}J_{H-N}$ decreases to −5.9 and −3.3 Hz, respectively, but remains negative. The last complex in this series, $H_3N-H^+\cdots NC-CN$ has a traditional $N-H^+\cdots N$ hydrogen bond with a relatively small N−N coupling constant of 7.6 Hz. $^{1}J_{N-H}$ approaches the value for H_3N-H^+, and $^{1h}J_{H-N}$ is small and positive. Thus, this series of complexes illustrates quite well how one- and two-bond coupling constants characterize hydrogen bond type.

The coupling constants for the next two series of complexes in which F−CN and H−CN are proton acceptors show similar behavior. There are seven complexes with HCN. The first, the protonated HCN dimer, has a symmetric hydrogen bond, the complexes with $H-CC-CN-H^+$ and $H_3C-CN-H^+$ have proton-shared hydrogen bonds, whereas the remaining four complexes with H_3N-H^+ and the three protonated aromatic rings (1,3,5-triazinium, pyrazinium, and pyridinium) are stabilized by traditional hydrogen bonds. The protonated dimers of H−CC−CN and H_3C-CN have symmetric hydrogen bonds, whereas that of NH_3 is asymmetric, but proton-shared. (The D_{3d} structure that has a symmetric $N\cdots H^+\cdots N$ hydrogen bond has values of $^{2h}J_{N-N}$ and $^{1}J_{N-H}$ of 17.2 and −26.6 Hz, respectively, at an N−H distance of 1.299 Å.)

In a previous study we were able to relate the values of $^{2h}J_{N-N}$ to the N−N distance for a set of 5 neutral and 8 protonated complexes, including complexes 9, 43−45, and 61. Can a similar relationship be established between $^{2h}J_{N-N}$ and the N−N distance for the 45 cationic complexes investigated in this study?

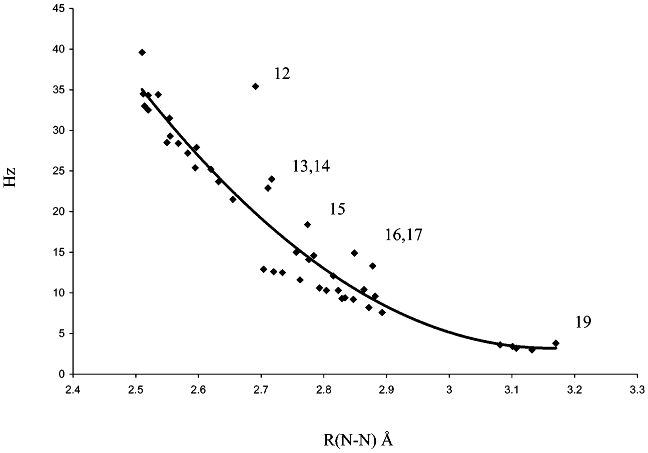

Figure 1. $^{2h}J_{N-N}$ versus the N−N distance for all complexes. The numbers on the graph refer to the numbers of the complexes in Table 3.

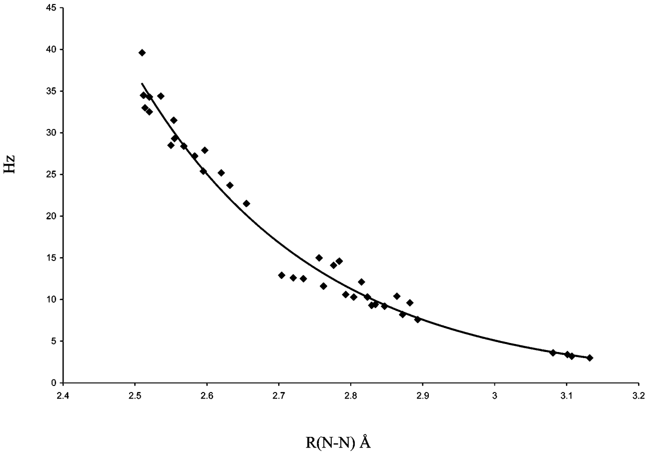

Figure 2. $^{2h}J_{N-N}$ versus the N−N distance for all complexes except those with NF_3 as the proton acceptor.

