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Ab Initio Study of the Influence of Trimer Formation on One- and Two-Bond Spin−Spin Coupling Constants Across an X−H−Y Hydrogen Bond: AH:XH:YH_3 Complexes for A, X = ^{19}F, ^{35}Cl and Y = ^{15}N, ^{31}P

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Ab initio equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) calculations have been carried out to investigate the effect of a third polar near-neighbor on one-bond ($^1J_{X-H}$ and $^{1h}J_{H-Y}$) and two-bond ($^{2h}J_{X-Y}$) spin−spin coupling constants in AH:XH:YH_3 complexes, where A and X are ^{19}F and ^{35}Cl and Y is either ^{15}N or ^{31}P. The changes in both one- and two-bond spin−spin coupling constants upon trimer formation indicate that the presence of a third molecule promotes proton transfer across the X−H−Y hydrogen bond. The proton-shared character of the X−H−Y hydrogen bond increases in the order XH:YH_3 < ClH:XH:YH_3 < FH:XH:YH_3. This order is also the order of decreasing shielding of the hydrogen-bonded proton and decreasing X−Y distance, and is consistent with the greater hydrogen-bonding ability of HF compared to HCl as the third molecule. For all complexes, the reduced X−H and X−Y spin−spin coupling constants ($^1K_{X-H}$ and $^{2h}K_{X-Y}$) are positive, consistent with previous studies of complexes in which X and Y are second-period elements in hydrogen-bonded dimers. $^{1h}K_{H-Y}$ is, as expected, negative in these complexes which have traditional hydrogen bonds, except for ClH:FH:NH_3 and FH:FH:NH_3. In these two complexes, the F−H−N hydrogen bond has sufficient proton-shared character to induce a change of sign in $^{1h}K_{H-Y}$. The effects of trimer formation on spin−spin coupling constants are markedly greater in complexes in which NH_3 rather than PH_3 is the proton acceptor.

Introduction

In a recent paper, Leopold and co-workers[1] employed microwave spectroscopy to investigate the influence of a polar near-neighbor on proton transfer in a complex with a strong hydrogen bond, FH:NH_3. The polar near-neighbor was HF, and in its presence, the hydrogen-bonded trimer FH:FH:NH_3 was formed. (For ease of discussion, AH:XH:YH_3 complexes will be referred to as trimers even though the three hydrogen-bonded monomers are not identical.) These researchers observed that formation of the trimer influenced the extent of proton transfer across the F−H−N hydrogen bond. Their observation leads naturally to the question of the extent to which trimer formation affects spin−spin coupling constants across hydrogen bonds.

In our previous studies, we investigated one- and two-bond spin−spin coupling constants across X−H−Y hydrogen bonds in complexes formed from the second-period elements C, N, O, and F.[2−14] Several reviews and books have surveyed studies carried out by various investigators of spin−spin coupling constants across hydrogen bonds.[15−18] The present study addresses the effect of the presence of a third molecule (AH) on one-bond ($^1J_{X-H}$ and $^{1h}J_{H-Y}$) and two-bond ($^{2h}J_{X-Y}$) spin−spin coupling constants across X−H−Y hydrogen bonds in AH:XH:YH_3 trimers. In the present study, A and X are the halogens ^{19}F and ^{35}Cl and Y is either ^{15}N or ^{31}P. The complexes investigated include ClH:FH:NH_3, FH:FH:NH_3, ClH:ClH:NH_3, FH:ClH:NH_3, ClH:FH:PH_3, FH:FH:PH_3, ClH:ClH:PH_3, and FH:ClH:PH_3. These are represented schematically in Figure 1, which shows a cyclic trimer.

In this paper, coupling constants for the AH:XH dimer will not be presented or discussed. Our previous study of HF clusters showed that there is a very strong and unusual distance and orientation dependence of F−F coupling constants.[10] We have also computed the Cl−Cl coupling constant for the equilibrium structure of $(HCl)_2$ and found it to be negligible at −0.3 Hz. Since a detailed study of the distance and orientation dependence of one- and two-bond coupling constants in the FH:ClH and ClH:FH complexes has not been carried out, the data required to examine how these couplings change in the AH:XH:YH_3 complexes are not available. Thus, our focus will be on the one-bond ($^1J_{X-H}$ and $^{1h}J_{H-Y}$) and two-bond ($^{2h}J_{X-Y}$) spin−spin coupling constants across the X−H−Y hydrogen bond and the changes in these coupling constants due to the presence of a polar near-neighbor in the trimer AH:XH:YH_3.

