Ab Initio EOM-CCSD Spin−Spin Coupling Constants for Hydrogen-Bonded Formamide Complexes: Bridging Complexes with NH_3, $(NH_3)_2$, H_2O, $(H_2O)_2$, FH, and $(FH)_2$

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EOM-CCSD spin−spin coupling constants across hydrogen bonds have been computed for complexes in which NH_3, H_2O, and FH molecules and their hydrogen-bonded dimers form bridging complexes in the amide region of formamide. The formamide one-bond N−H coupling constant [^1J(N−H)] across N−H···X hydrogen bonds increases in absolute value upon complexation. The signs of the one-bond coupling constants ^{1h}J(H−X) indicate that these complexes are stabilized by traditional hydrogen bonds. The two-bond coupling constants for hydrogen bonds with N−H as the donor [^{2h}J(N−X)] and the carbonyl oxygen as the acceptor [^{2h}J(X−O)] increase in absolute value in the formamide/dimer relative to the corresponding formamide/monomer complex as the hydrogen bonds acquire increased proton-shared character. The largest changes in coupling constants are found for complexes of formamide with FH and $(FH)_2$, suggesting that bridging FH monomers and dimers in particular could be useful NMR spectroscopic probes of amide hydrogen bonding.

Introduction

In addition to its intrinsic importance in many areas of chemistry as the simplest of amides,[1] formamide has been used as a model for the peptide bond and for hydrogen bonding involving peptides.[2–7] We have previously published several general papers[8–10] as well as an early theoretical one[11] dealing with formamide. Amide hydrogen bonding is of special interest since small solvent molecules like NH_3 and H_2O can form complexes in which solvent monomers or dimers can bridge the N−H and C═O groups.[12–18] Complexes of formamide with one NH_3, H_2O, or FH molecule and with the dimers of these molecules bridging the amide region are illustrated in Scheme 1.

Although there have been previous studies of spin−spin coupling constants for formamide and cyclic and open formamide dimers,[19,20] there have been no investigations of coupling constants across hydrogen bonds in complexes involving bridging solvent molecules in the amide region. Therefore, it is the purpose of this paper to present computed one- and two-bond spin−spin coupling constants across hydrogen bonds in complexes of formamide with NH_3, H_2O, FH, $(NH_3)_2$, $(H_2O)_2$, and $(FH)_2$ and to assess the variation in coupling constants as a function of the nature of the bridging group and the effect of hydrogen bonding on intramolecular one-bond N1−C2 and two-bond C2−H4 coupling constants of formamide.

Computational Methods

Structure optimizations were carried out at second-order Møller−Plesset perturbation theory (MP2)[21–24] as implemented in Gaussian 03,[25] with the 6-31+G(d,p) basis set.[26–29] The planar formamide monomer of C_s symmetry has one imaginary frequency corresponding to an out-of-plane distortion. However, the energy difference between this structure and the fully-optimized C_1 structure is negligible, and coupling constants computed for these two structures are essentially identical. Moreover, the formamide molecule is planar in all of the fully-optimized equilibrium complexes. These complexes have C_s symmetry, except for complexes of formamide with H_2O and $(H_2O)_2$, which have only C_1 symmetry. However, in these two complexes, all hydrogen-bonded atoms lie in the plane defined by the formamide molecule.

Coupling constants for the bridging complexes were evaluated using the equation-of-motion coupled-cluster singles and doubles method (EOM-CCSD) in the configuration interaction (CI)-like approximation,[30–33] with all electrons correlated, as implemented in ACES II.[34] For these calculations, the Ahlrichs[35] qzp basis set was used to evaluate coupling constants involving ^{13}C, ^{15}N, ^{17}O, and ^{19}F, and the qz2p basis was used for the hydrogen-bonded ^1H atoms. The Dunning cc-pVDZ basis[36,37] was placed on the remaining H atoms. Coupling constants for the formamide monomer were also computed with the qz2p basis on all H atoms. All terms that contribute to the total coupling constant, namely, the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi contact (FC), and spin−dipole (SD), were evaluated for formamide and its complexes, except for formamide/$(NH_3)_2$ and formamide/$(H_2O)_2$. Because of size and low symmetry, only the calculation of the FC terms was feasible for formamide/$(H_2O)_2$. The PSO, DSO, and FC terms were computed for formamide/$(NH_3)_2$, and the SD term was approximated from the SD terms in isolated formamide, formamide/NH_3, and $(NH_3)_2$. All calculations were performed on the Cray X1 or the Itanium cluster at the Ohio Supercomputer Center.

Results and Discussion

Coupling Constants for Formamide. Before examining spin−spin coupling constants for hydrogen-bonded complexes of formamide with the solvents ammonia, water, and hydrogen fluoride, it is appropriate to examine coupling constants for the formamide monomer since experimental data for many of these couplings are available. Table 1 presents a comparison of experimental and computed EOM-CCSD coupling constants.

