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Hydrogen Bonding, with Special Reference to O··H··O

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'One of the difficulties attending investigations of the hydrogen bond is that reliable determinations of the position of the hydrogen atom are difficult to make.'
(J. M. Robertson, *Organic Crystals and Molecules*, 1953)

1.1 INTRODUCTION AND BACKGROUND

1.1.1 Origins

Hydrogen bonding is used to describe a situation resulting from the process

$$A{-}H \quad + \quad B \quad \rightarrow \quad A{-}H\cdots B,$$

whereby the entities AH and B become attached to one another. It is a weak form of valency bonding, with an energy usually less than 10% of that associated with ordinary covalency. A and B, whether they be isolated atoms or parts of larger molecules, must be electronegative. Relatively strong hydrogen bonding is largely confined to cases where A and B are atoms of the three most electronegative elements – fluorine, oxygen and nitrogen. Though weak bonding sometimes occurs with chlorine, or bromine, or sulphur – even with carbon, when it is attached to very electronegative atoms – the interaction is then feeble and hard to distinguish from the general dispersion forces that operate between contiguous molecules.

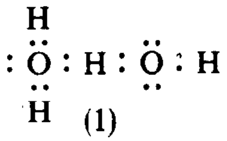
This Review is mainly concerned with systems in which A and B are both oxygen atoms.

From another, though related, point of view AH must be acidic; B must be basic. Within limits, increasing acid and basic strength favours hydrogen bonding. But, if the strengths become too great, an electrovalency will result:

$$A{-}H \quad + \quad B \quad \rightarrow \quad A{-}H\cdots B \quad \rightarrow \quad \bar{A} \quad + \quad H{-}\overset{+}{B}$$

Though the name, hydrogen bond, is more recent, the phenomenon was first explicitly recognised in the first decade of this century. For the roots of the concept we need to go back at least another century to the recognition of water as a remarkably unorthodox chemical compound. The simplest illustration of this is the boiling point, which is strangely high for material of molecular weight 18. No other material with a molecular weight less than 20 is not gaseous at ordinary temperatures. When physical chemistry began to develop, molecular association was recognised as the general cause of the abnormal behaviour of water in particular, and of other liquids in a lesser degree. These were usually compounds whose molecules included hydroxyl or amino groups: ROH, RNH_2, etc. Association could be correlated with the presence of such polar groups in the molecule.

The abnormality disappeared when the hydrogen atoms of the OH or NH_2 groups were replaced by a methyl group, for example. When the hydrogen atoms of water are so replaced, to yield dimethyl ether, the boiling point drops by 124 °C, despite more than a doubling of molecular weight. Many observations of this sort implied that the hydrogen atom is an essential link in the machinery of molecular association. By about 1907 certain chemists were bold enough to write formulae which carried the disturbing implication that hydrogen could behave as if it were bivalent: for instance, $F—H\cdots F$ or $H_2O\cdots H—O—H$. The meaning of the dotted line was obscure, though not any more so – at the time – than that of the ordinary chemical bonds. Then in 1920, Latimer and Rodebush wrote the electronic formula (1):



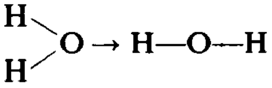
$$\overset{\textstyle H}{\underset{\textstyle H}{:\ddot{\underset{\cdot\cdot}{O}}:}}H:\ddot{\underset{\cdot\cdot}{O}}:H$$

(1)

The hydrogen bond was explicit, though this formula could hardly have been taken quite literally even in 1920.

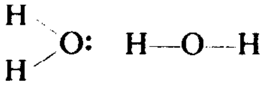
1.1.2 A note on the mechanism of hydrogen bonding

The causes of hydrogen bonding came within range of speculation, at the atomic level, after 1927. The first type of explanation, which we may term 'chemical', arose from a formal resemblance between the holding of two atoms or groups together by a hydrogen atom and coordination through a metal atom. Just as the complex $[Co(NH_3)_6]^{3+}$ was attributed to dative covalency ($H_3N \rightarrow Co$), so a dimerised water molecule might be formulated as



This was quickly rejected because the 1s orbital of hydrogen cannot accommodate two pairs of electrons*.

Proponents of a chemical mechanism then invoked the concept of resonance which Pauling had popularised. The hydrogen bond between (say) two water molecules might owe its stability to hybridisation between two electronic formulations (2a) and (2b):



(2a)

(2b)

This idea fell into disfavour when it was pointed out that form (b), as we have drawn it, would have a much higher energy than (a). Resonance stabilisation

---

*The contingency amendment, that the donated electron pair went into a second-shell orbital, was summarily rejected because this would be at too high an energy level. But Dr. Brian Webster opines that this objection is not necessarily so valid as it appeared to be in 1935.

would be significant only if the proton were centrally placed between the two oxygen atoms, or nearly so. This is certainly not true of most hydrogen bonds. However, in this Review we shall give prominence to some crystals which do have symmetrical, or quasi-symmetrical, O···H···O bonds. For such bonds, the resonance mechanism – or its more modern counterpart – may be important (see Section 1.7.1).

The second type of explanation, which may be labelled 'physical', attributes hydrogen bonding to a straightforward, classical electrostatic force. In the A—H B system, AH is necessarily dipolar in the sense symbolised below; and B, for similar reasons, carries a negative charge – a full charge if it is an anion (as in HF_2^-), a partial charge if it is part of a larger molecule. When in the mutual orientation

$$\overset{\delta-}{\mathrm{A}}\text{—}\overset{\delta+}{\mathrm{H}}\quad\overset{\delta-}{\mathrm{B}}$$

an attractive force operates between A and B. One advantage of this scheme was that it lent itself to simple quantitative calculations. Provided secondary effects were neglected, quite elementary calculations gave bonding energies of correct order of magnitude, at any rate for weak hydrogen bonds.