Method of Calculation

The structures of the dimers FH:NH_3, FH:PH_3, ClH:NH_3, and ClH:PH_3 and the trimers ClH:FH:NH_3, FH:FH:NH_3, ClH:ClH:NH_3, FH:ClH:NH_3, ClH:FH:PH_3, FH:FH:PH_3, ClH:ClH:PH_3, and FH:ClH:PH_3 were fully optimized at second-order Møller−Plesset theory[19−22] with the 6-31+G(d,p) basis set.[23−26] Vibrational frequencies were computed to ensure that all structures are equilibrium structures on their potential surfaces, although there is essentially free rotation of the NH_3 and PH_3 molecules about the hydrogen-bonding axis in some complexes. In the

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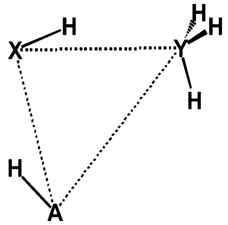

Figure 1. The trimer $AH{:}XH{:}YH_3$.

TABLE 1: Selected Distances (Å) and Angles (deg) and Binding Energies (kcal/mol) for $AH{:}XH{:}YH_3$ Trimers

trimer	R(X−Y)	R(X−H)	∠H−X−Y	∠A−X−Y	ΔE_e[a]
$ClH{:}FH{:}NH_3$	2.550	0.988	4	90	−7.1
$FH{:}FH{:}NH_3$	2.511	1.004	6	79	−10.6
$ClH{:}ClH{:}NH_3$	3.015	1.337	4	65	−5.1
$FH{:}ClH{:}NH_3$	2.917	1.381	5	62	−7.6
$ClH{:}FH{:}PH_3$	3.199	0.946	2	110	−5.0
$FH{:}FH{:}PH_3$	3.169	0.950	2	109	−7.4
$ClH{:}ClH{:}PH_3$	3.781	1.284	6	73	−3.1
$FH{:}ClH{:}PH_3$	3.729	1.288	9	65	−4.5

[a] MP2/6-31+G(d,p) electronic binding energies are computed relative to the dimer $XH{:}YH_3$ and the third polar molecule AH.

notation used in this paper, $AH{:}XH{:}YH_3$ implies that AH is the proton donor to XH, which is then the proton donor to YH_3. In some cyclic structures, YH_3 may also act as a proton donor to AH.

One-bond X−H ($^1J_{X-H}$) and H···Y ($^{1h}J_{H-Y}$) and two-bond X−Y ($^{2h}J_{X-Y}$) spin−spin coupling constants across X−H−Y hydrogen bonds have been computed using the ab initio equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) method in the configuration interaction (CI)-like approximation[27−30] with the Ahlrichs[31] qzp basis set on F, qz2p on P, Cl, and the hydrogen-bonded H, and Dunning's cc-pVDZ basis set on other hydrogens.[32,33] In the trimers, the in-plane H atom of NH_3 or PH_3 is also a potential proton donor (see Figure 1), so the qz2p basis set was also placed on it. In nonrelativistic theory, the total spin−spin coupling constant is a sum of four contributions: the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi-contact (FC), and spin−dipole (SD) terms.[34] All terms have been evaluated for all complexes, and all electrons have been correlated in the EOM-CCSD calculations.

The absolute shieldings (σ, ppm) of the H atoms in FH and ClH and the hydrogen-bonded hydrogens in the dimers and trimers were calculated using the gauge-invariant atomic orbitals (GIAO) formalism,[35] at the MP2 level with the same basis sets used for the coupling constant calculations. Structure optimizations were done using the Gaussian 98 suite of programs,[36] and coupling constants and shieldings were evaluated using ACES II.[37] All calculations were performed on the Cray SV1 or the Itanium Cluster at the Ohio Supercomputer Center.

Results and Discussion

Structures and Binding Energies. Table 1 presents selected MP2/6-31+G(d,p) structural data and binding energies for the eight trimers investigated in this study. Of particular interest is the open or cyclic nature of these complexes and the degree to which the X−H−Y hydrogen bonds deviate from linearity. As evident from Table 1, five of the trimers ($FH{:}FH{:}NH_3$, $ClH{:}ClH{:}NH_3$, $FH{:}ClH{:}NH_3$, $ClH{:}ClH{:}PH_3$, and $FH{:}ClH{:}PH_3$) are cyclic, as inferred from values of the A−X-Y angle that are <90°. The $ClH{:}FH{:}NH_3$ trimer has a Cl−F−N angle equal to 90°, which makes it borderline cyclic. Both complexes with FH as the proton donor to PH_3 ($ClH{:}FH{:}PH_3$ and $FH{:}FH{:}PH_3$) have open structures with tetrahedral X−F−P angles. Irrespective of whether the trimers have open or cyclic structures, the deviation of the X−H−Y hydrogen bond from linearity is relatively small, as seen from the values of the H−X−Y angle which are <10°. This slight deviation from linearity does not have a major effect on coupling constants.