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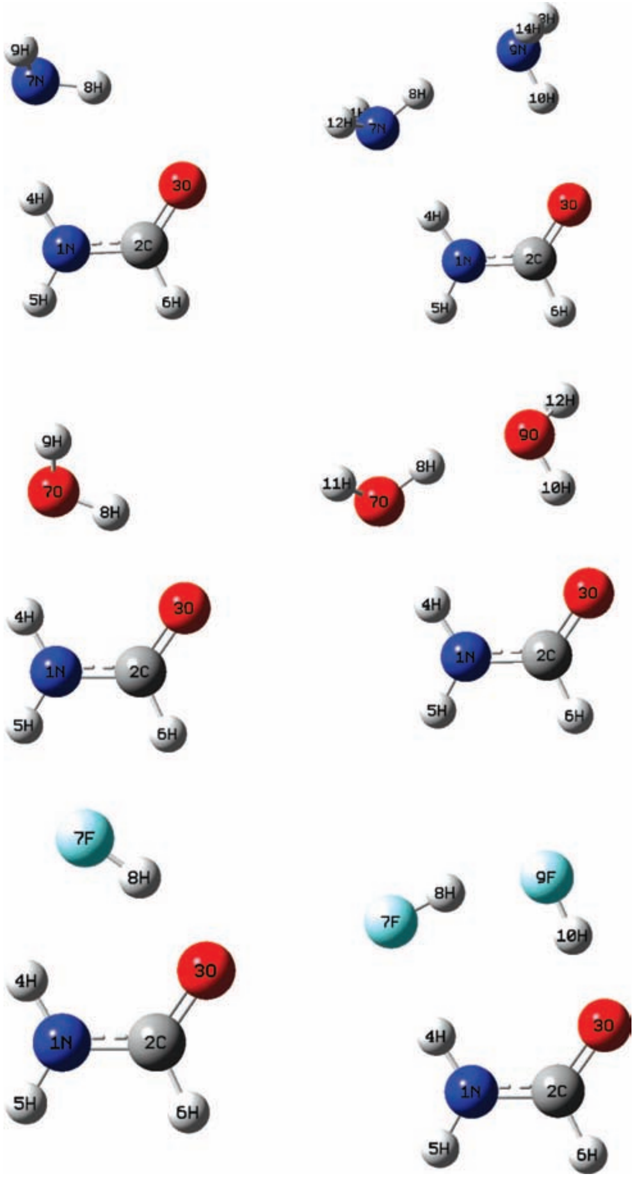
SCHEME 1: The Complexes of Formamide with One and Two Solvent Molecules, Illustrating the Numbering System



The components of J are given in Table S1. The experimental values are those given by Pecul, Leszczynski, and Sadlej in their study of formamide.[19] Values not reported by those authors have been taken from other sources.[38–41] There is good agreement between computed and experimental coupling constants as is evident from eq 1.

$$J_{calc} = (0.951 \pm 0.012)J_{exp} - (2.0 \pm 0.9) \qquad n = 10, r^2 = 0.9987 \quad (1)$$

This agreement and the agreement between computed and experimental couplings constants for hydrogen-bonded complexes[42,43] are important since experimental coupling constants for complexes of formamide with solvent molecules are not available.

Complexes of Formamide with Bridging Solvent Molecules. ***Structures.*** Table 2 presents hydrogen-bonded X−H and X−Y distances, H−X−Y angles, and binding energies for the complexes of formamide with bridging solvent monomers and dimers, designated as FMA/monomer and FMA/dimer. The complexes with a single bridging molecule have hydrogen bonds which deviate significantly from linearity. This deviation for the N1−H4···X7 hydrogen bond increases in the order FMA/NH_3 < FMA/H_2O < FMA/FH, while the deviation from linearity of the X7−H8···O3 hydrogen bond decreases in the same order. This is a reflection of the relative proton-donating and proton-accepting abilities of the solvent molecules, with NH_3 being the best acceptor for hydrogen bonding and FH the best donor. The deviations from linearity of the N1−H4···X7 and X9−H10···O3 hydrogen bonds are significantly reduced in complexes with dimers, as these are much better accommodated in the amide region. Not surprisingly, the binding energies of the complexes with bridging dimers are significantly greater than those with monomers. The N1−X7 distances increase in complexes with bridging dimers relative to complexes with bridging monomers when the solvent is NH_3 or H_2O