A plot of $^{2h}J_{N-N}$ versus the N−N distance is shown in Figure 1 Although these variables are obviously correlated, the correlation coefficient is only 0.933. Closer examination of Figure 1 shows that there are a set of points which lie significantly above the best-fit curve. These points are labeled and comprise the set of complexes with NF_3 as the proton acceptor. NF_3 is an electron-rich small molecule. The electron-withdrawing effects of the three fluorines on the N atom significantly lower its electron density to the extent that the proton affinity of NF_3 is similar to that of bases with sp hybridized N atoms. How the nitrogen electron density changes in both the ground and excited states of hydrogen-bonded complexes influences the computed values of $^{2h}J_{N-N}$, a second-order property. Removal of complexes 12−17 and 19 results in the plot shown in Figure 2, which has an improved correlation coefficient of 0.981.

The trendline shown in Figure 2 is a decaying exponential

$$^{2h}J_{N-N} = 795579\ \exp(-3.9868R) \qquad (1)$$

where R is the N−N distance. (This equation gives a slightly better fit than a second-order curve.) In a sense it is amazing that an equation that depends only on the N−N distance can fit the computed N−N coupling constants so well, because for a given N−N distance, $^{2h}J_{N-N}$ also depends on the N−H distance. However, the N−N and N−H distances are closely correlated in the equilibrium structures. Equation 1 can be used to predict the values of $^{2h}J_{N-N}$ for the 21 complexes for which coupling

TABLE 4: N−N and N−H Distances (Å) and Predicted Two-Bond ($^{2h}J_{N-N}$, Hz) and One-Bond ($^{1}J_{N-H}$, Hz) Coupling Constants Across N−H$^+$−N Hydrogen Bonds

order[a]	no./complex[b]	R(N−N)	$^{2h}J_{N-N}$[c]	R(N−H)	$^{1}J_{N-H}$[d]
1	30. pyridine−H$^+$···N≡C−C≡N	2.940	6.5	1.030	−91.9
2	29. pyrazine−H$^+$···N≡C−C≡N	2.900	7.6	1.035	−92.3
3	38. pyridine−H$^+$···N≡C−F	2.890	7.9	1.033	−91.7
4	27. 1,3,5-triazine−H$^+$···N≡C−C≡N	2.871	8.5	1.039	−94.0
5	37. pyrazine−H$^+$···N≡C−F	2.852	9.2	1.038	−92.0
6	51. pyridine−H$^+$···N≡C−C≡C−H	2.836	9.8	1.038	−91.1
7	56. pyridine−H$^+$···N≡C−CH$_3$	2.806	11.0	1.043	−90.6
8	50. pyrazine−H$^+$···N≡C−C≡C−H	2.796	11.5	1.046	−91.0
9	60. pyridine−H$^+$···1,3,5-triazine	2.771	12.7	1.064	−86.9
10	63. pyridine−H$^+$···NH$_3$	2.767	12.9	1.073	−84.8
11	55. pyrazine−H$^+$···N≡C−CH$_3$	2.766	12.9	1.052	−90.1
12	48. 1,3,5-triazine−H$^+$···N≡C−C≡C−H	2.763	13.1	1.053	−92.2
13	53. 1,3,5-triazine−H$^+$···N≡C−CH$_3$[e]	2.734	14.7	1.060	−90.9
14	59. pyrazine−H$^+$···1,3,5-triazine[e]	2.723	15.3	1.081	−83.8
15	65. pyridine−H$^+$···pyrazine[e]	2.701	16.8	1.085	−81.5
16	57. 1,3,5-triazine−H$^+$···1,3,5-triazine	2.672	18.8	1.107	−77.8
17	64. pyrazine−H$^+$···pyrazine	2.644	21.0	1.121	−69.9
18	66. pyridine−H$^+$···pyridine	2.638	21.5	1.119	−69.3

[a] The complexes are listed in order of decreasing N−N distance. [b] Complexes and number corresponding to Table 2. [c] Predicted value from eq 1. [d] Predicted value from eq 3. [e] Complexes with N−N and/or H−N distances at which $^{1h}J_{H-N}$ changes sign. $^{1h}J_{H-N}$ is predicted to be positive for complexes listed above these, and negative for those below.

constants were not computed, and these values are given in Table 4. The value of $^{2h}J_{N-N}$ for an N−N distance of 2.90 Å obtained from eq 1 is 7.6 Hz, consistent with the value of about 7 Hz reported experimentally for the N−N coupling constant across the N−H···N hydrogen bonds in the GC and AT base pairs at the same distance.[1] Hopefully, these predictions will be tested experimentally.

