Contents

1
Aspects of Hydrogen Bonding

J. C. SPEAKMAN
University of Glasgow

1.1 INTRODUCTION

The article on hydrogen bonding in the first volume of this series (hereinafter referred to as HB. 1) included a general elementary review of the subject with special reference to the study of O H···O bonds by crystallographic methods. There followed a report on some of the results then recently

published, coverage being to the end of 1971 approximately. In this second volume, we shall continue to be selective, concentrating on topics likely to be of more general interest from the literature to November, 1973. Many of the researches are of importance in other fields of chemistry, though they are considered here because they involve hydrogen bonding.

Mention should be made of a new general text: *Hydrogen Bonding* by Vinogradov and Linnell[1]. A supplement to Pimentel and McClellan's authoritative book (1960) has also been published[2] as well as a recent review of the theory of the hydrogen bond[3].

As before, we shall give interatomic distances in terms of the ångstrom: 1 Å = 10 pm. Estimated standard deviations of cited results are shown in parentheses; they should be accepted with the usual qualifications.

1.2 POLYMORPHS OF ICE

Definitive papers have now been published describing neutron diffraction (ND) work on the two forms of heavy ice, D_2O (II)[4] and D_2O (IX)[5]. The former is completely ordered with respect to the deuterons. (Whalley has stated[6] that were this structure disordered, its higher entropy might render it stable in conditions that could occur terrestrially. As ice (II) is denser than water, disastrous consequences might then ensue.)

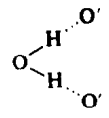
Ice (IX) has now had its structure more precisely determined than that of any other form of ice (see HB. 1, Figure 1.9). It is nearly completely ordered but has perhaps 4% of its deuterons in alternative sites. In general, there is little evidence in any form of ice for notable deviation of the water molecule from its gas-phase geometry, though this is not true for water in crystalline hydrates where experimental studies have been easier and much more numerous (see Section 1.3). In D_2O (IX), however, there is probably a significant lengthening of the hydrogen bonded O—D bonds. After correction for libration (see HB. 1, Section 1.6.4), O—D bond lengths average at 0.982(3) Å compared with 0.970 Å in the gas. The validity of the lengthening is supported by the O—D stretching frequency which is 2454 cm^{-1} in D_2O (IX) as against 2727 cm^{-1} in gaseous HOD. On the other hand, and more surprisingly, the D—O—D angles are not significantly below 104.5°, the gas-phase value, despite the circumstance that the acceptor angles, $O^1 \cdots D—O—D \cdots O^2$, are 98° and 101° for the respective molecules in D_2O (IX).

1.3 THE WATER MOLECULE IN SALT AND OTHER CRYSTALLINE HYDRATES

In salt hydrates, the water molecule engages in one, or more usually both, of two bonding roles: it directs one — sometimes both — of its lone pairs of electrons towards the (usually metallic) cation; or it donates its protons to form hydrogen bonds with the anion, either directly if this is a monatomic ion, or to the oxygen atoms of oxy anions. It may also be hydrogen-bonded to other water molecules. The possibilities have been classified in more detail[7].

To understand such bonding in hydrates, we need to know the positions

of the hydrogen atoms, preferably by ND but alternatively by less direct inference[8]. Ferraris and Franchini-Angela[9] have made a detailed statistical survey of some 90 water molecules whose structures have been determined accurately by ND in about 40 different crystalline hydrates. Amongst other features, the geometry of the hydrogen-bonded molecule (I) has been



(I)

examined. On an average, the water molecule in a hydrate has the dimensions, O—H = 0.96, O···O′ = 2.81, H···O′ = 1.88 Å, H—O—H = 108°, O′···(HOH)···O′ = 108°. The molecule itself is not much different from the isolated molecule.

However, the average dimensions have internal standard deviations larger than those of the individual values. The scatter is significant. The interpretation is that the water of hydration is acting as a 'flexible strain-absorber'. It helps to stabilise the interactions between charged ions by relieving any imbalance of bond strengths, in the sense of Pauling's electrostatic valency principles.

One of the correlations published in this paper is a histogram of the frequencies of occurrence of various O—H···O angles. As had been found previously, 180° is not the commonest angle: there is a maximum for the range 165–170° which has nearly twice as many examples as has the range 175–180°. This has been taken by various commentators as a possible indication of a preference for O—H···O bonds that are slightly bent. It has already been suggested (see, e.g. HB. 1, Section 1.3) that this deduction may be invalid. In a bond with O—H···O = 180°, the acceptor atom must lie somewhere on the O—H line produced beyond H. For an angle of (say) 165°, the acceptor has a wider choice: it is merely required to lie somewhere on the surface of the cone generated by rotating H···O about O—H. There is more phase-space in the latter situation and this must be taken into account in assessing the meaning of the histogram[10].

The hydrogen bonds occurring in hydrates are fairly weak bonds. For such, the effectiveness of the bonding will not be sensitive to small deviations of O—H···O from strict linearity. For stronger bonds, with O···O less than 2.5 Å, linearity is probably more important; but certainly some very short OHO bonds are not exactly linear.

