Very Strong Hydrogen Bonding

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1 Introduction

In 1968 Tuck reviewed the structures and properties of HX_2^- and HXY^- anions that have strong hydrogen bonds.[1] Since then there has been an upsurge in interest in this field, and strong hydrogen bonding has been detected in a variety of systems and not only in anions but between neutral molecules and cations. The literature is now extensive; this review deals mainly with the key developments of the past ten years.

2 Weak and Strong Hydrogen Bonds

The investigators of hydrogen bonds rely upon many techniques to detect their prey. The most important methods used are i.r. spectroscopy, *X*-ray and neutron diffraction, and ^1H n.m.r. spectroscopy, in that order. As far as possible the data are processed into the forms used by chemists to compare chemical bonds, *i.e.* bond lengths, bond angles, bond energies, and reactivities. Some data are not easily translated into these traditional modes of expression and the hydrogen bond is commonly discussed in terms of vibrational changes and proton chemical shifts.

To most chemists a hydrogen bond is a weak association between molecules and/or ions in which a link between a donor A–H and an acceptor B specifically involves the hydrogen atom. The attraction is explained simply as being predominantly electrostatic, between the positive end of a polar covalent bond, $A^{\delta-}$–$H^{\delta+}$, and a centre of high electron density on B, such as a non-bonding pair of electrons. Most hydrogen bonds are of this kind with A and B being the more electronegative elements F, O, N, Cl, *etc.* The notation A–H··B is self-explanatory and the term 'hydrogen bond' is used to refer to the H··B interaction.

However, not all hydrogen bonds are of this kind and it has been known for almost 40 years that in some hydrogen bonds the proton is not clearly bonded covalently to either A or B, but equally attracted to both of them. Called 'strong' or 'very strong' hydrogen bonding, the name now refers to the whole system and this is written A··H··B or preferably A–H–B. Many such systems are recognized and strong hydrogen bonding is yet another example of the versatility of the proton in chemical bonding.

But is strong hydrogen bonding really so different as to merit a separate category? While there are now overwhelming reasons for thinking this to be

[1] D. G. Tuck, *Progr. Inorg. Chem.*, 1968, **9**, 161.

so,[2,3] the belief in a clear distinction between weak and strong hydrogen bonding is not universal.[4] The purpose of this article is to convince the reader that there is such a thing as strong hydrogen bonding that is quantitatively different from normal hydrogen bonding. The criteria for classifying hydrogen bonds as weak or strong are summarized in Table 1.

Table 1 *Weak and strong hydrogen bonding*

Property	*Weak hydrogen bonding* A–H··B	*Strong hydrogen bonding* A–H–B
Bond length R(A··B)	Slightly less than the sum of the van der Waals radii of A and B[a]	Significantly less (> 30 pm) than the sum of the van der Waals radii of A and B
Location of H[b]	Near its parent[c] atom: $r(\text{A–H}) \simeq r_{\text{cov}}(\text{A–H})$	Centred, or roughly so, but not covalently near to A or B
Bond vibrational mode ν_{AH}	Broad bands and shifted to lower frequencies; still in 2000—3000 cm^{-1} region	Very broad bands in region below 1600 cm^{-1}
$\Delta\nu_{\text{AH}}/\nu_{\text{AH}}$[d]	<25%	>25%
$\nu_{\text{AH}}/\nu_{\text{AD}}$[e]	1.35 or less	Tends to 1 but may be >1.35 (see text and Fig. 3)
Bond energy	E(A–H··B) < 50 kJ mol^{-1} and most < 30 kJ mol^{-1} (measured)	E(A–H–B) > 50 kJ mol^{-1} and some > 100 kJ mol^{-1} (calculated)
Proton shielding; chemical shift	Slight downfield shift from $\delta(^1\text{H,AH})$ non-hydrogen-bonded	Large downfield shift, sometimes below 20 p.p.m.

[a] van der Waals radii: $r(N)$, 155 pm; r(O), 150 pm; $r(F)$, 140 pm; r(Cl), 175 pm; r(Br), 185 pm; ref: A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441; [b] most hydrogen bonds are linear or nearly so, depending upon local environmental forces; ref: I. Olovsson and P.-G. Jönsson, 'The Hydrogen Bond', ed. P. Schuster, G. Zundel, and C. Sandorfy, North-Holland, Amsterdam, 1976, pp. 403–408; [c] proton transfer from A to B may happen, but H will still be obviously *covalently* bonded to either A or B; [d] shift in stretching mode, $\Delta\nu_{\text{AH}}$ relative to non-hydrogen bonded-mode, ν^0_{AH}; [e] isotope frequency ratio

Some of the parameters of Table 1 need further explanation. Thus the strength of a weak hydrogen bond is defined simply as the enthalpy of the weak interaction between AH and B, which is usually an order of magnitude less than a

[2] I. D. Brown, *Acta Cryst.*, 1976, **32A**, 24.
[3] A. Novak, *Structure and Bonding*, 1974, **18**, 177.
[4] H. D. Megan, 'Crystal Structure: A Working Approach', W. B. Saunders, Philadelphia, 1973.

covalent single-bond energy. For a strong hydrogen bond the definition needs modifying because it is no longer desirable to label one interaction as covalent and the other as hydrogen bond. The hydrogen-bond energy, E(A–H–B), is defined with respect of the lower-energy components AH + B or A + HB.[5]

With the guidelines of Table 1 it is possible to classify a hydrogen bond in most cases, although there are some systems where not all the above information is to hand. Often recognition of a strong hydrogen bond relies on a single bit of evidence, which may be quite conclusive, *e.g.* a short R(A··B), or less so, such as a very broad band in the i.r. spectrum below 1500 cm^{-1}. Diffraction data and i.r. spectroscopy have given rise to their own ways of classification.

Speakman[6] has devoted 30 years to studying strong hydrogen bonding chiefly by X-ray diffraction. He categorized hydrogen bonds as types A or B, A having the proton located at a point of crystal symmetry, and B not so located.[7] The former are invariably short hydrogen bonds, the latter have the proton nearer one atom or the other. Refinements to his classification include pseudo-A (short but asymmetric bonds) and A_2 and B_2 (to cover acid salts of dibasic acids).[6]

Since i.r. spectroscopy has been so important in hydrogen-bond investigations it is not surprising to find a classification based on this. The spectrum of a hydrogen-bonding system is recognizable by its peaks in the i.r. region: these are broad, intense, and shifted from the non-hydrogen-bonding mode. Hadži recognized three types of spectra[8]—(i) the weak interaction in which the peaks are not far removed from the non-associated AH spectrum; (ii) the stronger hydrogen bond which gives a very broad band absorbing at 1600—3000 cm^{-1} with three discernible maxima which he called an ABC band;* and (iii) very strong hydrogen bonds which give a very broad band below 1600 cm^{-1} which he called the D band. These bands indicate an easily polarizable system, a characteristic of strong hydrogen bonds. A feature of D bands is the presence of 'windows' or narrow bands of i.r. transparency.[9] A few systems give spectra intermediate between (ii) and (iii) such as the chloroacetic acids with strong oxygen bases like pyridine N-oxide, alkyl sulphoxides, and phosphine oxides.[10a–g]

The best models for the vibrational modes of a strong hydrogen bond are the linear point groups $C_{\infty v}$ and $D_{\infty h}$ for A–H–B and A–H–A, respectively. There are

*These bands are caused by Fermi resonance of ν_{AH} with the in-plane, δ_{AH}, and out-of-plane, γ_{AH}, bending modes, *i.e.* $2\delta_{AH}$ and $2\gamma_{AH}$. Moreover it has been shown that the *minima* in the ABC band represent the overtone frequencies. *Cf.* M. F. Claydon and N. Sheppard, *Chem. Comm.*, 1969, 1431.

[5] J. Emsley and R. E. Overill, *Chem. Phys. Letters*, 1979, **65**, 616; W. J. Bouma and L. Radom, *ibid.*, 1979, **65**, 616.

[6] J. C. Speakman, *Structure and Bonding*, 1972, **12**, 141.

[7] J. C. Speakman, *J. Chem. Soc.*, 1961, 1164; *Chem. Comm.*, 1967, 32.

[8] D. Hadži, *Pure Appl. Chem.*, 1965, **11**, 435.

[9] J. C. Evans, *Spectrochim. Acta*, 1961, **17**, 129; 1962, **18**, 507.

[10] (*a*) D. Hadži, *J. Chem Soc.*, 1962, 5128; (*b*) D. Hadži and N. Kobilarov, *J. Chem. Soc.* (*A*), 1966, 439; (*c*) D. Hadži, H. Ratajczak, and L. Soboczyk, *ibid.*, 1967, 48; (*d*) D. Hadži, C. Klofatur, and S. Oblak, *ibid.*, 1968, 905; (*e*) S. Detoni, D. Hadži, R. Smerkolj, J. Hawranek, and L. Soboczyk, *ibid.*, 1970, 2851; (*f*) L. Golić, D. Hadži, and F. Lazarini, *Chem. Comm.*, 1971. 860; (*g*) D. Hadži and J. Rajnvajn, *J.C.S. Faraday I*, 1973, **69**, 151.

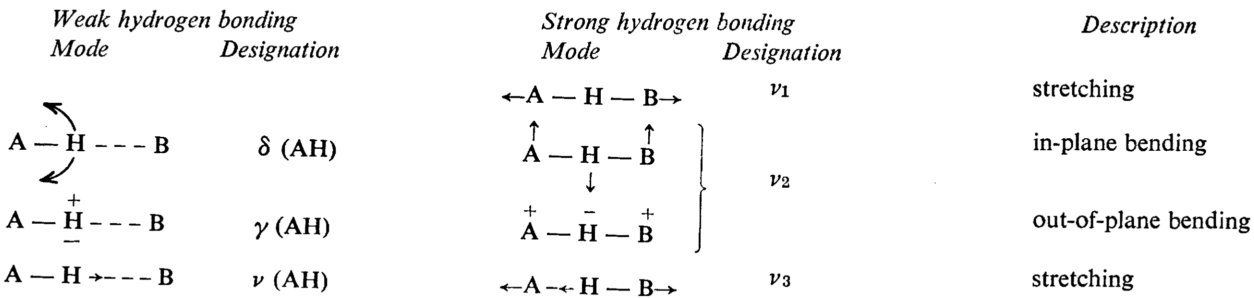


Figure 1 *The vibrational modes of a hydrogen bond*

hydrogen-bonded species with exactly these symmetries, *e.g.* $F–H–Cl^-$ and $F–H–F^-$, but in most cases the hydrogen bond will be part of a much larger system with fewer elements of symmetry overall. Nevertheless, if it is assumed that the bonds are linear and centred then the vibrational modes of the AHB moiety can be treated in the same way as a triatomic linear molecule. Figure 1 shows the vibrational modes of a strong hydrogen bond, compared to the equivalent weak bond modes. In a heteronuclear strong hydrogen bond all the modes are i.r.- and Raman-active; in a homonuclear bond with a centre of symmetry at H the ν_1 mode is Raman-active only and ν_2 and ν_3 are i.r.-active only.

For molecular vibrations the general order of frequency is $\nu_{as} > \nu_s > \delta$. However, if the masses of the outer atoms greatly exceed that of the central atom in a linear molecule the stretching mode $\nu_s(\nu_1)$ can vibrate with a frequency below that of bending modes, and this state of affairs is observed in some of the very strong hydrogen bonds. Even expecting this, it is not easy to analyse strong hydrogen-bond spectra—the i.r. region below 1600 cm^{-1} is overlaid by an immense band with superimposed maxima and 'windows'. The Raman spectra are clearer because the motion of the proton has less influence but *ipso facto* the spectrum is less useful.

Another method of classifying hydrogen bonds is that based on the potential well in which the H sits.[11,12] Four types of well can be envisaged (see Figure 2). At one extreme there is that of the weak bond with two energy minima and the proton in the lower one near its parent atom, 2(a). At the other extreme there is the very strong hydrogen bond with a single minimum, 2(d). Intermediate bonds with two equivalent minima separated by a high, 2(b), or low, 2(c), energy barrier are also postulated. The distance between A and B is the determining factor: as A and B draw closer the two minima merge into a single minimum.

To distinguish these various potential wells may not be easy, especially between the symmetric double minima with low barrier and the single minimum. Present diffraction techniques are not able to decide between them if a distance of less than 16 pm separates the minima in Figure 2(c). Elastic–inelastic neutron scattering may in the future differentiate them[13] but to date the best way of probing such finer details of hydrogen bonding has been by isotope exchange. Recent n.m.r. work with D, and even T, in place of H has proved very useful in identifying hydrogen bonds with a single minimum.[14]

Replacing the H of a hydrogen bond by D may be expected to cause changes in some or all of the physical properties of the bond. Singh and Wood[15] cal-

[11] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids', Benjamin, New York, 1968.

[12] S. N. Vinogradov and R. H. Linnell, 'Hydrogen Bonding', Van Nostrand-Reinhold, New York, 1971.

[13] H. Stiller, 'The Hydrogen Bond', ed. P. Schuster, G. Zundel, and C. Sandorfy, North-Holland, Amsterdam, 1976, Ch. 24.

[14] L. A. Altman, D. Laungani, G. Gunnarsson, H. Wennerström, and S. Forsén, *J. Amer Chem. Soc.*, 1978, **100**, 8264; G. Gunnarsson, H. Wennerström, W. Egan, and S. Forsén, *Chem. Phys. Letters*, 1976, **38**, 96.

[15] T. R. Singh and J. L. Wood, *J. Chem. Phys.*, 1969, **50**, 3572.