The theory of hydrogen bonding is surveyed in the standard monographs by Pimentel and McClellan[1] and by Hamilton and Ibers[2]. From a specialist position there is a recent review by Bratož[3]; and Murrell[4] has written a more elementary account for the general reader.

The molecular interactions we classify as hydrogen bonds cover a wide range, from the minimal, or notional, attraction in (say) N—H···Cl, to the strongest bonding in $[\mathrm{F}\text{—}\mathrm{H}\text{—}\mathrm{F}]^-$. Each exists in a molecular system that is stable in its own right. As Murrell has emphasised, it is artificial to divide the total molecular bonding energy amongst separate bonds, each with a bonding energy resolvable into components due to distinct forces. It is therefore dangerous to think we have clarified the situation when we say that the weak N—H···Cl bond and the very strong F—H—F differ merely in the relative participation in them of electrostatic and delocalisation forces. Nevertheless it comes naturally to many chemists to do just this.

1.1.3 Infrared spectra and hydrogen bonding

In this Review we are concerned with hydrogen bonding as it may be studied by crystal-diffraction methods. However, other methods require brief mention, one such being infrared spectroscopy.

An unperturbed hydroxyl group in a gaseous molecule is associated with a stretching frequency, which appears as a sharp absorption band centred near 3700 cm^{-1} (1.1×10^{14} Hz). The spectra of solutions of hydroxylic compounds in an inert solvent show a similar peak. When the hydroxyl enters into hydrogen bonding, this feature changes notably. The peak moves to lower frequency; it becomes less sharp; it also becomes broader, with enhancement of its integrated intensity. These changes are progressive with increasing strength of the hydrogen bonding. For instance, there is a smooth, inverse correlation between frequency and strength as indicated by the overall shortening of the O—H···O distance[1,2]. It can be followed down to frequencies of about 2000 cm^{-1}.

To get access to a range of measurable hydrogen bonds, we need to study crystalline solids. The interpretation of the spectra of solids is much more difficult than for gases. But it is clear that shortening of the bond is associated not only with a lowering of frequency, but also with more profound changes of spectrum in very strong bonds. This subject has been extensively studied by many authors, and reference may be made to recent articles by Hadzi[5] and Sheppard[6]. An example is shown in Figure 1.1, which is concerned with acetic acid and its sodium salts. The first spectrum (a) is that of solid acetic acid, in which the molecules are linked into infinite chains by moderately strong hydrogen bonds (3).

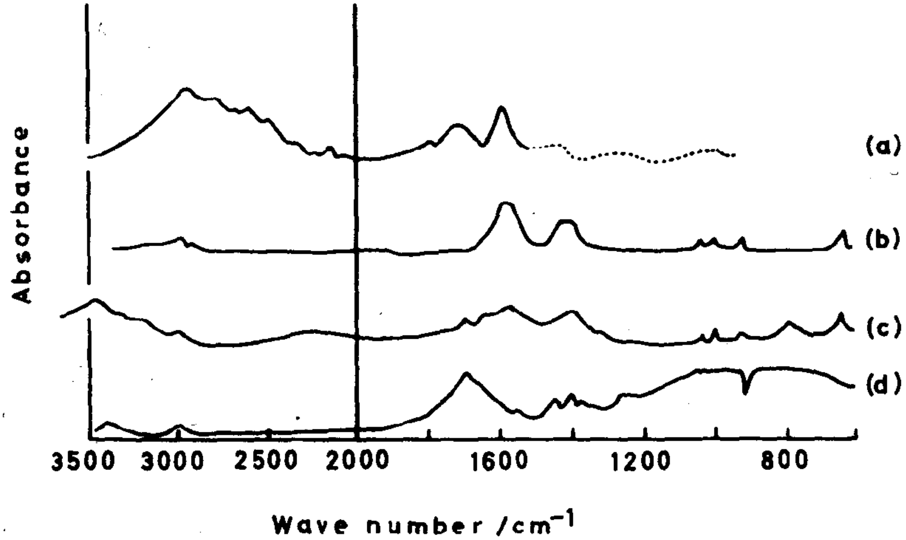
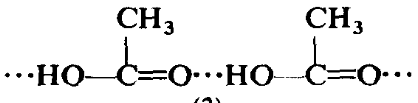


Figure 1.1 Infrared spectra of acetic acid and some salts: (a) crystalline acid; (b) sodium acetate; (c) sodium acetate trihydrate; (d) sodium hydrogen diacetate



$$\cdots HO-\overset{CH_3}{\overset{|}{C}}{=}O\cdots HO-\overset{CH_3}{\overset{|}{C}}{=}O\cdots$$

(3)

The large peak ~3000 cm^{-1} is attributable to the O—H stretching. The ~700 cm^{-1} lowering of frequency is typical. Figure 1.1(b) gives the spectrum of the anhydrous sodium salt, (c) that of its trihydrate. In (b) there is no peak attributable to OH: in (c) there is a broad peak near 3500 cm^{-1}, due to hydrogen-bonded water molecules. Figure 1.1(d) shows the spectrum of the *acid salt*, $NaH(CH_3CO_2)_2$, to which we shall refer later. This is characteristic of the spectra given by systems (particularly, but not necessarily, crystalline) with very strong O···H···O bonds. They have been classified by Hadži[5] as Type (ii) spectra. Sheppard has described them as 'remarkable spectra by any standards'. Their principal peculiarities are two: there is no peak unambiguously attributable to O—H stretching, though the peak near 1700 cm^{-1} in this case might possibly involve interaction of this mode with the C—O stretching; instead, there is a vast region of general absorption culminating near 900 cm^{-1}, sometimes known as the 'D band'. These features of Type (ii) spectra are diagnostic of very strong hydrogen bonding, and have led to successful predictions of unknown crystal structures[7].