1.4 THE HYDRATED 'HYDROGEN ION'

For over half a century it has been realised that the 'hydrogen ion' of aqueous-solution chemistry must be hydrated, and the formula H_3O^+ has been written, when necessary, to betoken the hydration. This particular entity has been characterised in many crystals. As long ago as 1924, Volmer noticed the similarity between the x-ray powder patterns of ammonium perchlorate and

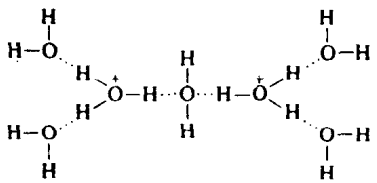
of the hydrate of perchloric acid: as the former was best represented as $NH_4^+ClO_4^-$, so $OH_3^+ClO_4^-$ was preferable to $HClO_4 \cdot H_2O$ for the latter. This suggestion has subsequently been confirmed by more direct experiments. From recent x-ray analyses, examples of crystals containing the 'oxonium ion' are $[H_3O^+]_2[O_3S \cdot CH_2 \cdot SO_3^{2-}]$ [11] and $[H_3O^+][CF_3 \cdot SO_3^-]$ [12].

In early x-ray work, the positions of the hydrogen atoms were merely inferred, and even now they are not accurately found. So there is a lack of firm information about the exact geometry of H_3O^+ in crystals. A recent account of a ND study of the monohydrate of toluene-*p*-sulphonic acid[13] therefore supplies valuable information. In this compound, the cation has no built-in crystal symmetry: the four atoms are all in general positions. All the same, its structure does not deviate significantly from the ideal of $3m$ (C_{3v}) symmetry. The O–H distances are 1.008, 1.011 and 1.013(8) Å, and the H–O–H angles are 109.2, 110.7 and 111.2(5)°. These results imply that the oxygen atom is 0.322 Å out of the plane of the three hydrogen atoms.

The finding agrees satisfactorily with one's expectations. However, it is fair to point out – as the authors do – that each hydrogen atom takes part in a strong hydrogen bond (O···O 2.528 Å, average), and that the acceptor oxygen atoms, belonging to three different sulphonate groups, lie in positions of approximate trigonal symmetry with respect to the oxonium ion. No doubt, in a less favourably symmetrical environment the H_3O^+ ion would be more distorted[12].

More hydrated species of the proton are well documented in the crystallographic literature. We instanced $H_5O_2^+$ in HB. 1, Section 1.4.4, and a recent example was found in x-ray work on the tetrahydrate of sulphuric acid, where '$H_2SO_4 \cdot 4H_2O$' turn out to be $[H_5O_2^+]_2[SO_4^{2-}]$ [14].

Almlöf, using x-rays[15], has found a complex hydrogen-bonded system in $HClO_4 \cdot 3.5H_2O$. In this crystal, two independent $H_9O_4^+$ units can be recognised, and they share the same water molecule. The entity (2) thus produced

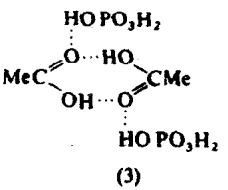


(2)

could be regarded as $H_{16}O_7^{2+}$, though it does not possess the crystal symmetry suggested by this simplified diagram. The hydrogen bonds to the central water molecule have O···O 2.68 and 2.61 Å; the other four bonds are even stronger with O···O 2.48–2.59 Å.

As is well known (e.g. see HB. 1, Section 1.1.1), acidity in the proton donor and basicity in the acceptor favour hydrogen bonding up to a point, but if they become too strong an ionised structure results. This is illustrated by ND work on the molecular compounds between acetic acid and a range of other acids. With sulphuric acid the crystal is ionic, being made up of $MeC(OH)_2^+$ and HSO_4^- [16]. With phosphoric acid, the dimeric hydrogen-bonded molecule

(3) is formed[17]. The intercarboxyl bonds [O···H···O 2.685(3) Å] are significantly longer than those in a normal carboxylic acid dimer (~2.64 Å).



(3)

Such weakening is attributable to the acceptance by each carbonyl oxygen atom of a second hydrogen atom from a phosphoric acid molecule.

1.5 SOME ACID SALTS

1.5.1 The bifluoride anion

For many years the FHF^- ion has been regarded as the firmest example — possibly the only sound example — of a symmetrical hydrogen bond. Structurally, it has been studied by particularly careful ND work on the sodium and potassium salts (MHF_2, where M = Na, K; see HB. 1, Section 1.6.2). According to a preliminary report[18], Williams and Schneemeyer have discovered by ND an unsymmetrical FHF^- ion in *p*-toluidinium bifluoride ($M^+ = C_7H_7NH_3^+$). In this crystal the anion has the geometry F···F = 2.260(4), F—H = 1.025(6), F···H = 1.235(6) Å; F—H···F = 178°. The distortion here is similar to, but more marked than, that in the intramolecular O—H···O bond reported by Schlemper *et al.*[19] (see HB. 1, Section 1.4.3), and similarly it may be attributed to the asymmetry of the crystal environment. Indeed, in the toluidinium bifluoride the asymmetry can be quantified simply. At each end the F(2)—H···F(1) anion accepts two hydrogen bonds from different —NH_3^+ groups; the N—H···F bonds to F(1) are stronger than those to F(2), the H···F distances being, respectively, 1.608, 1.675 and 1.777, 2.518 Å†. The stronger external bonding renders the corresponding internal (half-)bond the weaker, and the longer.

