Ab Initio Study of Hydrogen Bonding and Proton Transfer in 3:1 FH:NH_3 and FH:Collidine Complexes: Structures and One- and Two-Bond Coupling Constants across Hydrogen Bonds

Janet E. Del Bene*

Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555

José Elguero

Instituto de Química Médica, CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain

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Ab initio EOM-CCSD calculations have been performed on 3:1 FH:NH_3 complexes at their own optimized MP2/6-31+G(d,p) geometries and at the optimized geometries in the hydrogen-bonding regions of corresponding 3:1 FH:collidine complexes. The isolated gas-phase equilibrium 3:1 FH:NH_3 complex has an open structure with a proton-shared F_a-H_a-N hydrogen bond, while the isolated equilibrium 3:1 FH:collidine complex has a perpendicular structure with an F_a-H_a-N hydrogen bond that is on the ion-pair side of proton-shared. The F_a−N coupling constant ($^{2h}J_{F_a-N}$) for the equilibrium 3:1 FH:NH_3 complex is large and negative, consistent with a proton-shared F_a-H_a-N hydrogen bond; $^{2h}J_{F_b-F_a}$ is positive, reflecting a short F_b-F_a distance and partial proton transfer from F_b to F_a across the $F_b-H_b-F_a$ hydrogen bond. In contrast, $^{2h}J_{F_a-N}$ has a smaller absolute value and $^{2h}J_{F_b-F_a}$ is greater for the 3:1 FH:NH_3 complex at the equilibrium 3:1 FH:collidine geometry, consistent with the structural characteristics of the F_a-H_a-N and $F_b-H_b-F_a$ hydrogen bonds. Coupling constants computed at proton-transferred 3:1 FH:collidine perpendicular geometries are consistent with experimental coupling constants for the 3:1 FH:collidine complex in solution and indicate that the role of the solvent is to promote further proton transfer from F_a to N across the F_a-H_a-N hydrogen bond, and from F_b to F_a across the two equivalent $F_b-H_b-F_a$ hydrogen bonds. The best correlations between experimental and computed coupling constants are found for complexes with perpendicular proton-transferred structures, one having the optimized geometry of a 3:1 FH:collidine complex at an F_a-H_a distance of 1.80 Å, and the other at the optimized 3:1 FH:collidine geometry with distances derived from the experimental coupling constants. These calculations provide support for the proposed perpendicular structure of the 3:1 FH:collidine complex as the structure which exists in solution.

Introduction

In a series of landmark papers, Limbach et al. have reported the results of experimental studies of one- and two-bond spin−spin coupling constants across hydrogen bonds in Freon solutions at low temperature.[1−6] These investigators have observed sign changes of one-bond coupling constants as a function of temperature, and they have been able to relate their experimental values of $^{2h}J_{X-Y}$, $^{1}J_{X-H}$, and $^{1h}J_{H-Y}$ for X−H−Y hydrogen bonds to hydrogen-bond type and the degree of proton transfer. Recently, they have focused their efforts on complexes of FH with collidine (2,4,6-trimethylpyridine), presenting data for 1:1, 2:1, 3:1, and 2:3 FH:collidine complexes.[6]

The studies of Limbach et al., as well as a microwave spectroscopic study of the trimer FH:FH:NH_3 by Leopold et al.,[7] have led us to expand our own theoretical investigations of one- and two-bond coupling constants to hydrogen-bonded systems with multiple hydrogen bonds. We have employed ab initio equation-of-motion coupled-cluster singles and doubles theory to compute coupling constants in hydrogen-bonded systems, and we have demonstrated that the computed coupling constants obtained at this level of theory are reliable and in agreement with available experimental data. We have also observed the effects of full and partial proton transfer on one- and two-bond spin−spin coupling constants and have related these to hydrogen-bond type.[8] On the basis of our theoretical studies, we have made generalizations about the signs of $^{2h}K_{X-Y}$,[9] $^{1}K_{X-H}$,[10] and $^{1h}K_{H-Y}$,[11] where K_{A-B} is the reduced spin−spin coupling constant,

$$K_{A-B} \propto J_{A-B}/\gamma_A\gamma_B$$

and γ_A and γ_B are the magnetogyric ratios of A and B (^{13}C, ^{19}F, and ^{1}H positive; ^{15}N and ^{17}O negative).

After a study of the 1:1 FH:collidine complex using FH:NH_3 and FH:pyridine as models,[12] we investigated the structures and coupling constants associated with 2:1 FH:NH_3 and FH:collidine complexes.[13] We have now expanded our study to the 3:1 FH:collidine complexes, examining coupling across F−H−N and F−H−F hydrogen bonds. In this paper we present

(1) computed structures for 3:1 FH:NH_3 and FH:collidine complexes;

(2) computed coupling constants for 3:1 FH:NH_3 complexes at their own geometries and at the geometries of the corresponding 3:1 FH:collidine complexes;

(3) comparisons of our computed coupling constants with those measured experimentally; and

(4) relationships among the signs and magnitudes of coupling constants, hydrogen-bond type, and the degree of proton transfer.

