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Prediction of Hydrogen Bonds and Hydrogen Atom Positions in Crystalline Solids

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In the case of a hydrogen-containing inorganic crystal structure for which only the heavy atom positions are known, eight criteria can be used to predict the location of the hydrogen bonds and the positions of the hydrogen atoms: (1) the angles M–D–H will be at least 90° (and usually over 100°); (2) even when no hydrogen-bonding contact is made, the hydrogen atom will tend to be positioned as close as possible to potential hydrogen bond acceptor(s); (3) no hydrogen atoms will be located in the edges of coordination polyhedra around cations; (4) the requirement of linearity of hydrogen bonds is not important; (5) the hydrogen bond must be viewed in its complete environment $(M)_n\text{–}D\text{–H}\cdots A\text{–}(X)_m$; (6) the M–D and the A–X bond lengths are influenced by the hydrogen bond; (7) the D–H$\cdots A$ distance depends on the difference in the electrostatic bond strengths received by D and A; and (8) hydrogen atoms belonging to different donor groups should usually be at least 2·0 Å apart, because the van der Waals radius of the hydrogen atom is 1·0 Å. These criteria are based on considerations of electrostatic energy, bond strengths and bonding geometry as revealed by pertinent calculations, and an inspection of hydrogen-containing crystal structures determined by neutron diffraction. A computer program, *CALHPO*, which is based on the criteria, can be used to calculate hydrogen-atom positions. The program and the criteria are applied to $KH_5(PO_4)_2$, kinoite, $Na_2CO_3.H_2O$, α-$Al(OH)_3$, $Na_2S_2O_3.5H_2O$, and yugawaralite in order to reinterpret the hydrogen-bonding in these compounds. The criteria can also be used, *cum grano salis*, for the calculation of hydrogen atom positions in organic crystal structures.

Introduction

Hydrogen atoms covalently bonded to strongly electronegative atoms (like F, O, N, Cl, and S) are often involved in weak interactions with other neighboring electronegative atoms. This interaction, called a hydrogen bond, is usually viewed in terms of the three directly participating atoms: the donor D, the acceptor A, and the hydrogen atom, D–H$\cdots A$, where H$\cdots A$ is the hydrogen bond itself. The decision as to whether or not a particular arrangement represents a hydrogen bond can only be made without any doubt when we know the complete geometrical description of the arrangement, *i.e.* the bond distances D–H, H$\cdots A$ and the angle (D–H$\cdots A$). Specifically, the H$\cdots A$ separation should be shorter than the sum of the van der Waals radii of the hydrogen atom and the acceptor atom (Hamilton & Ibers, 1968, p. 14). Furthermore, we need an indication that the potential energy of the hydrogen atom has been influenced by the acceptor atom, as witnessed by the changes in characteristic frequencies of the vibrations involving the hydrogen atom. One useful measure of this is the D–H stretching frequency in the infrared. It occurs for the O–H groups which are not hydrogen-bonded, at wave numbers higher than 3600 cm^{-1}, but it is found empirically to be in the range 3600 to 1700 cm^{-1}, when the O–H group is involved in a hydrogen bond (Nakamoto, Margoshes & Rundle, 1955; Nakamoto, 1970).

The first condition can generally be ascertained only by a complete neutron diffraction analysis of a single crystal, because this is still the only way of arriving at unambiguous and precise values for the hydrogen atom positions. Whether or not the second criterion is met sometimes cannot be decided, because a crystal structure may be complicated, have many hydrogen atoms, and it may not be possible to assign each observed frequency to a particular bond. The common case with which we are usually confronted is a crystal structure determined by X-ray diffraction, with little or no information about the hydrogen atom positions. The heavy-atom positions are known, and we try to make reasonable inferences about the hydrogen bond distribution and the hydrogen atom positions. In this situation, we can be aided in our deductions by the considerable body of information that has been amassed in the past 20 years. An excellent review of this information and the methods employed has been presented by Hamilton & Ibers (1968). In this paper, the discussion is limited to the geometrical part of the question of the hydrogen bond: what can we tell about the hydrogen atom positions and the hydrogen bond, short of doing a neutron diffraction study, when we know the heavy-atom positions from an X-ray diffraction investigation?

