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Acid–Base Effects in Hydrogen Bonds in Crystals

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This paper reviews certain contributions to short hydrogen bonds from 'alternative structures'. Hydrogen bonds in crystals are discussed as a special case of the modern theory of acids and bases, applied to dissociation equilibrium within the crystals. Except when the bond is very short there must be two alternative basic sites, normally with different proton affinities. When the basicity is very different, there is no appreciable overlap between the potential energy curves describing these two sites; hydrogen bonding can be neglected. If there is some overlap, above 0° K. the crystal may contain a proportion of proton-transfer defect sites. When the proportion of transfer sites attains sufficiently large values co-operative proton-transfer effects must be present in the crystal. A survey of the geometrical arrangements found in crystals does not finally decide whether short bonds can be formed only as part of a co-operative system such as a spiral or network, though such structures are very common. In explaining various isotope effects, which are prominent in crystals containing short hydrogen bonds, it seems necessary to include a quantum mechanical contribution to individual hydrogen bonds. The overlap between two alternative structures may generally be expected to be closer for H than for D bonds, because of differences in zero-point vibrations.

Introduction

When the location of the hydrogen atom between two neighbouring groups in a crystal is discussed, quite sharp distinction is sometimes made between theories which account for the 'strength' of the bond wholly in terms of electrostatic calculations (cf. Davies, 1946) and theories which allow for some contribution from quantum mechanical effects (Robertson & Ubbelohde, 1939; Ubbelohde, 1949; Nordman & Lipscomb, 1951, 1953). It seems desirable to elucidate the various factors rather further; though the contributions from these different effects have been substantiated with varying degrees of success, much additional information is required in certain cases. One approach to the discussion of hydrogen bonds in crystals can be regarded as a special case of the modern theory of acids and bases.

1. The internal dissociation of *A*–H bonds in crystals

To discuss this, it is useful to start with possible dissociation processes of a proton bonded to each of two basic groups, considered *in vacuo*, i.e. as isolated from the rest of the structure. Without loss of generality we may consider the dissociation curves of two acids, AH and BH$^+$. The two imaginary dissociation curves are represented as Morse functions in Fig. 1(*a*) (curves X and Y).

This paper deals with strong hydrogen bond interaction in crystals which are known to contain hydrogen bonds with length shorter than about 2·75 Å. The substances quoted below can be classified according to the type of equilibrium present as follows:

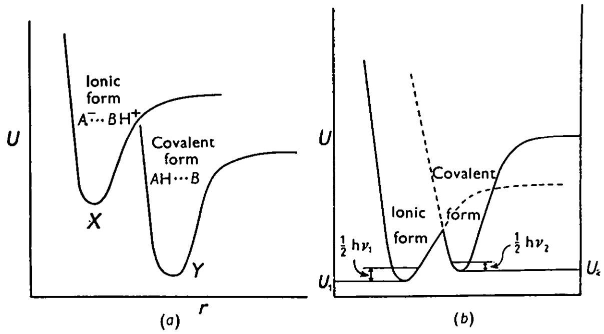

Fig. 1. (*a*) Potential energy curves for alternative distributions of the H atom. Case of poor overlap between alternatives.

(*b*) Potential energy curves for alternative distributions of the H atom. Marked overlap of the alternatives. Zero-point energies raise minimum energies as shown.

$$\begin{aligned} &AH\ldots AH \rightleftharpoons AH_2^+\ldots A^- \\ &AH\ldots A^- \rightleftharpoons A^- \ldots AH \\ &AH\ldots B \rightleftharpoons A^- \ldots BH^+ \end{aligned}$$

Table 1 shows a large number of known examples belonging to these three classes. By comparison with dissociation curves in the gas phase *in vacuo*, the situation will be different in electrolyte solutions. Obviously the potential energy curves may be greatly modified and the dissociation energy may be diminished by surrounding the pairs of molecules considered by

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Table 1. *Types of dissociation equilibria in crystals containing hydrogen bonds*

Dissociation equilibrium $AH\ldots AH \rightleftharpoons AH_2^+\ldots A^-$

Acids

Substance	$pK_{meas.}$ at 25° C.		Reference
Oxalic acid	(1)*	1·27	*Landolt–Börnstein Tabellen*
	(2)*	4·25	
Maleic acid	(1)	1·848	*Landolt–Börnstein Tabellen*
	(2)	6·067	
Salicylic acid	(1)	2·966	Böeseken & Ouwehand (1921)
	(2)	13·0†	Senter & Bulle (1912)
Tartaric acid	(1)	2·983	Jones & Soper (1934)
	(2)	4·342	
Furoic acid		3·2	*Handbook of Chemistry and Physics* (1945)
Formic acid		3·772	Harned & Embree (1934)
p-Chlorobenzoic acid		3·983	Saxton & Meier (1934)
Succinic acid	(1)	4·188	*Landolt–Börnstein Tabellen*
	(2)	5·393	
Glutaric acid	(1)	4·344	*Landolt–Börnstein Tabellen*
	(2)	5·420	
Adipic acid	(1)	4·424	*Landolt–Börnstein Tabellen*
	(2)	5·419	
Sebacic acid	(1)	4·57	Brown & Walker (1891)
	(2)	5·60	Chandler (1908)

* (1) and (2) refer to the 1st and 2nd dissociation constants respectively.
† At 20° C.