TABLE 2: $^{2h}J_{F-Y}$, $^1J_{F-H}$, and $^{1h}J_{H-Y}$ and Their Components (Hz) and Corresponding F−Y, F−H, and H−Y Distances (R, Å) for the HF Monomer and $FH{:}YH_3$, $ClH{:}FH{:}YH_3$, and $FH{:}FH{:}YH_3$ Complexes, with Y = N, P

complex	R	PSO	DSO	FC	SD	J
HF monomer	0.927	183.9	0.4	308.8	1.7	494.8[a]
$FH{:}NH_3$						
F−N	2.637	2.8	0.0	−45.2	−1.3	−43.7
F−H	0.963	108.8	1.3	325.5	−4.1	431.5
H−N	1.673	0.5	−0.5	2.9	−0.3	2.6
$ClH{:}FH{:}NH_3$						
F−N	2.550	3.2	0.0	−64.1	−1.6	−62.5
F−H	0.988	82.4	1.9	298.4	−5.7	377.0
H−N	1.565	0.5	−0.5	−0.1	−0.3	−0.4
$FH{:}FH{:}NH_3$						
F−N	2.511	3.5	0.0	−72.7	−1.5	−70.7
F−H	1.004	70.4	2.1	269.7	−6.3	335.9
H−N	1.517	0.5	−0.5	−2.3	−0.3	−2.6
$FH{:}PH_3$						
F−P	3.281	1.2	−0.1	191.6	6.6	199.3
F−H	0.938	150.8	1.0	329.0	−0.9	479.9
H−P	2.342	−1.0	1.1	−19.9	2.0	−17.8
$ClH{:}FH{:}PH_3$						
F−P	3.199	1.6	0.0	283.4	8.0	293.0
F−H	0.946	134.9	1.3	345.2	−2.4	479.0
H−P	2.254	−1.0	1.2	−17.5	2.3	−15.0
$FH{:}FH{:}PH_3$						
F−P	3.169	1.8	0.0	329.8	8.5	340.1
F−H	0.950	127.6	1.4	352.3	−3.2	478.1
H−P	2.219	−1.0	1.2	−15.3	2.5	−12.6

[a] The experimental value of $^1J_{F-H}$ is +529 Hz (Berger, S.; Braun, S.; Kalinowski, H.-O. *NMR Spectroscopy of the Non-Metallic Elements*; John Wiley and Sons: Chichester, U.K., 1997; p 386).

Although other structures on the potential surfaces were optimized, those reported in this paper are ones in which an in-plane Y−H bond is constrained to be cis to AH with respect to the X−Y line in order to allow for the formation of cyclic trimers, as illustrated in Figure 1. All of the trimers formed when YH_3 is NH_3 have no imaginary frequencies. When YH_3 is PH_3, two complexes, $FH{:}FH{:}PH_3$ and $FH{:}ClH{:}PH_3$, have one imaginary frequency less than -15 cm^{-1} corresponding to rotation of the PH_3 molecule about the X−P axis. In all trimers, this rotation is essentially free.

The binding energies reported in Table 1 have been computed relative to the dimer $XH{:}YH_3$ and the polar near-neighbor AH. It is interesting to note that for a given $XH{:}YH_3$, the trimer formed when the near-neighbor is HF is more stable than the trimer with HCl, a consequence of the stronger proton-donating ability of HF. The effects of the stronger A−H···X hydrogen bond when AH is FH will be manifest in the one-bond X−H and H−Y and two-bond X−Y spin−spin coupling constants discussed below.

Coupling Constants. Table 2 presents F−H, F−Y, and H−Y distances, the PSO, DSO, FC, and SD terms, and the total F−H, F−Y, and H−Y coupling constants for the HF monomer and the dimers and trimers in which FH is the proton donor to NH_3 or PH_3. Table 3 presents the corresponding data for complexes in which ClH is the proton donor. In these two tables, all distances and coupling constants for each complex are listed together. However, to facilitate analysis of the effects of trimer formation on coupling constants between pairs of atoms that

TABLE 3: $^{2h}J_{Cl-Y}$, $^{1}J_{Cl-H}$, and $^{1h}J_{H-Y}$ and Their Components (Hz) and Corresponding Cl−Y, Cl−H, and H−Y Distances (*R*, Å) for the HCl Monomer and ClH:YH_3, ClH:ClH:YH_3, and FH:ClH:YH_3 Complexes, with Y = N, P

complex	*R*	PSO	DSO	FC	SD	*J*
HCl monomer	1.270	14.8	0.0	22.9	0.4	38.1
ClH:NH_3						
Cl−N	3.131	0.4	0.0	−5.0	−0.2	−4.8
Cl−H	1.309	9.0	0.1	32.7	−0.4	41.4
H−N	1.822	0.4	−0.4	6.7	−0.2	6.5
ClH:ClH:NH_3						
Cl−N	3.015	0.4	0.0	−7.5	−0.3	−7.4
Cl−H	1.337	7.0	0.1	31.1	−0.5	37.7
H−N	1.682	0.4	−0.4	5.9	−0.2	5.7
FH:ClH:NH_3						
Cl−N	2.917	0.6	0.0	−10.1	−0.3	−9.8
Cl−H	1.381	4.8	0.1	25.6	−0.6	29.9
H−N	1.545	0.5	−0.4	1.7	−0.2	1.6
ClH:PH_3						
Cl−P	3.866	0.1	0.0	15.6	0.8	16.5
Cl−H	1.279	12.7	0.0	27.9	0.1	40.7
H−P	2.587	−0.7	0.8	−25.8	1.3	−24.4
ClH:ClH:PH_3						
Cl−P	3.781	0.1	0.0	22.0	0.9	23.0
Cl−H	1.284	11.8	0.1	29.5	0.0	41.4
H−P	2.508	−0.7	0.9	−29.7	1.4	−28.1
FH:ClH:PH_3						
Cl−P	3.729	0.1	0.0	26.4	0.8	27.3
Cl−H	1.288	11.3	0.1	30.2	−0.1	41.5
H−P	2.466	−0.7	0.9	−31.2	1.4	−29.6