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* Corresponding author. E-mail: jedelbene@ysu.edu.

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Methods

The structures of four 3:1 FH:NH$_3$ complexes have been optimized at second-order Møller−Plesset perturbation theory (MP2)[14−17] with the 6-31+G(d,p) basis set.[18−21] Included among these is a cyclic structure which is the global minimum on the potential surface. The other 3:1 FH:NH$_3$ complexes were optimized under specific constraints and include a second cyclic structure, a perpendicular structure, and an open "zigzag" structure. These complexes are designated as F_cH_c:F_bH_b:F_aH_a:NH$_3$, and are illustrated in Scheme 1. In all complexes, F_a-H_a is hydrogen-bonded to N, and F_b-H_b is hydrogen-bonded to F_a. In cyclic and open structures, F_c-H_c is hydrogen-bonded to F_b, while in perpendicular structures, F_b-H_b and F_c-H_c are equivalent and both are hydrogen-bonded to F_a. Corresponding 3:1 FH:collidine complexes were also optimized at MP2/6-31+G(d,p). In addition, a set of proton-transferred 3:1 FH:collidine complexes were optimized at fixed F_a-H_a distances, beginning at 1.60 Å and incrementing to 1.90 Å in steps of 0.10 Å.

Ab initio equation-of-motion coupled-cluster singles and doubles calculations (EOM-CCSD)[22−25] in the CI(configuration interaction)-like approximation with the Ahlrichs[26] qzp basis set on F and N, qz2p on the hydrogen-bonded H atoms, and Dunning's cc-pVDZ basis[27,28] on other hydrogens have been carried out to obtain one- and two-bond spin−spin coupling constants for 3:1 FH:NH$_3$ complexes. Total coupling constants were obtained as the sum of four contributions, namely, the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi-contact (FC), and spin−dipole (SD) terms.[29] These calculations were carried out on 3:1 FH:NH$_3$ complexes at their own geometries and on 3:1 FH:NH$_3$ complexes at the optimized geometries in the hydrogen-bonding regions obtained for corresponding 3:1 FH:collidine complexes. Geometry optimizations were carried out with the Gaussian 03 suite of programs,[30] and coupling constants were evaluated with ACES II.[31] All calculations were carried out on the Cray X1 or the Itanium cluster at the Ohio Supercomputer Center.

Results and Discussion

Structures of 3:1 FH:NH$_3$ and 3:1 FH:Collidine Complexes. Table 1 reports F−F, F−H, N−H_a, and F_a-N distances for the 3:1 FH:NH$_3$ complexes that are illustrated as structures 1−4 in Scheme 1. The cyclic structure 1 in which the in-plane N−H of NH$_3$ is "cis" to F_c and forms a distorted N−H−F_c hydrogen bond is the equilibrium structure on the potential surface. This structure is 1.1 kcal/mol more stable than structure 2 in which the in-plane N−H bond is "trans" to the hydrogen-bonding region. Structure 3 is the optimized perpendicular structure in which F_cH_c and F_bH_b are equivalent, and both are proton donors to F_a. This structure is 4.8 kcal/mol less stable than structure 1. Structure 4 is a "zigzag" structure which is 5.3 kcal/mol higher in energy than structure 1.

There is significant cooperativity in the F−H−F and F−H−N hydrogen bonds, as evident from the F−H, F−F, and F−N distances. Thus, all of the F−H−F hydrogen bonds have shorter F−F distances and longer F−H distances than the HF dimer which has F−F and hydrogen-bonded F−H distances of 2.776 and 0.932 Å, respectively, at MP2/6-31+G(d,p). The F_a-N distance in structure 1 is 2.425 Å, much shorter than the F−N distances of 2.637 and 2.511 Å, respectively, in 1:1 and 2:1 FH:NH$_3$ complexes. As expected, the F_a-H_a distance of 1.095 Å is longer than the distances of 0.963 and 1.004 Å found in the 1:1 and 2:1 FH:NH$_3$ complexes, respectively. Thus, even in the gas phase, the 3:1 FH:NH$_3$ complex has a proton-shared F_a-H_a-N hydrogen bond, and the F−H−F hydrogen bonds have increased proton-shared character. The perpendicular structure 3 has an F_a-H_a-N hydrogen bond which appears to have the greatest proton-shared character on the basis of its short F_a-N distance of 2.418 Å and its long F_a-H_a distance of 1.104 Å. The open zigzag structure 4 is the least stable and has the longest F_a-N and shortest F_a-H_a distances.