Dissociation equilibrium $AH\ldots B \rightleftharpoons A^-\ldots BH^+$

Acid hydrates

Substance	$K_{meas.}$ at 25° C.		Reference
$HNO_3.H_2O$		0·08	*Landolt–Börnstein Tabellen*
$HNO_3.3H_2O$			
Oxalic acid dihydrate	(1)	1·27	*Landolt–Börnstein Tabellen*
	(2)	4·25	
Acetylenedicarboxylic acid dihydrate		1·732	Ashton & Partington (1934)
		4·396	
Racemic acid hydrate	(1)	2·983	Jones & Soper (1934)
	(2)	4·342	

Dissociation equilibrium $AH\ldots A^- \rightleftharpoons A^-\ldots HA$

Acid salts

Substance	$K_{meas.}$ at 25° C.		Reference
$KHCO_3$		10·251	MacInnes & Belcher (1933)
$NaHCO_3$			
NH_4HCO_3			
$Na_2CO_3.NaHCO_3.2H_2O$			
KH bisphenylacetate		4·312	Frederick *et al.* (1934)
KH_2AsO_4		7·08	Hughes (1928)
KH_2PO_4	(1)	7·213	Guggenheim & Schindler (1934); Nims (1933)
$NH_4H_2PO_4$	(2)	12·32	Bjerrum & Unmack (1929)

media of dielectric constants greater than vacuum. For electrostatic reasons, the lowering of dissociation energy is likely to be proportionately less for the curve $BH^+ \rightarrow B+H^+$ than for $AH \rightarrow A^-+H^+$. As is well known, the relative strengths of acids depend to a considerable degree on the solvent. On passing to the crystalline state, an even greater change of local dielectric constant occurs in some cases. However, the situation depends so much upon what other nearest neighbours are present in a specific crystal, near the hydrogen bond, that specific effects must always be discussed in terms of particular examples. Neglecting such specific effects, the relative magnitudes of the dissociation constants K_{AH} and K_{BH^+} in aqueous solution may give some guide to the extent of overlap of the two possible potential energy curves.

The equilibrium constant K of the dissociation of an acid in the presence of a base $AH+B \rightleftharpoons A^-+BH^+$ may be represented in terms of the activities a of the various species as follows:

$$K = \frac{a_{BH^+} \times a_{A^-}}{a_{AH} \times a_B}.$$

This equilibrium may be considered in two stages:

(i) Dissociation of the acid:

$$AH \rightleftharpoons A^- + \text{proton}\ ,$$

where

$$K_{AH} = (a_{A^-} \times a_P)/a_{AH}.$$

(ii) Association of the proton with the base B. In the case of aqueous solutions the base is H_2O:

$$H_2O + \text{proton} \rightleftharpoons H_3O^+,$$

where

$$K_{H_3O^+} = (a_{H_2O} \times a_p)/a_{H_3O^+}\ .$$

For the distribution of the proton between the molecules A^-, and B,

$$K = K_{AH}/K_{BH^+}\ .$$

For the important case of crystalline acid hydrates it is not yet known at what value of K_{AH}, K is equal to unity. In practice, in calculating a figure ($K_{\text{meas.}}$) for the equilibrium constant of dissociation the activity of water is assumed unity so that

$$K_{\text{meas.}} = K \,.\, a_{H_2O}\ ,$$

but for the special case of hydrates the activity of water is required (see Bell (1943) for a discussion of probable values). Relevant information about these dissociation constants, where available, is given in Table 1.

In the absence of specific effects due to other molecules in the crystal, maximum overlap of the potential energy curves might be expected where $K_{AH} = K_{BH^+}$, i.e. when $K = 1$. On the other hand in cases where $K_{BH^+} \gg K_{AH}$, as for example for the groups in urea–paraffin adducts, where $B = -NH_2$ and $A^- = RCH_2^-$, the U ordinates of the potential energy curves lie very far from one another and the curves will not overlap at all (Schlenk, 1949; Redlich, Gable, Dunlop & Millar, 1950; Smith, 1952). Again, the fact that anhydrous HNO_3 shows no tendency to form short H bonds (the shortest $O \cdots O$ contact is 2·86 Å (Luzzati, 1951*a*, *b*)) may be interpreted on this basis as indication of the low basicity of the HNO_3 molecule as compared to H_2O. Because HNO_3 behaves as a strong acid in the crystal there is no overlap between potential curves for structures such as $H_2NO_3^+ \cdots OH^-$ or $HNO_3 \cdots OH_2$ with $NO_3^- \cdots OH_3^+$. To anticipate what follows, the view put forward for discussion is that the formation of strong hydrogen bonds requires considerable overlap of the potential energy curves for the two alternative structures. Quite generally, acids much stronger than those listed in Table 1 would not be expected to show short hydrogen bonds in the crystals, unless they crystallize together with more basic units of structure such as H_2O.

On the view that short hydrogen bonds will be formed in the crystals only when there can be appreciable overlap between alternative potential energy curves, it is clear that in the hydrides of the elements *both* basic and acidic character must be present for strong hydrogen bonding. The well known contrasts between HF and HCl, and H_2O and H_2S, in the solid state, are to be attributed in part to the fact that the second hydride in a family of elements is much less basic, and cannot readily hold protons.

2. Isolated proton transfer defects in crystals

The energy ε for transferring a proton from allegiance with atom A, to allegiance with atom B, is represented by the vertical distance between the two potential energy curves. Even when this distance is large, it is perfectly possible to discuss the statistical thermodynamics of isolated crystal defects arising from proton transfer. An equation of the Schottky type will be expected to apply for the fraction of isolated 'proton-transfer defects' in $(N-n)$ lattice sites, above 0° K.:

$$n/(N-n) = \exp(-\varepsilon/KT)\ .$$

Such isolated proton transfer defects are likely to be significant for the kinetics of certain physico-chemical processes in the crystals. As an extreme case, consider the proton transfer defect in an NH_4Cl crystal.

In the vapour phase, for the dissociation

$$NH_4Cl_s \rightarrow NH_{3_{\text{gas}}} + HCl_{\text{gas}}$$
$$\Delta G_{298\cdot 1^\circ K.} = +21\cdot 8 \text{ K.cal/mole}$$
$$\Delta H_{298\cdot 1^\circ K.} = +42\cdot 2 \text{ K.cal/mole}$$

(Stephenson, 1944). Since the lattice energy of NH_4Cl is estimated as 161·6 K.cal (Bleick, 1934), *gaseous* NH_4Cl will be completely dissociated. In the crystal the energy of proton transfer is substantially altered by the influence of nearest neighbours. Nevertheless, ε is likely to be sufficiently small for an appreciable proportion of isolated defects to be present in crystalline NH_4Cl. These might affect its kinetic properties. For example, each proton defect site lowers the potential barriers opposing 'rotation' of the NH_3 in the crystal. (By 'rotation' is meant statistical randomization of orientation of molecular axes in the crystal.) It may be that the rate of randomization in ammonium salts at the Λ points is determined by the formation of defects of this kind. Similarly, in ice, proton transfer defect sites $OH^- \cdots OH_3^+$ may be important in certain relaxation processes.