For all complexes listed in Table 3, $^{1}J_{N-H}$ values are negative. In general, the magnitude of $^{1}J_{N-H}$ will be similar to the magnitude of the corresponding protonated proton donor monomer when the hydrogen bond is traditional, but much less than that value as the proton-shared character of the N−H$^+$−N hydrogen bond increases. For example, the FC term is −149.0 Hz for HCNH$^+$, −138.1 Hz for the traditional hydrogen bond in HCNH$^+$···N$_2$, −97.9 Hz in HCN−H$^+$···NCF which has a hydrogen bond with significant proton-shared character, and −56.6 Hz for the symmetric hydrogen bond in HCN···H$^+$···NCH. For complexes in which the protonated base contains an sp-hybridized N atom, there is a linear relationship between the change in the monomer N−H distance (δR, Å) and the change in the FC term (δFC, Hz) for N−H coupling.

$$\text{sp:} \quad \delta\text{FC} = -393(\delta R) \tag{2}$$

However, when the N atoms are sp^2 or sp^3 hybridized, the relationship is quadratic.

$$\text{sp}^2\text{:} \quad \delta\text{FC} = -1940.5(\delta R)^2 - 31.7(\delta R) + 1.1 \tag{3}$$

$$\text{sp}^3\text{:} \quad \delta\text{FC} = -1206.4(\delta R)^2 - 51.7(\delta R) + 1.1 \tag{4}$$

The coupling constant for the complex is then given as

$$\text{FC}_c = \text{FC}_m - \delta\text{FC} \tag{5}$$

where FC$_c$ and FC$_m$ are the Fermi-contact terms in the complex and corresponding proton-donor monomer, respectively. The correlation coefficients for eqs 2−4 are 0.993, 0.995, and 0.994, respectively. The N−H distances and the computed FC terms for the monomers are given in Table 5.

The complexes listed in Table 4 that were not subjected to direct EOM-CCSD calculations are those with a protonated aromatic ring as the N−H donor. Because these complexes have sp^2 hybridized nitrogens, eq 3 has been used to predict values of $^{1}J_{N-H}$, and these are also given in Table 4. The corresponding second-order curve is shown in Figure 3. It should be noted that the range of δR values used to derive eq 3 is 0.074 Å, but this equation has been used to predict coupling constants for δR as large as 0.10 Å. The predicted values are most probably reasonable. However, this equation would not predict a reasonable value of $^{1}J_{N-H}$ for the transition structure of a protonated azine dimer because the curvature of the trendline is not correct at large values of δR. (δR is 0.265 Å for the D_{2d} structure of the protonated 1,3,5-triazine dimer.)

TABLE 5: N−H Distances (Å) and Fermi-Contact Terms (FC, Hz) for Protonated Bases

base	R(N−H)	FC
1. N≡N−H$^+$	1.038	−149.8
2. F$_3$N−H$^+$	1.045	−130.4
3. N≡C−C≡N−H$^+$	1.016	−163.4
4. F−C≡N−H$^+$	1.018	−154.6
5. H−C≡N−H$^+$	1.017	−149.0
6. H−C≡C−C≡N−H$^+$	1.012	−153.0
7. H$_3$C−C≡N−H$^+$	1.012	−147.9
8. 1,3,5-triazine−H$^+$	1.020	−94.2
9. H$_3$N−H$^+$	1.023	−73.5
10. pyrazine−H$^+$	1.019	−92.2
11. pyridine−H$^+$	1.017	−91.6

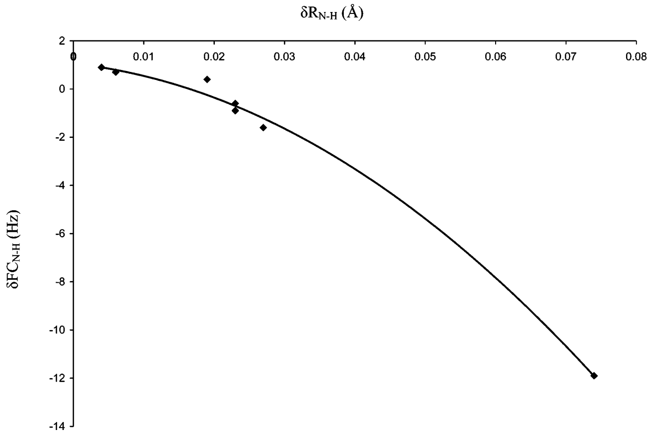

Figure 3. Change in the FC term for N−H coupling versus the change in the N−H distance in complexes relative to the corresponding sp^2 proton donors (eq 3).