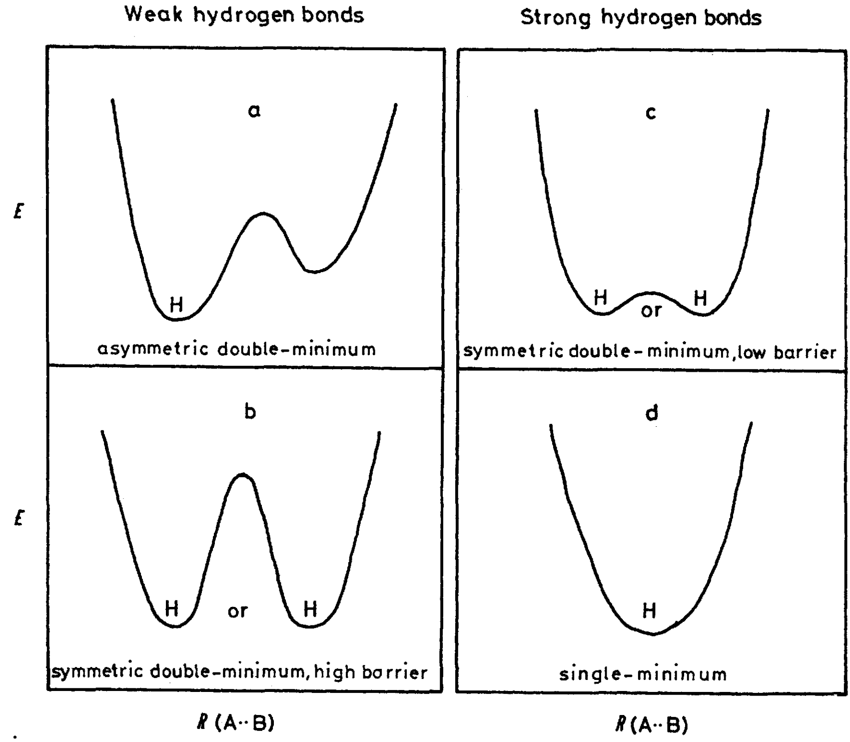


Figure 2 *Potential functions for hydrogen bonds*

culated that in the i.r. spectrum the isotope frequency ratio ν_{AH}/ν_{AD} would vary significantly from the expected 1.35 of non-hydrogen-bonding modes. The i.r. changes are dealt with by Novak[3] who shows graphically how this ratio first decreases with strong hydrogen bonds to a nil isotope effect, *i.e.* $\nu_{AH}/\nu_{AD} = 1$, but then for very short hydrogen bonds it increases to > 1 35. Figure 3 shows the relationship for OHO bonds.[3]

When D and T replace H there is a small but measurable effect on the n.m.r. chemical shift. The change in chemical shift, $\Delta\delta$, for strong hydrogen bonds can serve to distinguish the single-minimum kind from double-minimum–low-barrier kind.[14] Thus, for the hydrogen phthalate ion $\delta(\mathrm{H}) = 21.00, \Delta\delta(\mathrm{H,D}) = -0.15$, and $\Delta\delta(\mathrm{H,T}) = -0.25$ p.p.m., the negative changes indicating a single minimum, whereas for acetylacetone $\delta(\mathrm{H}) = 16.1, \Delta\delta(\mathrm{H,D}) = +0.61, \Delta\delta(\mathrm{H,T}) = +0.83$ p.p.m. and these positive shift values show a double-minimum situation.

Singh and Wood[15] also calculated that the internuclear separation $R(\mathrm{A}\cdot\cdot\mathrm{B})$ would increase on deuteriation if the system were a double minimum but decrease if it were a single minimum. Within experimental error strong bonds

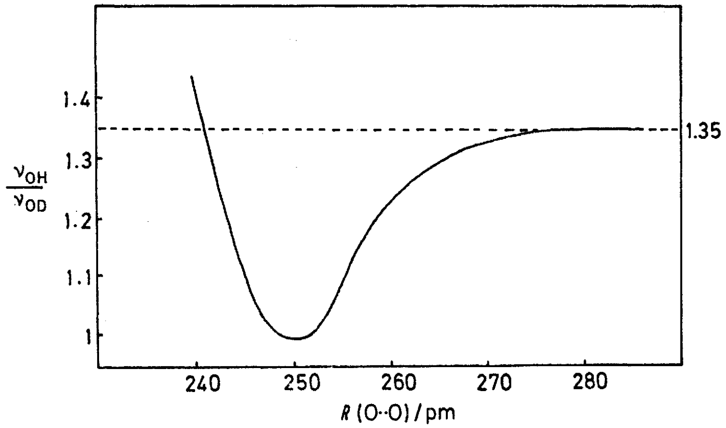


Figure 3 *Isotope frequency ratio ν_{AH}/ν_{AD} and hydrogen-bond length.*[3]

remain the same length on deuteriation, but few systems have been investigated. In any event deuteriation may itself change the potential function of the hydrogen bond from a single minimum with H to a double minimum with D. This is the interpretation of the differences observed in going from $CrHO_2$ to $CrDO_2$ and from $N_2H_5^+HC_2O_4^-$ to $N_2H_5^+DC_2O_4^-$; see pp. 104 and 107.

In discussing hydrogen bonding the word 'symmetry' can be ambiguous since there are several ways in which a hydrogen bond can be symmetric. A better designation is either homonuclear or heteronuclear (AHA or AHB) and centred and non-centred when talking of the proton's location. In writing the formulae of strongly hydrogen-bonded species the custom is to place the proton first, *e.g.* $NaHF_2$, sodium hydrogen difluoride, and $KH(CH_3CO_2)_2$, potassium diacetate. Certain well known species such as $H_5O_2^+$ are excluded from this.

In addition to two-atom hydrogen bonds there are three-atom bonds referred to as bifurcated bonds, $A\text{–}H\!:\!\begin{smallmatrix}\cdot B\\ \cdot B\end{smallmatrix}$, a term which unfortunately is also used to cover double hydrogen bonds $A\begin{smallmatrix}\diagup H\cdot\\ \diagdown H\cdot\end{smallmatrix}\!:\!B$. Neither of these kinds of bond will be covered in this review. We shall deal with the homonuclear bonds first, starting with the halogen group (X–H–X, O–H–O, N–H–N) then with the heteronuclear bond in the same general order (X–H–X′, X–H–O, X–H–N, O–H–N). The review will conclude with a few general remarks on the way in which very strong hydrogen bonding can be explained in terms of conventional chemical bonding theory.

3 Homonuclear Strong Hydrogen Bonds

A The Dihalide Anions, HX_2^-.—(i) *Difluorides.* Investigations into the structure of potassium difluoride were made as early as 1923 when an *X*-ray analysis reported[16] the incredibly short $R(F{\cdot\cdot}F)$ distance of 225 pm, exactly that which is accepted today. Thus began a spate of *X*-ray, i.r., and other measurements which questioned or supported the hypothesis that this ion had a centred H—see ref. 1 for details. That it was centred was finally resolved[17] by neutron diffraction in 1952, although it was later shown that this technique could not distinguish between a single-minimum bond and a double-minimum–low-barrier bond if the two positions were less than 16 pm apart.[18]

Table 2 lists the principal diffraction studies on difluoride salts. Together

Table 2 *Parameters of the difluoride ion* HF_2^-

Salt	*Diffraction method*	$R(F{\cdot\cdot}F)$ /pm	*Details*	*Ref.*
KHF_2	neutron, single crystal	—	linear ion, H centred	17
MHF_2*	*X*-ray	226	H not located	*a*
NH_4HF_2	*X*-ray, single crystal	227.2	,, ,, ,,	*b*
$LiHF_2$	*X*-ray	227	,, ,, ,,	*c*
$NaHF_2$	neutron	226.4	centred bonds	*d*
$NaDF_2$		226.5		
KHF_2	neutron	227.7	H centred†	18
p-$MeC_6H_4NH_3^+HF_2^-$	neutron	226.0	$F\overset{102.5}{—}H\overset{123.5}{—}F^-$‡ 178.1°	21

* M = Li, Na, K, Rb, Cs; † not possible to confirm single-minimum potential; ‡ see text.
[a] R. Kruh, K. Fuwa, and T. E. McEever, *J. Amer. Chem. Soc.*, 1956, **78**, 4256; [b] T. R. R. McDonald, *Acta Cryst.*, 1960, **13**, 113; [c] L. K. Frevel and H. W. Rinn, *Acta Cryst.*, 1962, **15**, 286; [d] B. L. McGraw and J. A. Ibers, *J. Chem. Phys.*, 1963, **39**, 2677.

these reveal a linear, symmetric ion with r(F–H) 113 pm, only 20 pm longer than the covalent bond of HF itself. In most salts the difluoride structure is unaffected by the accompanying cation. The short $R(F{\cdot\cdot}F)$ distance of 226.5 pm can be compared to the hydrogen-bond lengths of 249 pm in crystalline HF,[19] and 255 pm in cyclic HF polymers.[20] It is 54 pm less than the sum of the van der Waals radii (280 pm). Deuteriation make no difference to the bond length.

Not all crystals have perfectly symmetric HF_2^- ions. The *p*-toluidinium cation can displace the hydrogen from its centre site by forming a secondary $F{\cdot\cdot}H\text{–}N^+$ hydrogen bond to one end of the difluoride.[21] The overall length of the difluoride

[16] R. M. Bozorth, *J. Amer. Chem. Soc.*, 1923, **45**, 2128.
[17] S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, 1952, **20**, 704.
[18] J. A. Ibers, *J. Chem. Phys.*, 1964, **40**, 402.
[19] M. Atoji and W. N. Lipscomb, *Acta Cryst.*, 1954, **7**, 173.
[20] S. H. Bauer, J. Y. Beach, and J. H. Simons, *J. Amer. Chem. Soc.*, 1939, **61**, 19.
[21] J. M. Williams and L. F. Schneemeyer, *J. Amer. Chem. Soc.*, 1973, **95**, 5780.

bond remains unaffected. The i.r. data for this salt confirm the asymmetry[22]—Table 3.

Table 3 *Vibrational assignments of the difluoride ion*

Salt	*Technique*	ν_1 *Sym. stretch*	ν_2 *Bend*	ν_3 *Asym. stretch*	*Ref.*
KHF_2	i.r.	i.a.*	1225, 1274	1450	*a*
KHF_2	Raman	595, 604	i.a.	i.a.	*b*
KHF_2	i.r.	i.a.	1233	1473	*c*
KDF_2	i.r.	i.a.	885	1045§	*c*
KHF_2	i.r.	i.a.	1222	1450	*d*
NPr_4HF_2	i.r.	i.a.	1255, 1315	1900	*d*
$NaHF_2$	R, i.r.	630.5	1210, 1220	*ca.* 1500	*e*
KHF_2	R, i.r.	596, 603	1233	*ca.* 1450	*e*
p-$MeC_6H_4NH_3^+HF_2^-$	i.r.	450	1080, 1230	1740	22
$(Cs)HF_2$†	i.r.	i.a.	1217	1364	*f*
$NaHF_2$	i.r.	i.a.	1240	*ca.* 1500	24
$NaDF_2$	i.r.	i.a.	893	—‡	24
KHF_2	i.r.	i.a.	1238, 1263	1442	24
KDF_2	i.r.	i.a.	894, 911	—‡	24

* inactive; † argon matrix isolated; ‡ not reported; § isotope ratio = 1.4.
[a] G. L. Coté and H. W. Thompson, *Proc. Roy. Soc.*, 1951, **210A**, 206; [b] L. Couture and J. P. Mathieu, *Compt. rend.*, 1949, **228**, 555; 1950, **230**, 1054; [c] L. Jones and R. A. Penneman, *J. Chem. Phys.*, 1954, **22**, 781; [d] K. M. Harmon, I. Gennick, S. L. Madeira, and D. L. Duffy, *J. Org. Chem.*, 1974, **39**, 2809; [e] J. J. Rush, L. W. Schroeder, and A. J. Melveger, *J. Chem. Phys.*, 1972, **56**, 2793; [f] B. S. Ault, *J. Phys. Chem.*, 1978, **82**, 844.

If the difluoride ion has a centre of inversion at H, ν_1 will be i.r.-inactive. Table 3 summarizes the vibrational data, most of which prove the ion to have $D_{\infty h}$ symmetry. Agreement over band assignments is not unanimous for ν_3. The doublet observed in KHF_2 for ν_2 is due to lattice effects lifting the degeneracy of this mode, something that was not realized by the early i.r. investigators[23] who interpreted the doublet as indicative of an asymmetric difluoride hyrogen bond, as indeed it is in the *p*-toluidinium salt where a separation of 150 cm^{-1} is observed.[22]

Isotopic dilution of MDF_2 in MHF_2 and MHF_2 in MDF_2 (M = Na, K) gave values 893 cm^{-1} for ν_2 of $NaDF_2$ and 894 cm^{-1} and 911 cm^{-1} for ν_2 of KDF_2, where again site symmetry raises the degeneracy.[24] From this work also emerged a calculation of the charge distribution on the ion as

[22] K. M. Harmon, S. L. Madeira, and R. W. Carling, *Inorg. Chem.*, 1974, **13**, 1260.
[23] (*a*) J. A. A. Ketelaar, *J. Chem. Phys.*, 1941, **9**, 775; (*b*) *Rec. Trav. chim.*, 1941, **60**, 523. The assignment was corrected later in (c) J. A. A. Ketelaar and W. Vedder, *J. Chem. Phys.*, 1951, **19**, 654.
[24] R. D. Cooke, C. Pastorek, R. E. Carbon, and J. C. Decius, *J. Chem. Phys.*, 1978, **69**, 5.

$$\left[\begin{array}{ccc} -0.635e & & -0.635e \\ F & \text{———}H\text{———} & F \\ & +0.270e & \end{array}\right]^-$$

From Table 3 it is possible to calculate isotope frequency ratios, and these are in excess of 1.35, showing that the hydrogen bond is of the single-minimum kind. If other forces intervene, be they lattice or extra-hydrogen bonding, then the shape of the potential well may be changed. Partly substituted ammonium cations such as *p*-toluidinium[22] and triethylammonium[25] are the ones on which extra-hydrogen bonding has been detected.

The difluoride ion is a rare species in that it has three nuclei each with spin $\frac{1}{2}$ and as such would seem a promising target for n.m.r. spectroscopy. Yet despite several investigations it was not fully explored until the importance of the solvent was realized. Earlier work had failed to detect the expected doublet ^{19}F and triplet ^{1}H signals and the coupling constant $^{1}J_{HF}$ was unknown.[26] The same state of affairs pertained with HF itself. The researches of Fujiwara and Martin remedied all this.[27] The results in Table 4 are mainly from their work.