Whilst the case of NH_4Cl is chosen to illustrate the powerful effect of neighbouring atoms in the crystal in changing the degree of dissociation compared with the gas, the anion Cl^- is not likely to be a good base, in competition with NH_3, in the crystal, since NH_4Cl appears to show normal ionic distances.

In crystals exhibiting short hydrogen bonds acid–base effects are more important, and the possibility of wandering of protons from one defect site to another must be present. The activation energy U for a jump of a proton from either of one 'pair of sites' to a vacancy in a neighbouring pair need not be small compared with the energy difference between the pair of sites, so that high proton conductivity need not follow as a matter of course when there are short hydrogen bonds in the crystals. However, the mechanism of proton conductance does seem to play a dominant part in one or two cases so far studied with this problem in view. A clear example is found in the case of the acid sulphates (Rogers & Ubbelohde, 1950*a*, *b*). A case still under investigation is that of acetylene dicarboxylic acid dihydrate (Gallagher, Ubbelohde & Woodward, unpublished observations). Easy migration of the protons facilitates healing of sub-crystalline hybrids on passing through a thermal transition from single crystal to pseudo-single crystal and back again (Ubbelohde & Woodward, 1946).

3. Fraction of proton transfer sites in a crystal

In crystals, starting with an assumed model with 100% allegiance of the proton with one of the two groups, various methods so far developed to locate the protons are not sufficiently refined to permit close assessment of the fraction of defect sites arising from proton transfer to the alternative allegiance. Thermodynamically, unless the two potential energy minima are completely fused, above 0° K. the protons will always be distributed statistically between the positions available to them in the crystal. Although this is not precisely known at present, there is reason to suppose that the two minima even in a case such as $-O \cdots H{-}O \rightarrow -O{-}H \cdots O-$ do not become fused until the O–O distance falls markedly below 2·7 Å. A possible example of fused minima is Rochelle salt (Ubbelohde & Woodward, 1946). Because of the thermodynamics, experiments to locate protons in short hydrogen bonds should always be carried out at more than one temperature, and if possible at low temperatures.

The precision of the statistical location of the protons in hydrogen bond minima becomes important if the fraction of defects becomes sufficiently large to lead to co-operative effects, discussed in the next section. Methods proposed to locate the protons in hydrogen bond minima do not as yet give high statistical precision. They include:

(i) X-ray crystallographic 'difference maps' which locate the electron density approximately corresponding with the bonding of the proton to one of the groups. For example, in the nitric acid hydrates (Luzzati, 1953*a*, *b*) the peak electron density indicates that the structure is 'preponderatingly' $(OH_3^+) \cdots (NO_3^-)$, but the accuracy does not yet permit an assessment of the fraction of $(OH_2) \cdots (NO_3H)$ sites in the crystal. Similarly, Cochran (1953) has shown the intermolecular hydrogen bond in salicylic acid to be principally in the covalent form $OH \cdots O{=}C$.

(ii) Neutron-diffraction measurements locate the proton in KHF_2 crystals to within 0·1 Å of the centre of the F–H–F ion (Peterson & Levy, 1952). In KH_2PO_4 at room temperature the scattering density diagram shows an elliptical peak mid-way between the two oxygens in the O–H–O link, indicating that the two minima are 0·35 Å apart (Bacon & Pease, 1953). In the ferroelectric state the proton has been located in a minimum 0·21 Å from the centre. According to the polarity, all the protons in one domain occupy one set of minima nearest to the 'upper' or 'lower' oxygen. On reversing the polarity the protons jump to the other set of minima.

If the polarity of a domain in which the protons occupy the minima nearest to the upper oxygens is reversed then the protons will jump to the lower oxygens and vice versa (Bacon & Pease, 1954). Here again, the location is as yet too crude to say what fraction of the protons might occupy the alternative sites in a crystal such as KH_2PO_4.

(iii) Residual entropy measurements indicate the existence of more than one distinct location for each proton in ice (Giauque & Stout, 1936), KH_2PO_4 (Stephenson & Hooley, 1944), KH_2AsO_4 (Stephenson & Zettlemoyer, 1944*a*), $NH_4H_2PO_4$ (Stephenson & Zettlemoyer, 1944*b*), $NH_4H_2AsO_4$ (Stephenson & Adams, 1944) and $Na_2SO_4 . 10\,H_2O$ (Pitzer & Coulter, 1938), but do not give accurate estimates of statistical departures from the crystal arrangement of lowest energy as the temperature rises above 0° K. Direct studies of proton location have indicated less overlap at low temperatures in KH_2PO_4 (Frazer & Pepinsky, 1953; Bacon & Pease, 1954). It is not yet clear, however, whether this is a free energy or zero-point energy effect. Entropy measurements at different temperatures may decide this. Westrum & Pitzer (1949) have established that KHF_2 reaches zero entropy when cooled to 0° K. and does not possess residual randomness as in ice and other hydrogen bonded crystals, as mentioned above.

(iv) Crystalline symmetry in certain cases imposes at least statistical uniformity of distribution of the proton between two minima. One carefully studied example is potassium hydrogen bisphenylacetate for which the hydrogen bond length is 2·55 Å (Speakman, 1949).

(v) The shapes of magnetic resonance absorption spectra permit allocation of the protons to specific atoms in certain crystals (Purcell, 1948; Pake, 1950*a*, *b*; Richards & Smith, 1951; Smith & Richards, 1952). Crystals studied may be symbolised:

$(ClO_4)^- \cdots (OH_3)^+$	monohydrate and dihydrate
$(SO_4)^= \cdots (OH_3)^+$	monohydrate and dihydrate
$(NO_3)^- \cdots (OH_3)^+$	monohydrate and trihydrate
$(C_2O_4H_2) \cdots (H_2O)$	dihydrate

But this method gives neither the exact location of the proton, nor statistical estimates of the fraction of protons in the alternative position.