Experimental techniques

X-ray diffraction

The determination of hydrogen atom positions by X-ray diffraction is possible with a high degree of confidence in the presence of light atoms only. Therefore, the hydrogen atom positions found in crystal structures of organic compounds, where the heavy atoms are C, N, and O, are fairly reliable. In the presence of heavier atoms, the precision of the hydrogen atom coordinates is not only much lower, but the probability of making a completely wrong assignment increases sharply. The reason for this is the low scattering power of hydrogen for X-rays, so that the electron densities found in difference maps at the expected hydrogen atom sites are usually around 0·5 e.Å^{-3}. This means that they are of approximately the same height as the background peaks in even the most precise structure determinations. In several cases where a crystal structure has been determined accurately by both X-ray and neutron diffraction, the average distance between the hydrogen atom positions as found with these two methods is about 0·25 Å (Table 1). The angular deviation [H(X)–D–H(N)] for the 43 crystallographically different hydrogen atoms is 12°, which means that the deviations are not exclusively due to the fact that the observed D–H distances in X-ray determinations tend to be 0·1 to 0·2 Å shorter than in neutron diffraction determinations. Moreover, in the case of $MnCl_2.4H_2O$, the atom H(32) was misplaced in the X-ray structure determination by 0·7 Å, so that the acceptor atom of the hydrogen bond was not identifiable.

Infrared spectroscopy

It has been shown by Rundle & Parasol (1952), and subsequently corroborated by other investigators (for further literature see Hamilton & Ibers, 1968), that the D–H stretch vibration shifts to lower wave numbers as the distance $D\text{–H}\cdots A$ decreases. In the case of substances with only a few hydrogen bonds, the knowledge of this frequency can, therefore, be of help in the assignment of hydrogen bonds to particular interatomic distances in a known crystal structure. The major shortcoming of this method, namely of not being able to tell the direction of the O–H vector relative to the crystal structure, can be overcome by working with single crystals of known orientation and by measuring the pleochroism of the O–H stretch mode using polarized radiation (Tsuboi, 1950; Vedder, 1964). Since it is difficult to distinguish between contributions from different O–H groups, the method has been applied, so far, only to crystal structures with one O–H group per asymmetric unit.

Nuclear magnetic resonance

Pake (1948) has shown how the nuclear paramagnetic resonance absorption lines of hydrogen atoms in hydrates, which are due to the proton–proton spin interaction within the water molecule, can be interpreted to yield information about the length and direction of the H–H vector. Despite its inherent difficulties (El Saffar, 1966), the method was found to give reasonable results even in instances with many independent water molecules, as in the case of $FeSO_4.7H_2O$ (El Saffar, 1969). As of this date, the method has been applied in a quantitative way only to H_2O molecules.

Prediction of hydrogen bonds

Electrostatic energy calculations

The application of a simple point-charge model to several crystalline hydrates has shown that the orientations of the water molecules and the positions of the hydrogen atoms could be accurately predicted by searching for the configuration of minimum electrostatic energy (Baur, 1965*a*). In these calculations, which were performed with the computer program *MANIOC*, the heavy-atom parameters, including those of the water oxygen atom, were kept constant, while the positions of the hydrogen atoms were varied

Table 1. *Comparison of average deviations* (*both in terms of* d(H–H) *and angle* H–D–H) *between the hydrogen atom positions as determined by neutron diffraction* (N) *and*: (*a*) *X-ray diffraction* (X); (*b*) *electrostatic calculation* (El); (*c*) *geometrical calculation* (Geom)

The references indicated by the superscripts refer to the X-ray studies, the electrostatic calculations, and the geometrical calculations.