Table 4 ^{1}H *and* ^{19}F *n.m.r. data for difluorides*

Dihalides	$\delta(^{1}H)$/p.p.m.[a]	$\delta(^{19}F)$/p.p.m.[b]	$^{1}J_{HF}$/Hz	*Solvent*
(HF	7.64	−118.7	476	MeCN)
$Et_4N^+HF_2^-$	16.37	−83.35	120.5	MeCN
$Et_4N^+HF_2^-$	16.37	−82.70	118.8	$HCONMe_2$
$Et_4N^+HF_2^-$	16.27	−87.4	120.5	$MeNO_2$
$Et_3NH^+HF_2^-$ [c]	14.9	−94	139	

[a] from Me_4Si; [b] from CF_4; [c] ref. 28

Triethylammonium difluoride solutions in CH_2Cl_2 at −80 °C and at room temperature showed only slight variations in shielding and coupling constant that are probably solvent effects.[28] The authors deduced that the hydrogen was centred and that the cation did not exert a distorting effect. They also concluded that this was true of *p*-toluidinium difluoride also from n.m.r. studies on this compound in its solid state,[29] an observation that is at variance with the neutron-diffraction and i.r. observations.[21,22] A similar solid-state experiment on a single crystal of KHF_2 by Smith and Pratt[30a] showed the H to be centred and *r*(H–F) to be 113.8 pm within a linear ion, nicely in agreement with diffraction determinations. The same was true of the other alkali-metal difluorides.[30b]

[25] A. A. Lipovskii and S. A. Nikitina, *Zhur. neorg. Khim.*, 1965, **10**, 176.
[26] I.-T. Vang and F. I. Skripov, *Doklady Akad. Nauk S.S.S.R.*, 1961, **136**, 58; R. Haque and L. W. Reeves, *J. Amer. Chem. Soc.*, 1967, **89**, 250; J. Soriano, J. Shamir, A. Netzer, and Y. Marcus, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 209.
[27] (*a*) F. Y. Fujiwara and J. S. Martin, *Canada J. Chem.*, 1971, **49**, 3071; (*b*) *J. Amer. Chem. Soc.*, 1974, **96**, 7625, (*c*) *ibid.*, p. 7632.
[28] L. Gouin, J. Cousseau, and J. A. S. Smith, *J.C.S. Faraday II*, 1977, **73**, 1878.
[29] J. Cousseau, L. Gouin, E. K. C. Pang, and J. A. S. Smith, *J.C.S. Faraday II*, 1977, **73**, 1015.
[30] (*a*) J. C. Pratt and J. A. S. Smith, *J.C.S. Faraday II*, 1975, **71**, 596; (*b*) C. J. Ludman, T. C. Waddington, E. K. C. Pang, and J. A. S. Smith, *J.C.S. Faraday II*, 1977, **73**, 1003.

All the evidence points to the difluoride ion being the archetypal very short hydrogen bond with a single-minimum potential function: what then is its hydrogen-bond energy? There are many reasonable answers to this question—Table 5—but none is sufficiently reliable to be quoted in preference to the rest.

Table 5 *The hydrogen-bond energy of the difluoride ion*

Method	*Value*/kJ mol^{-1}	*Ref.*
Thermochemical K, Rb, $CsHF_2$	243	31
Thermochemical Me_4NHF_2	>155	32
Theoretical	167	*a*
Theoretical	217	*b*
Theoretical	234	*c*
Theoretical	213	*d*
Thermochemical (Li–Cs) HF_2	252	*e* (but see ref. 33)
Dipole interaction calculations	219	27(b)
Theoretical	222, 234	*f*
Thermochemical (Li–Cs)HF_2	176	33
Theoretical	214	138

[a] P. N. Noble and R. N. Kortzeborn, *J. Chem. Phys.*, 1970, **52,** 5375; [b] P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, 1970, **92,** 6101; [c] A. Neckel, P. Kuzmany, and G. Vinek, *Z. Naturforsch.*, 1971, **26a,** 569; [d] J. Almlöf, *Chem. Phys. Letters*, 1972, **17,** 49; [e] H. P. Dixon, H. D. B. Jenkins, and T. C. Waddington, *J. Chem. Phys.*, 1972, **57,** 4388; [f] A. Støgard, A. Strich, B. Roos, and J. Almlöf, *Chem Phys.*, 1975, **8,** 405.

Waddington was the first to tackle this thorny problem[31] and suggested the seemingly high value of *ca.* 240 kJ mol^{-1}, which was beyond the upper limit of a possible range of 113—230 kJ mol^{-1} that Ketelaar had suggested as likely many years before.[23b] A minimum value of 155 kJ mol^{-1} was deduced from the ΔH of reaction (1).[32] It was reasoned that lattice expansion from Me_4NF to Me_4-

$$Me_4NF(s) + HF(g) \rightarrow Me_4NHF_2(s) \qquad (1)$$

NHF_2 would be slight and the difference in lattice energies could be ignored, so that the ΔH of 155 kJ mol^{-1} did represent a likely value for the hydrogen-bond energy.

The debate over E(F–H–F) continues between those who favour thermochemical estimates, which rely on calculation of difluoride lattice energies, and those who favour *ab initio* theoretical calculations. The former have been recently helped by the publication of reliable $U(MHF_2)$ values:[33] 839 (M = Li); 788 (Na); 703 (K); 674 (Rb); 646 (Cs); 705 (NH_4) kJ mol^{-1}. As Table 5 shows, the theoretically derived values are generally higher than the thermochemical ones. The overall range is 155—252 kJ mol^{-1} and the mean is 212 kJ mol^{-1}. Under

[31] T. C. Waddington, *Trans. Faraday Soc.*, 1958, **54,** 25.
[32] S. A. Harrell and D. H. McDaniel, *J. Amer. Chem. Soc.*, 1964, **86,** 4497.
[33] H. B. D. Jenkins and K. F. Pratt, *J.C.S. Faraday II*, 1977, **73,** 812.

normal circumstances a bond this strong would correspond to a single covalent bond.

In addition to forming one hydrogen bond, a fluoride ion can act as a hydrogen-acceptor for two ($H_2F_3^-$), three ($H_3F_4^-$), and even four ($H_4F_5^-$) hydrogen fluorides. Some of these species are remarkably stable and promise further insights into strong hydrogen bonding.[34]

(ii) *Dichlorides.* Less work has been done on these, but they are of considerable interest to our investigation because of the comparisons to be made with the difluoride.

Dichlorides have been known for 70 years[35] and with a large counter-cation they are stable. Although $CsHCl_2$ can be made from CsCl and HCl at $-78\,°C$[36] attempts to prepare it from aqueous solution produce crystals of $CsCl,\frac{1}{3}(H_3O^+ HCl_2^-)$, which nevertheless contain this ion. A structural investigation suggested the ion was linear and symmetric, $R(Cl\cdot\cdot Cl) = 314$ pm, but the proton was not located.[37] A slightly longer $R(Cl\cdot\cdot Cl)$ of 322 pm was measured[38] in Me_4NHCl_2 and the hydrogen shown to be non-centred[39] by neutron diffraction: $[Cl\overset{136.8\text{ pm}}{\text{———}}H\overset{185.0\text{ pm}}{\text{———}}Cl]^-$. However, this particular hydrogen bond no longer qualifies as short, being only 28 pm less than twice the van der Waals radius of Cl (175 pm). In fact i.r. studies[40] revealed two types of dichloride and Me_4NHCl_2 belonged to the kind which gave three bands at *ca.* 200 (ν_1), *ca.* 1200 ($2\nu_2$), and 1520—1670 (ν_3) cm^{-1}; whereas another group of dichlorides, which included $CsCl,\frac{1}{3}(H_3O^+ HCl_2^-)$ and Et_4NHCl_2, gave only two bands at *ca.* 600 and *ca.* 1300 cm^{-1}.

The activity of ν_1 in the far-i.r. spectrum of Me_4NHCl_2 showed that its structure could not be $D_{\infty h}$. That it was $C_{\infty v}$, *i.e.* linear but not symmetric, was indicated by studies[41] on $CsHCl_2$ at 20 K which showed ν_2 at 631 cm^{-1}, and that the broad band at *ca.* 1200 cm^{-1} in these spectra was a strong first overtone, this being expected from $C_{\infty v}$.

Nuclear quadrupole resonance spectroscopy confirmed the existence of two configurations for HCl_2^-. ^{35}Cl frequencies were found at either 12 MHz [Et_4NHCl_2, Et_4NDCl_2, and $CsCl,\frac{1}{3}(H_3O^+HCl_2^-)$] indicative of a H-centred ion, or at 20 MHz (Me_4NHCl_2 and $CsHCl_2$) when the ion was non-H-centred. Deuteriation of the latter type caused a shift down of 0.8 MHz, but left the former type unchanged.[42] The n.q.r. spectrum of $Et_3NH^+HCl_2^-$ gave a signal at

[34] I. Gennick, K. M. Harmon, and M. M. Potvin, *Inorg. Chem.*, 1977, **16**, 2033, and refs. therein.
[35] The early refs. are given in R. West, *J. Amer. Chem. Soc.*, 1957, **79**, 4568.
[36] R. E. Valleé and D. H. McDaniel, *J. Amer. Chem. Soc.*, 1962, **84**, 3412.
[37] L. W. Schroeder and J. A. Ibers, *J. Amer. Chem. Soc.*, 1966, **88**, 2601.
[38] J. S. Swanson and J. M. Williams, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 271.
[39] J. M. Williams and S. W. Peterson, *Amer. Cryst. Assocn. Progr. Abs.*, Ottawa, Canada, 1970.
[40] J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, 1966, **70**, 11; 1969, **73**, 448.
[41] J. W. Nibler and G. C. Pimentel, *J. Chem. Phys.*, 1967, **47**, 710.
[42] C. J. Lundman, T. C. Waddington, J. A. Salthouse, R. J. Lynch, and J. A. S. Smith, *Chem. Comm.*, 1970, 405.

22.805 MHz at 195 K which split on cooling to 77 K.[43] This was explained as being due to extra-hydrogen bonding to the cation, $Et_3N^+–H\cdot\cdot[Cl–H–Cl]^-$.

Inelastic neutron scattering from $CsHCl_2$ and $CsDCl_2$ showed that the dichloride ions were non-linear.[44] The Raman and i.r. spectra confirmed $\nu_1 = 199$, $\nu_2 = 602, 660$, and $\nu_3 = 1670$ cm^{-1}. The reported isotope frequency shift of 1.40[41,44] is supportive of a single-minimum potential well, even for this non-centred hydrogen bond. It would seem that the potential well is sensitive to lattice forces, *i.e.* to the type of counter-cation; hence the differences observed in the i.r. and n.q.r. spectra.

Hydrogen-bond energies for HCl_2^- have been put forward. Some, based on thermochemical methods, gave values of 35 ($CsHCl_2$),[32] 49 (Me_4NHCl_2),[32] and 56 kJ mol^{-1} (Et_4NHCl_2).[45] From solution studies of HCl_2^- in sulpholane a value of E(ClHCl) > 59 kJ mol^{-1} was calculated.[46] Theoretical calculations[47] suggested a much higher bond energy of 121 kJ mol^{-1}, a figure supported by dipole interaction calculations[27b] that gave 104 kJ mol^{-1}.

Other experimental data on HCl_2^- are sparse but its dissociation constant, K, is reported[48] as 2×10^4 and the proton chemical shift, $\delta(^1H)$, as -13.92 p.p.m. for Bu_4NHCl_2 in MeCN.[27b] In the salts $RC{\equiv}CNHR_2'HCl_2$ the proton signal was a broad singlet at 8.5—9 p.p.m.[49].

(iii) *Dibromides.* The physical properties are collected in Table 6. The conclusion

Table 6 *Physical properties of the dibromide ion*

	Reference
R[Br··Br], CsBr, $\frac{1}{3}(H_3O^+HBr_2^-)$ = 335 pm	*a*
$\delta(^1H)$ = 10.15 p.p.m.	27b
K = 200	,,
E(BrHBr) = 54 kJ mol^{-1} (thermochemical)	45
E(BrHBr) = 93 kJ mol^{-1} (dipole calculations)	27b
Et_4NHBr_2 ν_1 i.a.; ν_2 633; ν_3 1350 (centred bond)	*b*
Me_4NHBr_2 ν_1 126; ν_2 1038; ν_3 1450 (non-centred bond)	*b*, 40
Bu_4NDBr_2; ν_2 870; ν_3 1297 ν_H/ν_D < 1.35	41, 50

[a] L. W. Schroeder and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 594; [b] J. C. Evans and G. Y.-S. Lo, *J Phys. Chem.*, 1967, **71**, 3942; 1969, **73**, 448.

[43] J. Cousseau, L. Gouin, L. V. Jones, G. Jugie, and J. A. S. Smith, *J.C.S. Faraday II*, 1973, **69**, 1821.
[44] G. C. Stirling, C. J. Lundman, and T. C. Waddington, *J. Chem. Phys.*, 1970, **52**, 2730.
[45] D. H. McDaniel and R. E. Vallee, *Inorg. Chem.*, 1963, **2**, 996.
[46] R. L. Benoit, M. Rinfret, and R. Domain, *Inorg. Chem.*, 1972, **11**, 2603.
[47] C. Thomson, D. T. Clark, T. C. Waddington, and H. B. Jenkins, *J.C.S. Faraday II*, 1975, **71**, 1942.
[48] Z. Pawlak, T. Jasiński, and C. Dobrogowska, *Roczniki Chem.*, 1974, **48**, 1609.
[49] J. Cousseau and L. Gouin, *Compt. rend.*, 1973, **277**, *C*, 351.

would again appear to show a strong hydrogen bond. Readers interested in di-iodides should consult refs. 27b, 41, 45, 50, and 51.

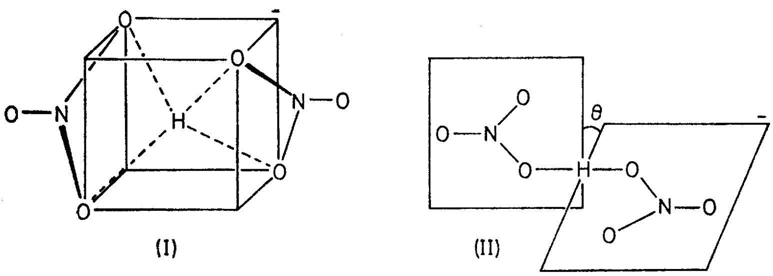
B The O–H–O Bonds.—The simplest bond of this type imaginable is $[H(O)_2]^{3-}$ and this is present in $CrHO_2$ and $CrDO_2$, which have been studied by *X*-ray[52] and neutron diffraction,[53] and n.m.r.,[54] i.r.,[55,56] and inelastic neutron scattering[56] spectroscopy. The value of $R(O\cdot\cdot O)$ was 249 pm for HO_2^{3-} and the proton was centred, but 255 pm for DO_2^{3-} which was non-centred. A similar difference was observed between $CoHO_2$ and $CoDO_2$.[57] These differences have been taken to mean a change from a double-minimum–low-barrier for HO_2^{3-} to a high barrier for DO_2^{3-}.

A natural example of a strong O–H–O bond is found in the mineral trona, $Na_3H(CO_3)_2,2H_2O$, in which two carbonate ions are joined by a short (250 pm) hydrogen bond.[58] Knowing that $H(CO_3)_2^{3-}$ exists prompts one to ask if other bisoxo-anions exist, and indeed several, such as $H(NO_3)_2^-$, $H(SO_4)_2^{3-}$, and $H(RCO_2)_2^-$, are known and have strong hydrogen bonds. There may even be mixed anions, although in these cases unless the strengths of the parent acids are similar an asymmetric hydrogen bond will result which may approximate to a weak bond with the proton nearer the weaker-acid oxygen.