(vi) Infra-red measurements indicate

$$(ClO_4)^- \cdots (OH_3)^+$$
$$(NO_3)^- \cdots (OH_3)^+$$

in crystals of perchoric acid monohydrate and nitric acid monohydrate (Bethell & Sheppard, 1953).

The extent to which specific interactions between nearest neighbours control proton distribution may be illustrated from the example of nitric acid monohydrate. Infra-red methods and X-ray difference maps indicate predominantly $(OH_3^+)(NO_3^-)$ in the crystal, though neither method gives the fraction of the alternative proton locations present. In the liquid, the structure is predominantly $(HNO_3)(OH_2)$, though no doubt there is a fraction of $(OH_3^+)(NO_3^-)$. The tendency of the nitrate ion to form association complexes in melts (Davis, Rogers & Ubbelohde, 1953) may in part explain this change of proton distribution on melting. In the crystal this tendency is balanced out by the crystal symmetry so that the basicity of the OH_2 can predominate.

4. Co-operative proton dissociation in crystals

When the difference ε between the minima of the potential energy curves is not large compared with kT, the number of proton transfer sites increases, and it is no longer possible to treat such lattice defects as independent. Co-operative interaction between lattice defects will occur when the potential energy curves X and Y (Fig. 1(*a*)) begin to overlap fairly closely. Though the crystals must exhibit a statistical distribution of protons between BH^+ and AH positions, it may prove difficult to construct a partition function giving the quantitative description of the distribution of the protons between these two positions when these are so close to one another that there is strong electrostatic interaction between neighbouring groups. From the purely geometrical standpoint co-operative effects might often be present when there are short intermolecular hydrogen bonds in crystal ions. A survey is presented in Table 2. From this table numerous geometrical possibilities for co-operative interaction between hydrogen bonds will be evident. Only class (*a*) contains a short hydrogen bond such that co-operation between hydrogen bonds is not geometrically evident.

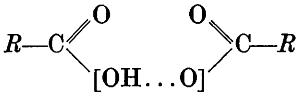
The problem to be discussed is whether proton transfer defects in co-operative hydrogen bond structures themselves co-operate sufficiently to affect the average hydrogen bond interaction. At present the possibility can be raised, but not decided. It would be important in permitting a possible explanation for the comparatively large changes in certain crystals containing hydrogen bonds, when the hydrogen is replaced by deuterium. If co-operative effects are significant, quite small changes (D for H) in the individual bonds could lead to fairly large overall changes in the crystals. The present experimental evidence indicates that isotope effects are quite large. So far as it goes, the evidence in Table 2 does not yet compel one to infer co-operative build-up in the crystal of small differences in the individual O–H–O bonds, since it is not yet possible to calculate how large the isotope effect may be in an isolated system. It remains for future work to determine whether in discussing isotope effects in crystals it is always necessary to consider quantum overlap effects in two and three dimensions in the systems described, or whether it is sufficient to discuss quantum effects in isolated O–H–O systems.

5. Quantum mechanical contributions to hydrogen bonds in crystals

On the present evidence it seems necessary and sufficient to consider quantum effects in the individual bonds to explain why some hydrogen bonds in crystals show special sensitiveness to isotope replacement, or to changes of lattice spacing due to thermal expansion, or to external compression (Ubbelohde, 1949). That such effects are present in many crystals, particularly when these contain short hydrogen bonds ($r \ngtr 2{\cdot}65$ Å), has now been verified by a number of distinct lines

Table 2. *Classification of crystals according to the geometrical possibilities for interaction of hydrogen bonds*

(*a*) Simple 'acid salt' dimer isolated by ionic and van der Waals forces from other hydrogen bonds



Crystal	H bond length (Å)	Donor → acceptor	Reference
KH bisphenylacetate	2·55	Carboxyl → O=C	Speakman (1949)

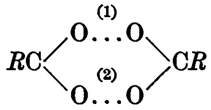
(*b*) Closed-circuit type

(i) Anhydrous

Hydrogen bonds (1) and (2) are equal in length. This system of hydrogen bonding gives rise to dimers in monocarboxylic acids and chains in the β-type dicarboxylic acids.

Table 2 (*cont.*)

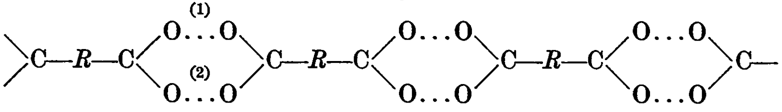
Monocarboxylic acids



Crystal	H bond length (Å)	Donor → acceptor	Reference
Lauric acid	2·56	Carboxyl → O=C	Vand *et al.* (1951)
Salicylic acid*	2·627	Carboxyl → O=C	Cochran (1953)
p-Chlorobenzoic acid	2·62	Carboxyl → O=C	Toussaint (1951, 1952)
Furoic acid	2·53	Carboxyl → O=C	Goodwin & Thompson (1954)
$KHCO_3$	2·61	Carboxyl → O=C	Nitta *et al.* (1952)

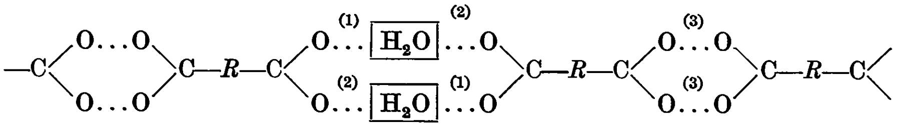
* There is also an intramolecular bond (2·590 Å) between carbonyl O and phenolic OH.

