

the total (unpolarized) emission intensities of the $0 \rightarrow j$ (x'' , y'' , and z'') transitions according to eq A17, where $\bar{\nu}_{0j}$ is the transition frequency.

$$I \propto \bar{\nu}_{0j}^4 D(0,j) \quad (\text{A17})$$

The magnetic circularly polarized luminescence (MCPL) intensity (ΔI) of the $0 \rightarrow j$ transition will be governed by eq A18.¹⁸

$$\Delta I \propto \bar{\nu}_{0j}^4 [D_-(0,j) - D_+(0,j)] \quad (\text{A18})$$

We have, then, for the $|0\rangle \rightarrow |x''\rangle$, $|y''\rangle$, and $|z''\rangle$ ${}^5D_0 \rightarrow {}^7F_1$ transitions

$$\Delta I(0,x'') \propto 2\bar{\nu}_{0x''}^4 \epsilon M^2 \quad (\text{A19})$$

$$\Delta I(0,y'') \propto -2\bar{\nu}_{0y''}^4 \epsilon M^2 \quad (\text{A20})$$

$$\Delta I(0,z'') = 0 \quad (\text{A21})$$

The influence of $H_{cf}(2,1) \neq 0$ on the intensity analysis A6-A8, above would be to (1) redistribute the total luminescence intensity (I) among the $|0\rangle \rightarrow |x''\rangle$, $|y''\rangle$, and $|z''\rangle$ transitions causing some intensity asymmetry between the $|0\rangle \rightarrow |x''\rangle$ and $|0\rangle \rightarrow |y''\rangle$ transitions and (2) induce some MCPL intensity (ΔI) in the $|0\rangle \rightarrow |z''\rangle$ transition as well as causing $|\Delta I(0,x'')| \neq |\Delta I(0,y'')|$.

Given our first-order treatment of magnetic field effects (see eq A6-A8), eq A19 and A20 show MCPL intensity to be linear in the magnetic field strength H . On the other hand, eq A15-A17 show that the total luminescence intensities will exhibit a field dependence only when $|\epsilon| \rightarrow 1$ (i.e., when $|\Delta_1(2,2)| \approx g\mu_B H$).

Classification of Spectra According to Cases I, II, and III of Section II (See Main Text). In section II of the main text three special cases are defined for the purpose of classifying the observed MCPL/TL spectra obtained for the $\text{Eu}(\beta\text{-diketonate})_3$ systems. This is a relatively "low-resolution" classification scheme with respect to making spectra-structure correlations, but it suffices for distinguishing between dominant axial or dominant nonaxial symmetry in the systems under study. Here we apply this classification scheme to the ${}^5D_0 \rightarrow {}^7F_1$ transition by using the analysis developed in this Appendix. Neglecting the low-symmetry $H_{cf}(2,1)$ crystal field component, we can make the following comments regarding cases I, II, and III.

Case I. This case corresponds to $H_{cf}(2,2) \gg H_{cf}(2,0)$ and $|\epsilon| \ll 1$. The TL spectrum should show three well-resolved bands with energies and relative intensities given by

$ 0\rangle \rightarrow j\rangle$	$ \Delta E_{0j} $	$I(0,j)/\bar{\nu}_{0j}^4$
$ 0\rangle \rightarrow x''\rangle$	$ E_1^0 + \Delta_1(2,2) $	M^2
$ 0\rangle \rightarrow y''\rangle$	$ E_1^0 - \Delta_1(2,2) $	M^2
$ 0\rangle \rightarrow z''\rangle$	$ E_1^0 $	M^2

The MCPL spectrum should show just two well-resolved bands with intensities $\Delta I(0,x'') \propto 2\bar{\nu}_{0x''}^4 \epsilon M^2$ and $\Delta I(0,y'') \propto -2\bar{\nu}_{0y''}^4 \epsilon M^2$. This case also admits $H_{cf}(2,1) \neq 0$, the effects of which are to give the $|0\rangle \rightarrow |z''\rangle$ transition some (weak) MCPL intensity and to cause both intensity and transition energy asymmetry in the TL spectrum.

Case II. This case corresponds to $H_{cf}(2,0) \gg H_{cf}(2,2)$ and $|\epsilon| > 1$. In this case both the TL and MCPL spectra should exhibit a strong magnetic field dependence according to

$ 0\rangle \rightarrow j\rangle$	$ \Delta E_{0j} $	$I(0,j)/\bar{\nu}_{0j}^4$	$\Delta I(0,j)/\bar{\nu}_{0j}^4$
$ 0\rangle \rightarrow x''\rangle$	$ E_1^0 - 1/2(1 + \epsilon^2)\Delta_1(2,0) + 2g\mu_B H\epsilon $	$(\epsilon^2 + 1)M^2$	$2\epsilon M^2$
$ 0\rangle \rightarrow y''\rangle$	$ E_1^0 - 1/2(1 + \epsilon^2)\Delta_1(2,0) - 2g\mu_B H\epsilon $	$(\epsilon^2 + 1)M^2$	$-2\epsilon M^2$
$ 0\rangle \rightarrow z''\rangle$	$ E_1^0 + \Delta_1(2,0) $	M^2	0

The energy separation between the $|0\rangle \rightarrow |x''\rangle$ and $|0\rangle \rightarrow |y''\rangle$ transitions is linearly dependent upon $H\epsilon$, collapsing to (near) zero when $H = 0$. In this case, corresponding to the presence of a very strong axially symmetric crystal field component, both the transition frequencies and the intensity distributions within the ${}^5D_0 \rightarrow {}^7F_1$ TL spectrum will exhibit a strong magnetic field dependence.