TABLE 1: Spin−Spin Coupling Constants (J, Hz) for Formamide[a]

coupling	J_{exp}[19]	interval[19,38–41] of exp. data	J_{calc}
^1J(N1−C2)	−14.82	−13.9/−14.8	−16.93
^1J(N1−H4)	−88.68	−87.0/−88.7	−89.53
^1J(N1−H5)	−91.49	−88.3/−92.7	−89.86
^1J(C2−O3)			27.63
^1J(C2−H6)	193.11	183.2/193.1	179.61
^2J(N1−O3)			0.69
^2J(N1−H6)	−13.49	−13.5/−21.5	−17.64
^2J(C2−H4)	−5.2	−5.2/−5.2	−2.34
^2J(C2−H5)	2.9	2.9/2.9	4.73
^2J(O3−H6)			−6.04
^2J(H4−H5)	2.9[38]	2.3/2.9	2.91
^3J(O3−H4)			1.68
^3J(O3−H5)			−0.65
^3J(H4−H6) (trans)	13.90	11.6/13.9	10.28
^3J(H5−H6) (cis)	2.25	1.6/2.3	0.48

[a] See Scheme 1 for atom numbering. Components of J are given in Table S1.

TABLE 2: Binding Energies (ΔE, kcal/mol), X−H and X−Y distances (R, Å), and H−X−Y Angles (°) for Bridging Complexes of Formamide with Solvent Molecules[a]

complex	R(X−Y)	R(X−H)	R(H···Y)	∠H−X−Y	ΔE
FMA/NH_3					9.3
N1−H4···N7	2.963	1.020	2.042	21	
N7−H8···O3	3.128	1.018	2.297	29	
FMA/$(NH_3)_2$					14.1[b]
N1−H4···N7	2.984	1.028	1.957	1	
N7−H8···N9	3.106	1.024	2.112	11	
N9−H10···O3	3.083	1.019	2.081	8	
FMA/H_2O					10.3
N1−H4···O7	2.891	1.014	2.058	29	
O7−H8···O3	2.812	0.976	1.941	22	
FMA/$(H_2O)_2$					16.4[b]
N1−H4···O7	2.918	1.022	1.899	4	
O7−H8···O9	2.740	0.981	1.796	13	
O9−H10···O3	2.783	0.981	1.814	7	
FMA/FH					12.8
N1−H4···F7	2.929	1.012	2.192	36	
F7−H8···O3	2.556	0.961	1.628	12	
FMA/$(FH)_2$					20.5[b]
N1−H4···F7	2.915	1.017	1.910	7	
F7−H8···F9	2.509	0.955	1.588	12	
F9−H10···O3	2.464	0.989	1.477	3	

[a] See Scheme 1 for numbering. The hydrogen bonds are N1−H4···X7 and X7−H8···O5 for the complexes with one solvent molecule. For complexes with the solvent dimer, the hydrogen bonds are N1−H4···X7, X7−H8···X9, and X9−H10···O3. [b] Binding energy relative to the solvent dimer.

TABLE 3: Spin−Spin Coupling Constants (Hz) across X−H···Y Hydrogen Bonds in Bridging Complexes of Formamide with Solvent Molecules[a]

complex	hydrogen bond	^{2h}J(X−Y)	^{1}J(X−H)	^{1h}J(H−Y)
		Complexes with NH_3[b]		
monomer	N1−H4···N7[c]	3.3	−92.0	2.8
dimer		5.4	−91.8	3.4
monomer	N7−H8···O3	1.2	−63.8	0.8
dimer	N9−H10···O3	1.9	−64.1	3.2
dimer	N7−H8···N9	3.0	−64.5	2.7
		Complexes with H_2O		
monomer	N1−H4···O7	1.9	−92.5 (−90.5)[d]	2.8
dimer		5.0	(−91.0)[d]	4.8
monomer	O7−H8···O3	2.6	−83.4	3.4
dimer	O9−H10···O3	(4.1)[d]		(6.3)[d]
dimer	O7−H8···O9	(4.6)[d]		(6.5)[d]
		Complexes with FH		
monomer	N1−H4···F7	0.5	−92.4	−3.4
dimer		−13.2	−93.0	−18.3
monomer	F7−H8···O3	−27.4	443.9	5.1
dimer	F9−H10···O3	−60.9	405.2	3.2
dimer	F7−H8···F9	11.0	480.6	−47.1

[a] The components of J are given in Table S2. [b] SD term set to 0.0 Hz for complexes with $(NH_3)_2$. [c] For formamide, R(N1−H4) = 1.008 Å; ^{1}J(N1−H4) = −89.4 Hz. This number was computed with the qz2p basis only on H4. The value in Table 1 of −89.5 Hz was computed with the qz2p basis set on all H atoms. [d] FC terms are given in parentheses if this term appears to be a reasonable approximation to J.