Compound	Δ(N,X)	Δ(N,El)	Δ(N,Geom)	Neutron study reference
$MgSO_4.4H_2O$	0·24 Å^a 15°	0·11 Å^b 6°	0·13 Å^c 9°	Baur, 1964*b*
$MnCl_2.4H_2O$	0·26 Å^d 13°	0·09 Å^e 5°	0·10 Å^c 6°	El Saffar & Brown, 1971
$Na_2HAsO_4.7H_2O$	0·22 Å^f 11°		0·18 Å^g 10°	Ferraris, Jones & Yerkess, 1971
$Cu(NH_4)_2(SO_4)_2.6H_2O$	0·24 Å^h 10°		0·13 Å^c 8°	Brown & Chidambaram, 1969
$BeSO_4.4H_2O$	0·12 Å^i 6°		0·09 Å^c 5°	Sikka & Chidambaram, 1969
$KAl_2(Si_3Al)O_{10}(OH)_2$		0·10 Å^j 6°	0·08 Å^c 4°	Rothbauer, 1971

a. Baur, 1962
b. Baur, 1965*a*
c. This work
d. Zalkin, Forrester & Templeton, 1964
e. Baur, 1965*b*
f. Ferraris & Chiari, 1970
g. Baur & Khan, 1970
h. Montgomery & Lingafelter, 1966
i. Dance & Freeman, 1969
j. Giese, 1971

until the positions of least electrostatic energy were found. The shape of the water molecule was held constant in these calculations: O–H = 0·97 Å and ∠H–O–H = 109·5°. The best agreement between calculated and experimental positions was found in the case of $BaCl_2.2H_2O$, for a charge of 0·5e on the hydrogen atoms and −1·0e on the water oxygen atom. This charge distribution was therefore used in determining the positions of least energy for the hydrogen atoms in $MgSO_4.4H_2O$, $Li_2SO_4.H_2O$, $C_4D_3N_3O_4.D_2O$, $Na_2Al_2Si_3O_{10}.2H_2O$, and $CuSO_4.5H_2O$. Positions calculated for 28 different hydrogen atoms in these six hydrates agreed, within 0·09 Å, with the experimental positions. More important, however, is that some of these correctly calculated hydrogen atoms were involved in extremely bent hydrogen bonds ($D\angle$–H···A as small as 140°), some were involved in clearly bifurcated bonds, and one was even located in a non-hydrogen bonded position, with H···O of 2·39 and 2·59 Å. The success of the electrostatic model in predicting these unconventional geometrical arrangements, as well as the hydrogen atom positions in essentially straight hydrogen bonds, shows the importance of the electrostatic contribution in the case of long hydrogen bonds of the type found in hydrates. Subsequently, the electrostatic approach, using *MANIOC*, was used for the prediction of hydrogen atom positions in salt hydrates for which no neutron diffraction data were available: $MnCl_2.4H_2O$ (Baur, 1965*b*); $CuSO_4.3H_2O$ (Zahrobsky & Baur, 1968); the antiferroelectric phase of $Cu(HCOO)_2.4H_2O$ (Soda & Chiba, 1968); $MnCl_2.2H_2O$, $KMnCl_3.2H_2O$, β-$RbMnCl_3.2H_2O$, $CsMnCl_3.2H_2O$, α-$RbMnCl_3.2H_2O$, $Cs_2MnCl_4.2H_2O$, and $Rb_2MnCl_4.2H_2O$ (El Saffar, 1970); and $MgSO_4.5H_2O$ (Baur & Rolin, 1972). Several of these predictions have been verified recently by neutron diffraction ($MnCl_2.4H_2O$ by El Saffar & Brown, 1971, and β-$RbMnCl_3.2H_2O$ by Jensen & Lehmann, 1970) and by nuclear quadrupole resonance and n.m.r. ($KMnCl_3.2H_2O$ and $CsMnCl_3.2H_2O$. DeJonge, Hijmans & Gevers 1971).

The simple electrostatic theory for predicting hydrogen atom positions is also applicable to hydrogen atoms which are not bonded to a water oxygen atom. Using *MANIOC*, Giese (1971) recently calculated the position of the hydrogen atom of a hydroxide group in $2M_1$ muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$. At the same time, the results of a neutron diffraction study of muscovite were published (Rothbauer, 1971), which fully confirmed Giese's prediction (Table 1). This is especially remarkable since this atom is not hydrogen-bonding: the three next oxygen atoms in directions in which hydrogen-bonding could be expected are at distances of 2·57, 2·68, and 2·69 Å from the hydrogen atom. Pedersen (1969) has applied the electrostatic method to a study of the conformation of H_2O_2 molecules in solids. Sequeira & Hamilton (1967) expanded the model in their investigation of the phosphonium ion in PH_4I and the ammonium ion in NH_4Br, by introducing a nonelectrostatic repulsion term of the 12–6 Lennard-Jones potential type. In this case, this was necessary because the electrostatic model by itself predicted the wrong positions for the hydrogen atoms. Lundgren, Liminga & Olovsson (1968, 1971) used this refined model to study the conformation of the hydrazinium ion in $LiN_2H_5SO_4$ and $N_2H_5HC_2O_4$. Here, the electrostatic model by itself already gave the same result as that of the calculation with the nonelectrostatic repulsion terms, but the authors were interested in an estimate of the energy barrier against rotation of the $-NH_3$ part of the hydrazinium ion; therefore, they had to introduce the nonelectrostatic repulsion terms.