1.2 CRYSTAL-STRUCTURE ANALYSIS AND HYDROGEN BONDING

Some of the earliest direct evidence of hydrogen bonding was derived from the x-ray analysis of crystals[8, 9]. It is still an important method. In principle it enables us to assign relative positions to all the atoms; when applied to a molecular crystal, it reveals hydrogen bonds *in situ*, whether between different molecules or between different parts of the same molecule.

1.2.1 x-Ray study of hydrogen bonds

x-Rays are scattered by the electron-density condensation around an atomic nucleus. Atoms therefore show up more prominently the greater the atomic number. Because the electron density associated with a hydrogen atom is low, hydrogen atoms are more difficult to find. In early x-ray work they were not located at all, and the evidence for hydrogen bonding was to that extent incomplete, though convincing enough. The typical experimental finding was a pair of oxygen atoms too far apart for them to be directly linked by covalency, yet too close together for them to be non-bonded. The Pauling value for the van der Waals radius of oxygen is 1.40 Å*, the covalent radius 0.66 Å (though the O—O distance in the hydrogen peroxide molecule is 1.50 Å). Thus any pair of atoms separated by a distance in the range 1.5–2.8 Å would be suspected of some form of liaison weaker than normal covalency. In practice distances significantly shorter than 2.4 Å are unknown. Hydrogen bonding would then be indicated by O···O distances between 2.4 and 2.8 Å.

The upper limit needs some increase to meet the following consideration. If there is to be any bonding, a hydrogen atom must be attached to one of the oxygens. Supposing this to be—as it must—nearly on the O···O line, we must add to the van der Waals radius of the acceptor oxygen atom the O—H distance at the donor, plus the van der Waals radius of the hydrogen; these amount, respectively, to ~1.0 and ~0.9 Å, giving a total O···O distance of 3.3 Å for the upper limit. (However this has been questioned by Bellamy[10].)

Application of this criterion to the results of x-ray work revealed many examples of O—H···O bonding, overall distances being mainly in the range 2.5–3.2 Å. Bonds with O···O > 2.75 Å came to be called 'long', whilst those between 2.5 and 2.6_5 Å were 'short'. We now have plenty of examples of bonds with O···O between 2.4 and 2.5 Å. These have had to be termed

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*As is still the almost universal practice amongst crystallographers, we express interatomic distances in ångstroms: 1 Å = 100 pm.

'very short' hydrogen bonds. They are of particular concern for us in this Review.

At the level of x-ray structure analysis implied above, participation of the hydrogen atom was deduced by inference. As there was always chemical evidence for the presence of hydrogen, and in a stereochemically reasonable position, the inference was strong. Improvements in x-ray methods substantiated the inference. In a modern analysis, based on more accurate intensity measurements, the small electron-density peak due to hydrogen can normally be detected, at any rate in crystals without elements of high atomic number. Such peaks show up better in the electron-density 'difference synthesis'—a Fourier series whose coefficients are $(F_o - F_c')$, where F_o is the observed structure amplitude (suitably phased) and F_c' is the structure factor calculated for all the heavier atoms, but omitting hydrogens. An example is given in Figure 1.2. With the mountains taken out, the foothills show up more prominently.

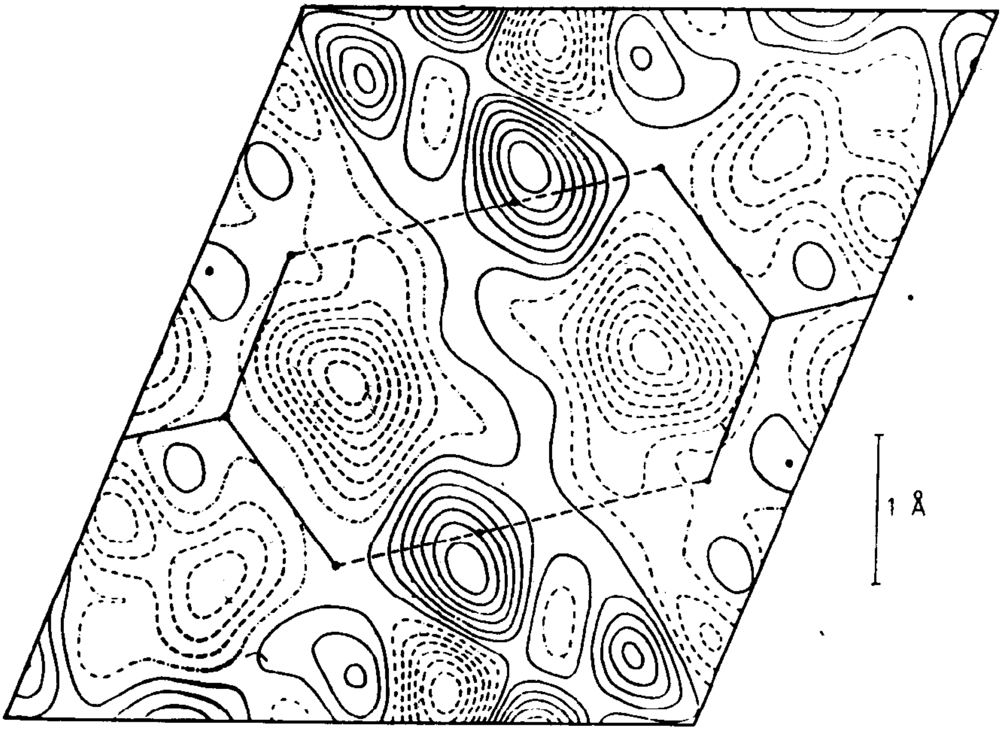

Figure 1.2 Electron-density 'difference' synthesis of the region between two carboxyl groups, based on the x-ray study of β-succinic acid (Negative contour lines are broken. The positions of the carbon and oxygen atoms of the carboxyl groups are indicated)
(From Robertson, J. M.[9], by permission of the Royal Society)