Dicarboxylic acids



Crystal	H bond length (Å)	Donor → acceptor	Reference
Sebacic acid	2·68	Carboxyl → O=C	Morrison & Robertson (1949*c*)
Adipic acid	2·68	Carboxyl → O=C	Morrison & Robertson (1949*b*)
β-Glutaric acid	2·7	Carboxyl → O=C	Morrison & Robertson (1949*d*)
β-Succinic acid	2·64	Carboxyl → O=C	Morrison & Robertson (1949*a*)
β-Oxalic acid	2·7	Carboxyl → O=C	Hendricks (1935)

(ii) Anhydrous circuits alternating with hydrated circuits



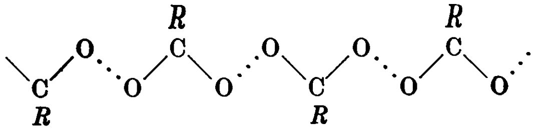
Crystal	H bond length (Å)	Donor → acceptor	Reference
Hydrate racemic acid	(1) 2·61	Carboxyl → O=C	Parry (1951)
	(2) 2·89	Water → O=C	
	(3) 2·72	Carboxyl → water	

These chains are connected by another H bond system, a parallelogram of H bonds between four OH groups of two molecules of tartaric acid. The lengths of the short and long sides are 2·75 and 2·83 Å respectively.

(*c*) Bond chains

Often arranged spirally in the crystals. Especially favourable for co-operative effects. Produces chains in monocarboxylic acids and sheets in the α-type dicarboxylic acids

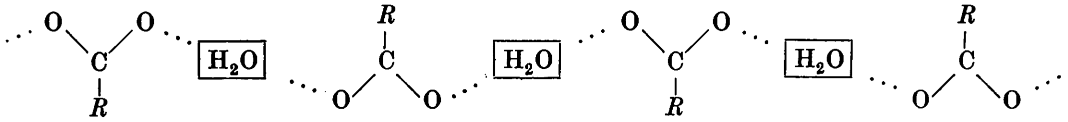
(1) Anhydrous



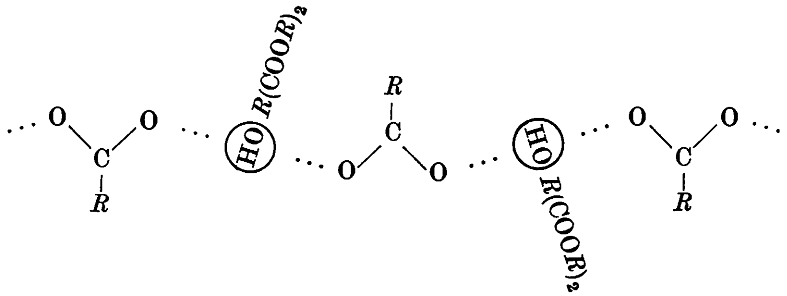
Crystal	H bond length (Å)	Donor → acceptor	Reference
α-Oxalic acid	2·71	Carboxyl → O=C	Cox *et al.* (1952)
Formic acid	2·58 (±0·03)	Carboxyl → O=C	Holtzberg *et al.* (1953)
$NaHCO_3$	2·55	Carboxyl → O=C	Zachariasen (1933)
NH_4HCO_3	—	Carboxyl → O=C	Brooks & Alcock (1950)

Table 2 (*cont.*)

(ii) With one molecule of water per carboxylic group



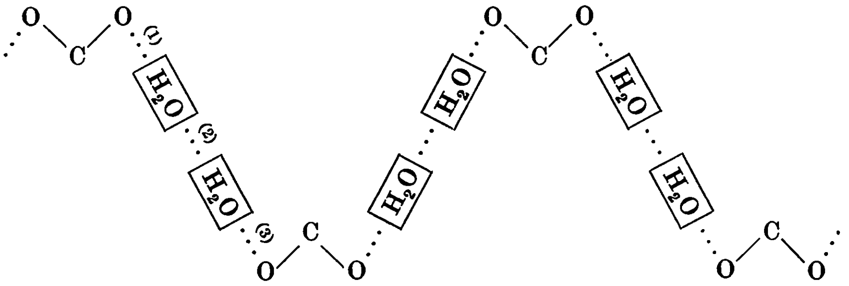
or an OH group of another molecule of the same species as in tartaric acid.



Crystal		H bond length (Å)	Donor → acceptor	Reference
Oxalic acid dihydrate	(1)	2·491	Carboxyl → water	Ahmed & Cruickshank (1953)
	(2)	2·885	Water → O=C	Dunitz & Robertson (1947*a*)
	(3)*	2·879	Water O=C	
Acetylenedicarboxylic acid dihydrate	(1)	2·56	Carboxyl → water	Dunitz & Robertson (1947*b*)
	(2)	2·89	Water → O=C	
	(3)*	2·82	Water → O=C	
Diacetylenedicarboxylic acid dihydrate	(1)	2·55	Carboxyl → water	Dunitz & Robertson (1947*c*)
	(2)	2·90	Water → O=C	
	(3)*	2·83	Water → O=C	
Tartaric acid	(1)	2·74	Hydroxyl → O=C	Stern & Beevers (1950)
	(2)	2·78	Carboxyl → hydroxyl	
	(3)*	2·87	Carboxyl → carboxyl	
	(4)	2·87	Hydroxyl → O=C	
	(5)	2·92	Hydroxyl → O=C	
$Zn.(CH_3.COO)_2.2H_2O$	(1)	2·49	Water → $^{-}$O−C	Nierkerk *et al.* (1953)
	(2)	2·74	Water → O=C	

* The sheets are joined by long hydrogen bonds (3) and in the case of tartaric acid, by (4) and (5) also.