TABLE 4: $^{1}J_{X-H}$, $^{2h}J_{X-Y}$, and $^{1h}J_{H-Y}$, Corresponding Fermi-Contact Terms (Hz), Reduced Coupling Constants [$^{1}K_{X-H}$, $^{2h}K_{X-Y}$, and $^{1h}K_{H-Y}$ (N A^{-2} m^{-3}) × 10^{19}], and Distances (Å) for AH:XH:YH_3 Complexes

X−H = F−H

complex	*R*	FC	$^{1}J_{F-H}$	$^{1}K_{F-H}$
HF monomer	0.927	308.8	494.8	43.8
FH:PH_3	0.938	329.0	479.9	42.4
ClH:FH:PH_3	0.946	345.2	479.0	42.4
FH:FH:PH_3	0.950	352.3	478.1	42.3
FH:NH_3	0.963	325.5	431.5	38.2
ClH:FH:NH_3	0.988	298.4	377.0	33.3
FH:FH:NH_3	1.004	269.7	335.9	29.7

X−Y = F−P

complex	*R*	FC	$^{2h}J_{F-P}$	$^{2h}K_{F-P}$
FH:PH_3	3.281	191.6	199.3	43.5
ClH:FH:PH_3	3.199	283.4	293.0	64.0
FH:FH:PH_3	3.169	329.8	340.1	74.2

X−Y = F−N

complex	*R*	FC	$^{2h}J_{F-N}$	$^{2h}K_{F-N}$
FH:NH_3	2.637	−45.2	−43.7	38.1
ClH:FH:NH_3	2.550	−64.1	−62.5	54.5
FH:FH:NH_3	2.511	−72.7	−70.7	61.7

H···Y = H···N

complex	*R*	FC	$^{1h}J_{H-N}$	$^{1h}K_{H-N}$
ClH:NH_3	1.822	6.7	6.5	−5.3
ClH:ClH:NH_3	1.682	5.9	5.7	−4.7
FH:ClH:NH_3	1.545	1.7	1.6	−1.3
FH:NH_3	1.673	2.9	2.6	−2.1
ClH:FH:NH_3	1.565	−0.1	−0.4	+0.3
FH:FH:NH_3	1.517	−2.3	−2.6	+2.1

X−H = Cl−H

complex	*R*	FC	$^{1}J_{Cl-H}$	$^{1}K_{Cl-H}$
HCl monomer	1.270	22.9	38.1	32.3
ClH:PH_3	1.279	27.9	40.7	34.5
ClH:ClH:PH_3	1.284	29.5	41.4	35.1
FH:ClH:PH_3	1.288	30.2	41.5	35.2
ClH:NH_3	1.309	32.7	41.4	35.1
ClH:ClH:NH_3	1.337	31.1	37.7	32.0
FH:ClH:NH_3	1.381	25.6	29.9	25.4

X−Y=Cl−P

complex	*R*	FC	$^{2h}J_{Cl-P}$	$^{2h}K_{Cl-P}$
ClH:PH_3	3.866	15.6	16.5	34.6
ClH:ClH:PH_3	3.781	22.0	23.0	48.2
FH:ClH:PH_3	3.729	26.4	27.3	57.2

X−Y = Cl−N

complex	*R*	FC	$^{1h}J_{Cl-N}$	$^{1h}K_{Cl-N}$
ClH:NH_3	3.131	−5.0	−4.8	40.2
ClH:ClH:NH_3	3.015	−7.5	−7.4	62.0
FH:ClH:NH_3	2.917	−10.1	−9.8	82.1

H···Y = H···P

complex	*R*	FC	$^{1h}J_{H-P}$	$^{1h}K_{H-P}$
ClH:PH_3	2.587	−25.8	−24.4	−5.0
ClH:ClH:PH_3	2.508	−29.7	−28.1	−5.8
FH:ClH:PH_3	2.466	−31.2	−29.6	−6.1
FH:PH_3	2.342	−19.9	−17.8	−3.7
ClH:FH:PH_3	2.254	−17.5	−15.0	−3.1
FH:FH:PH_3	2.219	−15.3	−12.6	−2.6

form the X−H−Y hydrogen bond, relevant distances, Fermi-contact terms, total coupling constants, and reduced spin−spin coupling constants are also presented in Table 4. These data are arranged so that coupling constants between the same pair of atoms in different complexes are grouped together. X−H data are listed in order of increasing X−H distance; H−Y and X−Y data are given in order of decreasing H−Y and X−Y distances, respectively. These orderings also correspond to the increasing stability of the grouped complexes.