The obvious interpretation is that an isolated bifluoride ion would have its proton moving in a symmetrical, *single-minimum** (but flattened) potential well. At a crystallographically symmetrical site, the bond retains its symmetry; at one that lacks symmetry, the point of minimum energy is readily displaced towards one of the fluorine atoms (see HB. 1, Figure 1.5).

Is the symmetry of HF_2^- in the simple alkali bifluorides merely a statistical effect, due to two opposite but equally probable orientations of F—H···F⁻, itself unsymmetrical and with a geometry like that specified above? This seems improbable. It is true that the ND measurements, considered alone, on $NaHF_2$ and KHF_2 can equally well be reconciled with a single-minimum potential, or with 'half-protons' vibrating less vigorously about two minima, provided these minima are *close together*. But a minimum 0.10 Å from the

* Or *effectively* single, and flattened, at the bottom of the well, relative to a parabolic shape.
† The last H···F distance is really too long for significant bonding.

mid-point, as found in the toluidinium bifluoride, is rather beyond the limits allowed by the ND measurements, for $NaHF_2$ in particular. There were, too, other reasons for supposing the anions in these latter salts to be genuinely symmetrical[20]

1.5.2 Symmetrical, or nearly symmetrical, OHO bonds

In HB. 1, Sections 1.4.1 and 1.4.2, the type-A acid salts of carboxylic acids were cited as a class of crystalline compounds in which very short, and effectively symmetrical O···H···O bonds have been found. Five more well-authenticated examples are now known to the reviewer. X-ray analyses have been reported on two type-A acid salts (MHX_2, where M is a univalent cation) of monocarboxylic acids (HX)[21, 22] and on two type-A_2 acid salts (MHY) of the symmetrically dicarboxylic acids (H_2Y)[23, 24]. There has also been reported a ND analysis[25] of RbHY, where H_2Y is oxydiacetic acid $O(CH_2CO_2H)_2$. Some particulars of the hydrogen bonding in these acid salts are listed in Tables 1.1 and 1.2, which are to supplement Tables HB. 1,

Table 1.1 Intercarboxylic hydrogen bonding in type-A acid salts, MHX_2.

HX	M	*Symmetry of bond*	O···O /Å	C—O··H /degrees	*Ref.*
Dichloroacetic	NH_4	$\bar{1}$	2.432(5)	114.8	21
m-Chlorobenzoic	K	$\bar{1}$	2.437(6)	111.6	22

Table 1.2 Intercarboxylic hydrogen bonding in type-A_2 acid salts, MHY

H_2Y	M	*Symmetry of bond*	O···O /Å	C—O··H /degrees	*Ref.*
Oxalic	N_2H_5	$\bar{1}$	2.457(1)	114.0	23
Acetylene-dicarboxylic	K (α form)	2	2.445(3)	116.2	24
Oxydiacetic	Rb	2	2.450(3)	116.1	25

1.3 and HB. 1, 1.4, respectively. Hydrazinium hydrogen oxalate has already appeared in Table HB. 1, 1.4, but the recent analysis[23] is more precise and to a large extent supersedes the earlier analyses.

The weighted averages for the O···O distances (including those from HB.1) are 2.443(2) Å for the monobasic series and 2.454(1) Å for the dibasic. This method of averaging and the resulting standard deviations of the means are based on the unrealistic assumption that all the hydrogen bonds in these different crystals have the same length*, whereas undoubtedly there is a

* The average for the dibasic series of 2.454 Å may have been unduly biased by the heavy weight given to the value for the acid oxalate with its very low standard deviation.

significant scatter within each series. Nevertheless, these acid salts constitute a notable set of crystals with very short hydrogen bonds, all lying across elements of symmetry.

The C—O···H angles found in the 47 most precise analyses all lie in the range 110.2–116.2°, with a mean ~115°. An angle near to this value seems to be necessary for optimal bonding between carboxyl groups.

Interest attaches to structures which just fail to achieve strict crystal symmetry with respect to the OHO bond. Three examples have a close relationship to the structures listed in Tables 1.1 and 1.2.

Thomas has studied the deuteriated acid salt $[N_2D_5^+][DC_2O_4^-]$ [23]. Apart from the hydrogen bond, this structure is closely similar to that of $[N_2H_5^+][HC_2O_4^-]$, but it belongs to the space group $P2_1$ which lacks the centres of symmetry included in $P2_1/m$, the space group adopted by the ordinary acid salt. The ODO bond therefore does not lie across a centre of symmetry. Location of the deuterium atom with x-ray data runs into difficulty with the KKM effect (see Section 1.5.3), but the atom seems to be more associated with one oxygen than with the other. The O—D···O distance is 2.466(2) Å. The increase of 0.009 Å should be significant, but there is evidence[26] that deuteriation may possibly change the character of hydrogen bonds that are short, but not 'very short'.