Thermodynamic evidence, in the form of association constants, $K(AHA^-)$, and i.r. data, has been collected by Pawlak which indicates that strong complexes may be formed between acetates, chloroacetates, nitrates, chlorides, iodides, benzoates, and pentachlorophenolate.[59] From what is now known of the more thoroughly investigated systems discussed below, there is every reason to expect very strong hydrogen bonding between these anions. However, for the purpose of this review we will confine ourselves to the better known combinations —dinitrate and dicarboxylates, and then deal with the other strong O–H–O bonds found in oximato-complexes and the diaquohydrogen cation $H_5O_2^+$.

(i) *The Dinitrate Ion*, $H(NO_3)_2^-$. This ion was first reported[60] in *trans*-$[Rhpy_4Cl_2]$-$H(NO_3)_2$. It was thought originally to have the H at the centre of a distorted tetrahedral configuration of four oxygen atoms,[61] a structure, Figure 4 (I), that

[50] J. A. Salthouse and T. C. Waddington, *J. Chem Soc. (A)*, 1966, 28.
[51] K. M. Harmon and P. A. Gebauer, *Inorg. Chem.*, 1963, **2**, 1319.
[52] K. M. Douglas, *Acta Cryst.*, 1957, **10**, 423.
[53] W. C. Hamilton and J. A. Ibers, *Acta Cryst.*, 1963, **16**, 1209.
[54] J. A. Ibers, C. H. Holm, and C. R. Adams, *Phys. Rev.*, 1961, **121**, 1620.
[55] R. G. Snyder and J. A. Ibers, *J. Chem. Phys.*, 1962, **36**, 1356; A. Benoit, *Spectrochim. Acta*, 1963, **19**, 2011.
[56] J. J. Rus and J. R. Ferran, *J. Chem. Phys.*, 1966, **44**, 2496.
[57] Yu. D. Kondrashev and N. N. Federova, *Doklady Akad. Nauk S.S.S.R.*, 1954, **94**, 229; R. G. Delaplane, J. A. Ibers, J. R. Ferraro, and J. J. Bush, *J. Chem. Phys.*, 1969, **50**, 1920.
[58] C. J. Brown, H. S. Peiser, and A. Turner-Jones, *Acta Cryst.*, 1949, **2**, 167; G. E. Bacon and N. A. Curry, *Acta Cryst.*, 1956, **9**, 82.
[59] Z. Pawlak, *Roczniki Chem.*, 1972, **46**, 75, 249, and 2069; with L. Sobczyk, *Adv. in Mol. Relax Processes*, 1973, **5**, 99; with Z. Szponar and C. Dobrogowska, *Roczniki Chem.*, 1974, **48**, 501.
[60] R. D. Gillard and R. Ugo, *J. Chem Soc. (A)*, 1966, 549.
[61] B. D. Faithful and S. C. Wallwork, *Chem. Comm.*, 1967, 1121.



(I) (II)

Figure 4 *Dinitrate configurations*

has some theoretical justification,[62] and for which the i.r. spectrum showed strong hydrogen bonding,[60] $\nu_s(OH)$ = 440 cm^{-1}. Recently a neutron diffraction study[63] of this complex salt showed two very similar configurations for the $H(NO_3)_2^-$ ion and both are linear as in Figure 4 (II). The bond length R(O··O) is 246.1 pm, the H is centred, the angle OHO is 168 °, and the dihedral angle θ is 96 °.

Initially, $CsH(NO_3)_2$, too, was believed to display a structure of type (I) although neither X-ray[64a] nor neutron[64b] diffraction could locate the proton. A later investigation[65] revealed it, however, and showed the correct arrangement to be non-coplanar nitrates linked by a single short and centred hydrogen bond [Fig. 4 (II): R(O··O), 246.8 pm; OHO, 172.6 °; θ, 75.4 °]. A similar structure was observed for $Ph_4AsH(NO_3)_2$ but with coplanar nitrates,[61] and for NH_4NO_3-$(HNO_3)_2$ with a dihedral angle, θ, of 83 °.[66]

It has proved possible, by i.r. and Raman studies, to distinguish between planar and non-planar arrangements for $H(NO_3)_2^-$ in a variety of salts.[67] The i.r. spectra show both conformations to be strongly hydrogen-bonded, having no OH absorptions above 1800 cm^{-1} but a strong bond absorption centred at *ca.* 600 cm^{-1}.

$H(NO_3)_2^-$ in acetonitrile solution has a chemical shift in the downfield region of 15—17 p.p.m.[67] as expected for an H-centred strong hydrogen bond.

(ii) *The Dicarboxylates*, $H(RCO_2)_2^-$. In 1972 Speakman wrote a comprehensive review (50 pp.) of very short hydrogen bonds of dicarboxylates,[6] and a useful tabulation of their R(O··O) values and ν_s(OHO) bands is to be found in Hadži and Orels' paper.[68] A selection of representative salts is listed in Table 7 especially where a neutron picture is available to fix the position of the proton. Most bonds

[62] R. Grunde, T. Solmajer, A. Azman, and D. Hadzi, *J. Mol. Struct.*, 1975, **24**, 405.
[63] J. Roziere, M. S. Lehmann, and J. Potier, *Acta Cryst.*, 1979, **35B**, 1099.
[64] (*a*) J. M. Williams, N. Dowling, R. Gunde, D. Hadži, and B. Orel, *J. Amer. Chem. Soc.*, 1976, **98**, 1581; (*b*) J. Roziere and C. V. Berney, *ibid.*, p. 1582.
[65] J. Roziere, M.-T. Roziere-Bories, and J. M. Williams, *Inorg. Chem.*, 1976, **15**, 2490.
[66] F. W. B. Einstein and D. G. Tuck, *Acta Cryst.*, 1969, **26B**, 1117.
[67] S. Detoni, L. Diop, R. Gunde, D. Hadži, B. Orel, A. Potier, and J. Potier, *Spectrochim. Acta*, 1977, **35A**, 443.
[68] D. Hadži and B. Orel, *J. Mol. Struct.*, 1973, **18**, 227.

Table 7 *Hydrogen-bond parameters for dicarboxylates*

Salt	*Diffraction method*	$R(\mathrm{O}\cdots\mathrm{O})$ /pm	*Details of hydrogen bond*	*Ref.*
Monocarboxylic acids				
$KH(HCO_2)_2$	*X*-ray	244.7	$\overset{179.5}{\mathrm{O}\underset{128}{-}\mathrm{H}\underset{116}{-}\mathrm{O}}$	*a*
$NaH(MeCO_2)_2$	,,	244.4	symmetric	*b*
$KH(MeCO_2)_2$	,,	247.6	asymmetric*	*c*
$KH(CF_3CO_2)_2$	,,	243.5	,,	72
,,	neutron	243.7	H-centred	72
$KH(PhCH_2CO_2)_2$	*X*-ray	244.3	H-centred	*d*
$KH(MeCO_2C_6H_4CO_2)_2$†	,,	245.5	symmetric	*e*
,,	neutron	244.8	H-centred	*f*
$KH(MeCH{=}CHCO_2)_2$	neutron	248.8	$\mathrm{O}\overset{114.1}{-}\mathrm{H}\overset{134.8}{-}\mathrm{O}$	*g*
Dicarboxylic acids				
$N_2H_5^+HC_2O_4^-$	*X*-ray	245.0	symmetric	69
,,	neutron	244.8	H-centred	70
$NaHC_2O_4,H_2O$	,,	257.1	$\underset{176°}{\mathrm{O}\overset{103.6}{-}\mathrm{H}\overset{153.7}{-}\mathrm{O}}$	71
$KH[CH_2(CO_2)_2]$‡	*X*-ray	245.9	intermolecular hydrogen-bonded polymer anion	*h*
,,	neutron	246.8	intermolecular hydrogen-bonded polymer anion	*i*
$KH[O(CH_2CO_2)_2]$§	neutron	247.6	$\underset{174.2°}{\mathrm{O}\overset{115.2}{-}\mathrm{H}\overset{132.8}{-}\mathrm{O}}$	*j*
$RbH[O(CH_2CO_2)_2]$	,,	244.9	$\underset{175°}{\mathrm{O}\overset{122.6}{-}\mathrm{H}\overset{122.6}{-}\mathrm{O}}$	*j*
$C_3H_5N_2^+[C_2H_2(CO_2)_2]^-$	*X*-ray	240.8	$\underset{178°}{\mathrm{O}\overset{106.3}{-}\mathrm{H}\overset{135.0}{-}\mathrm{O}}$	74
$CuH[C_2H_2(CO_2)_2]$	,,	240.9	H at mid point, but off-centre	73

* non-equivalent carboxylate groups, H not located; † aspirinate; ‡ malonate; § oxydiacetate.
[a] G. Larsson and I. Nahringbauer, *Acta Cryst.*, 1968, **24B**, 666; R. Tellgren, *Acta Cryst.*, 1978, **34A**, S296; [b] J. C. Speakman and H. H. Mills, *J. Chem. Soc.*, 1961, 1164; [c] M. Currie, *J.C.S. Perkin II*, 1972, 832; [d] Lj. Manojlović and J. C. Speakman, *Acta Cryst.*, 1968, **24B**, 323; [e] Lj. Manojlović and J. C. Speakman, *J. Chem. Soc.* (*A*), 1967, 971; [f] A. Sequeira, C. A. Berkebile, and W. C. Hamilton, *J. Mol. Struct.*, 1967–8, **1**, 283; [g] D. R. McGregor, J. C. Speakman, and M. S. Lehman, *J.C.S. Perkin II*, 1977, 1740; [h] J. G. Sime, J. C. Speakman, and R. Pathasarathy, *J. Chem. Soc* (*A*), 1970, 1919; [i] M. Currie and J. C. Speakman, *J. Chem. Soc* (*A*), 1970, 1923; [j] J. Albertson and I. Grenthe, *Acta Cryst.*, 1973, **29B**, 2751.

are *ca.* 244 pm but some are less than 240 pm. The cation can have a profound effect; thus potassium oxalate is a B-type salt (asymmetric) with $R(O\cdot\cdot O)$ 252.5 pm[69] whereas the hydrazinium salt is an A-type with a bond length of 245 pm.[70] The salt $NaHC_2O_4,H_2O$ has a non-centred bond which becomes lengthened on deuteriation from 257.1 pm to 259.3 pm.[71] The other weak hydrogen bonds in this crystal remain unaffected by deuteriation, which suggests that a profound change in the potential well is attributable to the heavier isotope. In $KD(CF_3CO_2)_2$ the bond changes neither its length nor its shape from that of $KH(CF_3CO_2)_2$.[72]

Lattice forces can play an unknown role in determining the orientation of the bulky dicarboxylate anions and various conformations are found, with the planes of the carboxylate groups lying at different dihedral angles with respect to one another, as well as variations in the arrangements of the carbonyl bonds and the R groups with respect of one another and the hydrogen bond. To minimize lattice effects it has been necessary to study intramolecular dicarboxylates and indeed these do display very short bonds. A much investigated system is the hydrogen maleate ion, $H[C_2H_2(CO_2)_2]^-$, but this too is not free of lattice forces. The copper(II) salt has a centred bond but with the proton lying above the plane of the molecule;[73] the imidazolium salt, $C_3H_5N_2^+$, has a non-centred bond,[74] as has the calcium salt.[75]

The shortest dicarboxylate bonds are found in potassium hydrogen chloromaleate[76] and pyridine-2,3-dicarboxylic acid,[77] shown in Figure 5. It is signifi-

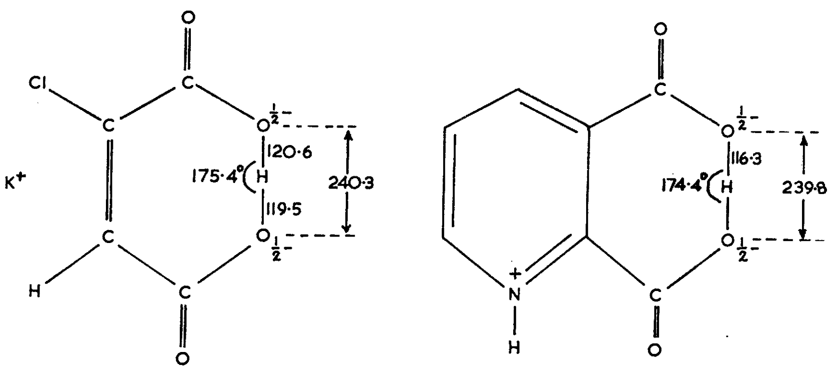


Figure 5 *Intramolecular dicarboxylates: potassium hydrogen chloromaleate and pyridine-2,3-dicarboxylic acid.*

[69] B. F. Pedersen, *Acta Chem. Scand.*, 1968, **22**, 2953.
[70] N. A. K. Ahmed, R. Liminga, and I. Olovsson, *Acta Chem. Scand.*, 1968, **22**, 88; A. Nilsson, R. Liminga, and I. Olovsson, *ibid.*, p. 719; J. Lindgren, J. De Villepin, and A. Novak, *Chem. Phys. Letters*, 1969, **3**, 84.
[71] R. Tellgren, J. O. Thomas, and I. Olovsson, *Acta Cryst.*, 1977, **33B**, 3500; R. Tellgren and I. Olovsson, *J. Chem. Phys.*, 1971, **54**, 127.
[72] A. L. MacDonald, J. C. Speakman, and D. Hadži, *J.C.S. Perkin II*, 1972, 825.
[73] C. K. Prout, J. R. Carruthers, and F. J. C. Rossotti, *J. Chem. Soc.* (*A*), 1971, 3342.
[74] M. N. G. James and M. Matsushima, *Acta Cryst.*, 1976, **32B**, 1708.
[75] H. Hsu and E. O. Schlemper, *Acta Cryst.*, 1978, **34B**, 930.
[76] R. D. Ellison and H. A. Levy, *Acta Cryst.*, 1965, **19**, 260.
[77] A. Krick, T. F. Koetzle, R. Thomas, and F. Takusagawa, *J. Chem. Phys.*, 1974, **60**, 3866.

cant that this latter compound, which is a neutral molecule, albeit a zwitterion, has the shortest O–H–O bond of any. Its non-centred proton is attributed to the molecule's dipole moment. Hydrogen bonds this short are 60 pm less than the sum of the two oxygen atoms' van der Waals radii (300 pm). Whether they are the single-minimum type can be gleaned from their i.r. and n.m.r. spectra.