The lesson to be learned from comparing the results of these calculations with the experimental results is that the positions of hydrogen atoms from various donor groups obey, reasonably well, a simple point-charge model, even in cases where the hydrogen atoms form bent or bifurcated bonds or are not involved in hydrogen bonding at all. This last statement appears to be true only as long as we are dealing with strongly electronegative donor and acceptor atoms. In the case of less electronegative atoms (such as P, I, and Br in PH_4I and NH_4Br), the nonelectrostatic contribution may become important, and the purely electrostatic model breaks down. For strongly hydrogen-bonding donors and acceptors, however, it is safe to assume that the hydrogen atoms will tend to occupy positions as far as possible from the cations (M) and from each other, and as close as possible to potential hydrogen bond acceptors.

These considerations are further supported by an inspection of the hydrogen bond geometries observed in crystal structures determined by neutron diffraction. The example shown in Fig. 1, taken from $MgSO_4.4H_2O$, demonstrates that even in a case where two less bent bonds could have been formed, the arrangement is

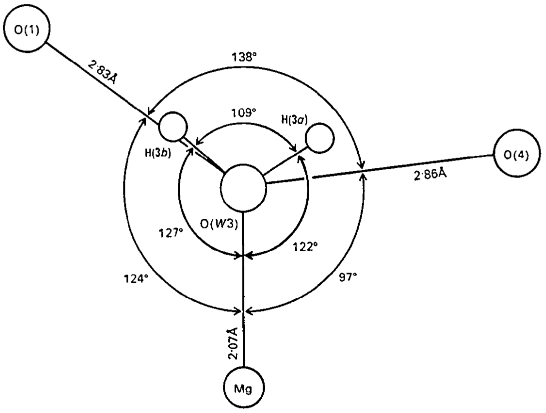

Fig. 1. Environment around oxygen atom O(W3) in $MgSO_4.4H_2O$ (Baur, 1962), determined by neutron diffraction. The angles do not add up to 360°, because the atoms are not exactly coplanar. The geometry demonstrates that linearity of hydrogen bonds is much less important than long cation–hydrogen distances and the constancy of the donor-group geometry (in this case a water molecule).

actually characterized by one essentially straight bond and one very bent bond with an angle [O(*W*)–H$\cdots$O] of 140°. The reason for this appears to be the gain in energy realized by the longer Mg–H separation that is allowed by the angle [Mg–O(*W*)–H] of 122°. In this particular case, the two O(*D*)$\cdots$O(*A*) distances have practically the same length. Therefore this bent hydrogen bond cannot be rationalized on the basis of the hydrogen bond angle [O(*D*)–H$\cdots$O(*A*)] *versus* hydrogen bond length [O(*D*)–O(*A*)] correlation established by Hamilton (1962). It should also be emphasized that none of the hydrogen-containing crystals studied so far by neutron diffraction exhibits a hydrogen bond located in the edge of a coordination polyhedron around a cation, thus bringing the hydrogen atom into coordinating contact with this cation.

Therefore, the following criteria can be established.

(1) The angles *M*–*D*–H will be at least 90° (and usually over 100°).

(2) Even when no hydrogen bonding contact is made, the hydrogen atom will tend to be positioned as close as possible to a potential hydrogen bond acceptor (or acceptors).

(3) No hydrogen atoms will be located in the edges of coordination polyhedra around cations.

(4) The requirement of linearity of hydrogen bonds is *not* important.