There is a rubidium hydrogen acetylenedicarboxylate which is isomorphous with the potassium salt listed in Table 1.2. This monoclinic α form (of RbHY) has not been studied in any structural detail. However, there has been an x-ray study of a triclinic β form of RbHY [27], with a comparison of the structures of α-KHY and β-RbHY. Chemically they are identical, and most of the geometric parameters are virtually identical. In each structure there are infinite chains of HY^- anions linked by OHO bonds, but whereas in the α form these bonds lie across twofold axes of the crystal, there is no symmetry constraint on the OHO bonds of the β form. The O···O distances differ: α form, 2.446(3); β form, 2.464(8) Å. Unfortunately, the difference is of dubious significance especially as different cations are involved. (The precision in the analysis of the rubidium salt was impaired by high absorption errors.)

Grenthe and co-workers have also reported[28] x-ray analyses of the isostructural (isomorphous?) monoclinic acid salts of oxydiacetic acid, NaHY and KHY. (They are not isomorphous with RbHY which belongs to the tetragonal system*.) Again, there are infinite chains of HY^- units, but in (Na/K)HY no crystal symmetry is involved in the chains. Though not symmetrical, the hydrogen bonds are short with O···O = 2.462(3) in NaHY and 2.480(2) Å in KHY, but slightly longer than the symmetrical bond in RbHY [2.450(3) Å]. Surprisingly, in view of the difficulty of locating hyurogen atoms with x-rays in such situations (see Section 1.5.3 and HB. 1, Section 1.2.3), the acidic hydrogen atoms were found in both NaHY and KHY at reasonable positions, 1.01–1.05 Å from one oxygen atom, and with C—O—H ≈ 115° in each.

* This is an uncommon situation. Whilst K, Rb and NH_4 salts are often isomorphous, it is very rare to find isomorphism between Na and K salts of organic acids, the sizes of the cations differing too much. $NaHX_2$ and KHX_2, where HX = acetic acid, crystallise in different systems and with totally different structures[29].

1.5.3 The Kroon–Kanters–McAdam (KKM) effect

This phenomenon is normally associated with short OHO bonds lying across a point of crystal symmetry (see HB. 1, Section 1.7.3.). A 'difference' electron-density synthesis, based on a precise x-ray study, may reveal a double peak which, at its face value, implies that the acidic hydrogen atom is disordered between alternative sites up to 0.5 Å on either side of the bond centre. One of the most striking examples, illustrated in HB.1, Figure 1.8 and reproduced in Figure 1.1(a), was discovered in an accurate study of potassium hydrogen *meso*-tartrate at 160 C[30]. The 'half-hydrogens' in this map are 0.37 Å away from the centre.

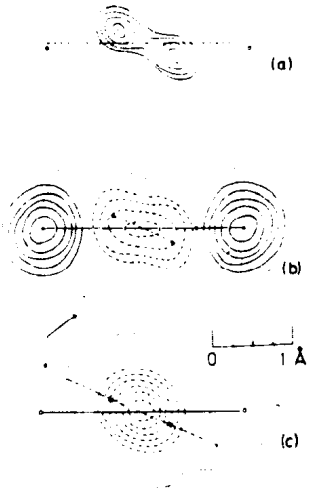


Figure 1.1 A short O···H···O bond in potassium hydrogen *meso*-tartrate. (a) Electron-density 'difference' synthesis, showing the KKM effect; (b) neutron-scattering density in the same region; (c) corresponding ND 'difference' synthesis, the scattering due to the oxygen atoms having been removed. [In (b) and (c), negative levels are shown by broken contour lines]

This crystal structure has now been examined by ND at room temperature[31]. Though the number of ND reflections measurable was much smaller, the shortness of the relevant hydrogen bond is confirmed; O···O = 2.474(13) Å as against 2.483(2) Å by x-rays. Figure 1.1(b) shows the neutron-scattering density in the same region as 1.1(a), the negative contours round the proton being represented by broken lines. The 'peak' corresponding to the proton is indeed elongated, but not sufficiently to indicate statistical half-protons ~0.74 Å apart. Figure 1.1(c) is a neutron 'difference' map, all nuclei having been taken out except the acidic proton. Though it is still elongated, the residual peak is even less compatible with 1.1(a) than is 1.1(b). Were the proton sites really 0.74 Å apart, they should be easily resolved in this ND map. Figures 1.1(b) and 1.1(c) could be explained by either of two models: (1) the proton has its point of minimum energy at the middle, but vibrates very anistropically with its greatest amplitude in a direction decidedly away from the direct O···O line, or (2) it occupies one or other of equivalent, alternative sites, perhaps as far as 0.15 Å (but not more) from the middle, with a reduced amplitude of vibration. In the case of this particular bond in potassium hydrogen *meso*-tartrate, the second explanation seems more likely. One reason is that, were the proton at the mid-point, the C···O···H angle would be very unfavourable at 131°.

It is relevant to point out that this hydrogen bond connects two extremely unorthodox carboxyl groups. For one thing, they break the almost universal rule that unequal C—O distances in the same carboxyl are matched by an inverse inequality in the C—C—O angles*. Typically, as in salicyclic acid dimer (see Section 1.6), C—O(1) = 1.308, C—O(2) = 1.237 Å; C—C—O(1) = 116, C—C—O(2) = 123°. In the *meso*-tartrate, corresponding dimensions are 1.297(1), 1.231(2) Å; 121.2, 117.3°. In view of these anomalies, the KKM effect in this bond might be exceptional; we notice also that the same crystal includes a second symmetrical OHO bond between more conventional carboxyl groups, and that the KKM effect at this second bond is rather less spectacular though easily detectable. However, there are numerous other examples[33].