The i.r. spectra of dicarboxylates have been discussed in several papers,[67,78] one of which[67] sought to relate the spectrum to the crystal structure classification proposed by Speakman.[6] A relationship between the two was established: type-A salts gave broad bands in the 1200—500 cm^{-1} region which shifted on deuteriation by a factor of 1.2—1.45. Pseudo-A-type salts, with short but asymmetrical bonds, gave similar bands which did not shift on deuteriation, *i.e.* $\nu_H/\nu_D = 1$.

Novak's work[78b] on the i.r. and Raman spectra of $NaH(CH_3CO_2)_2$, $NaD(CH_3CO_2)_2$, $NaH(CD_3CCO_2)_2$, and $NaD(CD_3CO_2)_2$ definitely established ν_s(OHO) at 320 cm^{-1}, ν_{as}(OHO) at 720 cm^{-1} with $\nu_{as}(OHO)/\nu_{as}(ODO) = 1.41$, δ(OHO) at 1540 cm^{-1} and γ(OHO) at 1285 cm^{-1}. The ν_{as}(OHO) band stretches from 400—1200 cm^{-1} with a 'window' at 914 cm^{-1} caused by ν(C—C) as shown by an intense Raman band at 932 cm^{-1}. The isotope evidence supports a single-minimum very strong hydrogen bond. Not all dicarboxylates have this potential function, as Table 8 shows. Even $KH(CH_3CO_2)_2$ appears[79] not to have it, but it may be that the isotope shift cannot distinguish a double- from a single-minimum

Table 8 *Asymmetric stretching mode and its isotopic frequency shift for dicarboxylates*

Salt	ν_{as}(OHO) /cm^{-1}	ν(OHO) /ν(ODO)	*Potential function*	*Ref.*
$KH(CH_3CO_2)_2$	1050	1.0	double minima	79
$NH_4H(ClCH_2CO_2)_2$	950	1.1	d.m.	79
$KH(Cl_2CHCO_2)_2$	1200	1.1	d.m.	79
$RbH(CCl_3CO_2)_2$	800	1.4	s.m.	78b
$KH(CF_3CO_2)_2$	800	1.4	single minimum	78d
$KH(PhCH_2CO_2)_2$	720	1.4	s.m.	79
$KH(PhCO_2)_2$	1150	1.2	d.m.	79
$KH(p\text{-}Cl.C_6H_4CO_2)_2$	1170	1.2	d.m.	79
$KH(CH_2CO_2)_2$*	950	1.4	s.m.	*a*

* succinate
[a] L. Angeloni, M. P. Marzocchi, D. Hadži, B. Orel, and G. Sbrana, *Chem. Phys. Letters*, 1974, **28**, 201

[78] (*a*) D. Hadži, M. Obradović, B. Orel, and T. Solmajer, *J. Mol. Struct.*, 1972, **14**, 439; (*b*) A. Novak, *J. Chim. phys.*, 1972, **69**, 1615; (*c*) P. J. Miller, R. A. Butler, and E. R. Lippincott, *J. Chem. Phys.*, 1972, **57**, 5451; (*d*) D. Hadži, B. Orel, and A. Novak, *Spectrochim. Acta*, 1973, **29A**, 1745.

[79] D. Hadži and B. Orel, *J. Mol. Struct.*, 1973, **18**, 227; R. Blinc, H. Dadži, and A. Novak, *Z. Elektrochem.*, 1960, **64**, 567; Lj. Manojlović and J. C. Speakman, *Acta Cryst.*, 1968, **24B**, 323.

situation for values of *ca.* 1.1. The chloroacetates vary with the extent of chlorine substitution (Table 8). ^{35}Cl n.q.r. spectroscopy shows both $KH(ClCH_2CO_2)_2$ and $KH(Cl_2CHCO_2)_2$ to have asymmetric hydrogen bonds but $KH(Cl_3CCO_2)_2$ to be symmetric.[80]

The difficulties with these systems are in deciding the exact centre of their very broad i.r. bands. In some dicarboxylates, such as the intramolecular ones like potassium hydrogen maleate, there has yet to be a positive identification of ν_{as}(OHO).[81] Whatever the difficulties in assigning this mode, the problem of locating ν_s(OHO) is not easy even though its i.r. inactivity/Raman activity should be a useful guide. Table 9 lists the few dicarboxylates for which most bands have been located.

Table 9 *Vibrational modes of some dicarboxylates*

Salt	ν_s(OHO) /cm^{-1}	ν_{as}(OHO) /cm^{-1}	δ(OHO) /cm^{-1}	γ(OHO) /cm^{-1}	*Ref.*
KH (maleate)	295	?*	1625, 1701	1025	80a, b
$NaH(CH_3CO_2)_2$	320	720	1540	1285	78b
$KH(CF_3CO_2)_2$	130	800	1480	*ca.*/1250	78d
$KH(CCl_3CO_2)_2$	133	850	1465	1215	78a

* Although this has been calculated as high as 2008 cm^{-1} (ref. 80b) it has yet to be identified. A band in the i.r. spectrum at 695 cm^{-1} could possibly be ν_{as} (OHO)

The ^1H n.m.r. spectra of $MH(CF_3CO_2)_2$ salts in CF_3CO_2H solution showed the chemical shift to depend on concentration and cation,[82] being lowest for Li^+ at 15.73 p.p.m. and furthest downfield for Me_4N^+ at 19.59 p.p.m. The heavier alkali metals have values of *ca.* 19 p.p.m. For $MH(CH_3CO_2)_2$ $\delta(^1H)$ again depended somewhat on M, but was *ca.* 16 p.p.m.,[83a] but the mixed system $H(CH_3CO_2,CF_3CO_2)$ was at 11.1 p.p.m., showing that the proton was nearer one of the oxygen atoms, presumably the acetate, in a double potential well.

Some protons are extremely deshielded such as those in potassium hydrogen phthalate, already mentioned with its negative isotope n.m.r. chemical shift $\Delta\delta$(H,D) indicating a single-minimum bond.[14] The same is true of potassium hydrogen maleate at $\delta(^1H)$ 20.32 p.p.m., and $\Delta\delta$(H,D) of -0.03 p.p.m. But a low δ value does not guarantee a single minimum, *e.g.* the hydrogen furan-3,4-dicarboxylate ion has $\delta(^1H)$ 20.3 p.p.m. but $\Delta\delta$(H,D) $+0.11$ p.p.m., meaning it is a double-minimum hydrogen bond.

The hydrogen-bond energy of O–H··O bond has been related to i.r. shifts, $\Delta\nu$(OH), and a thorough account of such correlations is covered by Joesten and

80 R. J. Lynch, T. C. Waddington, T. A. O'Shea, and J. A. S. Smith, *J.C.S. Faraday II*, 1976, **72**, 1980.
81 (*a*) K. Nakamoto, Y. A. Sarma, and G. T. Behnke, *J. Chem. Phys.*, 1965, **42**, 1662; (*b*) J. Maillob, L. Bardet, and R. Marignan, *J. Chim phys. Physiochim*, 1969, **66**, 522.
82 R. G. Jones and J. R. Dyer, *J. Amer. Chem. Soc.*, 1973, **95**, 2465.
83 (*a*) J. H. Clark and J. Emsley, *J.C.S. Dalton*, 1973, 2154; 1974, 1125; (*b*) J. Emsley, O. P. A. Hoyte, and R. E. Overill, *J. Amer. Chem. Soc.*, 1978, **100**, 3303.

Schaad.[84] The location of ν(OH) of acetic acid for monomer, hydrogen-bonded polymer, and sodium diacetate is 3583, 2875, and 720 cm^{-1}, respectively, giving shifts of 708 cm^{-1} and 2863 cm^{-1}. If the former corresponds to a bond energy of *ca.* 30 kJ mol^{-1} then the latter should mean, on a *pro rata* basis, a strong hydrogen-bond energy of *ca.* 120 kJ mol^{-1}.

Theoretical calculations[83b] have been possible for $H(HCO_2)_2^-$ and give R(O··O) 234 pm and E(OHO) 123 kJ mol^{-1}. This latter value is in excellent agreement with that from ion cyclotron resonance studies[85] of gas-phase anions, $H(RCO_2)_2^-$, which gave values of 125 kJ mol^{-1} for diacetate and dipproprionate.

Mixed bicarboxylate systems have been studied by Pawlack and co-workers[59,86] who have measured the stability constants $K(AHA')^-$ in dipolar aprotic solvents where A and A^- are a variety of substituted acetates. Values of $K(AHA')^-$ in the range 10^3—10^5 indicate strong associations in many cases, *e.g.* for the acetate–trifluoroacetate mixture in acetonitrile[87] $K(AHA')^- = 10^6$.

(iii) *Oximato-complexes.* Oximes and dioximes are used in gravimetric analysis and solvent extraction because they form stable inner-complex salts that are often insoluble in water. On formation of a complex, the oxime may lose a proton and dioxime complexes are often stabilized by the formation of a strong hydrogen bond.[88,89]

The tetradentate ligand 2,2′-(1,3-diaminoethane)bis(2-methylbutan-3-one) dioxime, HON:CMe·CMe_2·$NH(CH)_2NH$·CMe_2·CMe:NOH, EnOA for short, can wrap itself around metal ions such as Ni^{II}, Co^{II}, Cu^{II}, and Pt^{II} in a planar configuration. The propane derivative (PnAO) behaves similarly. Complexes are also formed by the bidentate ligands dimethylglyoxime, HON:CMe_2CMe:-NOH, DMG, and 2-amino-2-methyl-3-butanone oxime, NH_2·CMe_2·CMe:-NOH, AO. As ligands these oximes almost invariably lose a proton on complexing and the resultant oximato-group, $=N–O^-$, then acts as a hydrogen acceptor towards another oxime group to produce the short =N–O–H–O–N = hydrogen bond system, *e.g.* Figure 6. Table 10 lists the hydrogen-bond parameters for complexes with short bonds < 250 pm and where the proton was located. Some DMG complexes are known with bonds < 250 pm but many are > 260 pm.[90]

The short hydrogen bonds of Table 10 range from the perfectly centred bonds at the top of the list to the very asymmetric bonds at the bottom. In the complex $[Ni(EnAO–H)]NO_3,H_2O$ the proton of the hydrogen bond is nearer to one oxygen atom, r(OH) = 80 pm, than its normal covalent bond length, $r(OH, H_2O)$ = 96 pm. Truly a remarkable achievement.

Schlemper, responsible for most of the structures in Table 10, noted a relation-

[84] M. D. Joesten and L. J. Schaad, 'Hydrogen Bonding', Dekker, New York, 1974.
[85] R. L. Clair and T. B. McMahon, *Canad. J. Chem.*, 1979, **57**, 473.
[86] Z. Pawlak, *Roczniki Chem.*, 1973, **47**, 641.
[87] T. Jasinski, A. A. El-Harakany, F. G. Halaka, and H. Sadek, *Croat. Chem. Acta*, 1978, **51**, 1.
[88] G. R. Hedwig and H. K. Powell, *J.C.S. Dalton*, 1974, 47.
[89] G. I. H. Hanania and D. H. Irvine, *J.C.S. Dalton*, 1962, 2745.
[90] S. Bruckner and L. Randaccio, *J.C.S. Dalton*, 1974, 1017.

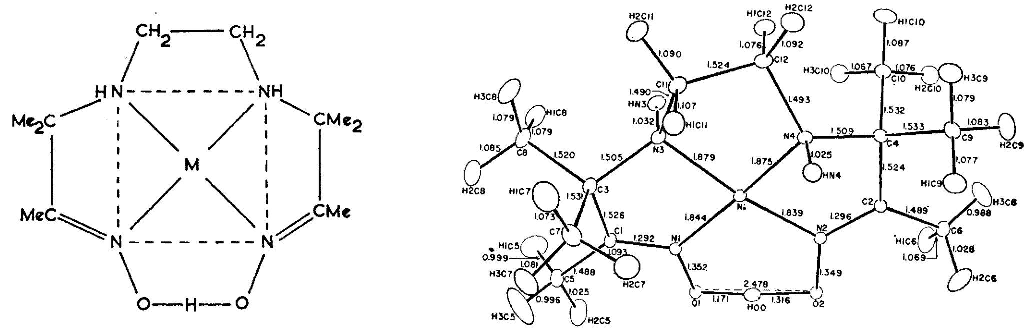


Figure 6 *Planar structure of dioxime complexes*
(Reproduced by kind permission from *Acta Cryst.*, 1978, **34B**, 438)

Table 10 *Dioxime complexes with short hydrogen bonds*

Complex	*Diffraction method*	R(O··O) /pm	r(O—H—O) /pm	/pm	OHO/°	*Ref.*
[Cu(PnAO–H)]ReO_4	X-ray	246	123	123	180	*a*
[Co(2AO–H)]Cl_2	,,	242.2	122	122	166.9	*b*
[Ni(2AO–H)]Cl.H_2O	neutron	242.0	118.7	124.2	169.9	*c*
[Co(PnAO–H)(NO_2)$_2$]^0	X-ray	243.2	119	126	168	*d*
[Ni(EnAO–H)]ClO_4	neutron	247.8	117.1	131.6	170.4	*e*
[Co(DMG)(CH_3)(H_2O)]	X-ray	248.6	111	138	—	*f*
[Pt(2AO–H)]Cl,3.5H_2O	neutron	247.2	108.7	138.9	173.8	*g*
[Co(PnAO–H)(CH_3)$_2$]	X-ray	246.1	99	153	—	*h*
[Ni(EnAO–H)]NO_3,H_2O	,,	247.4	80	168	169	*i*

[a] I. B. Liss and E. O. Schlemper, *Inorg. Chem.*, 1975, **14**, 3035; [b] E. O. Schlemper, S. J. LaPlaca, B. R. Davis, and W. C. Hamilton, *Acta Cryst.*, 1978, **34B**, 918; [c] E. O. Schlemper, S. J. LaPlaca, and W. C. Hamilton, *J. Chem. Phys.*, 1971, **54**, 3990; [d] R. K. Murman and E. O. Schlemper, *Inorg. Chem.*, 1973, **12**, 2625; [e] C. K. Fair and E. O. Schlemper, *Acta Cryst.*, 1978, **34B**, 436; [f] D. L. McFadden and A. T. McPhail, *J.C.S. Dalton*, 1974, 363; [g] E. O. Schlemper and C. K. Fair, *Acta Cryst.*, 1977, **33B**, 2482; [h] M. Caligaris, *J.C.S. Dalton*, 1974, 1628; [i] J. C. Ching and E. O. Schlemper, *Inorg. Chem.*, 1975, **14**, 2470.

ship between overall R(O··O) and the asymmetry of the bond Δ(O–H)—ref. *e* in Table 10. He extended this relationship to other very short O–H–O bonds. The effect of crystal packing around the oxime oxygens is the crucial factor in determining the locus of the proton. The shape of the O and H ellipsoids suggested that independent vibration of the proton along the bond axis is greater than that perpendicular to it, which suggests a rather broad single-minimum potential well in several of these bonds.