TABLE 6: Computed EOM-CCSD and Predicted N−N and N−H Coupling Constants (Hz) for Complexes with $(CH_3)H_2N-H^+$ as the Proton Donor[a,b]

complex	*R*(N−N) (Å)	computed $^{2h}J_{N-N}$	predicted $^{2h}J_{N-N}$
$(CH_3)H_2N-H^+\cdots N_2$	3.145	2.6	2.9
$(CH_3)H_2N-H^+\cdots NCF$	2.890	7.6	7.9
$(CH_3)H_2N-H^+\cdots NCH$	2.875	7.6	8.4
$(CH_3)H_2N-H^+\cdots NH_3$	2.776	12.4	12.4

complex	*R*(N−H) (Å)	computed $^{1}J_{N-H}$	predicted $^{1}J_{N-H}$
$(CH_3)H_2N-H^+\cdots N_2$	1.028	−73.7	−73.7
$(CH_3)H_2N-H^+\cdots NCF$	1.039	−73.6	−72.9
$(CH_3)H_2N-H^+\cdots NCH$	1.042	−73.4	−72.6
$(CH_3)H_2N-H^+\cdots NH_3$	1.080	−67.1	−67.2

[a] The N−H distance in $(CH_3)H_2N-H^+$ is 1.023 Å and $^{1}J_{N-H}$ is −72.9 Hz. [b] Values of $^{1h}J_{H-N}$ are positive for these complexes.

EOM-CCSD FC terms have been computed for all complexes with H_3N-H^+ as the proton donor, and these are given in Table 3. Equation 4 is a second-order equation that relates the change in the N−H distance in complexes with H_3N-H^+ as the proton donor to changes in $^{1}J_{N-H}$ (as approximated by the FC term). As a test of this equation, one-bond N−H coupling constants have been predicted for four complexes with $(CH_3)H_2N-H^+$ as the proton donor: $(CH_3)H_2N-H^+\cdots N_2$, $(CH_3)H_2N-H^+\cdots NCF$, $(CH_3)H_2N-H^+\cdots NCH$, and $(CH_3)H_2N-H^+\cdots NH_3$. The predicted N−N coupling constants obtained from eq 1 and FC terms for N−H coupling from eq 4 are given in Table 6, along with the directly computed EOM-CCSD FC terms for these complexes. There is good agreement between the predicted and computed N−N and N−H coupling constants. The protonated dimer, $(CH_3)H_2N-H^+\cdots NH_2(CH_3)$ has N−N and N−H distances of 2.704 and 1.113 Å, respectively. The predicted N−N and N−H coupling constants are +16.6 and −59.5 Hz, respectively.

Because none of the complexes in Table 4 have symmetric hydrogen bonds, values of $^{1h}J_{H-N}$ should be relatively small. Examination of both structural data in Table 2 and coupling constants from Table 3 suggests that some of the complexes in Table 4 have traditional hydrogen bonds, whereas the hydrogen bonds in others have acquired some proton-shared character. This implies that the sign of $^{1h}J_{H-N}$ will be positive for some complexes and negative for others. Figure 4 shows the signs of $^{1h}J_{H-N}$ for the 38 complexes listed in Table 3 plotted on a two-dimensional grid as a function of N−N and H···N distances. The perpendicular lines separate complexes with positive values of $^{1h}J_{H-N}$ in the upper-right quadrant from those with negative values of $^{1h}J_{H-N}$ in the lower left. The points in the upper right are associated with complexes that are stabilized by traditional hydrogen bonds, as indicated by a positive sign for $^{1h}J_{H-N}$ ($^{1h}K_{H-N}$ is negative). It is interesting to note that these points lie on a straight line that has a correlation coefficient of 0.993. Those complexes in the lower left quadrant have enough proton-shared character to make $^{1h}J_{H-N}$ negative ($^{1h}K_{H-N}$ positive). The best first-order fit of the data points only has a correlation coefficient of 0.87, reflecting the sensitivity of $^{1h}J_{H-N}$ to the nature of the base and the short N−N and H···N distances in this region. Figure 4 indicates that the N−N and H···N distances at which $^{1h}J_{H-N}$ changes sign are approximately 2.71 and 1.62 Å, respectively. Thus, complex 61 ($H_3N-H^+\cdots NH_3$) is just on the proton-shared side of this intersection with $^{1h}J_{H-N}$ equal to −0.3 Hz, and complex 62 (pyrazine-$H^+\cdots NH_3$) lies just on the other side of this intersection with $^{1h}J_{H-N}$ equal to 1.2 Hz. For complexes with N−N and N−H distances close to 2.71 and 1.62 Å, respectively, $^{1h}J_{H-N}$ will be close to 0 Hz, and not experimentally detectable. However, it should also be noted that $^{1h}J_{H-N}$ approaches zero asymptotically as the N−N distance increases. However, these two situations can be differentiated by the value of $^{2h}J_{N-N.}$ On the basis of Figure 4, complexes 1−12 in Table 4 are predicted to have $^{1h}J_{H-N}$ positive, whereas complexes 16−18 appear to have sufficient proton-shared character to make $^{1h}J_{H-N}$ negative. Complexes 13−15 lie near the crossover point, and $^{1h}J_{H-N}$ should be close to 0 Hz for these.