In this context, great interest attaches to the paper[23] by Thomas describing x-ray work on hydrazinium hydrogen oxalate, as well as its deuteriate. The former is a type-A_2 crystal, some details of which were given in Table 1.2, and the OHO bond is short and crystallographically symmetrical. Its carboxylate groups are equivalent and of unimpeachable orthodoxy: C—O(H) = 1.279(1), C—O = 1.224(1) Å; C—C—O(H) = 113.4, C—C—O = 120.3°. Further, the x-ray analysis is of high precision. At the end of the refinement, the 'difference' electron-density distribution was calculated over the region of the hydrogen bond. The outcome is represented by the three sections, from the three-dimensional distribution, shown in Figures 1.2(a), 1.2(b) and 1.2(c). This is very similar to the effect discovered by Kroon *et al.*[34] and reproduced in Figure 1.1(a), but here the setting is without abnormal

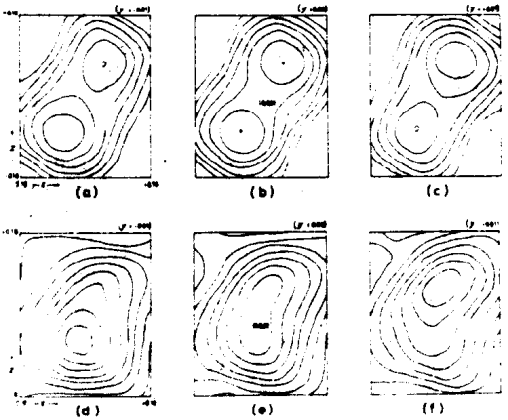


Figure 1.2 Electron-density 'difference' distribution near the short hydrogen bonds in (a), (b) and (c) hydrazinium hydrogen oxalate, and (d), (e) and (f) its deuteriate. In each case the density has been sampled at three levels: above, at, and below, the mid-point of the bond. [Reproduced, by permission, from (1973). *Acta Crystallogr.*, **B29**, 1769]

* The hydrogen maleate anion also breaks this rule. The severe strains arising from ring closure, by a very short intramolecular O···H···O bond, account for the anomaly[32].

features. It constitutes the best authenticated example so far of the KKM effect.

Some details of the situation are picked out in Figure 1.3, which represents a projection down the *b* axis. The origin is taken at the mid-point of the OHO bond and only half the actual bond is shown. Besides the relevant oxygen atom (O), P marks the position of peak density in Figure 1.2(a) and 1.2(c), and L marks the position found for the hydrogen atoms from a least-squares refinement based on a disordered model with two equivalent 'half-hydrogens' on either side of the centre of symmetry at the origin. P is 0.84 Å from the oxygen atom and L is 0.76(5) Å. Neither is an acceptable position for the proton and neither seems a very plausible position for the local electron-density maximum at, or very near to, the nucleus of the hydrogen atom.

The following interpretation of results such as those depicted in Figure 1.2(b) seems tenable. As is well known (see, e.g., HB. 1, Section 1.2.3), x-ray analysis which is otherwise precise always locates a hydrogen atom too close to the carbon, nitrogen or oxygen atom to which it is covalently bound. This is illustrated in Figure 1.4(a)*, which represents the $(F_X - F_N)$ 'difference' map in the region of a long hydrogen bond. (F_X is the x-ray structure factor observed; F_N that calculated, for x-rays, from the neutron-diffraction parameters of all the atoms.) The peak is ~0.7 Å from the right-hand atom, which is too close to be the true position of the hydrogen atom. Such errors are explained by the *asphericity effect*[35], though in an exaggerated form in this case since the bonding hydrogen atom has been included in calculating F_N. For strong practical reasons, x-ray analysis must always be organised on the assumption that the atoms are spherical masses of electron density. Such an assumption is not strictly valid (see Coppens, Chapter 2) and, although it works remarkably well in many cases, it fails particularly badly for a hydrogen atom bonded to an electronegative neighbour. For optimal matching of the actual, aspherical electron density round the hydrogen nucleus, the spherical-model atom has to be displaced nearer to the heavier atom. Now in regions including a symmetry element of the crystal, symmetry is built into any sort of structure refinement including a Fourier synthesis. The asphericity effect, forced to act both ways by the overall symmetry, will tend to pull apart any mass of electron density at the bond centre. It may produce the artefact illustrated in Figure 1.2(a). In Figure 1.4(b), we have forced symmetry on 1.4(a) and the result is very similar to the KKM effect.

Small errors in scaling our observed structure factors may have a large effect on the amount of electron density to be disposed of at our centre of symmetry, or other special position. So the exact type of effect produced is sensitive to scaling errors (see Coppens, Chapter 2).

Without any doubt, the three-dimensional map revealed in Figures 1.2(a), 1.2(b) and 1.2(c) is loaded with information about the electron-density

* Figure 1.4(a) is based on a photograph kindly supplied by Dr. J. O. Thomas of Uppsala. It actually covers an N—H···O bond, and it is an $(F_X - F_N)$ map, the positions of the atomic nuclei having been found by ND. A similar map for an O—H···O bond would have been more appropriate for our present purposes but Thomas' map has been used because it is based on very precise work. So far as the relevant details are concerned, the 'difference' map at a rather long O—H···O bond would be very similar. Figure 1.4(b) is a symmetrised map, obtained by averaging 1.4(a) with its own inversion about the mid-point; negative contours have been omitted for clarity in this case.