TABLE 4: Selected Distances (R, Å) and Coupling Constants (J, Hz) for Solvent Monomers and Dimers[a]

monomers	R(X7−H8)	^{1}J(X7−H8)
NH_3	1.012	−61.5
H_2O	0.963	−77.9
FH	0.927	494.8

dimers	R(X7−H8)	^{1}J(X7−H8)	R(X9−H10)	^{1}J(X9−H10)
$(NH_3)_2$	1.016	−64.7	1.013	−61.0
$(H_2O)_2$	0.970	−81.0	0.964	−81.7
$(FH)_2$	0.932	497.9	0.930	522.3
	R(X7−X9)	^{2h}J(X7−X9)	R(H8−X9)	^{1h}J(H8−X9)
$(NH_3)_2$	3.245	1.9	2.249	1.6
$(H_2O)_2$	2.914	1.3	1.946	4.8
$(FH)_2$	2.777	−39.5	1.856	−26.6

[a] See Scheme 1 for numbering. The components of J are given in Table S3.

but decrease when the solvent is FH. The X9−O3 distances in the complexes with bridging dimers are always shorter than the X7−O3 distances in the complexes with the solvent monomers. The N1−H4 distance is longer in the dimer complexes than that in the corresponding monomer complexes, while the X9−H10 distance increases in the dimer complex relative to the corresponding isolated dimer. The influence of such structural changes on spin−spin coupling constants will now be considered.

Spin−Spin Coupling Constants Across Hydrogen Bonds. Table 3 presents coupling constants ^{2h}J(X−Y), ^{1}J(X−H), and ^{1h}J(H−Y) across X−H···Y hydrogen bonds for complexes of formamide with solvent monomers and dimers. Table 3 is organized according to the nature of the solvent in the order NH_3, H_2O, FH. Under each solvent, the listing is according to the nature of the hydrogen bond. Coupling constants for the N1−H4···X7 hydrogen bond in the complex with the solvent monomer are given first, followed by corresponding data for the complex with the solvent dimer. Then, coupling constants are listed for the X7−H8···O3 and X9−H10···O3 hydrogen bonds in the complexes of formamide with the solvent monomer and dimer, respectively. The final entries in each section are coupling constants across the X7−H8···X9 hydrogen bond in formamide complexes with the solvent dimer. ^{1}J(X−H) for the solvent monomers and relevant coupling constants for the dimers are reported in Table 4. The numbering used for the complexes is illustrated in Scheme 1.

Total coupling constants across the hydrogen bonds in FMA/$(NH_3)_2$, which are reported in Table 3, have been estimated by setting the SD terms to 0.0 Hz, an approximation justified by the values of the SD terms for corresponding coupling constants in FMA/NH_3 and $(NH_3)_2$, which can be found in Tables S2 and S3. Only the FC terms for FMA/$(H_2O)_2$ have been computed, and these are reported for ^{2h}J(O−O) and ^{1h}J(H−O) since the FC terms appear to give an adequate approximation to these coupling constants in the FMA/H_2O complex and $(H_2O)_2$. Since the PSO terms make significant contributions to ^{1}J(O−H) but have not been evaluated, ^{1}J(O−H) coupling constants are not reported for FMA/$(H_2O)_2$.

Complexes of Formamide with Ammonia. Although the N1−N7 distance increases from 2.963 to 2.984 Å in FMA/$(NH_3)_2$ compared to that in FMA/NH_3, the two-bond N1−N7 coupling constant ^{2h}J(N1−N7) increases from 3.3 to 5.4 Hz, most probably reflecting a linear hydrogen bond in FMA/$(NH_3)_2$. ^{1}J(N1−H4) increases in absolute value from −89.4 Hz in formamide to −92.0 and −91.8 Hz in the complexes with NH_3 and $(NH_3)_2$, respectively. ^{1h}J(H4−N7) values are small and positive. Since the magnetogyric ratio of ^{15}N is negative and that of ^{1}H is positive, the reduced coupling constants ^{1h}K(H4−N7) are negative, indicating that the N1−H4···N7 hydrogen bonds are traditional.[44]

Both the intermolecular distance and the nonlinearity of the N−H···O3 hydrogen bond decrease in the formamide complex with $(NH_3)_2$ compared to that with NH_3, and ^{2h}J(N−O3) increases from 1.2 Hz in FMA/NH_3 to 1.9 Hz in FMA/$(NH_3)_2$. ^{1}J(N7−H8) is −63.8 Hz for FMA/NH_3, and ^{1}J(N9−H10) is −64.1 Hz for FMA/$(NH_3)_2$, both larger than the corresponding N−H coupling constants of the ammonia monomer (−61.5 Hz) and the N−H of the proton acceptor molecule in the ammonia dimer (−61.0 Hz). Since the magnetogyric ratio of ^{17}O is negative, positive values of ^{1h}J(H−O3) give negative values of ^{1h}K(H−O3), indicating traditional hydrogen bonds.[44]