1.2.2 The study of hydrogen bonds by neutron diffraction

Neutrons are scattered by the atomic nuclei. Though the scattering powers for 'thermal' neutrons ($\lambda \sim 1.0$ Å) show a general increase with rising atomic number of the scatterer, the increase is gradual and often over-ridden by special effects with particular nuclides. Table 1.1 compares some neutron-scattering factors with (average) values for x-ray scattering. For convenience, different kinds of units are used. With x-rays it is natural to base the scattering power on the number of electrons in the atom. The scattering effect of an atomic nucleus is expressed as an amplitude, which is of the order of the nuclear diameter ($\sim 10^{-12}$ cm). Thus, the amplitude for ^{12}C is 0.66×10^{-12} cm. It has recently become conventional to use a unit 10 times smaller than 10^{-12} cm. In SI this is defined as 10^{-15} m, and known as the fermi. The negative amplitude for H, and a few other nuclides, merely signifies that the act of scattering involves an unorthodox change of phase of the neutron-wave. It results in negative Fourier peaks for hydrogen atoms.

Table 1.1 Comparison of x-ray and neutron scattering factors

	H	D	C	O	F	Cl	Br
x-Rays (electrons) at $(\sin\theta)/\lambda = 0.3$	0.25		2.5	4.1	5.2	9.4	23.8
Neutrons (fermis)	−3.8	+6.5	+6.6	+5.8	+5.5	+9.9	+6.7

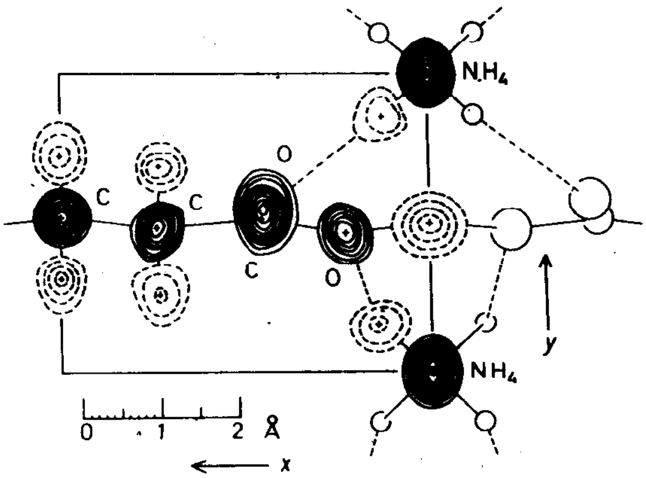

Figure 1.3 Neutron-scattering density in ammonium hydrogen glutarate, seen in the *c*-axial projection (The region covered includes rather more than half of a hydrogen–glutarate residue, $O_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2$, linked at each end to a similar residue by an O···H···O bond across a twofold axis, and two independent ammonium ions, which form N—H···O bonds to neighbouring oxygen atoms. Negative contours are represented by broken lines. See reference 11.)

We see that in x-ray analysis a hydrogen (or deuterium) atom is unfavourably recorded, compared with oxygen, by a factor of about 16. With neutrons. ordinary hydrogen is inferior to oxygen only by a factor of <2; whilst, if we use a deuteriated crystal the hydrogen is superior. There is an additional effect that makes deuteriation technically beneficial. Ordinary hydrogen nuclei produce a high background intensity because protons may scatter neutrons incoherently. This is avoided with deuterons. Figure 1.3 reproduces a neutron-scattering Fourier projection in which the positions of protons round two ammonium ions, each hydrogen-bonded to four oxygen neighbours, are clearly seen, as well as other hydrogen atoms[11].

1.2.3 Errors in hydrogen positions determined by x-rays

For reasons implied in Section 1.2.2, hydrogen atoms are much more precisely located by neutrons. In analyses of comparable quality, standard deviations of hydrogen positions based on x-ray intensities will be about ten times larger than those based on neutron intensities. (Against this neutron diffraction suffers two disadvantages: it is much more expensive, and it requires much larger crystals, which are often difficult to procure.)

The positions found by x-rays do not agree with those found by neutrons. In almost all cases A—H distances appear to be shorter by x-rays, and the difference is probably greater the more electronegative is A. This discrepancy is discussed by Hamilton and Ibers[2]. Recent analyses of glycollic acid, $CH_2OH{\cdot}CO_2H$, by x-ray[12] and neutron diffraction[13] illustrate this phenomenon particularly well. Some results are compared in Table 1.2*.

Table 1.2 Comparison of O—H distances (Å) in glycollic acid as found by analysis with x-rays (X) and neutrons (N)

Bond	1	2	3	4
X	0.934(25)	0.898(25)	0.819(26)	0.834(26)
N	1.003(2)	1.001(2)	0.971(2)	0.970(3)
Δ	−0.07	−0.11	−0.15	−0.14

These are typical differences; they are significant despite the higher uncertainty of the x-ray distances.