Case III. This case corresponds to $H_{cf}(2,2) > H_{cf}(2,0)$ and $|\epsilon| > 1$. In this case the transitions are characterized approximately by

$ 0\rangle \rightarrow j\rangle$	$ \Delta E_{0j} $	$I(0,j)/\bar{\nu}_{0j}^4$	$\Delta I(0,j)/\bar{\nu}_{0j}^4$
$ 0\rangle \rightarrow x''\rangle$	$ E_1^0 + (1 - \epsilon^2)\Delta_1(2,2) + 2g\mu_B H\epsilon $	$(\epsilon^2 + 1)M^2$	$2\epsilon M^2$
$ 0\rangle \rightarrow y''\rangle$	$ E_1^0 - (1 - \epsilon^2)\Delta_1(2,2) - 2g\mu_B H\epsilon $	$(\epsilon^2 + 1)M^2$	$-2\epsilon M^2$
$ 0\rangle \rightarrow z''\rangle$	$ E_1^0 $	M^2	0

From this analysis it is clear that the $|0\rangle \rightarrow |x''\rangle$ and $|0\rangle \rightarrow |y''\rangle$ components of the ${}^5D_0 \rightarrow {}^7F_1$ MCPL/TL spectra can provide effective probes of $H_{cf}(2,0)$ and $H_{cf}(2,2)$. The $|0\rangle \rightarrow |z''\rangle$ component can provide yet additional information about $H_{cf}(2,0)$ and $H_{cf}(2,2)$, as well as about $H_{cf}(2,1)$.

An Unexpectedly Strong Hydrogen Bond: Ab Initio Calculations and Spectroscopic Studies of Amide-Fluoride Systems

John Emsley,^{*1a} Deborah J. Jones,^{1a} Jack M. Miller,^{1b} Richard E. Overill,^{1c} and Roland A. Waddilove^{1a}

Contribution from the Department of Chemistry and the Computer Unit of King's College, University of London, Strand, London WC2R 2LS, England, and the Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1. Received January 29, 1980

Abstract: Ab initio LCAO-MO-SCF calculations have been performed on the formamide-fluoride, acetamide-fluoride and methylformamide-fluoride complexes to determine their equilibrium structures and the strength of the amide-fluoride hydrogen bond. At ca. 148 kJ mol⁻¹ it is the second strongest hydrogen bond known. The results of IR, ¹H and ¹⁹F NMR spectroscopic studies on solutions of alkali metal fluorides in these amides support this finding. Possible biochemical implications of this strong hydrogen bond are briefly discussed.

Strong hydrogen bonding is now recognized as a chemical interaction that is clearly distinguishable from normal hydrogen

bonding by a variety of measurements: short bond lengths, high bond energies, large IR band shifts, and large downfield chemical

shifts in the ^1H NMR spectrum.²

Ab initio calculations have been performed on several systems including $\text{H}(\text{HCO}_2)_2^-$,³ HCl_2^- ,⁴ H_3O_2^- ,⁵ and H_5O_2^+ ,⁶ for which the results indicate unusually high bond energies, generally in excess of 100 kJ mol^{-1} . Similarly, the difluoride ion, HF_2^- , has been found to have a bond energy in the region of 200 kJ mol^{-1} ,⁷ other very strong hydrogen bonds involving the fluoride ion for which ab initio values are available are RCO_2HF^- ($\text{R} = \text{H}, \text{CH}_3$)⁷ and HOHF^- .⁸ The amide-fluoride hydrogen bond, however, has not previously been reported upon.

Formamide, acetamide, and their *N*-methyl derivatives are the simplest models for the peptide linkage, $\text{RNH-COR}'$, which occurs throughout the polypeptide chains of all proteins. Consequently much effort has recently been devoted to investigating the structure, bonding, and spectra of these molecules by means of ab initio calculations.⁹⁻¹⁷ Their biologically important hydrogen bonding properties have attracted a lot of attention, with ab initio calculations on the formamide dimer,¹⁸⁻²¹ formamide-water,^{19,20,22-24} formamide-ammonia,²⁵ formamide-glyoxal,²⁶ and formamide-hydrogen sulfide²⁶ complexes.

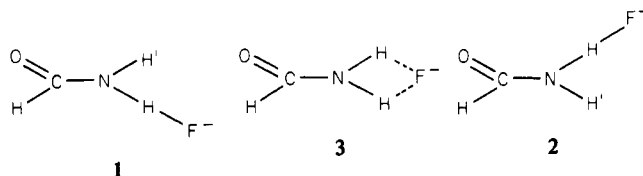
We now report that the hydrogen bonds between F^- and the simple amides formamide, acetamide, and methylformamide are stronger than any of these other amide hydrogen bonds and are stronger than those in the RCO_2HF^- and HOHF^- complexes; indeed they come second only to HF_2^- itself. This finding may have important biochemical implications.