One consequence of the electrostatic model is 'that there is no qualitative difference between a straight hydrogen bond... and the position of a hydrogen atom which does not form a hydrogen bond,.... Of course, there will remain a quantitative difference: in the first case there will be an energetically stronger interaction than in the latter case. Bent and bifurcated hydrogen bonds could be understood as intermediate stages between the two extremes' (Baur, 1965*a*). This raises a semantic question: is it especially difficult to distinguish between bifurcated bonds and cases where no hydrogen bonding occurs? From the standpoint of electrostatic energy, there is no such thing as 'no hydrogen bond', because there is always an electrostatic interaction, albeit small. The Hamilton & Ibers (1968) operational criterion, involving the sum of the van der Waals radii of the hydrogen atom and the acceptor atom, shows a practical way out of the dilemma: we know from experience that when the H–*A* distances are longer than this sum, usually no spectroscopic evidence for a hydrogen bond can be found. Its energy must be very small.

Extended electrostatic valence rule

Because the simple electrostatic model of the hydrogen bond is useful for an interpretation of most of its features, it appears justifiable to carry the simplification further and investigate the hydrogen bond in terms of the electrostatic valence rule. To do this, we cannot view just the part $D\text{–H}\cdots A$, but have to look at the valence balance of *D* and *A* as well. The immediate vicinity of the hydrogen bond can be represented schematically as $(M)_n\text{–}D\text{–H}\cdots A\text{–}(X)_m$, where *M* and *X* are each one or more cations (including additional hydrogen atoms) to which *D* and *A* are bonded. Each *D* and each *A* receives from the surrounding cations and hydrogen atoms a certain sum of the electrostatic bond strengths (Pauling, 1960), which we call p_D and p_A. It has been shown (Baur, 1970*a*) that the length of the hydrogen bond is strongly correlated with the difference $(\Delta p = p_D - p_A)$ between the bond strengths received by *D* and *A*:

$$d(D\text{–H}\cdots A) = (a + b\Delta p)\ \text{Å}, \tag{1}$$

where *a* and *b* are empirically derived constants. For the case where both the donor atom and the acceptor atom are oxygen atoms, $a = 2{\cdot}85$ (1) and $b = -0{\cdot}38$ (2). Values of *p* from $-0{\cdot}5$ to $+0{\cdot}8$ v.u. have been observed and found to correspond to hydrogen bond lengths of about 3·05 to 2·55 Å. The correlation coefficient between the bond lengths and Δp for 392 observations is $-0{\cdot}68$ which is statistically highly significant. The individual hydrogen bond lengths in $MgSO.5H_2O$ (Baur & Rolin, 1972) provide a good example of the validity of equation (1). An analogous relationship has been quantitatively established for N–H$\cdots$O bonds (Khan & Baur, 1972). The rarely occurring symmetrical hydrogen bonds are not covered by these correlations. Usually, they are formed between anions which both have small p_x values, and Δp is either zero or close to zero.

Table 2. *Dimensions of hydrogen-containing groups, based on neutron diffraction data and not corrected for thermal motion (modified from Baur,* 1970*b)*

Data for H_3O^+ are from $H_5O_2^+$ (Williams & Peterson, 1969, and private communication).

	Distance *D*–H			Angle H–*D*–H		
	Mean	Range	No. of values averaged	Mean	Range	No. of values averaged
Hydroxide, OH^-	0·98 Å	0·92–1·13 Å	16			
Water, H_2O	0·96	0·86–1·04	149	109°	102–116°	81
Hydronium, H_3O^+	1·00	0·99–1·00	3	112	109–113	3
Acid groups $(XO_n)H$:						
asymmetric H bond	1·04	0·97–1·09	9			
symmetric H bond	1·23	1·20–1·27	5			
NH_4, NH_3, NH_2	1·01	0·94–1·10	37	110	104–122	35