When we speak of the 'position of a hydrogen atom', we normally imply the position of the proton†. This is what neutron analysis finds. Associated with the proton there must be a local maximum of electron density. This maximum must coincide with the proton, or very nearly so. Allegedly, x-ray analysis finds it. But this may not be true, for the following reason. Because the hydrogen atom is near to its covalent, and electronegative, partner, the local electron-density cloud will be far from symmetrical. The model used for any atom, in structure refinement based on x-ray data, is a spherical electron-density condensation. (Any more sophisticated model is

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*Here, and elsewhere, we give standard deviations in parentheses. Thus 0.934(25 is short for the more conventional 0.934 ± 0.025. It is perhaps worthwhile to remind the reader that this is a measure of precision, not of accuracy. With some reservations, we may suppose the result unlikely to be in error by twice 0.025, and the true result very unlikely to be outside the limits 1.009–0.859. Not sensational news, in this case.

†More precisely, some sort of *mean* position. The differences between various sorts are not important in the context.

very difficult to handle.) The refinement procedure tries to fit this model to the non-spherical cloud implicit in the observational data. For a hydrogen it finds a 'best fit' when the sphere is displaced from the density maximum in a direction towards the more electronegative atom. The error (for we consider the x-ray result to be in error) will be greater the higher the electronegativity of the atom to which the hydrogen is covalently bonded.

1.3 THE GEOMETRY OF O—H···O BONDING

Conditions favourable to O—H···O bonding have been discussed by several authors, and their conclusions are summarised by Hamilton and Ibers[2]. The R—O—H angle is usually a little less than tetrahedral. This molecule will form a hydrogen bond with another oxygen atom, only if the O—H group points towards – or nearly towards – the acceptor atom. As hydrogen-bonding energies are not usually large enough to cause large changes in valency angles, this favourable orientation has to be achieved mainly by torsional adjustments. Exact alignment of O, H and O is not, of course, essential; but in strong hydrogen bonds O···H···O is always greater than (say) 160 degrees*. It is also advantageous if the conformational situation at the acceptor atom is such as to allow us to suppose that this atom presents a lone pair of electrons towards the donor.

In weaker hydrogen bonds these geometrical considerations become less important. In marginal cases the notion of a hydrogen bond ceases to have significance. The hydrogen atom of a peripheral hydroxyl group has to be somewhere. When circumstances do not allow it to form a palpable hydrogen bond, it may still minimise the total energy a little if it lies more or less in the direction of some rather distant negative atom.

Many, if not perhaps all, examples of the 'bifurcated' hydrogen bond can be explained away by an extension of the argument sketched in the previous paragraph. A proton may find a 'point of rest' – a point of minimum energy – more or less equidistant from two neighbouring acceptor atoms.

1.3.1 The Nakamoto–Margoshes–Rundle curve

In a very weak O—H···O liaison, the covalent bonding O—H is little affected, as is evidenced by the smallness of any change in the stretching frequency. The O—H will be more perturbed in a stronger liaison. It is intuitively reasonable to suppose that the O—H distance increases as O···O diminishes overall; and there is plenty of evidence to support this idea. The manner in which these distances may be inversely related is of interest.

A direct experiment in which the O—H distance is observed as a second oxygen atom approaches is impracticable. We have to depend on neutron-

---

*Histograms showing the frequency of occurrence of various O···H···O angles have been interpreted as showing a small preference for angles rather less than 180 degrees. It seems to the Author that this is based on a fallacy: if angles of 170, 180 and 190 degrees occurred with equal frequency, this could be misinterpreted to mean that 170 degrees was twice as common as 180 degrees.

diffraction measurements of the geometry at the hydrogen bonds in a series of different crystalline materials. For reasonable comparability the various hydrogen bonds should be in chemically similar situations. But this is impossible if we wish to cover a wide range of O···O distances. Consequently, a graphical plot of O—H *v.* O···O will yield a scatter of points, due partly to experimental errors, but—even if these errors could be eliminated—also to inherent differences in the O—H···O systems being compared. One of the first such graphs to be published was that of Nakamoto, Margoshes and Rundle (NMR)[14]. A later version, based on fuller experimental material, was given by Pimentel and McClellan[1]. We reproduce their (averaged) curve in Figure 1.4, the broken line. At its right-hand side, the curve has been drawn to converge on to a horizontal line at O—H = 0.96 Å—the bond-length in a gaseous water molecule. At the left-hand side, we show the straight line of slope 0.5 corresponding to truly symmetrical O···H···O bonds, supposing such bonds to exist. Similar graphs have been plotted for other hydrogen-bonded systems, such as F—H···F, N—H···O or O—H···N[1].