N−N and N−H coupling constants associated with the N7−H8···N9 hydrogen bond in FMA/$(NH_3)_2$ may be compared with corresponding coupling constants for $(NH_3)_2$. ^{2h}J(N7−N9) is 3.0 Hz, again larger than the value of 1.9 Hz for the ammonia dimer. ^{1}J(N7−H8) in the complex is −64.5 Hz and therefore similar to ^{1}J(N−H) for the hydrogen-bonded N−H in the ammonia dimer (−64.7 Hz). ^{1h}J(H8−N9) is 2.7 Hz in FMA/$(NH_3)_2$ compared to 1.6 Hz in the ammonia dimer.

Complexes of Formamide with Water. As was observed for the FMA/ammonia complexes, the intermolecular N1−O7 distance increases, the nonlinearity of the N1−H4···O7 hydrogen bond decreases, and ^{2h}J(N1−O7) increases from 1.9 to 5.0 Hz in FMA/$(H_2O)_2$ relative to that in FMA/H_2O. The absolute value of ^{1}J(N1−H4) increases from −89.4 Hz in formamide to −92.5 Hz in FMA/H_2O. This change reflects the corresponding increase in the FC term from −86.8 to −90.5 Hz. The small increase in the N1−H4 FC term for FMA/$(H_2O)_2$ suggests that the absolute value of ^{1}J(N1−H4) would increase slightly in this complex. ^{1h}J(H4−O7) is 2.8 Hz in the complex with the water monomer and estimated to be 4.8 Hz in the complex with the dimer. The reduced coupling constants ^{1h}K(H4−O7) are negative and consistent with the presence of traditional N1−H4···O7 hydrogen bonds.

Both the intermolecular distance and the nonlinearity of the O−H···O3 hydrogen bond decrease in the formamide complex with $(H_2O)_2$ compared to that with H_2O, and ^{2h}J(O−O3) increases from 2.6 Hz in FMA/H_2O to 4.1 Hz in FMA/$(H_2O)_2$. Hydrogen bond formation increases the absolute value of ^{1}J(O7−H8) from −77.9 Hz in the water monomer to −83.4 Hz in the FMA/H_2O complex. Positive values of ^{1h}J(H7−O3) and ^{1h}J(H9−O3) are again indicative of traditional hydrogen bonds.[44]

^{2h}J(O7−O9) and ^{1h}J(O9−H10) approximated using the FC terms are 4.6 and 6.5 Hz, respectively. Both of these values are larger than the corresponding coupling constants for $(H_2O)_2$, which are 1.3 and 4.8 Hz, respectively.

Complexes of Formamide with Hydrogen Fluoride. It has been observed previously that coupling constants involving hydrogen fluoride are extremely sensitive to geometry changes and hydrogen bond formation.[45] Therefore, it is not surprising that large differences are found among corresponding coupling constants in FMA/FH, FMA/$(FH)_2$, $(FH)_2$, and FH. ^{2h}J(N1−F7) is small but positive (0.5 Hz) in FMA/FH, and like ^{2h}K(F−F) for $(FH)_2$, ^{2h}K(N1−F7) is negative and an exception to the rule that reduced two-bond coupling constants across hydrogen bonds are positive.[46] However, ^{2h}K(N1−F7) increases in absolute value to −13.2 Hz in FMA/$(FH)_2$ as the N1−F4 distance and the nonlinearity of the hydrogen bond decrease, and ^{2h}K(N1−F7) is positive. ^{1}J(N1−H4) increases in absolute value from −89.4 Hz in formamide to −92.4 and −93.0 Hz in FMA/FH and FMA/$(FH)_2$, respectively. ^{1h}J(H4−F7) values are negative, indicating that the N1−H4···F7 hydrogen bonds are traditional.

The intermolecular F−O3 distance decreases dramatically in FMA/$(FH)_2$ relative to that in FMA/FH as the hydrogen bond approaches linearity. ^{2h}J(F7−O3) is −27.4 Hz in the formamide complex with the monomer and increases in absolute value to −60.9 Hz in the formamide complex with the dimer. ^{1}J(F7−H8) is 443.9 Hz for FMA/FH compared to that for the FH monomer (494.8 Hz). ^{1}J(F9−H10) is 405.2 Hz in FMA/$(FH)_2$, a value which is significantly reduced relative to ^{1}J(F−H) (522.3 Hz) for the FH molecule, which is the proton acceptor in $(FH)_2$. Positive values of ^{1h}J(H8−O3) and ^{1h}J(H10−O3) are indicative of traditional hydrogen bonds.