Theoretical Details

Ab initio LCAO-MO-SCF calculations were performed on formamide, acetamide, and methylformamide, their conjugate base anions, and their complexes with fluoride by using a version of

the program GAUSSIAN 70²⁷ which has been modified to accommodate 75 contracted basis functions and level shifters.²⁸ Partial geometry optimizations (bond lengths to within $\pm 1 \text{ pm}$, bond angles to within $\pm 0.1^\circ$) were carried out with the STO-3G basis set²⁹ by using standard univariate quadratic interpolation methods. The hydrogen bond energies were evaluated by using Dunning's [4s2p/2s1p] extended Gaussian basis set³⁰ with an *s* orbital scaling factor of $2^{1/2}$ and a *p* orbital exponent of 0.7 for the amide protons (except in the amido anions), while the scaling factors and *p* exponents for the other protons were all set to unity. This basis set is sufficiently complete to yield hydrogen bond energies which are stable against further basis set extensions⁷ and against "ghost orbital" corrections.³ Single-determinantal SCF wave functions are generally adequate for calculating the energies of strong hydrogen bonds between closed-shell molecules since the molecular extra correlation energy contributes only ca. 5% and the zero-point vibrational correlations are of a similar magnitude.^{8,31,32}

(i) **Formamide-Fluoride.** The recent electron diffraction structure for HCONH_2 by Kitano and Kuchitsu was used.³³ With the assumption that the N-H-F hydrogen bond is linear, the geometry of HCONH_2F^- was optimized to $\angle\text{CNH}' = 106.1^\circ$, $R_{\text{CO}} = 125 \text{ pm}$, $R_{\text{CN}} = 136 \text{ pm}$, $R_{\text{NH}} = 104 \text{ pm}$, $R_{\text{NH}} = 151 \text{ pm}$, and $R_{\text{HF}} = 99 \text{ pm}$ with the hydrogen bond trans to the carbonyl group (1) and to $\angle\text{CNH}' = 107.8^\circ$, $R_{\text{CO}} = 125 \text{ pm}$, $R_{\text{CN}} = 136 \text{ pm}$, $R_{\text{NH}} = 104 \text{ pm}$, $R_{\text{NH}} = 152 \text{ pm}$, and $R_{\text{HF}} = 98 \text{ pm}$ with the hydrogen bond cis to the carbonyl group (2). The intermediate structure (3), corresponding to the transition state for transfer of fluoride



between the two amide protons, was also optimized, yielding $R_{\text{CO}} = 123 \text{ pm}$, $R_{\text{CN}} = 139 \text{ pm}$, $R_{\text{NH}} = 102 \text{ pm}$, and $R_{\text{HF}} = 200 \text{ pm}$. The optimized structure of the formamide anion, HCONH^- , was found to have $R_{\text{NH}} = 105 \text{ pm}$, $R_{\text{CN}} = 135 \text{ pm}$, $R_{\text{CO}} = 126.5 \text{ pm}$, and $\angle\text{CNH} = 102.1^\circ$, with the amido proton cis to the carbonyl group (4).

(ii) **Acetamide-Fluoride.** The recent electron diffraction structure for CH_3CONH_2 by Kitano and Kuchitsu was used,³⁴ and the rotamer of CH_3CONH_2 with the carbonyl group eclipsed by a methyl C-H bond was verified to be the most stable conformation. For $\text{CH}_3\text{CONH}_2\text{F}^-$ we found $\angle\text{CNH}' = 105.6^\circ$, $R_{\text{CO}} = 126 \text{ pm}$, $R_{\text{CN}} = 137 \text{ pm}$, $R_{\text{NH}} = 104 \text{ pm}$, $R_{\text{NH}} = 151 \text{ pm}$, and $R_{\text{HF}} = 99 \text{ pm}$; the structure with fluoride bonded trans to the carbonyl group, as in 1, which is itself eclipsed by a methyl C-H bond, was found to be optimal. The optimized structure of the acetamido anion, CH_3CONH^- , was found to have $R_{\text{NH}} = 105 \text{ pm}$, $R_{\text{CN}} = 136 \text{ pm}$, $R_{\text{CO}} = 127 \text{ pm}$, and $\angle\text{CNH} = 101.7^\circ$, with the amido proton cis to the carbonyl group, as in 4, and the C-N bond eclipsed by a methyl C-H bond.

(iii) **Methylformamide-Fluoride.** The recent electron diffraction structure for $\text{HCON}(\text{CH}_3)\text{H}$ by Kitano and Kuchitsu was used,³⁴ and the most stable conformation of $\text{HCON}(\text{CH}_3)\text{H}$ was verified to have the *N*-methyl group cis to the carbonyl group with an *N*-methyl C'-H bond eclipsing the N-H bond. For $\text{HCON}(\text{CH}_3)\text{HF}^-$ we calculated $\angle\text{CNC}' = 113.3^\circ$, $R_{\text{CO}} = 125 \text{ pm}$, $R_{\text{CN}} = 136 \text{ pm}$, $R_{\text{NH}} = 152 \text{ pm}$, and $R_{\text{HF}} = 99 \text{ pm}$, and found the most

