Strong Hydrogen Bonding in the Polyfluorides: *ab initio* Calculations and a New Method of preparing Potassium Hydrogendifluoride

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Ab initio LCAO-MO-SCF calculations have been performed on the polyfluoride ions $H_nF_{n+1}^-$, n = 1—4, and the hydrogen fluoride polymers $(HF)_m$, m = 1—4, to determine their molecular configurations and the hydrogen-bond energies of the polyfluorides. All the polyfluorides are strongly hydrogen bonded and have structures in which a central fluorine acts as the acceptor to one to four HF molecules. The hydrogen fluoride polymers prefer open-chain arrangements. A safe and simple method of preparing $K[HF_2]$ in high yield is given.

VERY strong hydrogen bonding has emerged as a distinctly different kind of bonding from that of normal (weak) hydrogen bonding, and it can be found in a large variety of systems.[1] The earliest example of very strong hydrogen bonding recognized as such was that of the difluoride ion, HF_2^-, and although this simple ion has been studied for many years there is still disagreement over its hydrogen-bond energy. Methods of assessment based on thermochemical measurements have given values ranging from 155 [2] to 252 kJ mol^{-1},[3] while the energies derived theoretically are in the region 167 [4] to 234 kJ mol^{-1}.[5] The average of all reported values is 212 kJ mol^{-1}, which is in the region where there is now good reason for expecting the 'true' value to lie.[6] Other very strong hydrogen bonds involving the fluoride ion are weaker and have energies which fall below 150 kJ mol^{-1}: $F^- \cdots H_3BO_3$, $\Delta E = 149$ kJ mol^{-1};[7] $F^- \cdots H_2NCOR$, $\Delta E = 149$ kJ mol^{-1};[8] $F^- \cdots HO_2CR$, $\Delta E = 105$ kJ mol^{-1};[9] and $F^- \cdots H_2O$, $\Delta E = 101$ kJ mol^{-1}.[10]

When the fluoride ion is exposed to HF it can attach to itself one to four HF molecules. The experimentally determined structures of the polyfluorides show that these HF molecules are all hydrogen bonded to the central fluoride and in the case of H_2F_3 (ref. 11) and H_4F_5 (ref. 12) the hydrogen bonds are short, but not as short as the 226 pm found for $R(F \cdots F)$ in HF_2^-.[13] The structure of $H_3F_4^-$ was inferred to be of this type from i.r. spectral studies only [14] and the bond energy deduced to be *ca.* 40 kJ mol^{-1} which is comparatively weak.

There are few systems in which there are adjacent strong hydrogen bonds so that the polyfluorides offer a unique opportunity to explore whether such ions have several bonds of comparable energy or one strong bond and other weaker hydrogen bonds. We have calculated the hydrogen-bond energies and structures of these species by the method which we have previously found to be reliable for HF_2^- (ref. 9) and other systems.[7,8,15] The results of our present calculations have also led us to reformulate the definition of the bond energy of a strong hydrogen bond. The previous definition is shown to be of only limited application.[16]

THEORETICAL

Ab initio LCAO-MO-SCF calculations have been performed on the di-, tri-, tetra-, and penta-fluoride ions using a version of the program GAUSSIAN 76.[17] This program has recently been modified to perform level shifting of the Hartree–Fock Hamiltonian [18] directly in the atomic orbital basis to guarantee the convergence of the iterative SCF calculations.[19] Calculations have also been made on hydrogen fluoride and its polymers $(HF)_m$, m = 2—4.

Geometry optimizations (bond lengths to within ± 1 pm, bond angles to within $\pm 0.5°$) were performed with the split-valence 4-31G basis set,[20] using univariate quadratic interpolation procedures. All hydrogen bonds were assumed to be linear, and the HF polymers were assumed to be planar.