$^{2h}J_{X-Y}$. The two-bond spin−spin coupling constants listed in Table 4 include $^{2h}J_{F-N}$, $^{2h}J_{Cl-N}$, $^{2h}J_{F-P}$, and $^{2h}J_{Cl-P}$. For a given YH_3, the absolute value of the two-bond spin−spin coupling constant increases in the order XH:YH_3 < ClH:XH:YH_3 < FH:XH:YH_3. Since the two-bond spin−spin coupling constant $^{2h}J_{X-Y}$ is the one which appears to be most sensitive to hydrogen-bond type, these results indicate that the presence of a third molecule always increases the proton-shared character of the hydrogen bond. Moreover, the degree of proton sharing increases as the hydrogen-bond proton-donating strength of the third molecule increases. For each set of three complexes, the X−Y distance decreases as the proton-shared character of the hydrogen bond increases, as observed many times previously.[2−11]

As a specific example, consider the complexes FH:NH_3, ClH:FH:NH_3, and FH:FH:NH_3. In the dimer, the F−N distance is 2.637 Å and $^{2h}J_{F-N}$ is −43.7 Hz. In the trimer with ClH as the third molecule, the F−N distance decreases to 2.550 Å, while $^{2h}J_{F-N}$ increases (in absolute value) to −62.5 Hz. The trend continues as the F−N distance further decreases to 2.511 Å and the absolute value of $^{2h}J_{F-N}$ increases to −70.7 Hz when the third molecule is FH.

The data of Table 4 also show that all reduced two-bond spin−spin coupling constants ($^{2h}K_{X-Y}$) are positive, in agreement with our previous prediction.[12] Since the magnetogyric ratios of ^{19}F and ^{35}Cl are positive while that of ^{15}N is negative, both $^{2h}J_{F-N}$ and $^{2h}J_{Cl-N}$ are negative. One- and two-bond spin−spin coupling constants have been measured as a function of temperature by Limbach and co-workers for F−H−N hydrogen bonds in FH:collidine complexes.[38−40] The experimental F−N coupling constants are also negative and exhibit their largest absolute values when the hydrogen bond is a quasi-symmetric proton-shared hydrogen bond. Since the magnetogyric ratio of ^{31}P is positive, $^{2h}J_{F-P}$ and $^{2h}J_{Cl-P}$ are also positive.

$^1J_{X-H}$. Data for F−H coupling in the HF monomer, the dimers FH:NH$_3$ and FH:PH$_3$, and the four trimers ClH:FH:NH$_3$, FH:FH:NH$_3$, ClH:FH:PH$_3$, and FH:FH:PH$_3$ are listed in Table 4. In the monomer, the F−H distance is 0.927 Å and $^1J_{F-H}$ is 494.8 Hz. The weakest hydrogen bond is found in FH:PH$_3$, which has an F−H distance of 0.938 Å and a reduced value of $^1J_{F-H}$ equal to 479.9 Hz. The presence of a third molecule has a relatively small effect on the F−H distances and coupling constants in ClH:FH:PH$_3$ and FH:FH:PH$_3$. The F−H distances in these complexes are 0.946 and 0.950 Å, and the values of $^1J_{F-H}$ are 479.0 and 478.1 Hz, respectively. Thus, the variation in coupling constants in the complexes FH:PH$_3$, ClH:FH:PH$_3$, and FH:FH:PH$_3$ is less than 2 Hz. ClH:FH:PH$_3$ and FH:FH:PH$_3$ are the two open (noncyclic) trimers in the set.

The situation is quite different for complexes that have FH as the proton donor to NH$_3$. In FH:NH$_3$, the F−H distance is 0.963 Å and the F−H coupling constant decreases from the monomer value to 431.5 Hz. The presence of the third molecule has a dramatic effect, which increases as the hydrogen-bond proton-donating ability of the third molecule increases. The F−H distance increases to 0.988 Å in ClH:FH:NH$_3$ and 1.004 Å in FH:FH:NH$_3$. The F−H coupling constants decrease to 377.0 and 335.9 Hz, respectively. Thus, in these complexes with FH as the proton donor to NH$_3$, the presence of the third molecule increases the degree of proton transfer from F to N, thereby increasing the proton-shared character of the hydrogen bond. These results are in agreement with the conclusions of Leopold and co-workers, who observed that the presence of a polar near-neighbor promotes proton transfer from F to N in the FH:FH:NH$_3$ trimer.[1]

There are two other observations that can be made concerning F−H coupling constants from the data of Table 4. The first is that while the FC term and $^1J_{F-H}$ are both positive, the FC term is not a good approximation to $^1J_{F-H}$, since the PSO term is significant. The second observation is that the reduced F−H coupling constants ($^1K_{F-H}$) are also positive, in agreement with the generalization made based on hydrogen-bonded dimers that all C−H, N−H, O−H, and F−H reduced coupling constants are positive. Since the magnetogyric ratios of ^{19}F and ^{1}H are positive, $^1J_{F-H}$ is also positive, in agreement with experimental data.[13]