- (1) (a) Department of Chemistry, King's College, Strand, London WC2R 2LS, England. (b) Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1. (c) Computer Unit, King's College, Strand, London WC2R 2LS, England.
- (2) J. Emsley, *Chem. Soc. Rev.*, **9**, 91 (1980).
- (3) J. Emsley, O. P. A. Hoyte, and R. E. Overill, *J. Am. Chem. Soc.*, **100**, 3303 (1978).
- (4) C. Thomson, D. T. Clark, T. C. Waddington, and H. D. B. Jenkins, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1942 (1975).
- (5) B. O. Roos, W. P. Kraemer, and G. H. F. Dierksen, *Theor. Chim. Acta*, **42**, 77 (1976).
- (6) W. P. Kraemer and G. H. F. Dierksen, *Chem. Phys. Lett.*, **5**, 463 (1970).
- (7) J. Emsley, O. P. A. Hoyte, and R. E. Overill, *J. Chem. Soc., Perkin Trans. 2*, 2079 (1977); *J. Chem. Soc., Chem. Commun.*, 225 (1977).
- (8) G. Dierksen, W. Kraemer, and B. Roos, *Theor. Chim. Acta*, **36**, 249 (1974).
- (9) N. C. Baird and H. B. Kathpal, *Chem. Phys. Lett.*, **43**, 315 (1976).
- (10) L. Z. Stenkamp and E. R. Davidson, *Theor. Chim. Acta*, **44**, 405 (1977).
- (11) L. E. Nitzsche and E. R. Davidson, *J. Chem. Phys.*, **68**, 3103 (1978); *J. Am. Chem. Soc.*, **100**, 7201 (1978).
- (12) E. Oliveros, M. Riviere, C. Teichteil, and J.-P. Malrieu, *Chem. Phys. Lett.*, **57**, 220 (1978).
- (13) E. D. Stevens, J. Rys, and P. Coppens, *J. Am. Chem. Soc.*, **100**, 2324 (1978).
- (14) A. T. Hagler and A. Lapicciarella, *J. Am. Chem. Soc.*, **100**, 4026 (1978).
- (15) R. F. Nalewajski, *J. Am. Chem. Soc.*, **100**, 41 (1978).
- (16) N. R. Carlsen, L. Radom, N. V. Riggs, and W. R. Rodwell, *J. Am. Chem. Soc.*, **101**, 2233 (1979).
- (17) V. J. Klimkowski, H. L. Sellers, and L. Schäfer, *J. Mol. Struct.*, **54**, 299 (1979).
- (18) T. Ottersen and H. H. Jensen, *J. Mol. Struct.*, **26**, 355, 365 (1975).
- (19) J. F. Hinton and R. D. Harpool, *J. Am. Chem. Soc.*, **99**, 349 (1977).
- (20) A. Pullman, H. Berthod, C. Giessner-Prettre, J. F. Hinton, and R. D. Harpool, *J. Am. Chem. Soc.*, **100**, 3991 (1978).
- (21) S. Yamabe, K. Kitaura, and K. Nishimoto, *Theor. Chim. Acta*, **47**, 111 (1978).
- (22) T. Ottersen and H. H. Jensen, *J. Mol. Struct.*, **26**, 375 (1975); **28**, 220 (1975).
- (23) J. E. del Bene, *J. Chem. Phys.*, **62**, 1314, 1961 (1975).
- (24) J. E. del Bene, *J. Am. Chem. Soc.*, **100**, 1387, 1395 (1978).
- (25) T. Ottersen, H. H. Jensen, R. Johansen, and E. Wisloff-Nilssen, *J. Mol. Struct.*, **30**, 379 (1976).
- (26) P. Otto, S. Suhai, and J. Ladik, *Int. J. Quant. Chem., Quant. Biol. Symp.*, No. 4, 451 (1977).

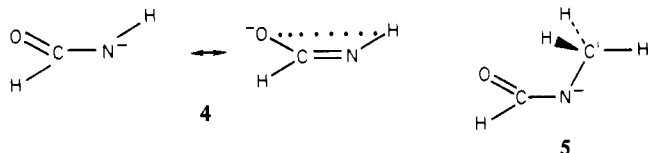
- (27) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSSIAN 70, Program 236, QCPE, Indiana University, 1971.
- (28) I. H. Hillier and V. R. Saunders, *Int. J. Quant. Chem.*, **7**, 699 (1973).
- (29) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (30) T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).
- (31) A. Støgaard, A. Strich, B. Roos, and J. Almif, *Chem. Phys.*, **8**, 405 (1975).
- (32) E. Clement, H. Kistenmacher, and H. Popkie, *J. Chem. Phys.*, **59**, 5842 (1973).
- (33) M. Kitano and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **47**, 67 (1974).
- (34) M. Kitano and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **46**, 3048 (1973).
- (35) M. Kitano and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **47**, 631 (1974).

Table I. Results of Calculations on the Amide-Fluoride Hydrogen Bond

molecule ^a	total energy, ^b hartrees
formamide	-168.898 482
formamido anion (4)	-168.286 115
formamide-fluoride (1)	-268.381 192
formamide-fluoride (2)	-268.370 184
formamide-fluoride (3)	-268.345 680
acetamide	-207.935 413
acetamido anion	-207.318 330
acetamide-fluoride	-307.412 886
methylformamide	-207.914 891
methylformamido anion (5)	-207.298 706
methylformamide-fluoride	-307.391 792
fluoride ion ^c	-99.414 059
hydrogen fluoride ^c	-100.038 590

^a For details of molecular geometries, see text. ^b Using [4s2p/2s1p] basis set. ^c From ref 7.

stable conformation to have F⁻ located trans to the carbonyl group, as in (1), with an *N*-methyl C'-H bond eclipsing the C-N bond. The methylformamido anion, HCONC'H₃⁻, was determined to have an optimal structure in which *R*_{CN} = 135.5 pm, *R*_{CO} = 126 pm and ∠CNC' = 109.1° with the *N*-methyl group cis to the carbonyl group and staggered with respect to the C-N bond (5).



Experimental Section

Formamide and methylformamide were dried over molecular sieves. The alkali metal fluorides were dried under vacuum at 100 °C. Solubilities were measured at 20 °C by evaporating the solvent from a weighed amount of solution and weighing the residual fluoride. Solutions, on standing for several days exposed to the atmosphere, deposited crystals of the corresponding difluoride salt.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer with NaCl optics. Nuclear magnetic resonance spectra were recorded on a Bruker HFX 90 spectrometer operating at 90 MHz (¹H) and 84.7 MHz (¹⁹F). The ¹⁹F NMR spectra of CsF in HCONHCH₃ showed a singlet with the following chemical shifts (ppm from external CFCl₃): -142.2 at 1.06 *m*, -138.6 at 1.45 *m*, -131.3 at 1.80 *m*, and -126.1 at 2.12 *m*. A plot of chemical shift δ vs. molality showed a linear relationship $\delta(^{19}\text{F}) = -159.8 + 15.5 m$.