The hydrogen-bond energy of the most stable conformation of each polyfluoride was then computed using the extended [4*s*2*p*/2*s*1*p*] basis set of Dunning [21] with an *s*-orbital sealing factor of $\sqrt{2}$ and a *p*-orbital exponent of 0.7 for the protons. This basis set has previously been shown to be sufficiently complete to yield hydrogen-bond energies which are stable against further basis-set extensions [9] and against 'ghost-orbital' corrections.[15] Single-determinant SCF wavefunctions are generally adequate for calculations of the energies of strong hydrogen bonds between closed-shell molecules since the molecular extra-correlation energy and the zero-point vibrational corrections are both small (*ca.* 5%).[22] The results of these calculations of the optimized conformations and their energies are given in Figures 1 and 2.

DISCUSSION

HF *Polymers*.—That the condensed phases of hydrogen fluoride contain zigzag (*i.e. trans, trans*) chains and rings of hydrogen-bonded polymers is mentioned in most textbooks of inorganic chemistry. The solid phase consists of infinite planar chains with $R(F \cdots F)$ 249 pm and angle HFH 120°.[23] Several theoretical studies of the dimer $(HF)_2$ have been carried out,[24a-g] the most recent ones showing that the open-chain form (II) is of lower energy than cyclic forms.[24f,g]

The trimer has been investigated by Swepston *et al.*[24g] using the 4-21G basis set for the *trans* open-chain form (III) and the cyclic form (V); the energy of the former was lower. The *cis* open-chain form (IV) was not considered, yet our results show this to be of even lower energy. The same conclusion was reached by del Bene and Pople [24c] regarding the *cis* and *trans* open-chain forms, although these authors used the minimal STO-4G

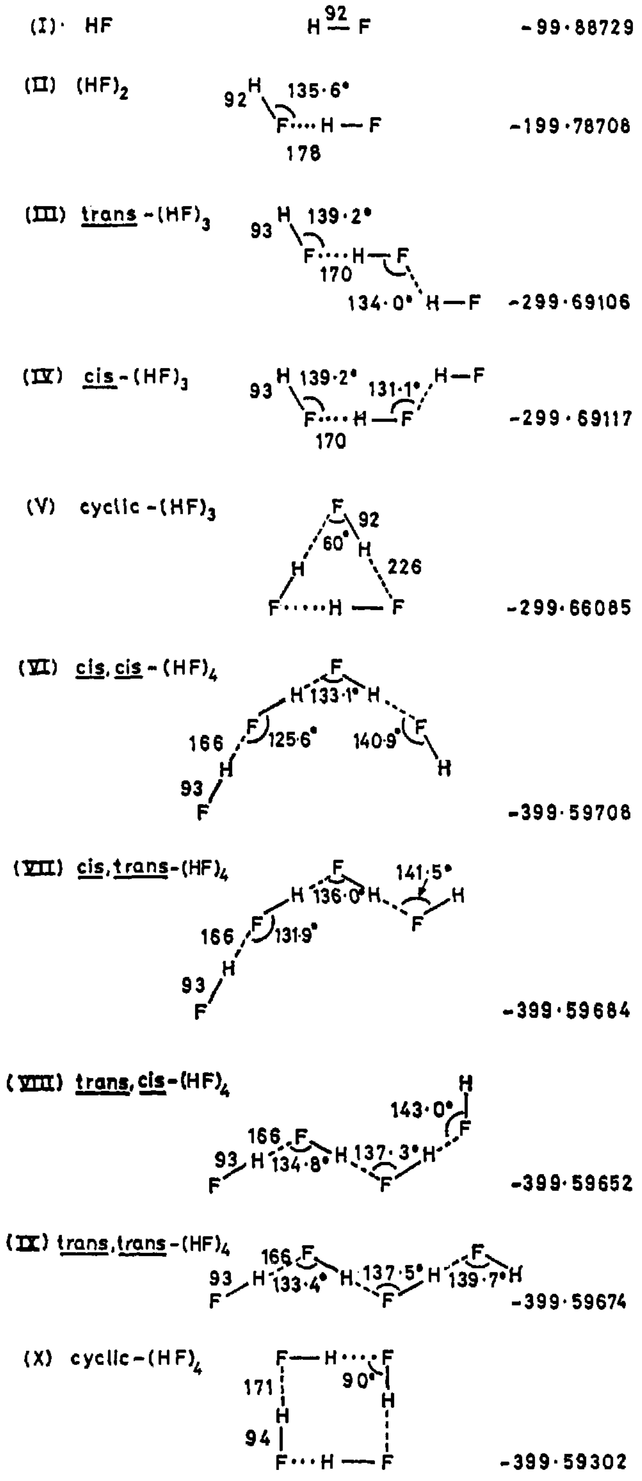

FIGURE 1 Optimized conformations of HF polymers and their calculated total energies, 4-31G basis set; bond lengths are given in pm, total energies in Hartrees

basis set which showed that the cyclic trimer was more stable than either.