F−F and F−H coupling constants associated with the F7−H8···F9 hydrogen bond in FMA/$(FH)_2$ are quite different from the corresponding coupling constants for $(FH)_2$. ^{2h}J(F7−F9) is 11.0 Hz and of opposite sign to that of $(FH)_2$ (−39.5 Hz). ^{1}J(F7−H8) in the formamide complex with $(FH)_2$ is 480.6 Hz, somewhat reduced relative to the FH dimer (497.9 Hz). ^{1h}J(H8−F9) has a much larger absolute value of −47.1 Hz compared to its FH dimer value of −26.6 Hz, and both hydrogen bonds are traditional since ^{1h}K(H−F) are negative. The large differences among corresponding coupling constants across hydrogen bonds in FMA/FH and FMA/$(FH)_2$ suggests that these would be excellent probes of bridging hydrogen bonds in the amide region.

Formamide Intramolecular Coupling Constants in Hydrogen-Bonded Complexes. Can changes in formamide intramolecular spin−spin coupling coupling constants be useful probes of hydrogen bonding? Two coupling constants which might be useful and which are amenable to experimental study are ^{1}J(N1−C2) and ^{2}J(C2−H4). Values of these coupling constants for formamide, FMA/NH_3, FMA/$(NH_3)_2$, FMA/H_2O, FMA/FH, and FMA/$(FH)_2$ are reported in Table 5. Full coupling data are given in Table S2. ^{1}J(N1−C2) is −16.6 Hz in the monomer and increases slightly in absolute value to −16.9, −17.2, and −17.3 Hz in the formamide complexes with NH_3, H_2O, and FH, respectively. The values of ^{1}J(N1−C2) for FMA/$(NH_3)_2$ and FMA/$(FH)_2$ increase further to −17.3 and −17.7 Hz, respectively. Thus, systematic changes are evident, although the magnitude of these changes is relatively small. The second intramolecular coupling constant, ^{2}J(C2−H4), increases in absolute value from −2.4 Hz in formamide to −2.6, −2.7, and −2.8 Hz in FMA/NH_3, FMA/H_2O, and FMA/FH, respectively. In contrast, ^{2}J(C2−H4) decreases to −1.4 Hz in FMA/$(NH_3)_2$, and at −2.3 Hz in FMA/$(FH)_2$, it is similar to the monomer value. Thus, while these coupling constants do change upon hydrogen bonding in the amide region, these changes are small relative to the changes which occur for the hydrogen-bonded N1−H4 coupling constant, which increases by at least 2.4 Hz in the complexes. However, since ^{1}J(N1−H4) is 0.2 Hz smaller in absolute value in FMA/$(NH_3)_2$ relative to that in FMA/NH_3 but 0.6 Hz greater in FMA/$(FH)_2$ relative to that in FMA/FH, this coupling constant does not appear to distinguish between bridging monomers and dimers. However, in conjunction with other coupling constants across hydrogen bonds, such distinctions may well be possible. Finally, it should be noted that the largest changes in ^{1}J(N1−H4) and ^{1}J(N1−C2) are found in the complex in which $(FH)_2$ bridges the amide region.

TABLE 5: Intramolecular N1−C2 and C2−H4 Distances (*R*, Å) and Spin−Spin Coupling Constants (*J*, Hz) for Formamide and Bridging Complexes of Formamide with Solvent Molecules[a]

complex	*R*(N1−C2)	^{1}J(N1−C2)	*R*(C2−H4)	^{2}J(C2−H4)
formamide[b]	1.361	−16.6	2.051	−2.4
FMA/NH_3	1.353	−16.9	2.050	−2.6
FMA/$(NH_3)_2$	1.349	−17.3[c]	2.085	−1.4[c]
FMA/H_2O	1.351	−17.2	2.049	−2.7
FMA/FH	1.347	−17.3	2.045	−2.8
FMA/$(FH)_2$	1.339	−17.7	2.064	−2.3

[a] The components of *J* are given in Table S2. No data are given for FMA/$(H_2O)_2$ since only FC terms were evaluated. [b] The coupling constants for the formamide monomer listed here are slightly different from those of Table 1, which were computed with the qz2p basis on all H atoms instead of only on H4. For consistency with the complexes, the formamide values listed here were computed with the qz2p basis on H4 and the cc-pVDZ basis on the remaining H atoms. [c] SD terms set to 0.0 Hz. See tables in the Supporting Information for a justification of this approximation.