The ¹⁹F NMR spectra of KF in solutions of HCONH₂·H₂O at a concentration of 1 g of KF per 10 g of solution gave the following chemical shifts (ppm from external CFCl₃): neat HCONH₂, -97.1, very broad signal; 0.39 mol fraction H₂O in HCONH₂, -106.7, broad signal; 0.71 mol fraction H₂O in HCONH₂, -112.3, sharp signal; pure H₂O, -118.5, sharp signal. A plot of chemical shift vs. mole fraction H₂O showed a linear relationship $\delta(^{19}\text{F}) = -97.1 - 21.4x_{\text{H}_2\text{O}}$.

Discussion

The results of our ab initio calculations are presented in Table I. It has recently been agreed that in order to impose a reasonable upper bound upon their magnitudes, the energies of very strong, asymmetric hydrogen bonds between two closed-shell molecules should be defined with respect to the pair of component molecules which are closer, either energetically or structurally, to the hydrogen bonded system.^{36,37} With use of either criterion it is clear that the amide-fluoride hydrogen bonds studied here should be defined with respect to the amido anion and hydrogen fluoride not to the amide and fluoride ions. A similar situation arose for the carboxylic acid-fluoride hydrogen bonds.^{36,37} For formamide-fluoride we have the linear distortion indices³⁷ $\Delta(\text{N}\cdots\text{H}) = 0.43$ and $\Delta(\text{F}\cdots\text{H}) = 0.09$, which illustrates the fact that the

Table II. League Table of the Strongest Hydrogen Bonds

system	hydrogen bond energy, kJ mol ⁻¹	basis	ref
[F-H-F] ⁻	214	[5s3p/3s1p]	7
[HCON(H)-H-F] ⁻	148	[4s2p/2s1p]	this work
[H ₂ O-H-OH ₂] ⁺	135	[5s4p1d/3s1p]	6
[HF-H-FH] ⁺	128	[5s4p1d/3s1p]	38
[HC(O)O-H-O(O)CH] ⁻	123	[4s2p/2s1p]	3
[Cl-H-Cl] ⁻	121	[4s2p1d/2s1p]	4
[HC(O)O-H-F] ⁻	105	[5s3p/3s1p]	7, 37
[HO-H-OH] ⁻	105	[5s4p1d/3s1p]	5
[HO-H-F] ⁻	96	[5s4p1d/3s1p]	8

amide N-H bond has been stretched almost five times more than the F-H bond of hydrogen fluoride. Our corresponding values for formic acid-fluoride⁷ are $\Delta(\text{O}\cdots\text{H}) = 0.45$ and $\Delta(\text{F}\cdots\text{H}) = 0.08$, clearly demonstrating the structural similarity of the two hydrogen bonds. Our theoretical energetics for formamide-fluoride may be summarized as follows: the hydrogen bond energy of 1 (relative to HCONH⁻ and HF) is 148 kJ mol⁻¹, the alternative structure 2 is less stable than 1 by 29 kJ mol⁻¹, and the barrier to transfer of fluoride ion between the two amide protons 1 and 2 via the transition state 3 is 93 kJ mol⁻¹.

For acetamide-fluoride the hydrogen bond energy is likewise 147 kJ mol⁻¹, but in the case of methylformamide-fluoride the strength of the hydrogen bond is slightly decreased to 143 kJ mol⁻¹.

These results unexpectedly place the amide-fluoride hydrogen bond as the second strongest type of hydrogen bond and the strongest heteronuclear hydrogen bond. On the basis of the most recent ab initio results available, a league table of the strongest hydrogen bonds has been drawn up (see Table II), which shows the amide-fluoride systems as one of a group of very strong hydrogen bonds with energies between 100 and 150 kJ mol⁻¹. It is interesting to observe from Table II that while the isoelectronic complexes H₃O₂⁺ and H₃F₂⁺ are calculated to have very similar hydrogen bond energies, the isoelectronic pair HF₂⁻ and H₃O₂⁻ differ by a factor of 2 in this respect. The formamide-fluoride system also has a significantly stronger hydrogen bond than its isoelectronic counterpart, formic acid-fluoride.

As far as we are aware, these are the first ab initio molecular structure calculations on amide-fluoride systems, and on the corresponding amido (amide conjugate base) anions. A brief discussion of the latter species, which is isoelectronic with the carboxylate anions, is therefore also of interest. Our geometry optimizations of these molecules show that, relative to their parent amides in the same basis set,³⁹ the C-N bond is shortened by 5 pm and the C=O bond is lengthened by 5 pm. This can be understood in terms of resonance between two structures (4) which delocalize the negative charge. In the case of the formamido and acetamido anions, the second of these resonance structures favors the formation of an intramolecular hydrogen bond which will further stabilize these anions. This is not possible with the methylformamido anion (5) and probably accounts for the slightly smaller hydrogen bond energy of this system.

How do these amide-fluoride hydrogen bond energies compare with those of other amide hydrogen bonds? The cyclic dimer (HCONH₂)₂ has hydrogen bond energies calculated at 41.4¹⁹ and 31.8 kJ mol⁻¹.²¹ The systems RCONHR'·H₂O, where R and R' can be either or both of H or CH₃, in which the amide acts as the hydrogen bond donor, have energies of 24.1 (R = R' = CH₃) to 26.8 (R = R' = H)²⁴ to 28.4 kJ mol⁻¹ (R = R' = H).¹⁹ Energies of this order are in the expected range for conventional, i.e., weak, hydrogen bonds, and this is the picture that emerges from other amide hydrogen bonds. Clearly the amide-fluoride hydrogen bond reported here is in a different category.