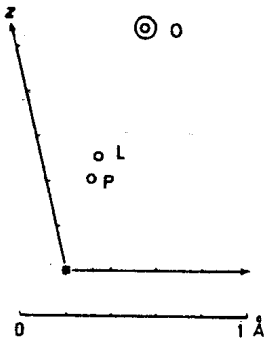


Figure 1.3 Some details of the hydrogen bonding in hydrazinium hydrogen oxalate; relative positions found for the oxygen atom (O), and for the electron density associated with the hydrogen atom (L) as found by least-squares analysis and (P) from the peak featured in Figure 1.2(b)

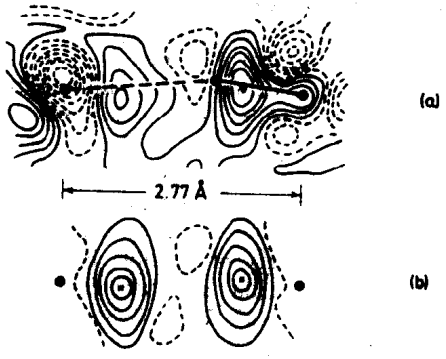


Figure 1.4 (a) The electron-density 'difference' distribution at a rather long hydrogen bond. (Zero and negative levels are shown by broken contour lines.) (b) Symmetrised version of (a). [The positions found by ND for the nuclei are marked by small filled circles; negative levels are omitted in (b).] [Based on work by Thomas —details in the footnote to p. 10]

distribution in a short 'symmetrical' hydrogen bond. The information is disguised, however, and the disguise is hard to penetrate. It should not be taken as a direct indication of the position, or positions, of the hydrogen atom.

Figures 1.2(d), 1.2(e) and 1.2(f) were derived in a similar way from the x-ray work on the deuteriated compound. Though the space group was now the unsymmetrical $P2_1$ the model of disordered 'half-deuterium' atoms was used as the basis for this 'difference' synthesis. Unlike the distribution explored in the upper half of Figure 1.2, there is now no constraint requiring strict centrosymmetry. Nevertheless, because all the heavier atoms are very close to the symmetrically related pairs of positions required by $P2_1/m$, there is a bias towards symmetry in the difference distribution as can be seen. The ODO bond in $[N_2D_5^+][DC_2O_4^-]$ appears to be unsymmetrical. Whether it is statically so (as we can symbolise by writing the formula O—D···O), or disordered with different proportions of the arrangements O—D···O and O···D—O, is uncertain. Certainly, when we ask what the lower half of the diagram tells us about the real position of the deuterium atom, we may well conclude that the disguise is even more impenetrable.

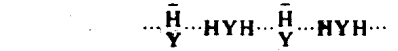
1.5.4 Neutron-diffraction studies of two 'super-acid' salts

The acid salts of the *dibasic* acids considered in the previous sections are normal in the sense that their existence is envisaged in elementary chemical theory: $H_2Y \rightarrow MHY \rightarrow M_2Y$. Acid salts of monobasic acids, on the other hand, are anomalous; HX should yield a salt MX, but not MHX_2, which in the elementary context can be regarded as a 'super-acid' salt of HX. Similarly, super-acid salts of dibasic acids are very common; the tetroxalates, $MH_3(C_2O_4)_2{\cdot}2H_2O$, are a long familiar example. Two super-acid salts from the dicarboxylic acid series have recently been examined by ND. They are both represented by the formula KH_3Y_2, H_2Y being malonic acid in one case[36] and succinic in the other[37].

Discrete H_2Y molecules and HY^- ions can be characterised in each salt, so that they are stoichiometrically identical, i.e. $K^+HY^-{\cdot}H_2Y$, but their crystal structures are wholly different. They are two more examples illustrating the almost infinite variety of possible hydrogen-bonding schemes[38] and how the details of a particular structure depend on a whole range of intermolecular, and intramolecular, forces, whose final effect is well beyond our present powers of prediction.

As in most acid salts of dicarboxylic acids, there are infinite chains of hydrogen-bonded units, such as those schematically illustrated in HB. 1, Section 1.4.2, structures (4)* and (5), though here without any participation of crystal symmetry in the chains. In the dimalonate[36], the chains consist of alternate H_2Y molecules and HY^- ions, and the situation may be stylised as in (4). The two O—H···O bonds donated by each HYH are non-equivalent. Their geometries (O···O, O—H and O—H···O) may be expressed as 2.543(8), 1.050(12) Å, 172° and 2.554(7), 1.018(12) Å, 163°, respectively.

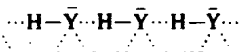
* Some of the symmetry symbols were accidentally lost during the final printing of structure (4).



(4)

The proton at one end of HY^- is donated to the carboxylate residue at the other and the six atoms of the ring thus completed are nearly co-planar. The intramolecular O—H···O bond has the dimensions 2.513(9), 1.023(14) Å, 155°.