The situation is quite different for optimized perpendicular and open 3:1 FH:collidine complexes, which are illustrated in Scheme 1 as structures 5 and 6, respectively. Shown in these two figures are the complexes in which the in-plane C−H bonds of the methyl groups in the 2 and 6 positions are "trans" to the hydrogen-bonding region. Structure 5 has two very low imaginary frequencies corresponding to methyl rotations, which are essentially free. The "trans" structure shown is 1.1 kcal/mol more stable than the "cis" structure. The 3:1 FH:collidine complexes are structurally and energetically distinct from the corresponding 3:1 FH:NH$_3$ complexes in several respects:

(1) The perpendicular 3:1 FH:collidine structure 5 is more stable than the open structure 6 by 1.6 kcal/mol. This is in contrast to the 3:1 FH:NH$_3$ complexes, where a cyclic structure is favored due to a stabilizing interaction between F_c and the ammonium hydrogens.

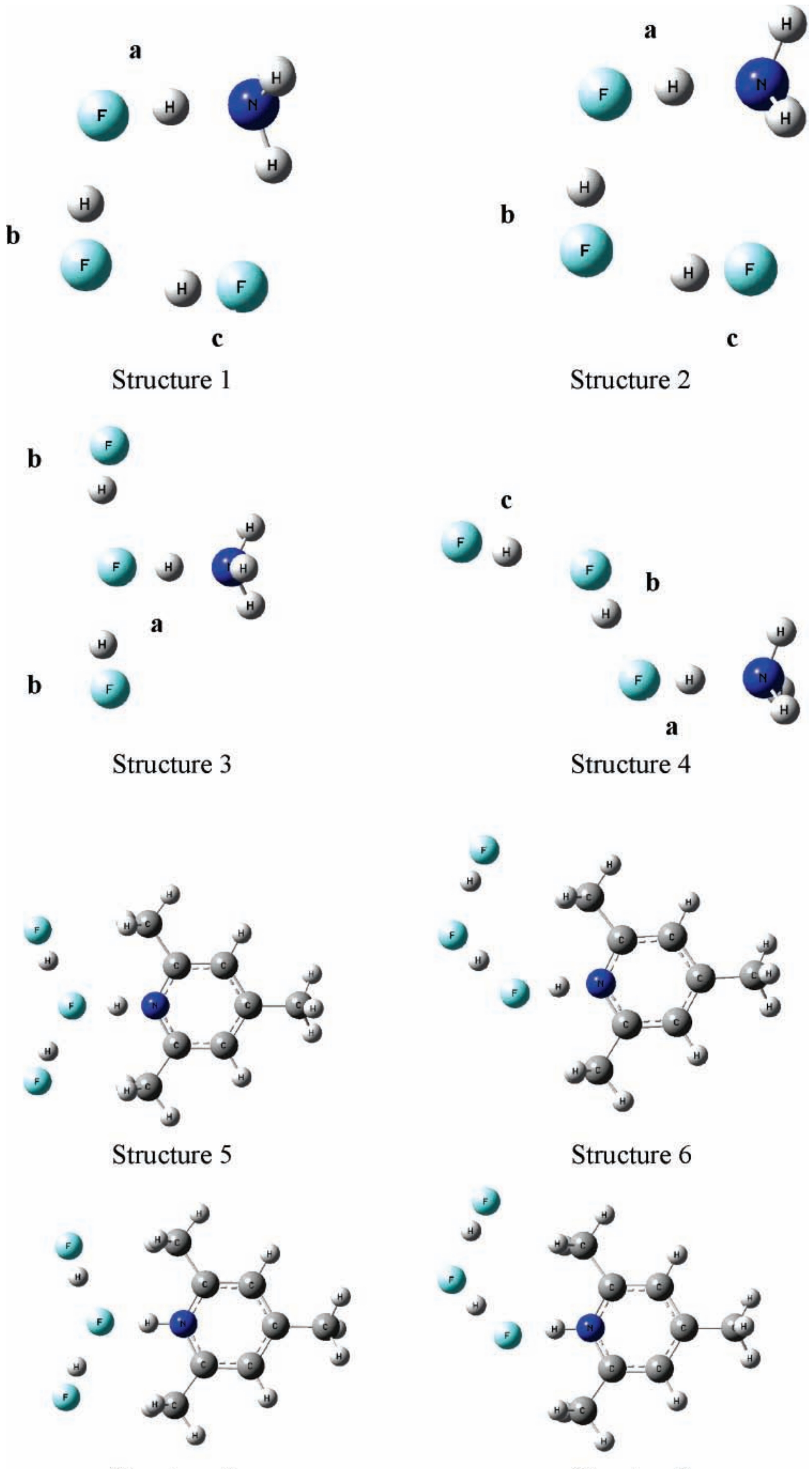
(2) Since collidine is a stronger base than NH$_3$, there is a greater degree of proton transfer from F_a to N in the perpendicular 3:1 FH:collidine structure 5 compared to the corresponding structure 3 with NH$_3$. This is evident from the longer F_a-H_a (1.340 vs 1.104 Å) and F_a-N (2.457 vs 2.418 Å) distances in structure 5. That is, even in the gas phase, the 3:1 FH:collidine complex has an F_a-H_a-N hydrogen bond that is on the ion-pair side of proton-shared.