Comparison of the amide-fluoride bond with other N-H⁺⁻ hydrogen bonds is not possible since unfortunately none has been calculated to date.² However there are results for the NH₃-HF

(36) W. J. Bouma and L. Radom, *Chem. Phys. Lett.*, **64**, 216 (1979).

(37) J. Emsley and R. E. Overill, *Chem. Phys. Lett.*, **65**, 616 (1979).

(38) G. H. F. Dierksen, W. von Niessen, and W. P. Kraemer, *Theor. Chim. Acta*, **31**, 205 (1973).

(39) J. E. del Bene, G. T. Worth, F. T. Marchese, and M. E. Conrad, *Theor. Chim. Acta*, **36**, 195 (1975).

combination⁴⁰ which show a minimum energy state $\text{H}_3\text{N}\cdots\text{H}-\text{F}$ with a hydrogen bond energy of 48.9 kJ mol^{-1} and the proton of the hydrogen bond residing nearer the fluorine than the nitrogen so that $R_{\text{HF}} = 105.4 \text{ pm}$, a value that compares well with the amide-fluoride situation. In the solid phase this system behaves as NH_4F with the hydrogen bonding between an ammonium cation and the fluoride anion, i.e., $^+\text{N}-\text{H}\cdots\text{F}^-$, as revealed by X-ray crystallography.⁴¹

Experimental evidence for fluorides KF, RbF, and CsF between amides and fluoride was sought from IR and NMR spectroscopic investigations of fluoride solutions in the solvents HCONH_2 and HCONHCH_3 , in which, rather surprisingly, potassium and cesium fluorides are soluble. Such solutions are metastable and the chief product of decomposition is, even more surprisingly, the corresponding difluoride. This salt settles out of solution. That a fluoride ion can abstract a proton from these solvents is in accord with our ab initio calculations which show that the proton resides near to the fluoride in the very strong hydrogen bond.

The alkali metal fluorides KF, RbF, and CsF are noted for their high solubilities in water, liquid HF, and aliphatic carboxylic acids, but little else.⁴² In all these solvents very strong hydrogen bonding plays a key role. Dimethylformamide, despite its relative permittivity of 36.1, is not a good solvent for KF, for example, dissolving barely any at room temperature. Replacement of one of the methyl groups of DMF with a proton has a remarkable effect on the relative permittivity, $\epsilon(\text{HCONHCH}_3) = 182$, and the solubility of KF, which is 83.7 g kg^{-1} . Replacement of both methyl groups produces HCONH_2 ($\epsilon = 111$) and the solubility of KF rises to 126 g kg^{-1} showing that this is not related to the polarity of the solvent but rather to its enhanced ability to solvate the anion. (Alkali metal cation solvation in these solvents involves the carbonyl oxygen end of the molecule.⁴³) Cesium fluoride in these two protic solvents has solubilities of 204.9 and 1204 g kg^{-1} , respectively. These high solubilities of fluorides are indirect support but are not real evidence of strong hydrogen bonding.

Dissolving KF in HCONH_2 produces a very viscous solution, reminiscent of the solutions produced by this salt in glacial acetic acid where strong hydrogen bonds break up the cyclic dimers of the solvent to form linear solvent polymers.⁴⁴ A saturated solution of KF in HCONH_2 will form a gel if left to stand. A hot saturated solution deposits crystals of $\text{KF}\cdot 3\text{HCONH}_2$ on cooling.

We are not the first to report on solutions of alkali metal fluorides in HCONH_2 . Somsen et al.⁴⁵ measured their heats of solution at 25°C , noting that LiF and NaF dissolve endothermically and KF, RbF, and CsF dissolve exothermically. The heat of solution of CsF is $-31.8 \text{ kJ mol}^{-1}$ which compares well with that of CsF in H_2O ($-34.0 \text{ kJ mol}^{-1}$)⁴⁶ and CsF in HCO_2H ($-63.3 \text{ kJ mol}^{-1}$).⁴⁶

Infrared Spectroscopy. The IR spectra of fluoride solutions in HCONH_2 did not reveal peaks that could be attributed to $\text{N}-\text{H}\cdots\text{F}$ hydrogen bonding; the $\text{N}-\text{H}\cdots\text{N}$ vibrational modes blanket out a large part of the spectrum. However, the spectrum of a saturated solution of CsF in HCONHCH_3 showed clearly a new and very broad band centered at 1600 cm^{-1} with an intensity equal to that of the neighboring carbonyl absorption. Other bands, but much weaker bands, appear at 1360 and 2000 cm^{-1} in the spectrum. Although the solvent itself has an intense $\text{N}-\text{H}$ bending mode at 1540 cm^{-1} , the new band at ca. 1600 cm^{-1} merges with it to produce a characteristic hydrogen bond stretching band which we identify as arising from the very strong $\text{N}-\text{H}\cdots\text{F}^-$ hydrogen bond.

A strong $\text{N}-\text{H}\cdots\text{F}^-$ bond has been reported in guanidinium

fluoride, $\text{C}(\text{NH}_2)_3^+\text{F}^-$,⁴⁷ and a broad band at 1650 cm^{-1} is observed in the IR spectrum of this salt which is not found in the spectra of the other guanidinium halides.