A study[91] of the thermodynamics of oximato-complexes of Cu^{II} showed that intramolecular hydrogen-bond formation gives rise to a positive entropy change, and this favourable change results if adjacent oxime and oximato-groups in the same complex come together to form a hydrogen bond. Such is the advantage of this that it may be done at the expense of overall ligand planarity. Intramolecular hydrogen bonding was assessed as adding $10^{3.5}$ to the stability of these oxime complexes.

I.r. evidence is lacking as yet, although the spectrum[92] of [Cu(EnAO–H)]$_2$$Br_2$ showed bands at 2300—2600 cm^{-1} (stretching) and 1730 and 1565 cm^{-1} (bending) which shifted on deuteriation by a ν_H/ν_D factor of 1.29. However, in this particular complex the hydrogen bonds are between oximato-groups attached to different Cu atoms, so that the complex is dimeric, and R(O··O) = 254.1 pm, longer than the values of Table 10, so that an isotopic ratio of this order would fit with a bond of this length if it were of a double-minimum kind.

[91] E. A. Daniel, F. C. March., H. K. J. Powell, W. T. Robinson, and J. M. Russell, *Austral. J. Chem.*, 1978, **31**, 723.
[92] J. W. Fraser, G. R. Hedwig, H. K. J. Powell, and W. T. Robinson, *Austral. J. Chem.*, 1972, **25**, 747.

N.m.r. evidence[93] from $[Ni(PnAO{-}H]^{2+}$ showed the hydrogen-bonding proton at 18.3 p.p.m. and at 19.1 p.p.m. in the oxidized product $[Ni(PnAO{-}6H)]^0$, and shifts of this magnitude would suggest a single minimum potential.

(iv) *The Diaquohydrogen Ion*, $H_5O_2^+$. This is now a well documented chemical entity* and being isoelectronic with HF_2^- might well be expected to have a strong hydrogen bond. Structurally it can vary quite a bit, principally as a result of rotation about the O–H–O axis. The actual bond length is found to fall in the range 241—244 pm.

A comprehensive review of $H_5O_2^+$ has been written.[94]

The diaquohydrogen ion consists of two water molecules linked through a strong hydrogen bond (Figure 7). There is a pyramidal configuration at each

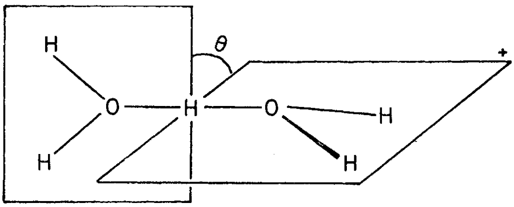


Figure 7 *The diaquohydrogen cation* $H_5O_2^+$

oxygen, although in some cases, such as in $HCl,2H_2O$ crystals, one of the oxygen's bonding arrangements is almost planar. The dihedral angle, θ, can vary from 0° to 180° which is called *trans*. Over 20 crystals have revealed themselves to harbour $H_5O_2^+$. A representative selection of conformations in which the proton has been located are listed in Table 11; in some cases the proton is centred.

The spectroscopic details of $H_5O_2^+$ are reviewed in depth by Williams.[96] The normal modes of the *trans*-conformer (15 in all) are given by Pavia and Giguère[97] but only the OHO vibrations are of interest here and these fall in the regions: 500—600 cm^{-1} [ν_s(OHO)], 1700—3500 cm^{-1} [ν_{as}(OHO)], and 800—1700 cm^{-1} [δ(OHO)]. The i.r. spectrum in, *e.g.*, $HBr,2H_2O$ and $HCl,2H_2O$ is complicated by broad bands due to weak hydrogen bonds of the terminal OH groups of $H_5O_2^+$; nevertheless the strong-hydrogen-bond bands in the latter hydrate were identified[98] at 484, 1000—1200, and 1082 cm^{-1}.

* Indeed, more was known about this species in crystals than about the much publicized H_3O^+ whose structure was not positively recorded until as late as 1973: J.-O. Lundgren and J. M. Williams, *J. Chem. Phys.*, 1973, **58**, 788.

93 E. G. Vassian and R. K. Murman, *Inorg. Chem.*, 1967, **6**, 2043.
94 J.-O. Lundgren and I. Olovsson, 'The Hydrogen Bond', ed. P. Schuster G. Zundel, and C. Sandorfy, North-Holland, Amsterdam, 1976, Ch. 10, pp. 473—526.
95 J.-O. Lundgren and I. Olovsson, *Acta Cryst.*, 1967, **23**, 996.
96 J. M. Williams, 'The Hydrogen Bond', ed. P. Schuster, G. Zundel, and C. Sandorfy, North-Holland, Amsterdam, 1976, Ch. 14, pp. 657—682.
97 A. C. Pavia and P. A. Giguère, *J. Chem. Phys.*, 1970, **52**, 3551.
98 A. S. Gilbert and N. Sheppard, *J.C.S. Faraday II*, 1973, **69**, 1628.

Table 11 *Diaquohydrogen* $H_5O_2^+$.

Salt hydrate	*Diffraction method*	r(O··O) /pm	r(O—H—O) /pm		OHO°	θ°	*Ref.*
$C_6O_2(NO_2)_2(OH)_2,6H_2O$*	neutron	245	118	127	176	0.5	*a*
$HBr.2H_2O$	,,	240	117	122	174.7	52.1	*b*
$HCl.2H_2O$	*X*-ray	241	*ca.* 119	*ca.* 128	*ca.* 180	54.7	95
$[C_6H_2(NO_2)_3SO_3H],4H_2O$†	neutron	243.6	112.8	131.0	175	105.7	*c*
trans-$[Co(en)_2Cl_2]Cl,2H_2O,HCl$	,,	243.1	121.6	121.6	180	180	99
$YH(C_2O_4)_2,3H_2O$	,,	244.2	122.1	122.1	178.2	‡	*d*
$YD(C_2O_4)_2,3H_2O$	,,	245.4	122.7	122.7	167.3	‡	*d*

* nitranilic acid; † picrylsulphonic acid; ‡ not quoted
[a] J. M. Williams and S. W. Peterson, *Acta Cryst.*, 1969. **25A**, S113; [b] R. Attig and J. M. Williams, *Angew. Chem. Internat. Edn.*, 1976, **15**, 491; [c] J.-O. Lundgren and R. Tellgren, *Acta Cryst.*, 1974, **30B**, 1937; [d] G. D. Brunton and C. K. Johnson, *J. Chem. Phys.*, 1975, **62**, 3797

The spectra are generally very complex and their analysis is a knotty problem. It seems that the proton moves in a broad, flat, anharmonic, single-minimum-potential well[99] which makes vibrational correlations hard to find and almost impossible to predict. Thus in the complex *trans*-$[Co(en)_2Cl_2]^+,H_5O_2^+,2Cl^-$ the calculated value for ν_s(OHO) was 350 cm^{-1} and yet it appears to absorb[99] at 980 cm^{-1}.

The calculated[100a] hydrogen-bond energy of $H_5O_2^+$ is 100 kJ mol^{-1} and this is in line with a value of 150 kJ mol^{-1} obtained from gas-phase experiments.[100b]

The diaquohydrogen cation is at the centre of such species as $H_7O_3^+$ and $H_9O_4^+$ which are better expressed as $H_5O_2^+,H_2O$ and $H_5O_2^+,2H_2O$. These species contain a central short hydrogen bond and longer normal hydrogen bonds to the third and fourth water molecules.[101] Even the cluster $H_{13}O_6^+$ has a *trans*-$H_5O_2^+$ at its core,[100] with R(O··O) of 239 pm, making it one of the shortest OHO bonds.

However, a much shorter OHO bond distance of 229 pm has recently been reported for the hydrated hydroxide ion, $H_3O_2^-$. This species is in effect the dihydroxide anion $H(OH)_2^-$ and the hydrogen bond is symmetrical.[102] The anion was discovered in the mixed salt $Na_2[Et_3MeN][Cr(PhCS{=}NO)_3]$,-$\frac{1}{2}NaH_3O_2,18H_2O$ which is a tris(thiobenzohydroximato)chromate(III) compound.

(v) *Other Strong* OHO *Hydrogen Bonds*. The hydrogen bonds in carboxylic acid dimers and polymers are weak but those of phosphorus acids can be strong. The R(O··O) of the hydrogen bond in $(p\text{-}ClC_6H_4O)_2PO_2H$ is 239.8 pm and crystallographically symmetrical.[103] Other short POHOP bonds have been discovered in dibenzyl phosphate (249.5 pm),[104a] the mineral monetite, $CaHPO_4$ (244 pm), and KH_2PO_4 (249 pm).[104b] In this last compound the unusual ferro-electric behaviour is attributed to the hydrogen bonding. Several of these ferro-electric crystals are known.[105]

The i.r. spectrum of $(p\text{-}ClC_6H_4O)_2PO_2H$ has a Hadži Type(ii) spectrum with no band above 1500 cm^{-1} that could be assigned to ν(OHO). Instead there were broad absorptions centred at 1410 and 1115 cm^{-1} that disappeared on deuteriation and which were labelled ν(OHO) and δ(OHO).[106]

Even H_3PO_4 can form a strong hydrogen bond to urea[107] and this particular

[99] J. Roziere and J. M. Williams, *Inorg. Chem.*, 1976, **15**, 1174.

[100] (*a*) A. F. Beecham, A. C. Hurley, M. F. Mackay, V. W. Maslen, and A. McL. Mathieson, *J. Chem. Phys.*, 1968, **49**, 3312; (*b*) P. Kebarle, A. Zolla, J. Scarborough, and M. Arshardi, *J. Amer. Chem. Soc.*, 1967, **89**, 6393.

[101] $H_7O_3^+$: R. Attig and J. M. Williams, *Inorg. Chem.*, 1976, **15**, 3057; $H_9O_4^+$: I. Taesler and J.-O. Lundgren, *Acta Cryst.*, 1978, **34B**, 2424; J.-O. Lundgren, *ibid.*, p. 2428; $H_{13}O_6^+$: R. A. Bell, G. G. Christoph, F. R. Fronczek, and R. E. Marsh, *Science*, 1975, **190**, 151.

[102] K. Abu-Dari, K. N. Raymond, and D. P. Freyberg, *J. Amer. Chem. Soc.*, 1979, **101**, 3688.

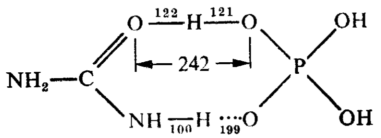
[103] M. Calleri and J. C. Speakman, *Acta Cryst.*, 1964, **17**, 1097.

[104] (*a*) J. D. Dunitz and J. S. Rollett, *Acta Cryst.*, 1956, **9**, 327; (*b*) D. W. Jones and D. W. J. Cruickshank, *Z. Krist.*, 1961, **116**, 101.

[105] V. H. Schmidt, 'The Hydrogen Bond', ed. P. Schuster, G. Zundel, and C. Sandorfy, North-Holland, Amsterdam, 1976, Ch. 23, pp. 1109—1169.

[106] D. Hadži and A. Novak, *Proc. Chem. Soc.*, 1960, 241.

[107] E. C. Kostansek and W. R. Busing, *Acta Cryst.*, 1972, **28B**, 2454.



urea-H_3PO_4 adduct

combination is remarkable for its phosphorylating abilities presumably through the hydroxyl group forming the strong bond, and activation that can be achieved by other strong bonds—see p. 121.

The mono-, di-, and tri-chloroacetic acids can act as hydrogen-bond donors to the acceptors Me_2SO, C_5H_5HO, Ph_3PO, *etc.*,[10a–g] forming bonds that have $\Delta H > 50$ kJ mol^{-1}, *e.g.* Cl_3CO_2H–Ph_2SeO $\Delta H = 67$ kJ mol^{-1}, Cl_3CO_2H–Ph_3PO $\Delta H = 58$ kJ mol^{-1}. I.r. changes are consistent with strong OHO bonding and a crystal structure of one of the adducts proved there to be a short hydrogen bond: R(O··O) in CCl_3CO_2–H–ONC_5H_5 is 241 pm.[10f]

Searching the literature[108] reveals evidence of many other potentially very strong hydrogen bonds and these are listed in Table 12. What to one chemist may be a hydrogen bond, to another is a proton transfer equilibrium, and some of these may turn out to be strong hydrogen bonds with a double minimum and high barrier. The subject is reviewed by Zundel.[109] It seems certain that many other strong OHO hydrogen bonds will turn up, some of which may well have important biochemical implications.

C The N–H–N Bonds.—(i) *Amine Base-Pair Cations.* The hypothetical cation $H_7N_2^+$, isoelectronic with $H_5O_2^+$, has yet to be characterized but substituted derivatives are known and have been shown to have strong hydrogen bonds of the type $[R_3N–H–NR_3]^+$. Although they were suspected from conductance studies on heterocyclic bases,[110] it was only relatively recently that hard evidence has shown them to exist.

The symmetric cations BHB^+, where B is pyridine or a substituted pyridine, show a doublet for ν_s(NHN) at *ca.* 2000 and 2500 cm^{-1} which is thought to arise from a double-minimum–low-barrier potential well.[111] For asymmetric base pairs $[B^1HB^2]^+$ the same effect was observed,[112] but the doublet structure was not observed[112] with non-heterocyclic base-pair cations such as $Me_3NHNMe_3^+$. The ν_s(NHN) is at 2100 cm^{-1} which is quite a large shift from the ν_s(NH) of the free base at 3170 cm^{-1}. The singlet nature of ν_s(NHN) here is thought to indicate a single minimum. In mixed heterocyclic–aliphatic base-pair cations the proton is

108 W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids', Benjamin, New York, 1968; and P. Schuster, G. Zundel, and C. Sandorfy, 'The Hydrogen Bond', 3 volumes, North-Holland, Amsterdam, 1976.
109 G. Zundel, 'The Hydrogen Bond', ed. P. Schuster, G. Zundel and C. Sandorfy, North-Holland, Amsterdam, 1976, Ch. 15, pp. 683—766.
110 I. M. Kolthoff, D. Stocesoca, and T. S. Lee, *J. Amer. Chem. Soc.*, 1953, **75**, 1834; J. F. Coetzee, G. R. Padmanabham, and G. P. Cummingham, *Talanta*, 1964, **11**, 93.
111 R. Clements, R. L. Dean, T. R. Singh, and J. L. Wood, *J.C.S. Chem. Comm.*, 1971, 1125; J. L. Wood, *J. Mol. Struct.*, 1972, **13**, 141.
112 R. Clements, R. L. Dean, and J. L. Wood, *J.C.S. Chem. Comm.*, 1971, 1127.