(3) In the perpendicular 3:1 FH:collidine structure, the two HF molecules hydrogen-bonded to F_a tend to bend away from the collidine molecule. The F_b-F_a-N angles are 94 and 114°, respectively, for structures 3 and 5.

Proton-transferred 3:1 FH:collidine complexes were obtained at a set of fixed F_a-H_a distances, and representative perpendicular and open complexes are shown as structures 7 and 8, respectively. F_a-N, $N-H_a$, F_b-F_a, F_b-H_b, F_c-F_b, and F_c-H_c distances for these complexes are also reported in Table 1. The long F_a-N and short $N-H_a$ distances are characteristic of complexes that are hydrogen-bonded ion-pairs, with decreased proton-shared character relative to structures 5 and 6. These differences are reflected in the computed one- and two-bond spin−spin coupling constants for these complexes.

One- and Two-Bond Coupling Constants $^{2h}J_{X-Y}$, $^{1}J_{X-H}$, and $^{1h}J_{H-Y}$ across X−H−Y Hydrogen Bonds for 3:1 FH:NH$_3$ Complexes at 3:1 FH:NH$_3$ Geometries. Fermi contact terms and total spin−spin coupling constants for complexes 1−4 are reported in Table 2. The two-bond F_a-N spin−spin coupling constants $^{2h}J_{F_a-N}$ are large and negative, ranging from −84 Hz in structure 4 to approximately −100 Hz in structures 1, 2, and 3. Since the magnetogyric ratio of ^{19}F is positive while that of ^{15}N is negative, the signs of the reduced two-bond F_a-N coupling constants are positive, consistent with the generalization that reduced two-bond coupling constants $^{2h}K_{X-Y}$ are positive for X−H−Y hydrogen bonds formed from second-period elements ^{13}C, ^{15}N, ^{17}O, and ^{19}F, except for $^{2h}K_{F-F}$ for the equilibrium HF dimer.[9] The largest F_a-N coupling constants are associated with structures 1, 2, and 3 which have hydrogen bonds with significant proton-shared character; the smallest is found for structure 4, which has the least proton-shared character. The one-bond F_a-H_a coupling constants $^{1}J_{F_a-H_a}$ are

SCHEME 1



Structure 1 Structure 2 Structure 3 Structure 4 Structure 5 Structure 6 Structure 7 Structure 8

positive, consistent with the generalization that $^1K_{X-H}$ is positive in hydrogen-bonded complexes.[10] However, values of $^1J_{F_a-H_a}$ are significantly smaller than $^1J_{F_b-H_b}$ and $^1J_{F_c-H_c}$ due to the longer F_a-H_a distances. The computed coupling constants $^{1h}J_{H_a-N}$ are

TABLE 1: Selected Distances (Å) for Optimized 3:1 FH:NH_3 and 3:1 FH:Collidine Complexes[a]

Optimized 3:1 FH:NH_3 Complexes

	F_a-N	F_a-H_a	F_b-F_a	F_b-H_b	F_c-F_b	F_c-H_c
structure 1	2.425	1.095	2.414	0.981	2.536	0.954
structure 2	2.437	1.074	2.429	0.975	2.555	0.950
structure 3	2.418	1.104	2.570	0.944	2.570	0.944
structure 4	2.490	1.019	2.488	0.959	2.658	0.938

Optimized 3:1 FH:Collidine Complexes

	F_a-N	F_a-H_a	F_b-F_a	F_b-H_b	F_c-F_b	F_c-H_c
structure 5	2.457	1.340	2.483	0.960	2.483	0.960
structure 6	2.410	1.235	2.367	0.999	2.541	0.951

Optimized 3:1 FH:Collidine Proton-Transferred Complexes[b]

	F_a-N	$N-H_a$	F_b-F_a	F_b-H_b	F_c-F_b	F_c-H_c
structures 7						
$F_a-H_a = 1.60$	2.655	1.055	2.434	0.971	2.434	0.971
$F_a-H_a = 1.70$	2.743	1.043	2.422	0.975	2.422	0.975
$F_a-H_a = 1.70$[c]	2.743	1.043	2.414	0.976	2.414	0.976
$F_a-H_a = 1.80$	2.836	1.036	2.412	0.978	2.412	0.978
$F_a-H_a = 1.90$	2.930	1.030	2.402	0.981	2.402	0.981
$F_a-H_a = 1.85$[d]	2.87	1.02	2.431	0.98	2.431	0.98
structure 8						
$F_a-H_a = 1.80$	2.789	1.036	2.282	1.112	2.419	0.979

[a] The hydrogen bonds are F_a-H_a-N and $F_b-H_b-F_a$; in the perpendicular structures, the third hydrogen bond is $F_c-H_c-F_a$, which is equivalent to $F_b-H_b-F_a$; in open and cyclic structures, the third hydrogen bond is $F_c-H_c-F_b$ (see Scheme 1, structures 1−4 for labeling). [b] The F_a-H_a distance was fixed during the optimizations. [c] In this complex, the in-plane C−H bond of the methyl groups in positions 2 and 6 are "cis" to the hydrogen-bonding region. [d] F_a-H_a, $N-H_a$, F_b-H_b, and H_b-F_a distances are taken from ref 6 and were held fixed for the optimization of the 3:1 FH:collidine complex.