¹⁹F NMR Spectroscopy. Cesium fluoride solutions in HCONHCH_3 show a downfield shift of the singlet of F^- with increasing concentration of CsF. Thus at least two environments are contributing to the signal and these are presumably the solvated fluoride, $\text{HCON}(\text{CH}_3)-\text{H}-\text{F}^-$, and the difluoride, HF_2^- . The latter should increase in concentration as the concentration of F^- increases and establishes an equilibrium with the HF which is formed as a consequence of the initial very strong hydrogen bond.

The downfield region is expected from the chemical shifts of HF and HF_2^- in DMF: $\delta(\text{HF}) -117.5$ (CF_4) and $\delta(\text{HF}_2^-) -83.4$ (CF_4).⁴⁸ At infinite dilution in HCONHCH_3 $\delta(\text{CsF}) -160$ (CFCl_3), which represents the chemical shift of the fluoride ion in the very strong $\text{HCON}(\text{CH}_3)-\text{H}-\text{F}^-$ bonding situation.

Solutions of KF in the mixed-solvent $\text{HCONH}_2\text{-H}_2\text{O}$ showed a linear relationship between $\delta(^{19}\text{F})$ and the mole fraction of water. This indicates that solvation of the anion is comparable for either of the solvent molecules, as would be expected if both were capable of forming a strong hydrogen bond.

Studies of $\text{Bu}_4\text{NBr-HCO}^{15}\text{NH}_2$ in the acetonitrile solutions showed hydrogen bonding between bromide and solvent and also that the trans proton forms a bond 3 kJ mol^{-1} more stable than of the cis proton.

¹H NMR Spectroscopy. Because of their high viscosity the spectra of KF- and CsF- HCONH_2 solutions are poorly resolved. The most noticeable change is the collapse of the doublet of the C-H proton to a broad singlet which means that the energy barrier to rotation about the molecule's C-N bond is reduced to allow free rotation of the NH_2 group. The formation of a strong hydrogen bond with its concomitant transfer of negative charge to the nitrogen atom localizes the amide's π system on the carbonyl group and away from the C-N bond, thus permitting the rotation. This very broad resonance of the NH_2 group remains in the same region of the spectrum.

Lithium chloride, bromide, and iodide salts are quite soluble in HCONH_2 , and at concentrations greater than 1:8 of LiX: HCONH_2 , the spectrum retains the doublet of doublets of the C-H group. The NH_2 signal, though still broad due to quadrupole moment broadening of ^{14}N , shows a clear triplet structure.⁴³ Curiously LiF is not very soluble in HCONH_2 at room temperature, and comparison could not be made with these lithium halide solutions.

Methylformamide has a complex set of bands at ca. 8 ppm in its ^1H NMR spectrum, as well as the CH_3 signals at 2-3 ppm. On addition of CsF the CH and NH_2 bands at ca. 8 ppm merge to a broad singlet. There also appears, at concentrations of CsF greater than 2 M, another weak singlet at ca. 5.8 ppm which we tentatively assign to the CH of the anion HCONCH_3^- and a multiplet at 1.2 ppm which we assign to the CH_3 group. It might be that exchange of protons between the solvent molecules and the HCONCH_3^- ion is slow on the NMR time scale. If HF_2^- is to exist in these solutions, as the ^{19}F NMR spectra suggest, then it presupposes the formation of HCONCH_3^- . A proton signal for HF_2^- was not observed—presumably since exchange between it and $\text{HCON}(\text{CH}_3)-\text{H}-\text{F}^-$ is rapid.

Biochemical Implications. Proteins are long-chain peptide polymers interconnected by hydrogen bonds formed between the N-H group of one amide fragment and the carbonyl group of another fragment on a parallel chain.⁴⁹ By such interpeptide hydrogen bonds the macromolecular structure is maintained. The strength of such hydrogen bonds is thought to be of the same order as that between simpler amides such as methylacetamide linear polymers and δ -valerolactam cyclic ones, where the hydrogen bond energies are 17.5^{50} and $30^{51} \text{ kJ mol}^{-1}$, respectively.

(40) M. S. Gordon, D. E. Tallman, C. Monroe, M. Steinbach, and J. Armbrust, *J. Am. Chem. Soc.*, **97**, 1326 (1975).

(41) H. W. W. Ardrian and D. Feil, *Acta Crystallogr., Sect. A*, **A25**, 438 (1969).

(42) J. Emsley, *J. Chem. Soc. A*, 2511 (1971).

(43) A. J. Lees, B. P. Straughan, and D. J. Gardiner, *J. Mol. Struct.*, **54**, 37 (1979).

(44) J. Emsley, *J. Chem. Soc. A*, 2702 (1971).

(45) G. Somsen and J. Coops, *Recl. Trav. Chim. Pays-Bas*, **84**, 985 (1965); **85**, 517 (1966).

(46) J. Emsley and O. P. A. Hoyte, *J. Inorg. Nucl. Chem.*, in press.

(47) O. D. Bonner, *J. Phys. Chem.*, **81**, 2247 (1977).

(48) J. S. Martin and F. Y. Fujiwara, *J. Am. Chem. Soc.*, **96**, 7632 (1974).

(49) S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding", Van Nostrand, New York, 1971, Chapter 9.

(50) I. M. Klotz and J. S. Frantzen, *J. Am. Chem. Soc.*, **84**, 3461 (1962).

(51) H. Susi and J. S. Ard, *Arch. Biochem. Biophys.*, **117**, 147 (1966).