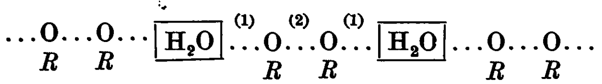
(iii) With two molecules of water per carboxyl group



Crystal		H bond length (Å)	Donor → acceptor	Reference
$NaK[O_2C.CHOH.CHOH.CO_2].4H_2O$ (Rochelle salt)	(1)	2·56	Water → $^{-}$O−C	Beevers & Hughes (1941)
	(2)	2·86	Water → water	
	(3)	3·07	Water → O=C	

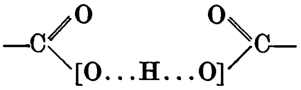
Table 2 (*cont.*)

(iv) Chain formed from two OH groups and one molecule of water

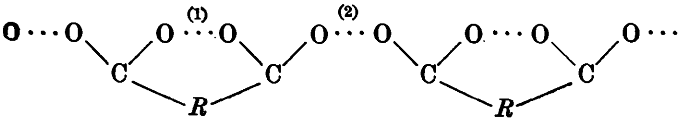


Crystal	H bond length (Å)		Donor → acceptor	Reference
K bis *p*-hydroxybenzoate	(1)	2·58	Hydroxyl → water	Speakman (1951)
	(2)	2·69	Hydroxyl → hydroxyl	

The carboxyl groups of two molecules are linked by a hydrogen bond (2·61 Å) of the acid salt type

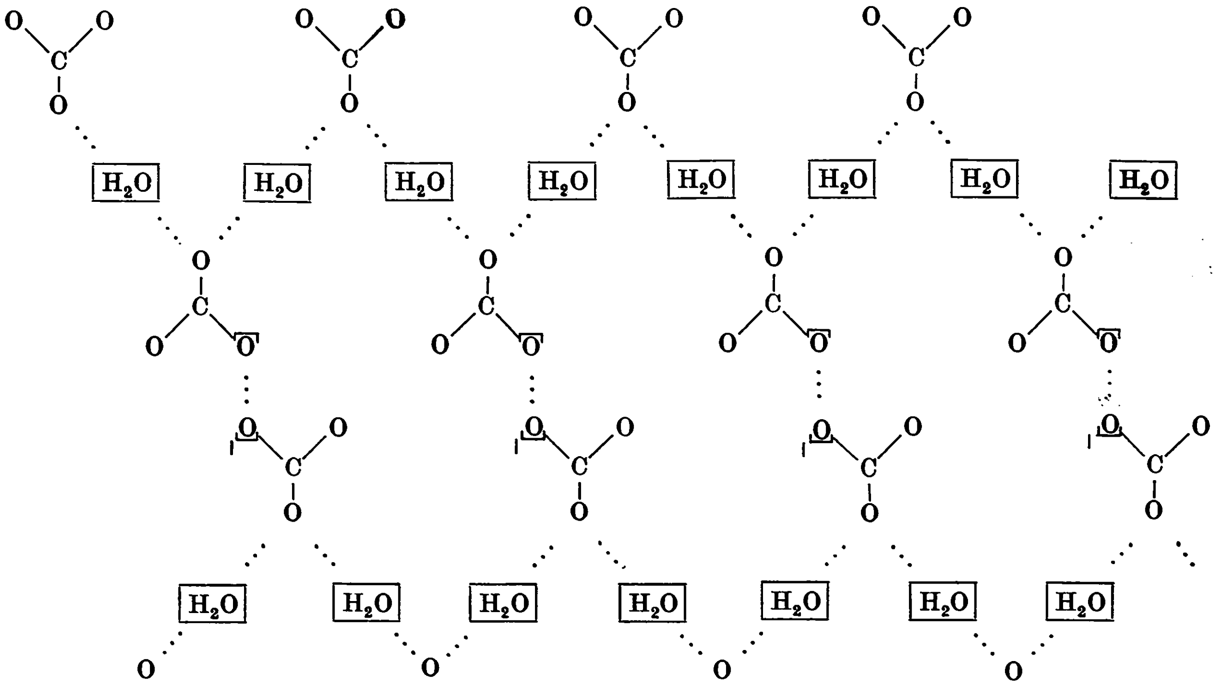


(v) Chain of alternating intra- and intermolecular bonds



Crystal	H bond length (Å)		Donor → acceptor	Reference
Maleic acid	(1)	2·46	Carboxyl → O=C	Shahat (1952)
	(2)	2·75	Carboxyl → O=C	

(i) Sheets bonded by hydrated chains and 'acid-salt' type linkages



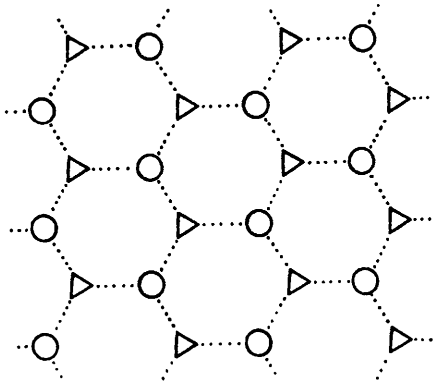
Crystal	H bond length (Å)		Donor → acceptor	Reference
$Na_2CO_3 . NaHCO_3 . 2H_2O$	(1)	2·72(±0·03)	Water → O=C	Brown *et al.* (1949)
	(2)	2·77(±0·03)	Water → O=C	
	(3)	2·53(±0·02)	Hydroxyl → $^-$O–C	

The Na^+ ions lie between the H bonded sheets.

Table 2 (*cont.*)

(*d*) Two-dimensional hydrogen-bonded systems

(ii) Sheets showing pseudo-trigonal symmetry and containing 1 molecule of water per X_nO_m molecule



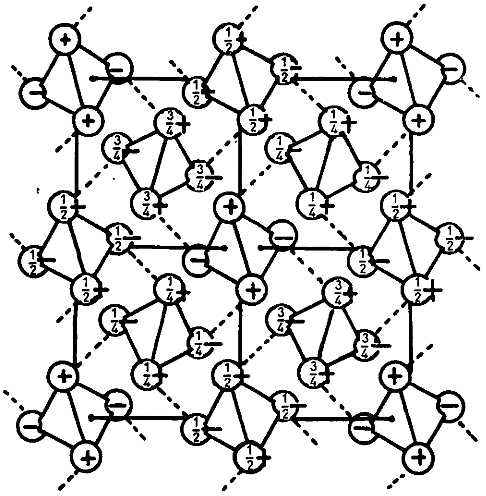
○ = H_2O △ = NO_3^-

Crystal	H bond length (Å)		Donor → acceptor	Reference
$HNO_3.H_2O$	(1)	2·54	Water → O=N	Luzzati (1951*a*, *b*)
	(2)	2·61	Water → O=N	
	(3)	2·68	=NOH → water	

(*e*) Three-dimensional network

(i) Phosphate–arsenate group

These possess tetragonal symmetry and the hydrogen bonds (all equivalent) lie nearly parallel to the basal plane (001).