TABLE 2: Selected FC Terms and Spin−Spin Coupling Constants (Hz) for 3:1 FH:NH_3 Complexes at 3:1 FH:NH_3 Geometries

	structure 1		structure 2		structure 3		structure 4	
	FC	*J*	FC	*J*	FC	*J*	FC	*J*
F_a-N	−102.3	−100.0	−100.6	−98.4	−101.7	−99.6	−86.0	−84.1
H_a-N	−19.0	−19.3	−15.4	−15.7	−21.2	−21.6	−5.4	−5.7
F_a-H_a	119.3	141.8	154.2	183.8	101.6	121.3	262.2	316.9
F_b-F_a	191.0	101.1	168.1	83.7	37.0	−20.2	132.7	69.0
F_b-H_b	353.3	435.9	359.1	447.0	354.1	486.2	387.5	492.3
H_b-F_a	−55.4	−52.9	−56.0	−53.4	−45.3	−42.8	−56.6	−53.7
F_c-F_b	73.4	13.5	55.7	−0.5			18.5	−17.1
F_c-H_c	373.5	489.0	369.6	491.7			356.2	499.0
H_c-F_b	−47.1	−44.2	−45.2	−42.3			−43.9	−41.1

TABLE 3: Selected FC Terms and Spin−Spin Coupling Constants (Hz) for 3:1 FH:NH_3 Complexes at 3:1 FH:Collidine Geometries[a]

					$F_a-H_a = 1.8$ Å			
	structure 5		structure 6		structure 7		structure 8	
	FC	*J*	FC	*J*	FC	*J*	FC	*J*
F_a-N	−78.0	−77.8	−97.8	−95.1	−20.9	−20.2	−25.9	−25.0
$N-H_a$	−54.1	−54.7	−41.0	−41.5	−75.9	−77.0	−73.4	−74.6
H_a-F_a	−62.0	−67.4	−22.4	−22.5	−24.1	−25.2	−28.8	−30.0
F_b-F_a	109.1	27.0	312.1	208.7	194.8	83.2	472.1	311.8
F_b-H_b	348.9	459.8	337.4	406.8	326.9	420.2	140.3	163.6
H_b-F_a	−63.6	−60.9	−54.7	−51.6	−70.9	−68.5	58.5	70.1
F_c-F_b			74.8	17.1			187.7	89.2
F_c-H_c			360.8	482.2			342.1	430.6
H_c-F_b			−55.3	−52.2			−60.5	−57.4

[a] Labels correspond to those shown in Scheme 1 for structures 1−4.

negative and make ${}^{1h}K_{H_a-N}$ positive, which is indicative of the proton-shared character of the F_a-H_a-N hydrogen bonds.[11]

It was observed previously that although the FC term for F−F coupling in the HF dimer is positive, ${}^{2h}J_{F-F}$ is negative but becomes positive at shorter F−F distances and is strongly dependent on the orientation of the hydrogen-bonded pair.[32] It is interesting to note that structures 1, 2, and 4 have F_b-F_a distances which vary from 2.414 to 2.488 Å and are therefore much shorter than the F−F distance of 2.776 Å in $(HF)_2$. For these structures, both the FC terms and ${}^{2h}J_{F_b-F_a}$ are positive. However, structure 3 has a longer F_b-F_a distance of 2.570 Å, a positive FC term, but a negative total coupling constant ${}^{2h}J_{F_b-F_a}$ due to a large negative contribution from the PSO term. The FC contributions to ${}^{2h}J_{F_c-F_b}$ are also positive, but ${}^{2h}J_{F_c-F_b}$ is positive only in structure 1 which has the shortest F_c-F_b distance. ${}^{2h}J_{F_c-F_b}$ is essentially 0 Hz in structure 2 and negative in structure 4. The one-bond coupling constants ${}^{1}J_{F_b-H_b}$ and ${}^{1}J_{F_c-H_c}$ are very large and positive, varying from 436 to 499 Hz, while the corresponding one-bond coupling constants ${}^{1h}J_{H_b-F_a}$ and ${}^{1h}J_{H_c-F_b}$ are negative, ranging from −41 to −54 Hz. Positive ${}^{1}K_{X-H}$ and negative ${}^{1h}K_{H-Y}$ indicate that $F_b-H_b-F_a$ and $F_c-H_c-F_b$ are traditional hydrogen bonds.