In the calculation of the p_x, it is assumed that D receives 0·83 v.u. ($\frac{5}{6}$) of the bond strength donated by the hydrogen atom, while A receives the balance, that is 0·17 v.u. ($\frac{1}{6}$). Since the M–D and the A–X distances are also influenced by the bond strengths received by D (or A), the lengths of these cation–anion bonds can give us clues as to the existence of hydrogen bonds and can help us to identify the donor and the acceptor groups. To do this quantitatively, we have to apply rule 3 of Baur (1970*a*) which relates the bond strengths with the bond lengths within a coordination polyhedron and gives, for an individual bond distance $d(M\text{–}D)$ [or $d(A\text{–}X)$] within a polyhedron:

$$d(M\text{–}D)=[d(M\text{–}D)_{\text{mean}}+b\Delta p_x]\ \text{Å}\,, \tag{2}$$

where M is any cation, D is any anion, $d(M\text{–}D)_{\text{mean}}$ and b are empirically derived constants for a given pair of M and D in a given coordination, and Δp_x is the difference between the individual p_x and the mean p_x for the coordination polyhedron around M: $\Delta p_x=p_x-p_{x(\text{mean})}$. Values of $d(M\text{–}D)_{\text{mean}}$ and b have been derived for 14 different cases (Baur, 1970*a*). Thus, the following additional criteria have to be considered when making predictions about hydrogen bonds and hydrogen atom locations.

(5) The hydrogen bond must be viewed within its complete environment $(M)_n\text{–}D\text{–H}\cdots A\text{–}(X)_m$.

(6) The M–D and the A–X bond lengths are influenced by the hydrogen bond.

(7) The $D\text{–H}\cdots A$ distance depends on the difference in the electrostatic bond strength received by D and A.

Geometrical calculations

Based on the principles presented above, it is usually possible to specify the atoms to which the hydrogen atoms are covalently bonded and which atoms are hydrogen bond acceptors (if any). Once the general distribution of the hydrogen bonds is deduced, the positional coordinates of the hydrogen atoms can be calculated using the known dimensions of hydrogen-bond donor groups. The shape of these groups in very different crystalline environments is reasonably constant (Table 2.) Such geometrical calculations are very simple and straightforward, but are also tedious;

Table 3. *Hydrogen atom coordinates* ($\times 10^3$) *calculated with CALHPO*

The donor and acceptor atoms are identified, the D–A and H–A distances are given. For some of the longer distances, H–A, the name 'acceptor' may be not quite appropriate, because the hydrogen bonding interaction must be extremely weak. Polyfurcated arrangements are indicated by two or three atom numbers for A. In these cases, the average distances are given.

$KH_5(PO_4)_2$:							
	x	*y*	*z*	*D*	*A*	*D*–*A*	H–*A*
H(24)	438	255	024	O(2)	O(4)	2·59 Å	1·61 Å
H(38)	561	084	296	O(3)	O(8)	2·64	1·66
H(54)	707	922	129	O(5)	O(4)	2·59	1·61
H(68)	129	972	452	O(6)	O(8)	2·57	1·59
H(71)	032	207	163	O(7)	O(1)	2·41	1·20
Kinoite:							
H(1)	400	099	948	O(*h*7)	O(5,*h*6)	3·16	2·40
H(2)	616	066	400	O(*h*6)	O(3)	2·68	1·70
$Na_2CO_3.H_2O$:							
H(1)	153	917	084	O(*W*4)	O(1,3)	3·04	2·29
H(2)	908	922	097	O(*W*4)	O(3)	2·68	1·77
α-$Al(OH)_3$, arrangement I:							
H(2)	300	990	411	O(2)	O(2,3,4)	3·16	2·43
H(3)	251	220	593	O(3)	O(4)	2·92	1·94
H(4)	478	370	326	O(4)	O(2,3)	3·16	2·41
α-$Al(OH)_3$, arrangement II:							
H(2)	316	990	416	O(2)	O(2,3,4)	3·16	2·41
H(3)	051	128	684	O(3)	O(2,4)	3·19	2·42
H(4)	297	264	413	O(4)	O(3)	2·92	1·94
$Na_2S_2O_3.5H_2O$:							
H(9)	721	042	173	O(8)	S(1)	3·25	2·42
Yugawaralite:							
H(12)	895	201	119	O(*W*1)	O(2)	3·04	2·17
H(113)	899	313	142	O(*W*1)	O(13)	3·32	2·44
H(215)	828	290	629	O(*W*2)	O(15)	3·05	2·09
H(26)	830	177	645	O(*W*2)	O(6)	3·16	2·20
H(313)	656	329	253	O(*W*3)	O(3)	2·92	1·95
H(34)	572	249	332	O(*W*3)	O(*W*4)	3·15	2·20
H(44)	345	150	267	O(*W*4)	O(4)	2·98	2·11
H(46)	463	117	428	O(*W*4)	O(6)	3·28	2·49