Crystal	H bond length (Å)	Donor → acceptor	Reference
KH_2PO_4	2·53* 2·44† 2·51‡§	Hydroxyl → O=P	Frazer & Pepinsky (1953)
$NH_4H_2PO_4$	2·49	Hydroxyl → O=P	Ueda (1948)
KH_2AsO_4	2·54	Hydroxyl → O=As	Helmholtz & Levine (1942)

* At room temperature. † At 126° K. ‡ This is the orthorhombic form. § At 116° K.

Table 2 (*cont.*)

(ii) Miscellaneous

This includes crystals which have a complicated three-dimensional network of H bonds, in which no series of linkages takes precedence over any other. Co-operative H bonding is likely to operate in all directions in the crystal, the degree depending upon the strength of the bonds involved.

Crystal	H bond length (Å)		Donor → acceptor	Reference
$HNO_3.3H_2O$	(1)	2·49	Water → water	Luzzati (1953*a*, *b*)
	(2)	2·57	Water → water	
	(3)	2·62	Water → O=N	
	(4)	2·73	Water → O=N	
	(5)	2·75	NOH → water	
	(6)	2·79	Water → O=N	
	(7)	2·81	Water → water	
Ice		2·76	Water → water	Barnes (1929)

Table 3. *Equivalent* bond length changes on replacing* H *by* D

(Measured values)

Crystal	r_{AB} (Å)	Δr ($r_D - r_H$) ($\text{Å} \times 10^{-3}$)	Reference
Oxalic acid dihydrate	2·491	+40·5	Robertson & Ubbelohde (1939)
Acetylene dicarboxylic acid dihydrate	2·56	+34·0	Gallagher *et al.* (1954)
Succinic acid	2·64	+18† approx.	Robertson & Ubbelohde (1939)
Ice	2·76	+1·5	Megaw (1934)
β-Resorcinol	2·75	No measurable effect	Robertson & Ubbelohde (1939)
	2·70		
Urea	2·99	Small contraction	Ubbelohde (1939)
$NH_4H_2PO_4$	2·49	+10·0	Ubbelohde & Woodward (1942)
KH_2PO_4	2·52	+9·7	Ubbelohde (1939)
KH_2AsO_4	2·54	+8·0	Dickson & Ubbelohde 1950
$CuSO_4.5H_2O$	—	Small contraction	Ubbelohde (1939)
KHF_2	2·26	Small contraction	Ubbelohde (1939)

* These are calculated from expansions of the unit cell on the basis of assumptions discussed in the various individual papers.

† This figure was estimated from measurements in a crystallographic zone which is now known to be the least favourable for accurate determination.

Table 4. *Effect of isotope replacement on ferroelectric transition temperatures*

Crystal	Lower Curie point (°K.)		ΔT ($T_D - T_H$) (°K.)	Upper Curie point (°K.)		ΔT ($T_D - T_H$) (°K.)	Reference
	H	D		H	D		
Rochelle salt	255–258	250–251	−4	296	308	+12	Davies (1927); Kurchatov & Kurchatov (1933): Hablützel (1939); Holden & Mason (1940)
$NH_4H_2PO_4$	—	—	—	147–148	230–242	82–94	Stephenson *et al.* (1953); Matthias (1952)
KH_2PO_4	—	—	—	121·97	213·0	+91·0	Stephenson *et al.* (1953)
$NH_4H_2AsO_4$	—	—	—	215·8	298·6	+82·8	Stephenson *et al.* (1953)
KH_2AsO_4	—	—	—	95·57	162·0	+66·4	Stephenson *et al.* (1953)
RbH_2AsO_4	—	—	—	109·9	177·8	+67·9	Stephenson *et al.* (1953)
CsH_2AsO_4	—	—	—	143·3	212·4	+69·1	Stephenson *et al.* (1953)

of research. The most striking of these quantum effects arises when hydrogen is replaced by deuterium. This replacement localises any changes in the crystal to the immediate neighbourhood of the $AH \cdots B$ regions. Effects established so far can be summarized in general terms. When a 'short' hydrogen bond is present in the crystal ($r \ngtr 2{\cdot}75$ Å), in all the examples yet investigated there is a marked expansion of the crystal lattice on replacing H by D (Table 3). For crystals containing longer H bonds (2·65–2·8 Å), so far as these have been studied, any expansion on replacing H by D is only small. As illustrated in Table 4, isotope replacement can also have a striking influence on thermodynamic transition temperatures, e.g. of the ferro-electric ⇌ para-electric type.

Thermal expansion

Less simple but equally important quantum effects arise in the thermal expansions of crystals containing hydrogen bonds. Since thermal expansion is determined in principle by the entire vibrational spectrum of the crystal, it is only when certain force fields have quite abnormal properties that they *dominate* the crystal behaviour and can be picked out to give information about the hydrogen bonds. This may be the case, particularly, for crystals containing short hydrogen bonds in a cooperative system, and no competitive stronger forces between the molecules. For example, the direction of the isotope effect for oxalic acid dihydrate makes an angle of only 22° from the direction of the overall thermal expansion in the same crystal plane, indicating that in this plane of this particular crystal lattice the O · · · HO forces provide the dominant vibrations controlling the thermal behaviour. For acetylenedicarboxylic acid dihydrate, which can be considered as a related structure, the thermal expansion in the plane containing the short hydrogen bonds (010) shows a marked anisotropy with maximum at 22° to the maximum isotope effect (Gallagher, Ubbelohde & Woodward, 1954). In other directions in the crystal, changes of atomic coordinates with change in temperature are more complex.