The same order of stability is found for the tetramers, *i.e. cis,cis* > *cis,trans* > *trans,cis* > *trans,trans* > cyclic. This is at variance with the published structure of $(HF)_n$ in the solid[23] but the zigzag (*trans,trans*) configuration is presumably the best conformation for efficient packing. The *cis,cis* form has also been computed to be more stable than the other forms by del Bene and Pople.[24c]

The Polyfluorides.—How do the calculated structures of these ions, given with their energies in Figure 2, compare with those observed? The trifluoride, $K[H_2F_3]$ has ions with the calculated angular arrangement (XII) but a central angle in the crystal of either 130 or 139°,[11] depending upon the crystal site. The hydrogen-bond lengths $R(F \cdots F)$ were 233 pm which compares well with the 238 pm of (XII), the protons were not located.

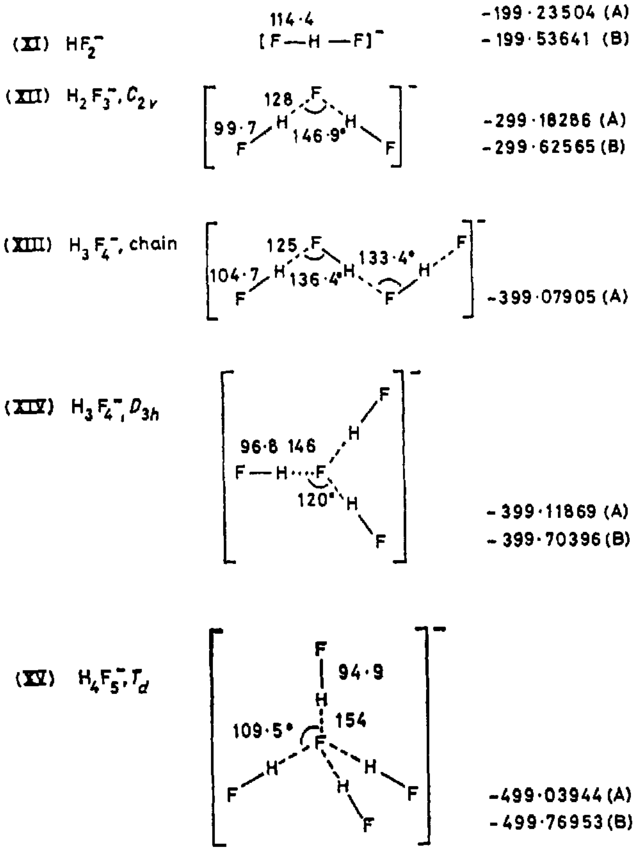

FIGURE 2 Optimized conformations, 4-31G basis set, of the polyfluorides $H_nF_{n+1}^-$, $n = 1$—4, and their calculated total energies, 4-31G (A) and $[4s2p/2s1p]$ (B) basis sets. Bond lengths are given in pm and total energies in Hartrees. The 4-31G energy for F^- is -99.247 82 Hartrees

The structure of $K[H_3F_4]$ has been explored only by low-temperature i.r. spectroscopy[14] which nevertheless revealed a planar D_{3h} configuration as in (XIV). Pyramidal C_{3v} conformations were tried for (XIV) on the likely assumption that the remaining lone pair on the central fluoride which is not involved in the hydrogen bonding would be stereochemically active. However, such conformations for $H_3F_4^-$ were of higher energy than the planar conformation, where the non-bonding orbital is essentially the p_π orbital of the central fluorine. The bond energy of $H_3F_4^-$ was estimated to be only *ca.* 40 kJ mol^{-1}.[14] Structure (XIII) was also investigated but found to be of higher energy than structure (XIV).