Effect of Hydrogen Bonding with Formamide on Coupling Constants of the Solvent Dimers. What changes in the one- and two-bond coupling constants for the dimers $(NH_3)_2$, $(H_2O)_2$, and $(FH)_2$ should be expected when these dimers bridge the N1−H4 and O3 hydrogen-bonding sites in formamide? Answering this question is facilitated by comparing the reduced coupling constants ^{1}K(X7−H8), ^{1h}K(H8−X9), and ^{2h}K(X7−X9) for FMA/dimer complexes to those for the isolated dimers, which are reported in Table 6. Using reduced coupling constants eliminates the dependence on the signs of the magnetogyric ratios of the coupled atoms; it is in terms of the reduced coupling constants that generalizations have been made. The structures of the dimers as well as the negative values of the reduced coupling constants ^{1h}K(H8−X9) indicate that the isolated dimers are stabilized by traditional hydrogen bonds. It is anticipated that the cooperative effect associated with the formation of additional hydrogen bonds by the dimers should increase the proton-shared character of the X7−H8···X9 hydrogen bond.[47,48]

TABLE 6: Changes (δ) in Reduced Coupling Constants ^1K(X7−H8), ^{1h}K(H8−X9), and ^{2h}K(X7−X9) [(N A^{-2} m^{-3}) × 10^{19}] for $(NH_3)_2$, $(H_2O)_2$, and $(FH)_2$ upon Complexation with Formamide

complex	^1K(X7−H8)	^{1h}K(H8−X9)	^{2h}K(X7−X9)
$(NH_3)_2$	53.1	−1.3	15.4
FMA/$(NH_3)_2$	53.0	−2.2	24.3
δ	−0.1	−0.9	+8.9
$(H_2O)_2$	49.7	−2.9	5.9
FMA/$(H_2O)_2$		−4.0	20.8
δ		−1.1	+14.9
$(FH)_2$	44.0	−2.4	−3.7
FMA/$(FH)_2$	42.5	−4.2	1.0
δ	−1.5	−1.8	+4.7

As an X−H···Y hydrogen bond acquires increased proton-shared character by partial proton transfer, the following changes should occur in the reduced coupling constants.

1. ^{2h}K(X−Y) increases, reaches a maximum at a quasi-symmetric proton-shared hydrogen bond, and then decreases as H approaches Y.[42]

2. ^1K(X−H) is positive initially, decreases, passes through zero, and becomes negative as H approaches Y. Such changes have been observed experimentally[49] for the FH/collidine dimer and characterized theoretically.[50]

3. ^{1h}K(H−Y) is negative but eventually increases, passes through zero, and becomes positive as H approaches Y. The changes in the one-bond coupling constants along the proton transfer coordinate reflect the interchange of the roles of proton-donor and proton-acceptor molecules.

It is apparent from Table 6 that ^{2h}K(X7−X9) increases upon complexation of the dimers with formamide, suggesting that these hydrogen bonds have acquired increased proton-shared character. The increased proton-shared character of the X7−H8···X9 bonds is also reflected in a significant decrease of the X7−X9 distance. It was noted above that ^{2h}K(F−F) for equilibrium $(FH)_2$ is negative,[45] and as such, this is an exception to the generalization that ^{2h}K(X−Y) is positive. However, ^{2h}K(F7−F9) does become positive at the shorter F−F distance in FMA/$(FH)_2$.

The X7−H8 distance in the dimer increases upon complexation with formamide, and eventually, ^1K(X7−H8) must decrease, but that is not seen in the data reported in Table 6. However, it has been observed previously that for small displacements of H along the proton-transfer coordinate, ^1K(X−H) may increase before it decreases,[51] and that is observed for FMA/$(NH_3)_2$, where the change in this coupling constant is very small. What might at first appear to be the most puzzling and contradictory result is the observation that ^{1h}K(H8−X9) is more negative in the FMA/dimer than that in the isolated dimer. However, a closer examination of how this one-bond coupling constant changes along the proton-transfer coordinate can resolve this apparent discrepancy. Figure 1 shows the change in ^1J(F−H) for the FH/NH_3 dimer as a function of the F−H distance, that is, as a function of the degree of proton transfer from F to N. Limbach et al.[49] observed a sign change in ^1J(F−H) as a function of the degree of proton transfer in the FH/collidine complex, and their interpretation was supported by EOM-CCSD calculations.[50] Figure 1 shows that as H approaches N, the J curve passes through 0.0 Hz at a F−H distance of approximately 1.25 Å, exhibits a minimum value at approximately 1.45 Å, and then asympotically approaches zero at longer F−H distances. On the basis of this curve, if the F−H distance in a complex is initially greater than 1.45Å and then decreases, ^{1h}J(H−F) would decrease before it increased and changed sign. This is most probably the situation which leads to a decrease in ^{1h}K(H8−X9) in the FMA/dimers relative to that in the isolated dimers.