Table 12 *Possible strong* OHO *hydrogen bonds*

System	*Suspected hydrogen bond*	*Evidence*	*Ref.*
$(MeCONH_2)_2HCl$	COHOC	i.r.	*a*
$RCO_2H,RCONH_2$	COHOC	$R(O\cdots O)$ = 248 pm	*b*
HNO_3,H_2O	NOHON	i.r.	*c*
$Na_3H(SO_4)_2$	SOHOS	$R(O\cdots O)$ = 243.4 pm	*d*
$Bu_4N^+H(C_6Cl_5O)_2^-$, *etc.*	COHOC	i.r.	*e*
LiOH,H_2O	HOHOH	theoretical E = 105 kJ mol^{-1}, $R(O\cdots O)$ = 246.5 pm, sym.	*f*
MeOH,KOH	COHOH	i.r.	*g*
MH_2PO_2,RCO_2H (M = Na, K; R = H, CH_3, *etc.*)	POHOC	i.r., n.m.r.	*h*
acetylacetone (enol form)	COHOC	n.m.r., $\Delta\delta$(H,D)	*i*, 14
H_3PO_2, H_3PO_3, H_3PO_4	POHOP	i.r.	*j*
2-mesitaldehyde,$HClO_4$	COHOC	$R(O\cdots O)$ = 245 pm	*k*
isolumine, HBr, $2H_2O$	COHOC	$R(O\cdots O)$ = 245 pm	*l*

[a] N. Albert and R. M. Badger, *J. Chem. Phys.*, 1958, **29**, 1193; [b] L. Leiserowitz and F. Nader, *Acta Cryst.*, 1977, **33B**, 2719; [c] M. Leuchs and G. Zundel, *J. Phys. Chem.*, 1978, **82**, 1632; [d] M. Cabbi, G. Ferraris, and G. Invaldi, *Acta Cryst.*, 1979, **35B**, 525; [e] Z. Pawlak, *Adv. Mol. Relax. Processes*, 1973, **5**, 99; Z. Pawlak, J. Magoński, and T. Jasiński, *J. Mol. Struct.*, 1978, **47**, 329; [f] I. Gennick and K. M. Harmon, *Inorg. Chem.*, 1975, **14**, 2214; B. O. Roos, W. P. Kraemer, and G. H. F. Diercksen, *Theor. Chim. Acta*, 1976, **42**, 77; [g] D. Schiöberg and G. Zundel, *J.C.S. Faraday II*, 1973, **69**, 771; [h] J. H. Clark, J. Emsley, and T. B. Middleton, *J.C.S. Dalton*, 1979, 1693; [i] S. I. Chan, L. Lin, D. Chitter, and P. Dea. *Proc. Nat. Acad. Sci. USA*, 1970, **65**, 316; H. Lowrey, C. George, P. D'Autonio, and J. Karle, *J. Amer. Chem. Soc.*, 1971, **93**, 6339; A. L. Andreassen and S. H. Bauer, *J. Mol. Struct.*, 1972, **12**, 381. [j] M. Leuchs and G. Zundel, *Canad. J. Chem.*, 1979, **57**, 487; [k] C. D. Fisher, L. H. Jensen, and W. M. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 33; [l] M. F. Mackay, Ph.D. Thesis, Melbourne University, 1967, reported in ref. 100a.

nearer the aliphatic nitrogen.[113] The isotope frequency ratio is *ca.* 1.25, which is indicative of a double minimum.[3] If the groups on nitrogen are too bulky they may prevent hydrogen-bond formation; thus $Et_3NHNEt_3^+$ is not formed.[114]

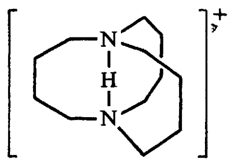
Pawlack has measured the stability constants of many cations of type BHB^+ in acetone, which is not the ideal solvent, and shown some appreciable $K(BHB^+)$ values.[115a] The bipyridyl cation in $MeNO_2$ has $K(BHB^+) = 4.5 \times 10^3$, and i.r. and ^1H n.m.r. spectroscopy [$\delta(^1H)$ = 10.52 p.p.m.] were consistent with a double-minimum situation.[115b]

Hydrazinium salts display NHN bonds linking these cations together in a polymeric array,[116] not surprising when one considers that this cation, H_2N–

[113] R. L. Dean, F. N. Masri, and J. L. Wood, *Spectrochim Acta*, 1975, **31A**, 79.
[114] B. Borah and J. L. Wood, *J. Mol. Struct.*, 1974, **22**, 237.
[115] (*a*) Z. Pawlak, *Roczniki Chem.*, 1972, **46**, 1163; (*b*) 1973, **47**, 347.
[116] N_2H_5X (X = Cl, Br): K. Sakurai and Y. Tomiie, *Acta Cryst.*, 1952, **5**, 289, 293; $N_2H_5H_2PO_4$: R. Liminga, *Acta Chem. Scand.*, 1965, **19**, 1692.

NH_3^+, has both a donor and an acceptor site. N_2H_5,HC_2O_4, already mentioned for its short OHO bonds in the oxalate anion,[69,70] also has $R(N{\cdot\cdot}N) = 287.2$ pm, which is fairly short, in the cation chains.

The most unusual example of this kind of hydrogen bond is the recently reported 1,6-diazabicyclo[4.4.4]tetradecanium ion in which a proton is encaged:[117]



The strength of this bond is shown by its low ν(NHN) at 1400 cm^{-1} and $\delta(^1H)$ at 17.5 p.p.m., both values representing lower limits of frequency and shielding for a proton between two nitrogen atoms, in a single-minimum well.

(ii) *The Hexacyanometal Acids*, $H_nM(CN)_6$. The best known is $H_3Co(CN)_6$ in which octahedra of $Co(CN)_6^{3-}$ are three-dimensionally linked *via* CN–H–NC hydrogen bonds. *X*-Ray diffraction[118] could not determine whether the H was in a single- or double-minimum well, but it was within ± 19 pm of the centre of a very short hydrogen bond, $R(N{\cdot\cdot}N) = 258.2$ pm, to be compared with twice the van der Waals radius of N, *i.e.* 310 pm. Calculations predicted a double-minimum–low-barrier potential function,[119] but to all intents the bond is centred, and investigations of $D_3Co(CN)_6$[120] show this to be so as well as showing no lengthening of the bond on deuteriation, $R(N{\cdot\cdot}N) = 259.3$ pm. The stretching mode was allocated to an absorption at 560 cm^{-1} which shifted to 430 cm^{-1} on deuteriation.[118] This isotope shift of 1.30 is larger than that in $H_3Fe(CN)_6$ (where a weaker hydrogen bond is found but where $\nu_H/\nu_D = 1$) so that it might represent a single-minimum well.

The following solid acids also appear to have centred NHN bonds: $H_3Ru(CN)_6$, $H_3Ir(CN)_6$, $H_2Pd(CN)_4$, and $H_2Pt(CN)_4$ as shown by a very broad band centred at *ca.* 750 cm^{-1}. The acids $H_4Fe(CN)_6$, $H_4Ru(CN)_6$, and $H_4Os(CN)_6$ are thought to have non-centred bonds,[121] and in $H_3Fe(CN)_6$ the r(N–H) distances are 113 and 162 pm and the angle at hydrogen is 150.3°.[118]

4 Heteronuclear Strong Hydrogen Bonds

A The Mixed Dihalide Anions, HXY^-.—All combinations are known[27,45,50,122a–c]

[117] D. W. Alder, A. Casson, and R. B. Sessions, *J. Amer. Chem. Soc.*, 1979, **101**, 3652.
[118] R. Haser, B. Bonnet, and J. Roziere, *J. Mol. Struct.*, 1977, **40**, 177.
[119] H. U. Güdel, *J. Chem. Phys.*, 1972, **56**, 4984.
[120] H. U. Güdel and A. Ludi, *J. Chem. Phys.*, 1970, **53**, 1917; and with P. Fischer, 1972, **56**, 674.
[121] D. F. Evans, D. Jones, and G. Wilkinson, *J. Chem. Soc.*, 1964, 3164.
[122] (*a*) J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, **70**, 20; (*b*) *ibid.*, p. 543; (*c*) R. L. Benoit, M. Rinfret, and R. Domain, *Inorg. Chem.*, 1972, **11**, 2603.

and although the expected asymmetry of the hydrogen bond is indicated there has been little interest shown in these ions, apart from the mixed fluoride–halides whose n.m.r. and i.r. parameters are given in Table 13. Considering the

Table 13 *The fluoride–halide ions*, HFX^-

	$HFCl^-$	$HFBr^-$	HFI^-	*Ref.*
$\delta(^1H)$ p.p.m. Me_4Si	10.43	8.88	7.4	27c
$\delta(^{19}F)$ p.p.m. CF_4	−83.3	−83.2	−82	27c
$^1J_{HF}$/Hz	403.4	427.1	437	27c
ν_1/cm^{-1}	275	220	180	122b
ν_2/cm^{-1}	823, 863	740	635	122b
ν_3/cm^{-1}	*ca.*2710	*ca.*2900	*ca.*3200	122b

high values of ν_3, the asymmetric stretching frequency, they would seem to be more like normal hydrogen bonds with the proton located much nearer one atom than the other—and the $\delta(^1H)$ values support this.

Deuteriation of $HClBr^-$ and the isotope shift this produces in the i.r. led to conflicting results but all showed the weak hydrogen-bond shift[50] of 1.34[50] or slightly less[41,122a] at *ca.* 1.25.

B The F–H–O Bonds.—(i) *Fluoride–Water.* HF and H_2O form a hydrogen bond $H_2O{\cdot\cdot}HF$ that can only be described as a normal, weak interaction[123] of around 26 kJ mol^{-1}. Calculated values for this pair[124] are 39 and 32 kJ mol^{-1}. On the other hand the calculated energy for the hydrogen bond between water and a fluoride ion, $HOHF^-$, is 101 kJ mol^{-1} and $R(O{\cdot\cdot}F)$ = 241 pm,[125] or 98.2 kJ mol^{-1} and 252 pm with a slightly bent bond, OHF = 173 °.[126*]

Although theoretical calculations indicate a strong and short hydrogen bond, in metal fluoride hydrates the hydrogen-bond distances are much larger than the above values. Few such structures have been determined, however, so it may be unwise to generalize. A comparison of the geometry of hydrogen bonding in such salts has recently been published by Simonov and Bukvetsky.[127] In their analysis they find the average $R(O{\cdot\cdot}F^-)$ to be 268.2 pm with a range 256—286 pm, and an average angle OHF of 170 °. The sum of the van der Waals radii of O and F is 290 pm so that only $R(O{\cdot\cdot}F)$ < 260 pm is really good evidence of a strong bond.

Short bonds have been reported in $ZnF_2,4H_2O$[128] (257 pm, OHF^- = 175 °)

* The anomalous, weak-acid behaviour of HF in water has been explained, not in the usual terms of involving HF_2^-, but as due to a strong hydrogen bond $H_2O^+–H–F^-$: P. A. Giguère, *Chem. Phys. Letters*, 1976, **41**, 598.

123 R. K. Thomas, *Proc. Roy. Soc.*, 1975, *A*, **344**, 579.

124 P. Kollman and L. C. Allen, *J. Chem. Phys.*, 1970, **52**, 5085; P. Kollman, A. Johannsen, and S. Rothenberg, *Chem. Phys. Letters*, 1974, **24**, 199.

125 G. H. F. Diercksen and W. P. Kraemer, *Chem. Phys. Letters*, 1970, **5**, 570.

126 H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, 1973, **58**, 5627

127 V. I. Simonov and B. V. Bukvetsky, *Acta Cryst.*, 1978, **34B**, 355.

128 B. V. Bukvetsky, S. A. Polishchuk, and V. I. Simonov, *Kristallografiya*, 1973, **18**, 956.

and $RbVF_4,2H_2O$[129] (256 pm, 178 °) but in neither case was the proton centred and in fact r(O–H) was less than 100 pm in both cases, indicating that it still was covalently bound to its parent water molecule. Short and linear OHF^- bonds are found[130] in $(NH_4)_2$ $[Cr(H_2O)_6]F_5$ where $R(O\cdot\cdot F)$ = 253—257 pm. Because the water molecules are ligands this may explain their enhanced hydrogen-bonding ability.

When a fluoride ion finds itself only in the company of very large cations it becomes very hydroscopic, and hydrates of tetra-alkylammonium fluorides are readily formed. These compounds have some very unusual features, and it is not yet clear what is the crystal environment about the fluoride. The hydrates Me_4NF,xH_2O, x = 1,2,3, show[131] broad bands in several parts of the spectrum and the ν_H/ν_D ratios were ambiguously 1.32—1.42. The trihydrates $F(H_2O)_3^-$ may have a tetrahedral arrangement of the four electronegative atoms with six hydrogen bonds lying along each edge of the tetrahedron.[132]

(ii) *Fluoride–Carboxylic Acids.* Metal fluorides are only soluble to an appreciable degree in water, liquid HF, and aliphatic carboxylic acids. In all three solvents hydrogen bonding between solvent and fluoride is partly responsible for the very high solubilities.[133a] For instance, glacial acetic acid will dissolve more than its own weight of CsF to form a solution noteworthy for some unusual physical properties.