The pentafluoride, $K[H_4F_5]$, has been studied by *X*-ray crystallography,[13] revealing a slightly distorted tetrahedral arrangement as in (XV) with $R(F \cdots F) = 245$, $R(H \cdots F) = 176$, and $R(H–F) = 70$ pm. Although asymmetric, these hydrogen bonds are still very short and therefore likely to be strong.[1]

Apart from HF_2^-, on which a great deal of theoretical work has been done,[4,5,9,25] the higher fluorides are reported on here for the first time. In addition we have carried out calculations on HF_2^- with various large basis sets (Table 1) to establish further the basis-set stability of the hydrogen-bond energy.

TABLE 1

Basis-set dependence of the hydrogen-bond energy in HF_2^-

Basis set	ΔE/kJ mol^{-1}
4-31G	262
6-31G**	239
[4*s*2*p*/2*s*1*p*]	220
[4*s*2*p*1*d*/2*s*1*p*]	217
[5*s*3*p*/3*s*1*p*]	214
[5*s*3*p*1*d*/3*s*1*p*]	214

The trifluoride species was also calculated by the larger basis set [4*s*2*p*1*d*/2*s*1*p*] which gave −299.638 50 Hartrees (XII). The tetrafluoride (XIV) likewise gave −399.723 94 Hartrees. The pentafluoride could only be studied with the [4*s*2*p*/2*s*1*p*] basis set and considering the foregoing trends it was not thought to justify the computer time required to study the linear forms using the larger basis set. Clearly the formation of hydrogen bonds to a central fluoride is the preferred situation.

Precisely how the hydrogen-bond energies of these bonds are to be defined is open to debate. The previously agreed definition,[16] that the energy of a strong hydrogen bond should be defined with respect to the lower-energy pair of component molecules, *i.e.* AH + B or A + HB, now needs revision. This definition is appropriate when considering systems with a single strong hydrogen bond such as HF_2^-. However, when considering the higher polyfluorides there are two ways of defining the hydrogen-bond energy: first to use the energy difference in equation (1) as defined previously; [16] or secondly to define the mean hydrogen-bond energy of all bonds as in equation (2).

$$\Delta E_1 = E(H_nF_{n+1}^-) - E(H_{n-1}F_n^-) - E(HF) \quad (1)$$

$$\Delta E_2 = (1/n)[E(H_nF_{n+1}^-) - nE(HF) - E(F^-)] \quad (2)$$

These two methods are the respective equivalents of the individual bond-dissociation energies and the mean bond energies of a covalent molecule such as H_2O. Table 2 gives the hydrogen-bond energies calculated by both methods. We believe that for systems with more than one strong hydrogen bond the purely abstract approach to energies of Bouma and Radom [16a] needs supplementing by the definition of energies ΔE_2 which takes into account the chemical nature of the system. Table 2 shows, as might be expected, a progressively decreasing hydrogen-bond energy with each addition of HF to F^-. Extrapolation to $H_5F_6^-$ using ΔE_1 would predict an additional hydrogen-bond energy of <40 kJ mol^{-1}, but at the price of steric overcrowding, so that this species is not likely to be stable with respect to $(H_4F_5{\cdot}HF)^-$ in which an HF molecule is hydrogen bonded to the inner sphere of solvent HF molecules.

TABLE 2

Hydrogen-bond energies (kJ mol^{-1}) of the polyfluorides [a]

	Hydrogen bond-dissociation energy, ΔE_1 [b]	Mean hydrogen-bond energy, ΔE_2 [c]
HF_2^- (XI)	220	220
$H_2F_3^-$ (XII)	133	177
$H_3F_4^-$ (XIV)	104	152
$H_4F_5^-$ (XV)	71	132

[a] Calculated with E(HF) = −100.038 59 Hartrees and $E(F^-)$ = −99.414 06 Hartrees for the basis set [4*s*2*p*/2*s*1*p*]. [b] Calculated from equation (1). [c] Calculated from equation (2).