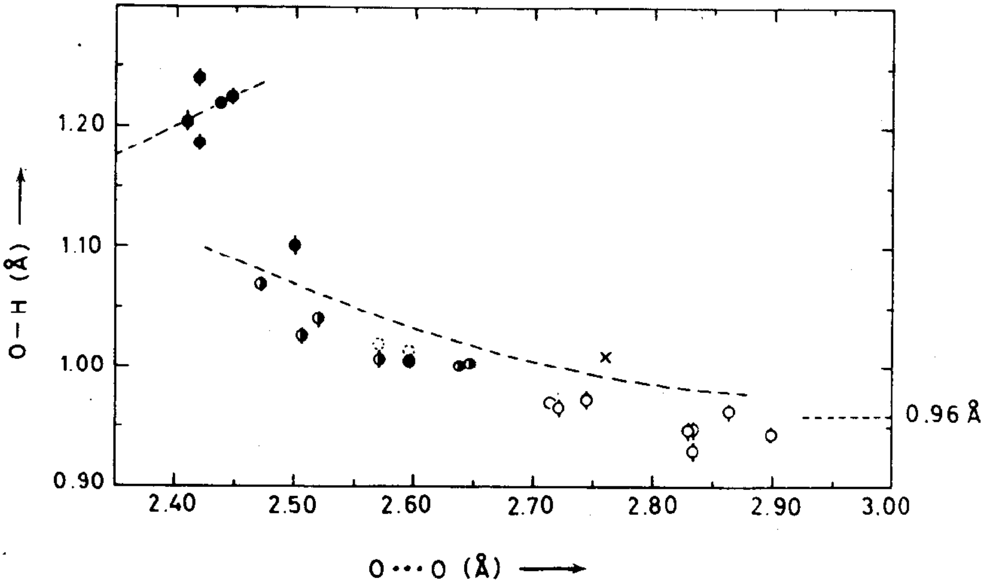

Figure 1.4 The Nakamoto–Margoshes–Rundle curve of Pimentel and McClellan[1] (broken lines), and some points from recent neutron analyses (The circles represent O···H···O bonds, and the vertical line in each the standard deviation of the O—H distance. The filled circles are for systems in which both donor and acceptor are carboxyl groups (or groups of similarly strong acidity); half-filled circles systems in which carboxyl is the donor; open circles systems in which it is the acceptor. The broken circles, in two cases, show the effect of applying an estimated correction for libration. The cross is for the O—D···O bonds in 'heavy' ice.)

For O···O > 2.6 Å the general trend of the NMR curve is well defined. At shorter distances the trend becomes less certain, and more interesting. Reliable experimental results are few in their region. Possibly we are approaching a catastrophic situation, where the O—H···O bond—rather suddenly, perhaps discontinuously—changes character and becomes O···H···O. In this Review we are particularly concerned with these short bonds.

In Figure 1.4 we have also plotted some recent results from fairly precise neutron-diffraction work (marked by circles). We have restricted the points to bonds where the O···H···O angle is greater than 160 degrees, and to systems in which a carboxyl group (or one of similar acidity) is involved as donor, or acceptor, or both. Though our sample is not large, we notice that it does not make a good fit with the Pimentel and McClellan version of the NMR curve. The points suggest that the curve ought to be pulled down in its central and right-hand parts, and to rise much more steeply to the left. The difference may be partly due to our restrictions on the choice of hydrogen bonds.

The O—H distances plotted are the values uncorrected for the effects of librational motion. The correction is small, and difficult to assess, between hydrogen-bonded molecules (see Section 1.6.4). If it had been applied, it would increase O—H, though not enough to reach the curve.

In heavy ice[15] the O···O distance is 2.76 Å and the mean O—D 1.00(1) Å if corrected for libration. This result is represented in Figure 1.4 by a cross, which fits the curve better.

1.3.2 The potential-energy diagram for O··H··O bonds

Relevant to our discussion is a graph representing the variation of potential energy as the proton moves along a straight line between two fixed oxygen atoms. Some conceivable situations are described by the curves of Figure 1.5. The first (a) could correspond to a long bond between a hydroxyl group and an uncomplicated keto group. The (mean) position of the proton lies at the lower minimum in the normal state: $-\mathrm{O}-\mathrm{H}\cdots\mathrm{O}{=}\mathrm{C}\!<$; at the higher minimum in the less stable tautomeric alternative: $-\bar{\mathrm{O}}\cdots\mathrm{H}-\overset{+}{\mathrm{O}}{=}\mathrm{C}\!<$.

A potential-energy curve of this type obtains in most O—H···O bonds. The second curve (b) corresponds to a situation where the bond, though still rather long, has exact, or virtual, symmetry. A familiar example, with virtual symmetry, is ice. There are alternative positions for the proton; diffraction methods find a statistical 'half-proton' in each[*].

As the overall O···O distance decreases, the energy barrier separating the double minima will diminish in height, as shown in (c), and ultimately disappear, leaving a single-minimum curve, which might be of the parabolic shape indicated by curve (e), or of the flattened shape (d). (There is now theoretical support for the sequence (c), (d) and (e) from quantum-mechanical calculations on simple model systems[16].) Curves (d) and (e) represent genuinely symmetrical O···H···O bonds, and correspond to the line of 0.5 slope at the left-hand side of Figure 1.4.

Curve (e) would apply to an ideally symmetrical bond, in which the

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[*] Such symmetry of the potential-energy curve in ice would be valid only in a restricted sense. Were a single proton to move to the other site, without sympathetic movements elsewhere in the crystal domain, it would find itself in an energetically less favoured situation.

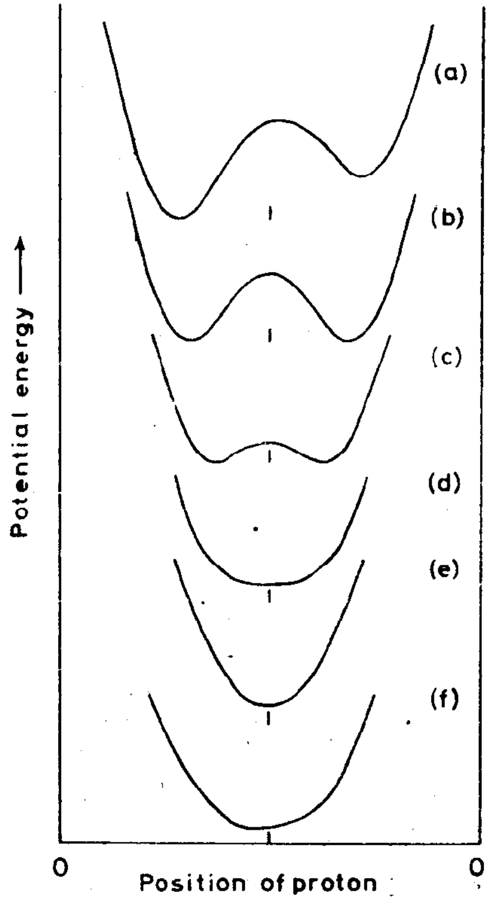


Figure 1.5 The variation of potential energy as a proton moves along the line between two oxygen atoms (The various curves correspond to different, hypothetical, situations.)

proton would vibrate harmonically about the mid-point. Somewhere between (c) and (e) a complication arises when the energy barrier is only about as high as the vibrational zero-point level. Such a situation may result in an effective potential-energy curve of the flattened shape drawn in (d); with the trough no longer parabolic, the vibration of the proton along the bond – an asymmetric stretching – will be anharmonic.