One- and Two-Bond Coupling Constants for 3:1 FH:NH_3 Complexes at 3:1 FH:Collidine Geometries. Table 3 reports Fermi-contact terms and total coupling constants for 3:1 FH:NH_3 complexes at the geometries in the hydrogen-bonding region taken from corresponding optimized 3:1 FH:collidine complexes. Structures 5 and 6 are the optimized perpendicular and open structures, respectively. The data given for structures 7 and 8 refer to complexes in which the F_a-H_a distance is 1.80 Å, and proton transfer has occurred.

The signs of the one- and two-bond coupling constants for structures 5−8 indicate that the F_a-H_a-N hydrogen bonds are on the ion-pair side of proton-shared, having structural and spectroscopic characteristics similar to those of traditional hydrogen bonds with the roles of X and Y reversed. (When $Y-H^+$ is the proton-donor to X^-, the Y−H bond is slightly elongated relative to the isolated cation, the infrared Y−H stretching frequency is red-shifted relative to the monomer, ${}^{1}K_{Y-H}$ is positive, and ${}^{1h}K_{H-X}$ is negative.[33]) In these complexes values of ${}^{1}K_{N-H_a}$ are positive and ${}^{1h}K_{H_a-F_a}$ are negative, indicating that the $N-H_a\cdots F_a$ hydrogen bonds are traditional, ion-pair hydrogen bonds. Absolute values of ${}^{1}K_{N-H_a}$ are greater in structures 7 and 8, which have shorter $N-H_a$ distances. It is difficult to judge the degree of proton-shared character from ${}^{1h}K_{H_a-F_a}$ in these complexes, since the F_a-H_a coupling constant passes through zero along the proton-transfer coordinate and exhibits a maximum negative value before asymptotically approaching zero. However, ${}^{2h}K_{N-F_a}$ is much smaller in absolute value in structures 7 and 8 compared to structures 5 and 6, indicating that the latter two structures have greater proton-shared character.

Although two-bond F−F coupling constants exhibit both distance and orientation dependencies, ${}^{2h}K_{F_b-F_a}$ for structures 5−8 are positive, most probably reflecting the short F_b-F_a distances. The one-bond F_b-H_b coupling constants (${}^{1}K_{F_b-H_b}$) are also positive, as expected. ${}^{1h}K_{H_b-F_a}$ values are negative in complexes 5, 6, and 7, indicating that these $F_b-H_b-F_a$ hydrogen bonds are traditional. In structure 8, ${}^{1h}K_{H_b-F_a}$ is positive and ${}^{2h}J_{F_b-F_a}$ has its maximum value, indicating that the $F_b-H_b-F_a$ hydrogen bond in the open proton-transferred structure has significant proton-shared character.

Comparison of Computed and Experimental Coupling Constants. The open structures 6 and 8 have two distinguishable two-bond F−F and four distinguishable one-bond F−H coupling constants associated with the nonequivalent $F_b-H_b-F_a$ and $F_c-H_c-F_b$ hydrogen bonds. However, only one F−F coupling constant and three distinguishable F−H coupling constants, one

TABLE 4: Spin-Spin Coupling Constants (Hz) for 3:1 FH:NH$_3$ Complexes at 3:1 FH:Collidine Geometries

F_a-H_a (Å)	F_a-N	$N-H_a$	H_a-F_a	F_b-F_a	F_b-H_b	H_b-F_a
structure 5						
1.340	−77.8	−54.7	−67.4	27.0	459.8	−60.9
structures 7						
1.60	−37.5	−72.5	−48.5	63.3	434.3	−67.6
1.70	−27.7	−75.2	−35.9	74.2	426.9	−68.4
1.80	−20.2	−77.0	−25.2	83.2	420.2	−68.5
1.90	−14.7	−78.2	−16.9	91.9	413.8	−68.2
ref 6[a]	−20.4	−78.6	−22.0	76.1	423.5	−63.0
exptl[b]	c	−90	−45	99	400	−38

[a] F_a-H_a, $N-H_a$, F_a-H_b, and F_a-H_b distances estimated from experimental data in ref 6. These distances were held fixed during the optimization of a 3:1 FH:collidine complex. [b] Ref 6. [c] Coupling to F_a could not be resolved in the ^{15}N NMR signal in ref 6.

corresponding to F_a-H_a coupling in the $N-H_a-F_a$ hydrogen bond, were measured experimentally for a 3:1 FH:collidine complex. Thus, coupling constants for optimized and proton-transferred open structures are not compatible with experimental data. For example, the open structure 6 has two F−F coupling constants of 209 and 17 Hz; the proton-transferred structure 8 with an F_a-H_a distance of 1.80 Å has two F−F coupling constants of 312 and 89 Hz; the experimental value of the F−F coupling constant is 99 Hz.