A Safe and Simple Synthesis of $K[HF_2]$.—Sodium and potassium difluorides are available commercially, produced by the reaction of the corresponding carbonate or hydroxide and hydrofluoric acid.[26] More recently it has been reported that prolonged stirring of a suspension of NaF in dilute hydrochloric acid at 50 °C will also yield $Na[HF_2]$.[27] Another method advocates the use of pyridine to precipitate the more soluble $K[HF_2]$ and $Rb[HF_2]$ from solutions of the corresponding fluoride in 40% HF solution.[28]

We have discovered that good yields of $K[HF_2]$ can be obtained from KF dissolved in aqueous acetic acid. The method is eminently suited to laboratory synthesis since it gives a high-grade crystalline material without recourse to hydrofluoric acid. The $K[HF_2]$ crystals will grow from such solutions provided there is at least 65% (w/w) CH_3CO_2H and not more than 95% (w/w). The optimum rate of crystal growth is from a $H_2O–CH_3CO_2H$ (1 : 1) solution.

To potassium fluoride (87 g, 1.5 mol) dissolved in water (150 cm^3) was slowly added glacial acetic acid (150 g) with stirring and the solution allowed to stand at room temperature. Potassium difluoride crystals form and the yield of these was 25 g (42%, based on F) after 1 h, 42 g (72%) after 3 d, and 58 g (98%) after 10 d. Cooling the solution to 0 °C caused more rapid crystal formation but of smaller crystals. The product was filtered off, dried at 120 °C, and identified by i.r. spectroscopy. It was shown by ^{1}H n.m.r. spectroscopy to be free from CH_3CO_2H, and analysed as 99% pure by titration with alkali solution. The chief impurities were sulphate (0.08%) and sodium (0.02%) from the original, laboratory grade KF.

Potassium fluoride solutions in glacial acetic acid deposit crystals of $KF{\cdot}2CH_3CO_2H$,[29] but with water present $K[HF_2]$ is produced. The amount of water present has to be at least 5% by weight but the yield from such a solution is only 2% $K[HF_2]$ after 3 d. This rises to 12% after 3 d in a 25% solution and 37% after

3 d with a 40% water solution. Too much water (>50%) reduces the yield of $K[HF_2]$ since it increases the solubility of this salt in the solution.

The conventional explanation for this reaction would be that the formation of HF in equation (3) leads to $K[HF_2]$ as in (4). Recent ideas concerning the nature of

$$F^- + CH_3CO_2H \longrightarrow HF + CH_3CO_2^- \qquad (3)$$

$$K^+ + F^- + HF \longrightarrow K[HF_2] \qquad (4)$$

hydrofluoric acid solutions show that HF molecules as such are not present as was previously postulated.[30] The chief species is the strongly hydrogen-bonded $H_2\overset{+}{O}{-}H{-}F^-$, so that equations (5) and (6) are presented as a better summary of the reaction.

$$CH_3CO_2HF^- + H_2O \rightleftharpoons CH_3CO_2^- + H_2\overset{+}{O}HF^- \qquad (5)$$

$$H_2\overset{+}{O}HF^- + K^+ + F^- \rightleftharpoons K[HF_2]\downarrow + H_2O \qquad (6)$$

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REFERENCES

[1] J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91.

[2] S. H. Harrell and D. H. McDaniel, *J. Am. Chem. Soc.*, 1964, **86**, 4497.

[3] H. P. Dixon, H. D. B. Jenkins, and T. C. Waddington, *J. Chem. Phys.*, 1972, **57**, 4388; H. D. B. Jenkins and K. F. Pratt, *J. Chem. Soc., Faraday Trans. 2*, 1977, 812.

[4] P. N. Noble and R. N. Kortzeborn, *J. Chem. Phys.*, 1970, **52**, 5375.

[5] A. Neckel, P. Kuzmany, and G. Vinek, *Z. Naturforsch., Teil A*, 1971, **26**, 569; A. Støgard, A. Strich, B. Roos, and J. Almlöf, *Chem. Phys.*, 1975, **8**, 405.

[6] T. C. Waddington, personal communication.