A recent and comprehensive compilation of the hydrogen bonding in amino acids, peptides, and related molecules⁵² shows that N-H...X⁻ (X = Cl and Br) bonds are appreciably longer and therefore weaker than hydrogen bonds to other likely acceptors such as acetate, phosphate, and sulfate oxygen atoms. No instances of N-H...F⁻ systems appear to have been subjected to crystal structure determination.

From our calculations and studies it seems certain that the F⁻ ion competes successfully for the N-H bond in amide systems. Other N-H bonds could also be affected. Considering the prevalence of hydrogen bonding involving N-H in biological systems, including DNA, it may well be important to avoid undue exposure in high concentrations of fluoride ion, which may be able to disrupt them.

The profound biological effects that are being linked to the simple fluoride ion such as genetic damage, birth defects, allergy

responses, and cancer⁵³ are difficult to explain as arising from the chemistry of this ion, which in aqueous solution is stable and not active in bond-forming or bond-breaking reactions, being a very weak nucleophile. We believe that we have found, in its strong hydrogen bonding potential toward the NH group of amides and related biomolecules, an explanation of how this reputedly inert ion could disrupt key sites in biological systems. By the same token it may also explain why fluoride is an essential element in low concentrations, use being made of the N-H...F⁻ hydrogen bond as an intermediate step in reactions involving amides.

Acknowledgment. The authors wish to thank NATO for a travel grant (J.E. and J.M.M.) and the Science Research Council of Great Britain for a maintenance grant (D.J.J.).

(52) S. N. Vinogradov, *Int. J. Peptide Protein Res.*, **14**, 281 (1979).

(53) G. L. Waldbott, A. W. Burgstahler, and H. L. McKinney, "Fluoridation: the Great Dilemma", Coronado Press, Lawrence, Kansas, 1978.

NMR Study of Molecular Reorientation under Fivefold Symmetry — Solid Permethylferrocene[†]

D. E. Wemmer, D. J. Ruben, and A. Pines*

Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. Received March 24, 1980

Abstract: The ring reorientation in permethylferrocene has been studied by using high-resolution solid-state ¹³C NMR. The constraints which symmetry places upon the number and types of motional parameters which may be determined from the NMR spectrum are discussed. From comparison of the experimental line shapes in the slow reorientation temperature range with theoretical models for random rotations and symmetry-related jumps, it is concluded that the reorientation occurs as jumps between symmetry-related orientations with jumps of $2\pi/5$ highly favored over $4\pi/5$. The activation energy derived for the jump process is 13.5 kJ/mol.

1. Introduction

NMR has long played an important role in the study of molecular motion in the solid state.^{1,2} However, most of the experiments to date have been low resolution in nature, observation of narrowing of dipolar broadened lines or measurement of relaxation times T_1 and $T_{1\rho}$, and thus are limited in ability to distinguish among different types of molecular motion. Recent advances in solid state NMR techniques³ have made available high-resolution line shapes for chemical shielding and thus the possibility for much more detailed analysis of molecular motions in the solid state. Early studies of this type were made in cases for which the motion is of sufficiently high symmetry to reduce the powder line shape to a single sharp line.^{4,5,7} In such cases it is possible to distinguish experimentally between models of rotational diffusion and jumps between symmetry-related orientations, in spite of the fact that the rapid motion line shapes are the same. Theoretical⁶ and experimental^{7,8} work has shown that similarly detailed information may also be obtained in cases where the motion is of lower symmetry.

In this paper we present an analysis of ring rotation in permethylferrocene, using the high-resolution approach. This case is of particular interest because of the C_5 symmetry, which requires two parameters, corresponding to jumps of $2\pi/5$ and $4\pi/5$ for a jump model. Though it may be possible to distinguish the relative probability of such jumps by using neutron scattering,⁹ no such analysis has yet been successfully completed. However,

since the different types of jumps lead to different kinds of averaging in the ¹³C line shapes, the relative probability may be ascertained through analysis of line shapes obtained in the slow-exchange temperature region.

2. ¹³C Line Shapes for Limiting Cases of Motion

In rigid powder solids, high-resolution ¹³C spectra may be completely characterized by one, or more possibly overlapping chemical shielding tensors. If a carbon is at a site of low symmetry, then its line shape is the well-known tensor powder pattern calculated first by Bloembergen and Rowland.¹⁰ If some rapid molecular motion occurs (rapid meaning that the correlation time is much shorter than the inverse of the spectral width involved), then this tensor must be averaged over the motion with an appropriate angular weighing function. If the motion is isotropic, as in plastic phases, then the chemical shielding tensors are reduced to just their trace. If the motion is a uniform uniaxial rotation,

(1) H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.*, **18**, 162 (1950).

(2) E. R. Andrew, *J. Chem. Phys.*, **18**, 607 (1950).

(3) M. Mehring, "NMR: Basic Principles and Progress", Vol. 11, Springer Verlag, Heidelberg, 1976.

(4) H. W. Spiess, *Chem. Phys.*, **6**, 217 (1974).

(5) H. W. Spiess, R. Grose, and U. Haeberlen, *Chem. Phys.*, **6**, 226 (1974).

(6) A. Baram, Z. Luz, and S. Alexander, *J. Chem. Phys.*, **64**, 4321 (1976).

(7) D. Wemmer, Ph.D. Thesis, University of California, Berkeley, 1979.

(8) D. Wemmer, D. J. Ruben, and A. Pines, to be submitted for publication.

(9) J. Tomkinson, private communication.

(10) N. Bloembergen and T. J. Rowland, *Acta Metallurgica*, **1**, 731 (1955).

[†]Taken in part from the Ph.D. Thesis of D. E. Wemmer, Lawrence Berkeley Laboratory Report No. LBL-8042, 1978.