In the disuccinate[37], the main chain consists only of HY^- ions linked by a single type of bond [2.579(9), 1.009(12) Å; 178°]. In a manner suggested by (5), the H_2Y molecules hang as festoons from the main chain. The two bonds



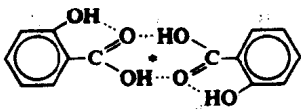
(5)

attaching H_2Y to the chain have the dimensions 2.573(11), 0.991(12) Å, 163° and 2.630(10), 0.996(15) Å, 172°.

All the unsymmetrical hydrogen bonds along these two types of chain are significantly longer than the symmetrical bonds along the chains in the simple (KHY) acid salts of malonic and succinic acids (see HB. 1, Table 1.4).

1.6 SALICYCLIC ACID AND α-RESORCINOL

Recent ND work throws light on the intramolecular hydrogen bond in salicyclic acid[39]. The dimer (6), in which the asterisk marks the position of a



(6)

crystallographic centre of symmetry, was one of the first systems in which hydrogen atoms engaged in hydrogen bonding were located from electron-density 'difference' maps (Cochran, 1953). The detailed geometry of the intramolecular bond is pictured in Figure 1.5, which is based on the ND study. Were we to ignore the proton, whose exact position was hitherto uncertain, the O(2)···O(3) distance corresponds to a rather strong hydrogen bond; for instance, it would be judged to be much stronger than the bond in ice and about as strong as the intermolecular O—H···O bonds which hold the dimer together. However, we then see that the C—O(3)···O(2) and C—O(2)···O(3) angles, each less than 90°, are very unfavourable. Location of the proton, as shown in the diagram, now enables us to examine the consequences of this misfit in detail; the O(3)—H distance and the C—O(3)—H angle differ hardly at all from those in the molecule of gaseous phenol, while the O(3)—

H···O(2) angle is far below the optimum (180°) for hydrogen bonding. On the other hand, H···O(2) is much less than the sum (2.4 Å; see the footnote to p. 19) of the van der Waals' radii of hydrogen and oxygen. The general impression is of a strong repulsion between H and O(2) only just compensated by electrostatic attraction. The proton must lie somewhere on the circle it generates when O H is rotated about C—O. It finds a position of minimum energy at the place shown in the diagram, only about 0.04 Å from the mean plane of the other five atoms of the chelate ring. There is, perhaps, no very positive act of bonding.

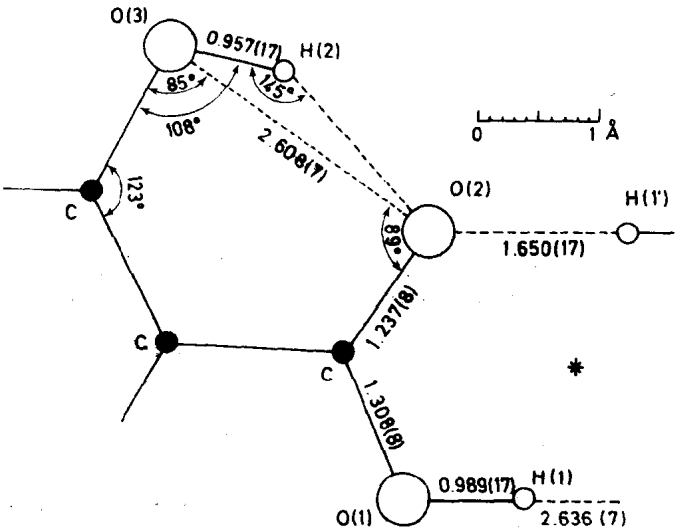


Figure 1.5 Some geometric details of the hydrogen bonding in salicyclic acid dimer as found by ND. (Distances in Å, with standard deviations in parentheses; the asterisk marks the position of a centre of symmetry)

Nakamoto, *et al.* drew attention[40] to a close inverse correlation between the overall length of an O—H···O bond and the decrease ($\Delta\nu$) in the O—H stretching frequency below that of an unperturbed hydroxyl group (~3700 cm^{-1}). In the spectrum of solid salicyclic acid, there are two frequencies due to O—H stretchings at 3225 and 2564 cm^{-1}. There are the two hydrogen bonds with O···O equal to 2.636 and 2.608 Å. The allocation must be anomalous. The lower frequency has to be associated with the longer intercarboxyl bond since there is a band at 2630 cm^{-1} in the spectrum of the methyl ether of salicyclic acid, while the higher frequency has to be associated with the shorter bond since methyl salicylate has a band at 3220 cm^{-1}. In a nearly straight bond, a $\Delta\nu$ value of 475 cm^{-1} would correspond to an O···O distance of 2.8 Å. It indicates a weak bond, which is undoubtedly true in this case, despite an O···O distance of only ~2.6 Å.

The same workers[39] have reported a precise ND analysis of *α*-resorcinol (*m*-dihydroxybenzene), one of the earliest hydrogen-bonded structures to be studied by x-rays (Robertson, 1936). There are two rather weak intermolecular

hydrogen bonds with the geometries O···O = 2.717(5), O—H = 0.989(5) Å, O—H···O = 175.9°, and 2.731(5), 0.991(7) Å, 165.7°

1.7 HYDROGEN BONDING IN HYDRATED COPPER ACETATE

X-Ray work by van Niekerk and Schoening (1953) showed that copper(II) acetate monohydrate contained the dimeric molecule $Cu_2(C_2H_3O_2)_4$, this affording one of the first examples of a direct metal–metal bond. This crystal has now been studied by precise ND analysis[41]. [The Cu—Cu distance is now refined to 2.6143(17) Å.]