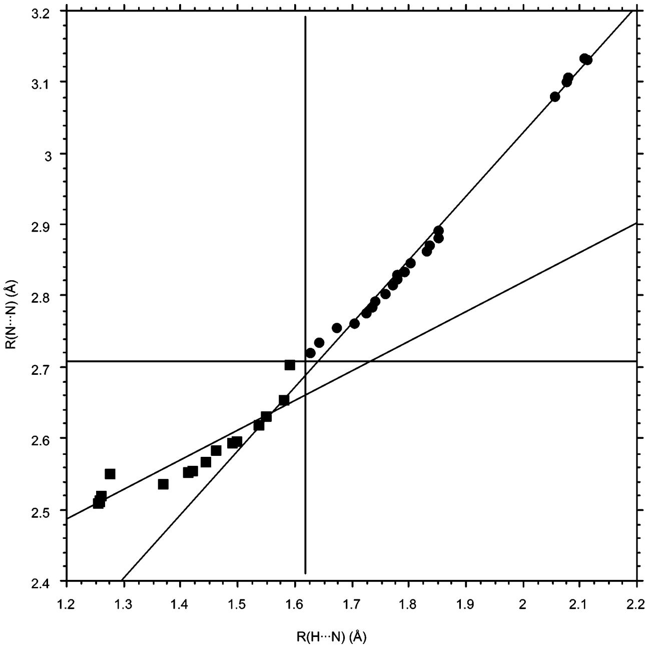

Figure 4. Signs of $^{1h}J_{H-N}$ as a function of N−N and H···N distances (Å). Data from Table 3. Key: (■) $^{1h}J_{H-N}$ negative; (●) $^{1h}J_{H-N}$ positive.

Conclusions

A systematic ab initio study of $^{15}N-^{15}N$ and $^{15}N-^{1}H$ spin−spin coupling constants has been carried out for a series of complexes formed from 11 nitrogen bases with experimentally measured proton affinities. When these complexes are arranged in order of increasing proton affinity of the proton-acceptor base and, for a given proton acceptor, increasing order of proton affinity of the protonated N−H donor, trends in distances and signs of coupling constants are evident that are indicative of the nature of the hydrogen bond.

1. All two-bond spin−spin coupling constants ($^{2h}J_{N-N}$) are positive and decrease as the N−N distance increases.

2. All one-bond N−H coupling constants ($^{1}J_{N-H}$) are negative ($^{1}K_{N-H}$ are positive). When the hydrogen bond is symmetric, the absolute value of $^{1}J_{N-H}$ is much less than it is in the protonated N−H donor monomer. For complexes in which an sp hybridized N atom is the proton donor, changes in $^{1}J_{N-H}$ upon complex formation are linearly related to changes in the corresponding N−H distances. When the nitrogen of the proton donor is sp^2 or sp^3 hybridized, changes in $^{1}J_{N-H}$ are quadratically related to changes in the corresponding N−H distances.

3. One-bond H···N coupling constants ($^{1h}J_{H-N}$) are positive for traditional hydrogen bonds but become negative when the hydrogen bond acquires sufficient proton-shared character. The N−N and H···N distances at which a change of sign occurs are approximately 2.71 and 1.62 Å, respectively.

4. The equations developed in this study from relationships between coupling constants and distances can be used to predict

values of ${}^{2h}J_{N-N}$ and ${}^{1}J_{N-H}$, and the sign of ${}^{1h}J_{H-N}$, for complexes that are too large for EOM-CCSD calculations.

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Supporting Information Available: Full reference citations for refs 36 and 37. This material is available free of charge via the Internet at http://pubs.acs.org.

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