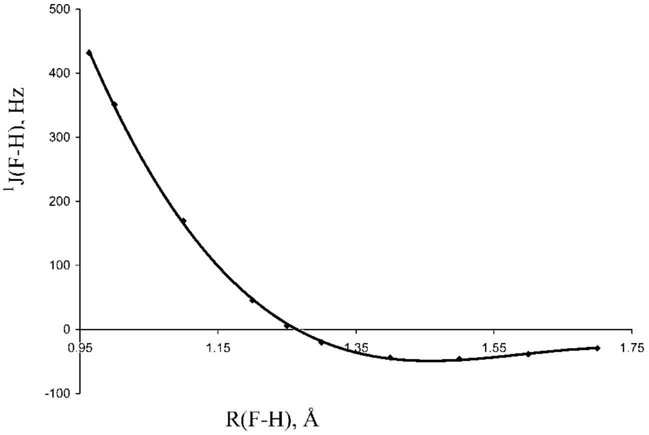


Figure 1. ^1J(F−H) versus the F−H distance for the FH/NH_3 complex. As proton transfer occurs, ^1J(F−H) changes sign and eventually becomes ^{1h}J(H−F).

Concluding Remarks

In this study, EOM-CCSD spin−spin coupling constants across hydrogen bonds have been computed for complexes in which NH_3, H_2O, and FH molecules and their hydrogen-bonded dimers form bridging complexes in the amide region of formamide. The results of these calculations support the following statements.

For complexes with ammonia and water monomers and dimers:

1. For both ammonia and water as the bridging solvent, the hydrogen bond N1−X7 distance increases in going from FMA/monomer to FMA/dimer, but ^{2h}J(N1−X7) always increases. The increase in ^{2h}J(N1−X7) in the FMA/dimer is due in part to the approach toward linearity of the N1−H4···X7 hydrogen bond. Hydrogen bonding with either the solvent monomer or dimer increases the absolute value of ^1J(N1−H4) relative to formamide.

2. For the X−H···O3 hydrogen bond, the X−O3 distance and the nonlinearity of the hydrogen bond are reduced in the formamide complex with the dimer relative to that for the complex with the monomer, and ^{2h}J(X−O3) increases. ^1J(X−H) always increases in absolute value in the complexes relative to ^1J(X−H) in the corresponding monomer and dimer.

For complexes of formamide with FH and $(FH)_2$:

3. Large differences are found in corresponding coupling constants for FH, $(FH)_2$, FMA/FH, and FMA/$(FH)_2$. ^{2h}J(N1−F7) is small but positive in FMA/FH and becomes large and negative in FMA/$(FH)_2$ as the N1−F7 distance and the nonlinearity of the hydrogen bond decrease. ^1J(N1−H4) increases in absolute value in the complexes relative to that in formamide. ^{2h}J(F−O3) increases significantly in absolute value in going from FMA/FH to FMA/$(FH)_2$. ^1J(F−H) decreases dramatically in FMA/FH and FMA/$(FH)_2$ relative to the corresponding coupling constants for FH and $(FH)_2$. The large changes in these coupling constants suggest that bridging FH monomers and dimers could be particularly useful probes of amide hydrogen bonding.

4. Traditional hydrogen bonds are found in the formamide complexes. They have increased proton-shared character in FMA/dimer relative to that in the corresponding FMA/monomer and isolated dimer.

5. ^{2h}J(X7−X9) increases in the FMA/dimer complex relative to that in the isolated dimer. Although ^1J(N7−H8) has similar

values in FMA/$(NH_3)_2$ and $(NH_3)_2$, ^{1}J(F7−H8) decreases significantly in FHM/$(FH)_2$ relative to that in $(FH)_2$.

6. Formamide intramolecular coupling constants change only slightly upon hydrogen bonding with solvent monomers and dimers, with the largest changes occurring for ^{1}J(N1−H4).

In the not too distant past, it might have been concluded that small values of or small changes in coupling constants would put many spin−spin coupling constants forever out of the reach of NMR spectroscopists. However, this is now really not so. Dramatic progress has been made in techniques for measuring small couplings and in the determination of coupling constants for nuclei with spin greater than 1/2, (eg., ^{17}O).[52] Moreover, ^{nh}J coupling constants have been measured for proteins in solution[38] and in very low temperature experiments[53] since, in both environments, the molecules have restricted conformational freedom. Recently, Söntjens et al.[43] measured ^{2h}J(N−N) couplings in solution and verified the relationship between ^{2h}J(N−N) and the N−N distance proposed earlier by Del Bene and Bartlett[54] and subsequently expanded to a much larger set of complexes.[51] Finally, the measurement of ^{nh}J values in the solid state[55] opens enormous opportunities for determining spin−spin coupling constants across hydrogen bonds in crystals.

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Supporting Information Available: The components of J in Tables S1, S2, and S3 and full citations for refs 25 and 34. This material is available free of charge via the Internet at http://pubs.acs.org.

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