Investigations of the solutions and solvates of alkali-metal fluorides in formic, acetic, propionic, and butyric acids show that very strong hydrogen bonding between F^- and RCO_2H is formed.[133b,134] The monosolvates, MF,RCO_2H, gave Type(ii) spectra with strong broad absorptions centred on 1490 cm^{-1}, ν(OHF), 1165, and 990 cm^{-1}. The $\delta(^1H)$ of the hydrogen bond is dependent upon concentration and counter-cation but is measured[135] as *ca.* 14.5 p.p.m. Calculated values for $\delta(^1H)$ are 7 p.p.m. downfield of this and this difference has been used to deduce the location of the cation.[136]

It has been shown from ^{19}F n.m.r. spectra of KF in HCO_2H that $\delta(^{19}F)$ is due to two main environments F^- and HF in dilute solutions (0.06—0.5 M), the ratio being *ca.* $4F^-$:1HF at 0.5 M. At higher concentrations HF_2^- and $(HF)_n$ probably also contribute to $\delta(^{19}F)$.[137]

Calculations on HCO_2HF^- and $CH_3CO_2HF^-$ gave $R(O\cdot\cdot F)$ values of 237 and 239 pm and bond energies of 249 and 250 kJ mol^{-1} relative to the acid + fluoride.[138] These calculations also show that the proton is likely to reside in a single-minimum potential well and near the fluoride so that the actual hydrogen-

129 B. V. Bukvetsky, L. A. Muradyan, R. L. Davidovich, and V. I. Simonov, *Soviet J. Coord. Chem.*, 1976, **2**, 869.
130 W. Massa, *Z. anorg. Chem.*, 1977, **436**, 29.
131 K. M. Harmon and I. Gennick, *Inorg. Chem.*, 1975, **14**, 1840.
132 I. Gennick, K. M. Harmon, and J. Hartwig, *Inorg. Chem.*, 1977, **16**, 2241.
133 (*a*) J. Emsley, *J. Chem. Soc. (A)*, 1971, 2511; (*b*) *ibid.*, p. 2702.
134 J. Emsley and O. P. A. Hoyte, *J.C.S. Dalton*, 1976, 2219.
135 J. H. Clark and J. Emsley, *J.C.S. Dalton*, 1973, 2154.
136 J. W. Akitt, *J.C.S. Faraday I*, 1977, **73**, 1622.
137 C. Coulombeau, C. Beguin, and C. Coulombeau, *J. Fluorine Chem.*, 1977, **9**, 483.
138 J. Emsley, O. P. A. Hoyte, and R. E. Overill, *J.C.S. Perkin II*, 1977, 2079.

bond energy should be defined relative to carboxylate + HF in which case it is 105 kJ mol^{-1} but still a very strong bond.[5]

A crystal-structure determination of a metal fluoride–carboxylic acid solvate has yet to be performed. Recently the presence of fluoride ions in carboxylic acids has been shown to lead to enhanced NOE of the anomalously large values which the carbonyl carbons of these acids display.[139] Ion cyclotron resonance studies on gas-phase ions have led to values of 178 and 82 kJ mol^{-1} for the energies $MeCO_2H + F^-$ and $MeCO_2^- + HF$.[85]

The effect on the chemistry of carboxylic acids when they form such a strong hydrogen bond is demonstrated by the increased nucleophilicity of the carboxylic group, which then becomes able to form esters by attack of alkyl halides.[140] The use of fluorides to stimulate a large variety of molecules to unusual chemical behaviour by the formation of hydrogen bonds, presumed strong, has been reported by Clark and Miller. Condensations,[141a,b] alkylations,[141c] sulphenylations,[141d] and Michael additions[141e] are areas in which fluorides have produced interesting results. Polymer-immobilized fluoride can also be used.[141e]

(iii) *Other Strong* F–H–O *Bonds*. The shortest R(O··F) so far measured (238.3 pm) was that between HF and the hydrogen phosphite anion in the compound KH_2PO_3,HF.[142] Though very short, and presumably with a single minimum, the hydrogen was far off-centre and the bond was bent, 145 °. The r(F–H) distance was 94 pm, almost the same as r_{cov}(HF), 92 pm, and the $r(^-O–H)$ distance was 155 pm.

Recently, compounds of the type $Bu_4NF(oxime)_2$ have been prepared and studied by ^1H, ^{13}C, ^{19}F n.m.r., i.r., and u.v. spectroscopy, and shown to have strong hydrogen bonding of the type F^----H–ON=CR^1R^2 in which the H may be in an asymmetric double-minimum potential well.[141f]

The adducts $Te(OH)_6$,2KF and $Te(OH)_6$,NaF have fluoride atoms acting as the acceptor towards three OH groups and these hydrogen bonds are 258 pm long although with slightly different OHF angle, 159 °, 161 °, and 175 °.[143] The i.r. spectra have broad bands at: 2720 cm^{-1} [ν(OHF), $\Delta\nu$(OH) = 380 cm^{-1}]; 1160, 1190 [δ(OHF)]; 935, 890, and 815 [γ(OHF) split into three bands corresponding to the three OHF bonds], and 255 cm^{-1} [ν_s(OHF)].

A formal negative charge on oxygen or fluoride seems a prerequisite for strong OHF bonding. Without this, only normal, weak hydrogen bonding occurs, *e.g.* R_2O + HF forms bonds[144] with E(OHF) = *ca.* 30 kJ mol^{-1}.

139 J. M. Miller, R. K. Kanippayoor, J. H. Clark, and J. Emsley, *J.C.S. Chem. Comm.*, 1979, 758.
140 J. H. Clark and J. Emsley, *J.C.S. Dalton*, 1975, 2129; with O. P. A. Hoyte, *J.C.S. Perkin I*, 1977, 1091.
141 (*a*) J. H. Clark and J. M. Miller, *J. Amer. Chem. Soc.*, 1977, **99**, 498; (*b*) *J.C.S. Perkin I*, 1977, 2063; (*c*) *ibid.*, 1977, 1743; J. M. Miller, K. H. So, and J. H. Clark, *Canad. J. Chem.*, 1979, **57**, 1887; (*d*) *ibid.*, 1978, **56**, 141; (*e*) *J.C.S. Chem. Comm.*, 1978, 466; (*f*) J. H. Clark, *Canad. J. Chem.*, 1979, **57**, 1481.
142 H. Altenburg and D. Mootz, *Acta Cryst.*, 1971 **27B**, 1982.
143 R. Allman and W. Haase, *Inorg. Chem.*, 1976, **15**, 804; R. Allman, *Acta Cryst.*, 1976, **32B**, 1025.
144 M. Tsuda, H. Touhara, K. Nakanishi, K. Kituara, and K. Morokuma, *J. Amer. Chem. Soc.*, 1978, **100**, 7189.

C. The F–H–N Bond.—The sum of the van der Waals radii of N and F is 295 pm and no R(F··N) distance has been reported shorter than 270.8 pm in NH_4F.[145] In $(NH_4)_2[Cr(H_2O)_6]F_5$ the NHF bonds are 272 pm.[130]

There is some i.r. evidence for strongish NHF bonding in $NH_3D^+F^-$; the relatively low $\nu_1(NH_3D^+)$ at 2182 cm^{-1} in this salt is lower than in any other ammonium salt which was probed by studying it as NH_3D^+.[146] The Raman and i.r. spectra of guanidium fluoride, $C(NH_2)_3{}^+F^-$, also suggest a type of hydrogen bonding that is not present in the corresponding chloride.[147]

D The X–H–O Bonds.—Crystal data for R(Cl··O), R(Br··O), and R(I··O) show none to have the necessary shortening to qualify as a strong hydrogen bond.[148] However, Yamdagni and Kebarle[149] studied the hydrogen bonding between Cl^- and hydroxy-compounds in the gas phase and reported ΔH values that indicate strong hydrogen bonding: $E(Cl^-HOH)$, 55 kJ mol^{-1}; $E(Cl^-HOMe)$, 59; $E(Cl^-HOPh)$, 82; $E(Cl^-HO_2CCH_3)$, 91; and $E(Cl^-HO_2CH)$, 156 kJ mol^{-1}. Similar combinations, studied in sulpholane as the solvent, gave enthalpies below 20 kJ mol^{-1} for all of them.[150] Calculations on the $[ClHOH]^-$ system suggest a strong hydrogen-bond interaction.[151]

E The X–H–N Bonds.—Ault and Pimentel[152] have shown that a very strong bond, centred and with a single minimum, is formed in a 1:1 complex of NH_3 and HCl isolated in a nitrogen matrix at 15 K. The estimated bond energy was 40—85 kJ mol^{-1}. Theoretical calculations predict E(NHCl) = 82 kJ mol^{-1} and r(N–H) = 124 pm, r(H–Cl) = 162 pm, *i.e.* R(N··Cl) = 286 pm.[153]

Measured R(N··Cl) distances in Et_3NHCl,[154a] Me_3MHCl,[154b] and Me_2NH_2-Cl[154b] are longer than this at *ca.* 310 pm but nevertheless are appreciably shorter than the sum of the van der Waals radii, 360 pm, and so qualify as short hydrogen bonds.

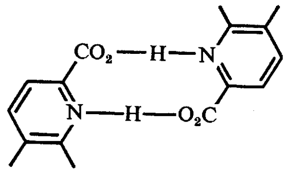
The i.r. spectra of NH_4X show N–H··X^- bonds but none gave a shift $\Delta\nu/\nu_0$ for the N–H stretching vibration that was over 25%.[3]

Recently ^{79}Br n.q.r. studies have indicated strong hydrogen bonding in $C_6H_5NH_3Br$ of the type N–H–Br.[155]

F The O–H–N Bonds.—An unexpectedly strong hydrogen bond with biological

145 H. W. W. Adrian and D. Feil *Acta Cryst.*, 1969, **25A**, 438; B. Morosin, *Acta Cryst.*, 1970, **26B**, 1635.
146 O. Knop, I. A. Oxton, and M. Falk, *Canad. J. Chem.*, 1979, **57**, 404.
147 O. D. Bonner, *J. Phys. Chem.*, 1977, **81**, 2247.
148 J. R. Clark, *Rev. Pure Appl. Chem. Australia*, 1963, **13**, 50.
149 R. Yamdagui and P. Kebarle, *J. Amer. Chem. Soc.*, 1971, **93**, 7139.
150 S. Y. Lam, C. Louis, and R. L. Benoit, *J. Amer. Chem. Soc.*, 1976, **98**, 1156.
151 L. Piela, *Chem. Phys. Letters*, 1973, **19**, 134.
152 B. S. Ault and G. C. Pimentel, *J. Chem. Phys.*, 1973, **77**, 1649.
153 E. Clementi, *J. Chem. Phys.*, 1967, **46**, 3851; 1967, **47**, 2323; and with J. N. Gayles, 1967, **47**, 3837.
154 (*a*) F. Genet, *Bull. Soc. Fr. Min. Crist.*, 1965, **88**, 463; (*b*) J. Lindgren and I. Olovsson, *Acta Cryst.*, 1968, **24B**, 549, 554.
155 W. Pies and A. Weiss, *Bull. Chem. Soc. Japan*, 1978, **51**, 1051.

significance has been reported between a phenanthroline ring nitrogen and a carboxylic acid group as evidenced by i.r. data.[156]



This kind of hydrogen bond may be a single-minimum but more likely is a double-minimum type in which case the system can be viewed as a proton-transfer equilibrium. Studies of phenols and amines have been made[157] to measure the extent of proton transfer which can range from 0%, *e.g.* $C_6H_5OH\cdots NH_2Pr^n$, to 100%, *e.g.* $C_6Cl_5O\cdots HNH_2Pr^n$. The combination 2,3-$C_6Cl_2H_3OH$ + Pr^nNH_2 gave an unexpected 84% transfer and an i.r. spectrum with a very broad band extending from 3000 down to 800 cm^{-1}. The conclusion was that this particular combination produced a centred hydrogen bond.

The gas-phase hydration energies of pyridinium ions show hydrogen-bond energies in excess of 50 kJ mol^{-1}, *e.g.* $C_5H_5N^+$–N–OH_2, E = 63 kJ mol^{-1}, which may indicate that bonds of this kind have an important role to play in the chemistry of many organic base systems.[158]

5 Strong Hydrogen Bonding Theory

Advanced theories of hydrogen bonding have been proposed[83,159,160] as well as more general approaches to the subject.[161] But what of very strong hydrogen bonds? Is there a simple way of viewing these which is not an affront to the chemists' traditionally held views of the single valency of hydrogen and at the same time is more than simple electrostatic attraction, albeit modified by exchange, polarization, charge transfer, and coupling energies?[162] Morokuma has proposed a theory[163] based on combinations of these energies.

A recent text[164] speaks of hydrogen as showing 'divalent character' in hydrogen-bonding situations, and makes the comparison between these and donor–acceptor complexes on the basis of electron migration, pointing out the extra

[156] D. Smith, P. J. Taylor, J. Vause, and W. S. Waring, *J.C.S. Chem. Comm.*, 1978, 369.
[157] G. Zundel and A. Nagyreni, *J. Phys. Chem.*, 1978, **82**, 685, and refs. therein.
[158] W. R. Davidson, J. Sunner, and P. Kebarle, *J. Amer. Chem. Soc.*, 1979, **101**, 1675, and refs. therein.
[159] P. Schuster, 'The Hydrogen Bond', ed. P. Schuster, G. Zundel, and C. Sandorfy, North-Holland, Amsterdam, 1976, Ch. 2, pp. 25—164.
[160] L. C. Allen, *J. Amer. Chem. Soc.*, 1975, **97**, 6921; with P. Kollman, *Chem. Rev.*, 1972, **72**, 283.
[161] I. D. Brown, *Chem. Soc. Rev.*, 1978, **7**, 352.
[162] K. Morokuma, *Accounts Chem. Res.*, 1977, **10**, 294.
[163] H. Umeyama and K. Morokuma, *J. Amer. Chem. Soc.*, 1977, **99**, 1316.
[164] J. N. Murrell, S. F. A. Kettle. and J. M. Tedder, 'The Chemical Bond', Wiley, Chichester, 1978, p. 298.

factor of electrostatic attraction in the no-bond state that is usually absent for donor–acceptor complexes. In very strong, single-minimum, centred hydrogen bonds the hydrogen atom is forming two covalent, electron-pair bonds. The best analogy is with a Lewis adduct, the hydrogen acting as a Lewis acid and accepting an electron pair from another atom. Clearly the 1*s* orbital cannot be used for this purpose and the lowest unoccupied level is the 2*s*.

In HF_2^- the bond length r(H–F) is 113 pm which is longer than first-row-element bonds to hydrogen, except r(B–H) = 119 pm, but shorter than second-row covalent bonds, the shortest of which r(H–Cl) = 128 pm. In the dicarboxylates r(O–H) is *ca.* 120 pm.

In a centred, symmetrically bonded system it is meaningless to apportion the energy of the system other than equally between the two bonds. For HF_2^- the total bond energy is (566 + 212) kJ mol^{-1} giving each bond in this ion a bond energy value of 389 kJ mol^{-1}, which by all normal criteria we would judge to be a strong single covalent bond. We can compare this bond energy with other bond energies of hydrogen and find it stronger than the single monovalent bonds that hydrogen forms to B, Si, P, and S. For the dicarboxylate bond E(O–H) is *ca.* 310 kJ mol^{-1}, still quite strong.

Clearly, bonds this strong represent one extreme of hydrogen bonding in which it behaves as a Lewis acid in its own right. Other bonds may come close to this model but the hydrogen-bonded system is very susceptible to the slightest of environmental forces, as this review has shown, and can deviate from the centred bond quite markedly. Moreover, the proton is unable to impose its own potential effectively on the space between the two other nuclei because its nuclear charge is so much less. Thus it may find itself in a double-minimum well, defined by the other nuclei, with a barrier of a height that may constrict its motion. If the barrier is high, the proton is constrained to the well defined by its parent atom and behaves merely as a weak centre of positive attraction towards a negative centre some distance away, which is the classical picture of hydrogen bonding.