The water molecule fits into the structure in a way typical of salt hydrates (see Section 1.3). The hydrogen-bonding scheme involves eight-membered rings like that illustrated in Figure 1.6. Formally, such a ring closely resembles the ring closed by the pair of hydrogen bonds in a carboxylic acid dimer [see structure (6) and Figure 1.5]. In copper acetate there are, in fact, two independent types of eight-membered ring. One type lies about the centre of symmetry, marked by an asterisk in the diagram. For this ring, the resemblance to (6) is increased by the circumstance that all eight atoms are nearly co-planar. This is a necessary condition in doubly hydrogen-bonded carboxyls.

However the similarity, though pleasing to the eye, must not be taken too seriously. The dimensions given in the diagram show that the hydrogen bonding in this case is very weak; O—H···O is nearly 0.3 Å longer than in typical carboxylic acids, and the condition of co-planarity is not nearly so stringent. The rings of the second type are chemically identical with that shown in Figure 1.6 and most of the dimensions are about the same. But

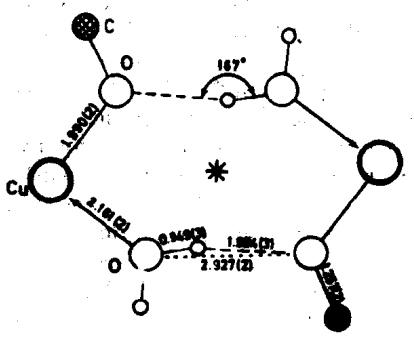


Figure 1.6 Part of the hydrogen-bonding pattern in hydrated copper acetate as found by ND. (Distances in Å)

instead of a centre, a crystallographic twofold axis passes through the middle of the ring and the eight atoms are far from co-planar. Four atoms constituting each half of the ring do indeed lie in the same plane, but the ring is buckled through ~62° about a line joining the oxygen atoms of the two water molecules. Evidently a ring of the sort shown in the diagram is compliant in adapting itself to its environment.

1.8 PRECISION NEUTRON-DIFFRACTION ANALYSES OF AMINO ACIDS

1.8.1 General

The late Walter Hamilton initiated at the Brookhaven National Laboratory a project for the 'precision neutron-diffraction structure determination of protein and nucleic acid components'. This is enabling the protons to be located with standard deviations normally in the range 0.001–0.003 Å, and in most cases it has also improved the precision with which the heavier atoms had been found by x-rays. Some of the advantages of ND were summarised in HB. 1, Section 1.2.2. One advantage, not mentioned, is that the vibrational behaviour of atoms is more directly and more accurately studied by ND. Neutrons are scattered by the atomic nuclei which are virtually points so far as thermal neutrons are concerned. X-Rays, on the other hand, are scattered by the total electron density around the individual atoms in the crystal. When the density around a given atom is found to be non-spherical or distorted in any other way from the ideal shape of the atom, it is hard to differentiate distortion due to bonding from that due to the various modes of vibration which the atom may be undergoing (see Coppens, Chapter 2). For this reason, amongst others, ND is inherently a more accurate method for studying crystal structure in all its aspects — always provided we restrict the word 'structure' to the description of the positions and motions of the atomic centres only.

Twelve papers have been published from Brookhaven at the time of writing. They deal with (Part I) L-alanine[42], (II) diglycylglycine hydrochloride hydrate[43], (III) *a*-glycine[44], (IV) orthorhombic L-histidine[45], (V) L-arginine dihydrate[46], (VI) L-asparagine hydrate[47], (VII) L-lysine hydrochloride dihydrate[48], (VIII) *β*-L-glutamic acid[49], (IX) 4-hydroxy-L-proline[50], (X) L-tyrosine and its hydrochloride[51], (XI) L-serine hydrate and DL-serine[52], and (XII) the base-pair 9-methyladenine–1-methylthymine[53]. In addition, from Bombay, there are papers describing ND work on L-glutamic acid hydrochloride[54] and the aminosulphonic acid L-cysteic acid monohydrate[55].

These papers are a mine of precise information of many kinds. In this short review we shall confine ourselves to matters directly, or indirectly, connected with hydrogen bonding. In nearly every case, all hydrogen atoms attached to oxygen or nitrogen take part in hydrogen bonding, in accord with Donohue's rule: 'A structure (is most stable) in which all possible hydrogen bonds are formed. . . . It is exceedingly rare to find an "unused" hydrogen atom'[56]. Dihydrated L-asparagine involves an exception. The protons of its *a*-amino group are unused although the group accepts a proton from an $\rangle$NH group of another molecule.

An elementary structural problem with amino acids concerns the particular tautomeric form adopted by the molecule. In most cases the zwitterionic structure (7) was inferred long ago from indirect evidence, subsequently confirmed and amplified by traditional x-ray analysis. Consideration of structures (8) and (9), for instance, suggests that the carboxyl group should