Returning to the individual potential energy curves for AH and BH$^+$, the effect of the vibrational quanta of these two bonds on the closeness of overlap can be discussed quite generally. When there is overlap, each potential curve will be affected by the other. But neglecting this, a highly simplified statement is as follows:

If the two potential energy curves lie at U_1 and U_2 above a reference zero, then at 0° K. the difference in the energy ε_{21} will be the distance between the minima of the two curves U_2–U_1. Allowing for zero-point energies,

$$\varepsilon_{21} = U_2 - U_1 + \tfrac{1}{2}h(\nu_2 - \nu_1)\ .$$

Normally the curve with lower potential energy has the stronger force constants and $\nu_2 = \alpha\nu_1$ where $\alpha < 1$. Then

$$\varepsilon_{21} = (U_2 - U_1) + \tfrac{1}{2}h\nu_1(\alpha - 1)\ .$$

On replacing H by D, very approximately the U's are the same, but $\nu_{\mathrm{H}} = \sqrt{2} \times \nu_{\mathrm{D}}$. Then

$$\varepsilon_{21\mathrm{H}} - \varepsilon_{21\mathrm{D}} = \tfrac{1}{2}h\nu_{1\mathrm{H}}(\alpha - 1)(1 - 1/\sqrt{2})\ .$$

This is essentially negative, showing the overlap of the energies is normally closer for the H compound at 0° K. Because of this closer overlap, any quantum mechanical contribution to the energy of the hydrogen bond is greater for the H compound than for the D compound. In the absence of any other explanation, this appears to be the reason why short H bonds are measurably shorter than short D bonds. More detailed quantum-mechanical discussions have been proposed by Nordman & Lipscomb (1951, 1953) (see also Rundle, 1953). It may be noted that the basic reason for an isotope effect in short hydrogen bonds leading to an expansion on replacing H by D is here considered to be the effect of differences of zero-point energy on the overlap of two potential energy curves. This is obviously a much oversimplified means of introducing quantum effects. More precise treatments of the problem have been indicated by Coulson (1954 *a*,*b*).

A geometrical illustration of the need to include zero-point energy considerations when discussing the location of H atoms in hydrogen bonds follows from known amplitudes of vibration of protons in crystals. For protons, such amplitudes may be as high as 0·4 Å. Temperature studies suggest that most of this will persist on cooling to 0° K., i.e. most of it is zero-point energy.

Suppose the proton has been 'located' at a distance of 1·05 Å from one of a pair of oxygen atoms distant 2·50 Å apart. Its zero-point energy brings about an overlap with the alternative location, to beyond the mid-point of the O–O bond. Unless the overlap of the potential energy curves is very poor, owing to greatly different basicities, a quantum mechanical interaction between the two sites must follow.

6. Other properties of the crystals as affected by quantum mechanical differences in the H and D compounds

The argument describes the situation of 0° K. As the temperature rises, the D bonds will at first exhibit a more rapid energy intake than the H bonds. This will tend to enhance the expansion (D for H). Up to the present, corrections of measured isotope effects to 0° K. have not proved feasible. The treatment of Nordman & Lipscomb (1951) rather overemphasizes thermal as distinct from the zero-point energy effects in short hydrogen bonds.

If there is an overlap of two alternative structures, changes of bond length can have particularly marked effects on the properties of the hydrogen bonds. This appears to explain, at least qualitatively, the sensitiveness of crystals containing short hydrogen bonds to changes of temperature, and of external pressure. Two closely overlapping curves, as in Fig. 2, may approximate to a potential energy curve with exceptionally large anharmonicity of vibrations of the H or D atom owing to exceptionally large departures from a parabolic form of the potential energy curve near its minimum.

The effect of compression on the extent of overlap is also marked, since the minima of the two curves shift fairly rapidly with decreasing separation of the A and B atoms. If an external electric field is acting, this shift of the minima alters the polarization of the hydrogen bond, owing to the jump of the proton from one minimum to the other under the action of the field (Ubbelohde & Woodward, 1946; Bacon & Pease, 1954).

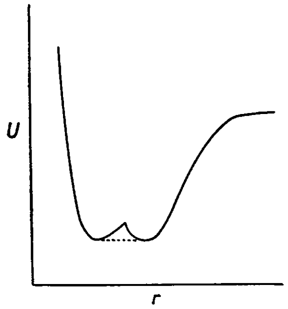


Fig. 2. Single potential energy curve with two minima for case of marked overlap.

This probably explains the remarkable piezo-electric properties of crystals such as Rochelle salt. Co-operative interaction through a system of hydrogen bonds can only lead to polar properties if crystal symmetry permits this and does not require cancelling out of polarization in alternate chains. Less obvious consequences of co-operative interaction may however prove to be quite as important for the interpretation of short hydrogen bonds in crystals.

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The Crystal Structure of Co_2Si*

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The crystal structure of Co_2Si has been redetermined from single-crystal X-ray data. The structure given by Borén, Ståhl & Westgren is incorrect. Co_2Si belongs to space group D_{2h}^{16}–*Pnam*, with 8 cobalt atoms and 4 silicon atoms in positions 4(*c*): $\pm(x, y, \frac{1}{4}; \frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{4})$ with parameters Co_I: $x = 0{\cdot}038$, $y = 0{\cdot}218$; Co_{II}: $x = 0{\cdot}174$, $y = 0{\cdot}562$; Si: $x = 0{\cdot}702$, $y = 0{\cdot}611$. Co_2Si is isostructural with Rh_2Ge and has a distorted Ni_2In structure.

The programming of the calculation of the (001) Fourier projection on the I.B.M. No. 701 calculator is also described.

Introduction

A structure for Co_2Si was first proposed by Borén, Ståhl & Westgren (1935). Because it was apparently the first of a type, the *Strukturbericht* (1937) designated the Co_2Si structure, as proposed by the above authors, the *C*-37 type. Since its publication, apparently no other structure isomorphous with Co_2Si has been reported. Kripiakevich (1951) has shown that the structure reported by Borén *et al.* is a distorted Ni_2In structure.

One of us (S. G.) became interested in the Co_2Si structure while working on the rhodium–germanium system (Geller, 1955). The phase Rh_2Ge seemed to be isomorphous with Co_2Si. That is, there was a striking qualitative similarity between the powder photographs of the two compounds. Work with powder samples on

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