On the basis of their experimental data, the authors of ref 6 proposed a perpendicular proton-transferred structure for the 3:1 FH:collidine complex (structure 7). Table 4 presents computed values of coupling constants for proton-transferred complexes with perpendicular structures, along with the experimentally measured coupling constants $^1J_{N-H_a}$, $^{1h}J_{H_a-F_a}$, $^{2h}J_{F_a-F_b}$, $^1J_{F_b-H_b}$, and $^{1h}J_{H_b-F_a}$. It is significant that the signs and relative magnitudes of the computed coupling constants for perpendicular proton-tranferred complexes (structures 7) over a range of F_a-H_a distances are consistent with experimental data. This implies that the characterization of the nature of these hydrogen bonds on the basis of computed coupling constants is most probably correct.

Computed coupling constants for a perpendicular 3:1 FH:NH$_3$ complex at the optimized gas-phase 3:1 FH:collidine geometry are given for structure 5 in Table 4. It is interesting to note that the signs of coupling constants even for the gas-phase structure of the 3:1 complex are consistent with the signs determined experimentally. However, the $N-H_a$ coupling constant is too small (−55 Hz) compared to the experimental value (−90 Hz) and the F_a-H_a coupling constant is too large (−67 vs −45 Hz). Moreover, the computed F_b-F_a coupling constant (27 Hz) is too small relative to experiment (99 Hz). These data suggest that the gas-phase $N-H_a-F_a$ hydrogen bond has too much proton-shared character while the $F_b-H_b-F_a$ hydrogen bond has too little relative to the hydrogen bonds that exist in solution. Thus, the presence of the solvent promotes proton transfer from F_a to N and from F_b to F_a.

Table 4 also reports computed coupling constants for perpendicular structures 7 in which proton transfer across the F_a-H_a-N hydrogen bond was imposed by lengthening the F_a-H_a distance. The experimental $N-H_a$ and H_a-F_a coupling constants are negative for these complexes, giving positive $^1K_{N-H_a}$ and negative $^{1h}K_{H_a-F_a}$, an indication that these ion-pair hydrogen bonds have little proton-shared character. There is no significant change in $^1J_{N-H_a}$ as the F_a-H_a distance increases from 1.60 to 1.90 Å in perpendicular proton-transferred complexes, since the $N-H_a$ distance varies by less than 0.03 Å. The computed $N-H_a$ coupling constants are too small relative to experiment, but this is not unexpected since the computed values refer to N−H coupling in ammonium, whereas the experimental value refers to collidinium.[34] (The computed N−H coupling constant for the ammonium ion is −75 Hz, while that for pyridinium is −92 Hz.) In contrast, $^{1h}J_{H_a-F_a}$ does vary with the F_a-H_a distance, decreasing from −49 to −17 Hz as this distance increases from 1.60 to 1.90 Å. These computed values sweep through the experimental value of −45 Hz. $^{2h}J_{N-F_a}$ also decreases from −38 to −15 Hz as the F_a-H_a distance increases. Unfortunately, coupling to F_a could not be resolved experimentally in the ^{15}N NMR signal.

The data of Table 4 show that as the F_a-H_a distance increases from 1.60 to 1.90 Å, $^{2h}J_{F_b-F_a}$ increases from 63 to 92 Hz, and $^1J_{F_b-H_b}$ decreases from 434 to 414 Hz. The values of these coupling constants at the longer F_a-H_a distances approach the experimental values of 99 Hz for $^{2h}J_{F_b-F_a}$ and 400 Hz for $^1J_{F_b-H_b}$. These comparisons indicate that the degree of proton transfer from F_b to F_a increases as the F_a-H_a distance increases, and that the $F_b-H_b-F_a$ hydrogen bonds in the optimized gas-phase structures of these 3:1 FH:collidine complexes have too little proton-shared character relative to the $F_b-H_b-F_a$ hydrogen bonds which exist in solution. That is, the solvent induces proton transfer across the $F_b-H_b-F_a$ hydrogen bond from F_b to F_a. $^{1h}J_{H_b-F_a}$ is −68 Hz and does not change as the F_a-H_a distance varies from 1.60 to 1.90 Å, since the H_b-F_a distance varies by only 0.01 Å. The computed values of $^{1h}J_{H_b-F_a}$ are too large relative to the experimental coupling constant of −38 Hz.