[7] J. Emsley, V. Gold, J. Lucas, and R. E. Overill, *J. Chem. Soc., Dalton Trans.*, 1981, 783.

[8] J. Emsley, D. J. Jones, J. M. Miller, R. E. Overill, and R. A. Waddilove, *J. Am. Chem. Soc.*, 1981, **103**, 24.

[9] J. Emsley, O. P. A. Hoyte, and R. E. Overill, *J. Chem. Soc., Perkin Trans. 2*, 1977, 2079.

[10] G. H. F. Diercksen and W. P. Kraemer, *Chem. Phys. Lett.*, 1970, **5**, 570.

[11] J. D. Forrester, M. E. Senko, A. Zalkin, and D. H. Templeton, *Acta Crystallogr.*, 1963, **16**, 15.

[12] B. A. Coyle, L. W. Schroeder, and J. A. Ibers, *J. Solid State Chem.*, 1970, **1**, 386.

[13] J. A. Ibers, *J. Chem. Phys.*, 1964, **40**, 402.

[14] I. Gennick, K. M. Harmon, and M. M. Potvin, *Inorg. Chem.*, 1977, **8**, 7033; K. M. Harmon and I. Gennick, *J. Mol. Struct.*, 1977, **38**, 97.

[15] J. Emsley, O. P. A. Hoyte, and R. E. Overill, *J. Am. Chem. Soc.*, 1978, **100**, 3303.

[16] (*a*) W. J. Bouma and L. Radom, *Chem. Phys. Lett.*, 1979, **64**, 216; (*b*) J. Emsley and R. E. Overill, *ibid.*, 1979, **65**, 616.

[17] Quantum Chemistry Program Exchange, 1978, vol. 10, p. 368.

[18] I. H. Hillier and V. R. Saunders, *Int. J. Quantum Chem.*, 1973, **7**, 699.

[19] R. E. Overill, *King's College Computing Bull.*, 1980, **K5**, 10/1.

[20] W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.

[21] T. H. Dunning, *J. Chem. Phys.*, 1970, **53**, 2823.

[22] G. Diercksen, W. Kraemer, and B. Roos, *Theor. Chim. Acta*, 1974, **36**, 249; E. Clementi, H. Kistenmacher, and H. Popkie, *J. Chem. Phys.*, 1973, **59**, 5842.

[23] M. Atoji and W. N. Lipscomb, *Acta Crystallogr.*, 1954, **7**, 173.

[24] (*a*) L. C. Allen and P. A. Kollman, *J. Am. Chem. Soc.*, 1970, **92**, 4108; (*b*) G. H. F. Diercksen and W. P. Kraemer, *Chem. Phys. Lett.*, 1970, **6**, 419; (*c*) J. E. del Bene and J. A. Pople, *J. Chem. Phys.*, 1971, **55**, 2296; (*d*) W. von Niessen, *Theor. Chim. Acta*, 1973, **31**, 297; (*e*) R. C. Kerno and L. C. Allen, *J. Am. Chem. Soc.*, 1978, **100**, 6587; (*f*) M. Remko, *Adv. Mol. Relaxation Processes*, 1978, **12**, 221; (*g*) P. N. Swepston, S. Colby, H. L. Sellers, and L. Schafer, *Chem. Phys. Lett.*, 1980, **72**, 364.

[25] P. A. Kollman and L. C. Allen, *J. Am. Chem. Soc.*, 1970, **92**, 6101; J. Almlöf, *Chem. Phys. Lett.*, 1972, **17**, 49.

[26] M. Hudlicky, ' Chemistry of Organic Fluorine Compounds,' Macmillan, New York, 1962, pp. 49—63.

[27] F. Narbeshuber, A. Schmidt, and F. Weinrotter, G.P. 1,132,547/1962 (*Chem. Abstr.*, **57**, 10778i).

[28] M. K. Chaudhuri and P. K. Chaudhuri, *Chem. Ind.* (*London*), 1979, 88.

[29] J. Emsley, *J. Chem. Soc. A*, 1971, 2702.

[30] P. A. Guiguère and S. Turrell, *J. Am. Chem. Soc.*, 1980, **102**, 5473.