Table 4 also reports the one-bond Cl−H coupling constants in the HCl monomer, the dimers ClH:NH$_3$ and ClH:PH$_3$, and the trimers ClH:ClH:NH$_3$, FH:ClH:NH$_3$, ClH:ClH:PH$_3$, and FH:ClH:PH$_3$. Formation of the dimer ClH:PH$_3$, which has the weakest hydrogen bond among all complexes, leads to an increase in the Cl−H bond length. However, both the FC terms and $^1J_{Cl-H}$ also increase in the complex. The Cl−H bond length increases in the complexes in the order ClH:PH$_3$ < ClH:ClH:PH$_3$ < FH:ClH:PH$_3$ < ClH:NH$_3$, and the FC term also increases in the same order. However, the total coupling constant varies within this group of complexes by less than 1 Hz. The constancy of $^1J_{Cl-H}$ is primarily a result of a counterbalancing of the contributions of the PSO and FC terms.

The situation is quite different for the trimers with ClH as the proton donor to NH$_3$. Relative to ClH:NH$_3$, the Cl−H distance in ClH:ClH:NH$_3$ and FH:ClH:NH$_3$ increases from 1.309 to 1.337 and 1.381 Å and the Cl−H coupling constant decreases from 41.4 Hz in the dimer to 37.7 and 29.9 Hz, respectively, in the two trimers. Once again, the influence of the third molecule on the X−H coupling constant is greater in the complexes with the stronger proton acceptor NH$_3$ compared to PH$_3$.

Table 4 also shows that the reduced spin−spin coupling constants ($^1K_{Cl-H}$) are positive in all complexes. Thus, the generalization that all reduced spin−spin coupling constants for second-row proton donors C−H, N−H, O−H, and F−H are positive appears to extend to the third period for Cl−H. Since the magnetogyric ratio of ^{35}Cl is positive, $^1J_{Cl-H}$ is also predicted to be positive.

In ref 13, a linear relationship was obtained between X−H coupling constants and X−H distances times the square of the Pauling electronegativity of X for a set of 16 monomers that have C−H, N−H, O−H, and F−H as proton donors, and 64 hydrogen-bonded dimers formed by these donors. These complexes also have second-period elements as proton acceptors. The data for the F−H and Cl−H donors in the complexes AH:FH:YH$_3$ and AH:ClH:YH$_3$ obtained in the present study also fit this same relationship.

$^{1h}J_{H-Y}$. In our previous study of X−H−Y hydrogen bonds with X and Y second-period elements, it was observed that all reduced coupling constants $^{1h}K_{H-Y}$ are negative for traditional hydrogen bonds. However, for a symmetric X−H−X hydrogen bond, both $^1K_{X-H}$ and $^{1h}K_{H-X}$ must be equal and positive. This implies that, somewhere along the proton-transfer coordinate, $^{1h}K_{H-Y}$ must change sign. For a complex stabilized by a traditional hydrogen bond, this sign change was found to occur along the proton-transfer coordinate not far from the equilibrium structure.[14] That $^{1h}K_{H-Y}$ and subsequently $^1K_{X-H}$ change sign along the proton-transfer coordinate is in agreement with experimental data obtained by Limbach et al.,[37−39] and this provides insight into why H−Y spin−spin coupling constants for specific complexes may not be experimentally detectable.

To what extent do the signs of $^{1h}K_{H-Y}$ in the trimers follow the patterns noted above? Table 4 presents $^{1h}K_{H-N}$ values for dimers and trimers with NH$_3$ as the proton acceptor molecule. It has been noted above that in the series ClH:NH$_3$, ClH:ClH:NH$_3$, and FH:ClH:NH$_3$, $^{2h}J_{Cl-N}$ increases in absolute value, a sign that the hydrogen bond is acquiring increased proton-shared character. The changes in $^{1h}K_{H-N}$ are consistent with this observation, since in the same series $^{1h}K_{H-N}$ becomes less negative, with values of −5.3, −4.7, and −1.3 (N A^{-2} m^{-3}). However, progress along the proton-transfer coordinate is apparently not sufficient to induce a change of sign in $^{1h}K_{H-N}$ in this series. This is not the case in the series FH:NH$_3$, ClH:FH:NH$_3$, and FH:FH:NH$_3$. $^{1h}K_{H-N}$ is −2.1 in FH:NH$_3$, is slightly positive in ClH:FH:NH$_3$ with a value of +0.3, and then increases to +2.1 (N A^{-2} m^{-3}) in FH:FH:NH$_3$. Thus, the presence of FH induces sufficient proton transfer in FH:FH:NH$_3$ to cause a change of sign in $^{1h}K_{H-N}$.