1.4 CRYSTALLOGRAPHICALLY SYMMETRICAL HYDROGEN BONDS

1.4.1 Acid salts of monobasic acids

The great majority of hydrogen bonds that have been studied by crystal-diffraction methods do not possess any symmetry by virtue of their crystallographic situation. An important, and long-recognised, exception is the

F—H—F bond in the bifluorides of some alkali metals. We shall return to this later (Section 1.5). It was only in 1949 that analogously symmetrical O—H—O bonds were first reported[17,18]. They were in structures where the two participating oxygen atoms are related by a crystallographic symmetry element, such as a centre of inversion. Granted that a hydrogen bond exists between them (which must be so with $O \cdots O \approx 2.5$ Å), the hydrogen atom can (without finesse) only be placed at the mid-point.

A typical example, which has been extensively studied[19–24], is potassium hydrogen bisphenylacetate, KHX_2, where HX = phenylacetic acid, $C_6H_5{\cdot}CH_2{\cdot}CO_2H$. According to elementary theory, this monobasic acid should form only the one series of neutral salts (e.g. KX). In fact, acid salts of monocarboxylic acids are common, a number of examples (accidentally discovered) being recorded in the literature[25], and many more being preparable.

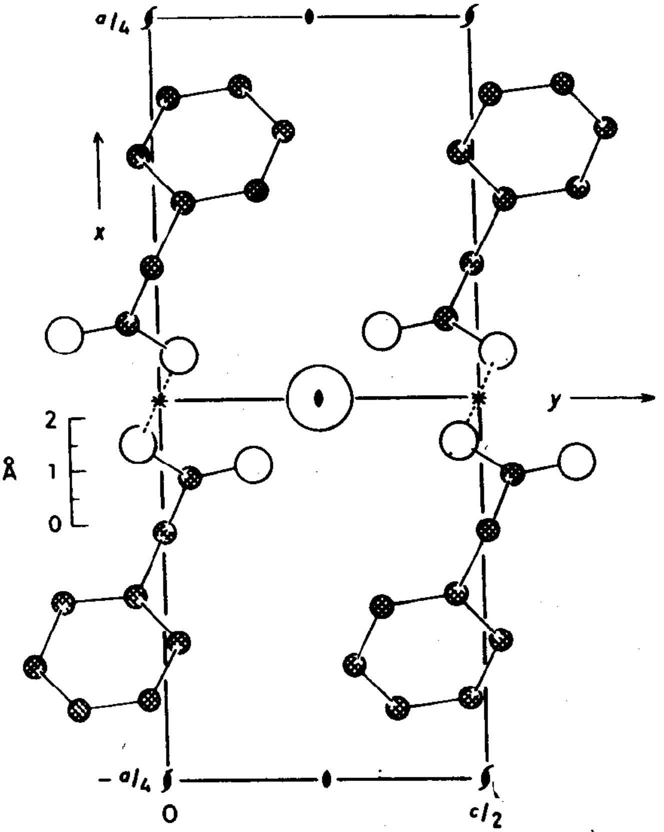


Figure 1.6 The crystal structure of potassium hydrogen bisphenylacetate, in its *b*-axial projection[19] (The larger open circles represent K^+ ions, the smaller, oxygen atoms; the cross-hatched circles, carbon. The short $O \cdots H \cdots O$ bond lies across a centre of symmetry denoted by an asterisk.)

Potassium hydrogen bisphenylacetate crystallises in the monoclinic space group *I*2/*a* (No. 15). As No. 15 is an eighth-order space group, and as the unit cell contains four KHX_2 units, we have the implications that the asymmetric unit is only half of KHX_2, that the potassium ion and the acidic hydrogen atom are in positions of special symmetry and that the two

X units of the formula are crystallographically equivalent. x-Ray structure analysis led to the results represented in Figure 1.6. The two phenylacetate residues are related by a centre of symmetry, at which the hydrogen atom is effectively situated: the $[X\cdots H\cdots X]^-$ unit is thus centrosymmetric, with $O\cdots H\cdots O = 2.443(4)$ Å. This is a very short bond.

Acid salts of stoichiometric formula MHX_2, where M is a univalent cation, whose crystal structures turn out to be of this symmetrical character, have been classified as Type *A*[26,27]. Their structures are more properly formulated as $M^+ (XHX)^-$. (In contrast, some other acid salts have crystal structures in which X^- and HX can be distinguished, so that $M^+X^-\cdot HX$ would be a more appropriate formula. These are classified as Type *B*.)

Study of Type *A* acid salts of a number of monocarboxylic acids, by x-ray and neutron diffraction, shows them all to contain very short $O\cdots H\cdots O$ bonds. Results from the structure analyses that have been carried out with moderate precision are collected in Table 1.3. Duly weighted according to the standard deviation of each measurement, the results lead to the mean value $O\cdots O = 2.447(2)$ Å. Although there is no *a priori* reason for supposing that all these hydrogen bonds have exactly the same length, the agreement is impressive. All $C—O\cdots O$ angles are in the range 110–115 degrees.