On the basis of their experimentally measured coupling constants, Limbach et al. proposed a perpendicular structure for the 3:1 FH:collidine complex in solution, with $N-H_a$ and F_a-H_a distances of 1.02 and 1.85 Å, respectively, and F_b-H_b and F_a-H_b distances of 0.98 and 1.46 Å, respectively.[6] A 3:1 FH:collidine complex was optimized with these distances held fixed, and the structural parameters from the optimized complex that describe the hydrogen-bonding region were used to construct a corresponding 3:1 FH:NH$_3$ complex. The coupling constants computed for this structure are also given in Table 4. Not surprisingly, the computed coupling constants associated with the $N-H_a-F_a$ hydrogen bond in this complex are similar to those computed for the 3:1 FH:collidine complex at an F_a-H_a distance of 1.80 Å, which has similar $N-H_a$ and F_a-H_a distances. At the experimental distances for the $F_b-H_b-F_a$ hydrogen bond, the computed values of $^{2h}J_{F_b-F_a}$ and $^1J_{F_b-H_b}$ are 76 and 424 Hz, respectively, similar to those computed for a complex with the F_a-H_a distance equal to 1.70 Å. However, $^{2h}J_{F_b-F_a}$ is too small and $^1J_{F_b-H_b}$ is too large relative to the experimental values of 99 and 400 Hz, respectively, The computed coupling constant $^{1h}J_{H_b-F_a}$ at the experimental geometry is −63 Hz, which is slightly closer to the experimental value of −38 Hz. The only notable structural difference related to the $F_b-H_b-F_a$ hydrogen bond between the computed structure at an F_a-H_a distance of 1.70 Å and the structure based on the experimental distances is the orientation of the $F_b-H_b-F_a$ moiety as described by the $N-F_a-F_b$ angle, which is 109° in the former and 103° in the latter. Thus, coupling constants associated with the $F_b-H_b-F_a$ hydrogen bond once again exhibit both distance and orientation dependencies. A statistical analysis using a correlation matrix indicates that the best correlations between computed and experimental coupling constants are found for the perpendicular structure 7 at an F_a-H_a distance of 1.80 Å and for the perpendicular structure with the experimentally derived $N-H_a$, F_a-H_a, F_b-H_b, and F_a-H_b distances. This same analysis predicts a value of −19 Hz for $^{2h}J_{N-F_a}$. Thus, the computed coupling constants for perpendicular proton-transferred 3:1 FH:NH$_3$ complexes at the geometries of the corresponding 3:1 FH:collidine complexes and at the experimentally derived geometry support the proposed perpendicular proton-transferred structure as the one which exists in solution.

Conclusions

Ab initio EOM-CCSD calculations have been performed on 3:1 FH:NH$_3$ complexes at their own optimized MP2/6-31+G(d,p) geometries and at the geometries in the hydrogen-bonding regions of corresponding optimized 3:1 FH:collidine complexes. The results of these calculations support the following statements.

(1) The most stable 3:1 FH:NH$_3$ complex has a cyclic structure stabilized by F−H−N, F−H−F, and a distorted N−H−F hydrogen bonds. In contrast, the most stable 3:1 FH:collidine complex has a perpendicular structure in which two FH molecules are hydrogen-bonded to the third F atom (F$_a$) which forms the F_a-H_a-N hydrogen bond. The isolated gas-phase equilibrium structure of the 3:1 FH:NH$_3$ complex has a proton-shared F_a-H_a-N hydrogen bond, while the 3:1 FH:collidine complex has an F_a-H_a-N hydrogen bond that is on the ion-pair side of proton-shared.

(2) The F_a-N coupling constants ($^{2h}J_{F_a-N}$) in the cyclic, open, and perpendicular structures of 3:1 FH:NH$_3$ complexes are large and negative, consistent with proton-shared F_a-H_a-N hydrogen bonds. For these complexes, $^{2h}J_{F_b-F_a}$ is positive, a consequence of short F_b-F_a distances and partial proton transfer from F$_b$ to F$_a$. $^{2h}J_{F_a-N}$ has a smaller absolute value in the zigzag structure, which has the least amount of proton-shared character, and $^{2h}J_{F_b-F_a}$ is negative.

(3) The signs and magnitudes of one- and two-bond spin−spin coupling constants computed for 3:1 FH:NH$_3$ complexes at optimized 3:1 FH:collidine geometries indicate that the complexes with collidine have ion-pair F_a-H_a-N hydrogen bonds with less proton-shared character than the hydrogen bonds in the corresponding 3:1 FH:NH$_3$ complexes. In particular, $^{2h}J_{F_a-N}$ is less negative at the 3:1 FH:collidine geometries, $^1K_{N-H_a}$ is positive, and $^{1h}K_{H_a-F_a}$ is negative, indicating that these complexes are stabilized by traditional ion-pair hydrogen bonds. Positive values of $^1K_{F_b-H_b}$ and negative values of $^{1h}K_{H_b-F_a}$ indicate that the $F_b-H_b-F_a$ hydrogen bonds are traditional.

(4) Coupling constants for 3:1 FH:NH$_3$ complexes computed at proton-transferred 3:1 FH:collidine perpendicular geometries are consistent with experimental coupling constants for the 3:1 FH:collidine complex in solution. The presence of the solvent appears to promote further proton transfer from F$_a$ to N across the F_a-H_a-N hydrogen bond as well as from F$_b$ to F$_a$ across the $F_b-H_b-F_a$ hydrogen bonds.

(5) The best correlations between experimental and computed coupling constants are found for two perpendicular structures, one at the optimized 3:1 FH:collidine geometry with an F_a-H_a distance of 1.80 Å, and the other at the optimized 3:1 FH:collidine geometry on the basis of distances derived from the experimental coupling constants. These calculations provide support for the proposed perpendicular structure of the 3:1 FH:collidine complex as the structure which exists in solution.

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