Does the fact that $^{1h}K_{H-N}$ changes sign in the series of complexes with FH as the proton donor to NH$_3$ (FH:NH$_3$, ClH:FH:NH$_3$, and FH:FH:NH$_3$) but not in the corresponding series with ClH as the donor (ClH:NH$_3$, ClH:ClH:NH$_3$, and FH:ClH:NH$_3$) indicate that the hydrogen bonds in the complexes with FH have greater proton-shared character? Although the change of sign of $^{1h}K_{H-N}$ could be used to support this interpretation, the differences in $^{1h}K_{H-N}$ in the two series may simply be a reflection of the much longer H−N distances in the complexes with ClH as compared with FH. Moreover, previous studies of the structures of complexes with hydrogen halides as proton donors to nitrogen bases[41] and of the effects of external electric fields applied along the hydrogen-bonding axis on F−N and Cl−N distances and coupling constants in ClH:NH$_3$ and FH:NH$_3$ complexes indicate that a proton-shared hydrogen bond is more readily formed when ClH is the proton donor. Thus, for the ClH:NH$_3$ complex, the Cl−H−N hydrogen bond becomes a quasi-symmetric proton-shared hydrogen bond at a field strength of ~0.0055 au. At this field strength, the Cl−N distance is shortest and $^{2h}J_{Cl-N}$ exhibits its maximum absolute value.[42] In contrast, a field of 0.0250 au is required to produce a quasi-symmetric proton-shared F−H−N hydrogen bond in the FH:NH_3 complex, as judged by the same criteria. This is as expected, since the F−H bond is much stronger than the Cl−H bond.

For complexes with PH_3 as the proton acceptor molecule, $^{1h}K_{H-P}$ is always negative. This is another indication that the hydrogen bonds in these complexes are traditional hydrogen bonds with only a very limited amount of proton-shared character. In the series ClH:PH_3, ClH:ClH:PH_3, and FH:ClH:PH_3, $^{1h}K_{H-P}$ is always negative but surprisingly increases with decreasing H−P distance. This behavior may be related to the very long Cl−P and H−P distances in Cl−H−P hydrogen bonds. It is also possible that, along the proton-transfer coordinate, the reduced FC terms and $^{1h}K_{H-P}$ can exhibit extreme negative values before increasing and changing sign. In contrast, complexes with F−H−P hydrogen bonds show the expected pattern, decreasing from −3.7 to −3.1 to −2.6 ($N\ A^{-2}\ m^{-3}$) in FH:PH_3, ClH:FH:PH_3, and FH:FH:PH_3, respectively. However, once again, the long F−P and H−P distances limit the degree of proton-shared character of the hydrogen bond and $^{1h}K_{H-P}$ does not become positive.

Reduced Coupling Constants and NMRTWM. In a previous paper, the nuclear magnetic resonance triplet wave function model (NMRTWM) was proposed as a model for obtaining insight into the signs of spin−spin coupling constants.[43] NMRTWM focuses on the Fermi-contact term, which is an excellent approximation to the two-bond X−Y spin−spin coupling constant $^{2h}J_{X-Y}$ across an X−H−Y hydrogen bond, except for F−F coupling in $(HF)_2$.[10] In the sum-over-states expression for the FC term, contributions arise from excited triplet states that couple to the ground state through the Fermi-contact operator.[34,44] NMRTWM states that the sign of the contribution from a particular excited triplet state is related to the nodal pattern of the triplet state wave function and the resulting alignment of nuclear magnetic moments. If the wave function has the same sign at atoms X and Y, then the magnetic moments of X and Y have a parallel alignment and the sign of the contribution to the reduced FC term is negative. Conversely, if the wave function has opposite signs at atoms X and Y, then the nuclear magnetic moments of these atoms have an antiparallel alignment and the contribution to the reduced X−Y Fermi-contact term is positive. Although the Fermi-contact term may or may not be a good quantitative approximation to the one-bond X−H and H−Y coupling constants, it is usually the dominant term, with the same sign as the total coupling constant. Thus, NMRTWM has been used to gain insight into the signs of both one- and two-bond coupling constants across hydrogen bonds.

For hydrogen-bonded dimers stabilized by traditional hydrogen bonds, all two-bond reduced spin−spin coupling constants ($^{2h}K_{X-Y}$) are positive,[12] covalent one-bond X−H coupling constants ($^{1}K_{X-H}$) are positive,[13] and hydrogen-bond one-bond H−Y coupling constants ($^{1h}K_{H-Y}$) are negative.[14] All of these signs are consistent with the dominance of low-energy triplet states that have one node (or an odd number of nodes) intersecting the X−Y hydrogen-bonding axis between X and H and no nodes (or an even number of nodes) intersecting the H−Y hydrogen bond. The signs of the reduced X−Y and X−H Fermi-contact terms and reduced coupling are positive in all trimers, as evident from Table 4, as expected for complexes with traditional hydrogen bonds. The H−Y reduced FC terms and reduced coupling constants are negative in all trimers except ClH:FH:NH_3 and FH:FH:NH_3. As noted above, the F−H−N hydrogen bonds in ClH:FH:NH_3 and FH:FH:NH_3 have sufficient proton-shared character to induce a change of sign in $^{1h}K_{H-Y}$. This is also consistent with the observation that both $^{1}K_{X-H}$ and $^{1h}K_{H-Y}$ are positive as hydrogen bonds acquire increased proton-shared character. The dominant triplet state wave functions for one-bond couplings must then be those with one node (or an odd number of nodes) intersecting the X−H bond and one node (or an odd number or nodes) intersecting the H−Y bond.