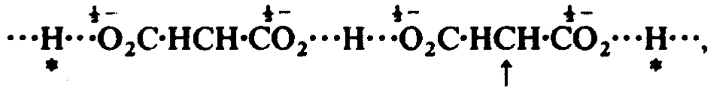
Table 1.3 Summary of inter-carboxyl hydrogen bonding in some Type *A* acid salts, MHX_2, of monocarboxylic acids

((N) indicates a neutron study; standard deviations are in parentheses.)

HX	M	*Symmetry of bond*	$O\cdots H\cdots O$ (Å)	*Reference*
Phenylacetic	K	$\bar{1}$	2.443(4)	24
p-OH-benzoic	K(hydrate)	$\bar{1}$	2.458(6)	62
Acetic	Na	2	2.444(10)	63
Cinnamic	NH_4	$\bar{1}$	2.51(3)	64
p-Cl-benzoic	K	$\bar{1}$	2.457(13)	65
Trifluoroacetic	Cs	$\bar{1}$	2.38(3)	66
	K	$\bar{1}$	2.435(7)	66
			2.437(4) (N)	11
	K	$\bar{1}$	2.455(5)	17
			2.448(4) (N)	49
Aspirin	Rb	$\bar{1}$	2.48(2)	68
Anisic	K	2	2.476(18)	69

1.4.2 Acid salts of symmetrical dicarboxylic acids

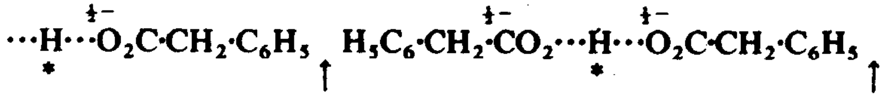
That a dibasic acid, H_2Y, should form an acid salt (MHY) is in accordance with the book of classical chemistry. What is unexpected is that the 'half-salts' of many symmetrical dicarboxylic acids are found, by structure analysis, to have their carboxyl groups crystallographically equivalent. Potassium hydrogen malonate, for example[28], does not have a crystal structure corresponding to the classical formula $K^+ \ {}^-O_2C\cdot CH_2\cdot CO_2H$. Instead, there are infinite hydrogen–anion chains (4),



$$\cdots\underset{*}{H}\cdots\overset{\frac{1}{2}-}{O}_2C\cdot HCH\cdot C\overset{\frac{1}{2}-}{O}_2\cdots H\cdots\overset{\frac{1}{2}-}{O}_2C\cdot H\underset{\uparrow}{C}H\cdot C\overset{\frac{1}{2}-}{O}_2\cdots\underset{*}{H}\cdots,$$

(4)

where the asterisks and arrows stand, respectively, for centres of symmetry at the hydrogen atoms and for axes of twofold symmetry passing through the methylene carbon atoms. This scheme presents a complete analogy with that in Type *A* acid salts of monocarboxylic acids, as can be seen if we represent the anion structure of potassium hydrogen bisphenylacetate (Figure 1.6) as in (5).



$$\cdots\underset{*}{H}\cdots\overset{\frac{1}{2}-}{O}_2C\cdot CH_2\cdot C_6H_5\;\underset{\uparrow}{\;}\;H_5C_6\cdot CH_2\cdot C\overset{\frac{1}{2}-}{O}_2\cdots\underset{*}{H}\cdots\overset{\frac{1}{2}-}{O}_2C\cdot CH_2\cdot C_6H_5\;\underset{\uparrow}{\;}$$

(5)

In potassium hydrogen malonate, whose crystal structure is shown in Figure 1.7, the symmetrical O···H···O bond is very short (see Table 1.4). We classify salts of dibasic acids with this structural pattern as Type A_2 [27].

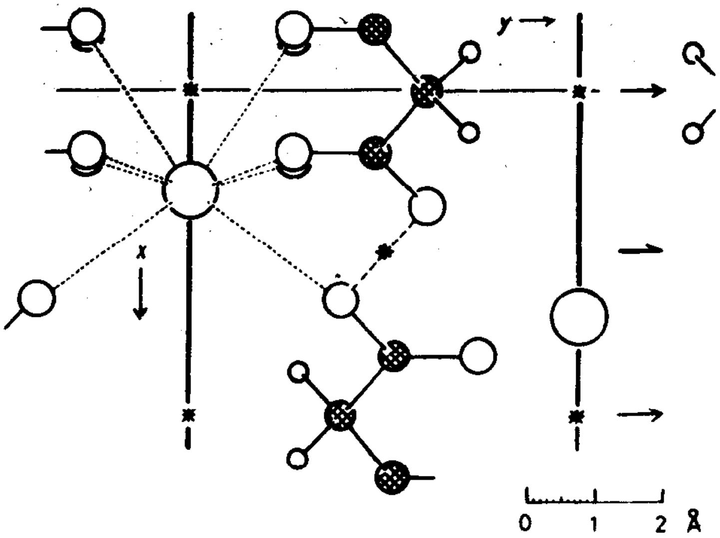


Figure 1.7 The crystal structure of potassium hydrogen malonate, in its *a*-axial projection[27,28] (The smallest open circles represent methylenic hydrogen atoms. Other conventions are explained in the caption to Figure 1.6.)

In Table 1.4 we summarise the results at present available for the hydrogen bonds in Type A_2 acid salts. The weighted average length is O···O = 2.450(2) Å. All C—O···O angles are in the range 110–115 degrees.

The hydrogen bonds collected in Tables 1.3 and 1.4 constitute a remarkable set. Apart from some chelated systems which we shall mention later, they represent the shortest O···H···O bonds that have been measured with any precision. The great majority of them lie across crystallographic centres of symmetry, so that the O···H···O angle is necessarily (identically) 180 degrees. For the exceptions, in which the bond is symmetrical about a