TABLE 5: Selected Distances (Å) and Chemical Shieldings (ppm) of X−H Hydrogen Atoms in Monomers and in XH:YH_3 and AH:XH:YH_3 Complexes with X−H−Y Hydrogen Bonds

species	R(X−Y)	R(X−H)	σ
FH		0.927	29.0
FH:NH_3	2.637	0.963	21.4
ClH:FH:NH_3	2.550	0.988	18.5
FH:FH:NH_3	2.511	1.004	17.2
FH:PH_3	3.281	0.938	26.3
ClH:FH:PH_3	3.199	0.946	24.7
FH:FH:PH_3	3.169	0.950	24.1
ClH		1.270	31.1
ClH:NH_3	3.131	1.309	22.5
ClH:ClH:NH_3	3.015	1.337	19.2
FH:ClH:NH_3	2.917	1.381	15.5
ClH:PH_3	3.866	1.279	28.4
ClH:ClH:PH_3	3.781	1.284	27.3
FH:ClH:PH_3	3.729	1.288	26.7

Shieldings of Hydrogen-Bonded Protons. The computed shieldings of the hydrogen atoms in the monomers FH and ClH and of these atoms hydrogen-bonded to NH_3 or PH_3 in dimers and trimers are listed in Table 5. The shielding of the H atoms decreases in the order XH > XH:YH_3 > ClH:XH:YH_3 > FH:XH:YH_3. This order is indicative of decreased electron density on the hydrogen-bonded X−H proton. It is consistent with the changes in coupling constants described above and indicative of increasing proton-shared character of the hydrogen bond in the series.

Conclusions

Ab initio EOM-CCSD one- and two-bond spin−spin coupling constants ($^{1}J_{X-H}$, $^{1h}J_{H-Y}$, and $^{2h}J_{X-Y}$) across X−H−Y hydrogen bonds have been calculated for the dimers XH:YH_3 and trimers AH:XH:YH_3 for A, X = ^{19}F, ^{35}Cl and Y = ^{15}N or ^{31}P. The results of these calculations support the following statements.

(1) For a given YH_3, the absolute value of the two-bond spin−spin coupling constant ($^{2h}J_{X-Y}$) increases in the order XH:YH_3 < ClH:XH:YH_3 < FH:XH:YH_3. Thus, the presence of a third molecule (AH) increases the proton-shared character of the X−H−Y hydrogen bond. Furthermore, the degree of proton sharing increases as the hydrogen-bond proton-donating strength of AH increases. Thus, the computed two-bond X−Y spin−spin coupling constants support the results of a microwave spectroscopic study of the FH:FH:NH_3 complex,[1] which also indicates that the presence of a third polar molecule promotes proton transfer across the F−H−N hydrogen bond.

(2) All reduced two-bond X−Y coupling constants ($^{2h}K_{X-Y}$) for trimers AH:XH:YH_3 are positive, irrespective of whether X and/or Y are second- or third-period atoms. These results are consistent with a previous study which showed that all $^{2h}K_{X-Y}$ for X and Y second-period elements are positive, with the exception of $^{2h}K_{F-F}$ for $(HF)_2$.

(3) The presence of a third polar molecule has only a small effect on one-bond X−H coupling constants when PH_3 is the proton acceptor. In contrast, when NH_3 is the acceptor, the X−H coupling constants decrease in the order $XH:NH_3 > ClH:XH:NH_3 > FH:XH:NH_3$. This order is consistent with the order of increasing proton-shared character of the X−H−Y hydrogen bond.

(4) All reduced one-bond X−H spin−spin coupling constants are positive, as previously observed for dimers with X a second-period element. This generalization still applies when the third-period atom is Cl and Cl−H is the proton donor.

(5) With the exception of $ClH:FH:NH_3$ and $FH:FH:NH_3$, reduced one-bond H$\cdots$Y spin−spin coupling constants ($^{1h}K_{H-Y}$) are negative, as expected for complexes with traditional hydrogen bonds. However, for the trimers $ClH:FH:NH_3$ and $FH:FH:NH_3$, the presence of the third molecule induces sufficient proton-shared character of the F−H−N hydrogen bond to change the sign of $^{1h}K_{H-Y}$. The value of $^{1h}K_{H-Y}$ is greater in $FH:FH:NH_3$ than in $ClH:FH:NH_3$.

(6) The absolute shieldings of the hydrogen-bonded protons decrease in the order $XH > XH:YH_3 > ClH:XH:YH_3 > FH:XH:YH_3$. The changes in the shieldings are consistent with the changes in coupling constants and are indicative of increasing proton-shared character of the X−H−Y hydrogen bond in the series of complexes.

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