therefore, it is preferable to perform them on a computer (program *CALHPO* Baur, 1969). *CALHPO* allows the hydrogen atoms of a donor group to be arranged along specified lines or planes in the crystal structure, or at specified angles from these lines or planes. The lines and planes are defined by indicating the coordinates through which they go. Within a certain plane, the group can be arranged in such a way as to have maximum distances of the hydrogen atoms from a specified cation or cations and thus simulate the electrostatic repulsion between these atoms.

Once the hydrogen atom positions are calculated, it is possible to find out how long the H···*A* distances are, and whether they could correspond to hydrogen bonded contacts by applying the criterion of Hamilton & Ibers (1968). In crystal structures for which the positions of several hydrogen atoms have been calculated, the H–H distances should also be carefully checked. According to Pauling (1960), the van der Waals radius of the hydrogen atom is 1·2 Å. However, two hydrogen atoms can come into a contact, 1·5 Å in length, when they are covalently bonded to the same electronegative atom (as in the water molecule). Under special circumstances, such as the tight packing of hydroxide groups in $Mg(OH)_2$ (Zigan & Rothbauer, 1967), hydrogen atoms that belong to different groups can come as close as 1·93 Å. In cases where the same electronegative atom is acting as both the donor and the acceptor atom in different hydrogen bonds, the H–H distance between the donated and the accepted hydrogen atom can be as short as 2·05 Å. H–H distances of 2·2 Å are quite common in a variety of hydrogen-containing compounds. Therefore, it would seem that the van der Waals radius of 1·2 Å proposed for the hydrogen atom by Pauling (1960) is slightly too large. Thus a further criterion for the assignment of hydrogen atom positions is:

(8) Hydrogen atoms belonging to different donor groups should usually be at least 2·0 Å apart, because the van der Waals radius of the hydrogen atom is 1·0 Å.

The new value of the van der Waals radius of the hydrogen atom means that according to the distance criterion of Hamilton & Ibers (1968), only H···O distances shorter than 2·4 Å should be considered to be hydrogen bonds. This is particularly obvious in a case like $Mg(OH)_2$, where each hydrogen atom is surrounded by three oxygen atoms at a distance of 2·46 Å, but the O H stretch frequency is 3649 cm^{-1} (Hexter, 1958), which means it is as high as in the free OH radical or in H_2O in the vapor phase (Nakamoto, 1970). The proposal that the van der Waals radius of hydrogen is 1·0 Å leads to the same numerical values of the distance criterion for hydrogen bonds as given by Hamilton (1968), according to whom the H···*A* distance should be 0·2 Å smaller than the sum of the radii of hydrogen and the acceptor atom (based on $r_{H(vdW)} = 1{\cdot}2$ Å). The advantage of the new, smaller value of the radius is that it helps to rationalize both the observed H–H distances and the H···*A* distances.

The 'geometrical' hydrogen atom positions of the compounds mentioned in Table 1 were calculated using *CALHPO*. The agreement between neutron diffraction results and geometrically calculated positions is not quite as good as with the electrostatically calculated positions. But in all cases where it can be compared, the agreement is better than it is for the comparison between neutron and X-ray results. Especially instructive is the case of $Na_2HAsO_4.7H_2O$. The crystal structure of this compound was determined by X-ray diffraction independently by Ferraris & Chiari (1970), who reported the hydrogen atom positions as found in a difference synthesis, and by Baur & Khan (1970) who calculated the positions using *CALHPO*. The subsequent neutron diffraction study (Ferraris, Jones & Yerkess, 1971) confirmed that the calculated positions are nearer to the true positions than are the X-ray positions (Table 1). Another example of a verification of calculated hydrogen atom positions is provided by the n.m.r., study of $FeSO_4.7H_2O$ (El Saffar, 1969) which fully confirmed (average deviation only 0·07 Å) the positions calculated previously (Baur, 1964*b*).

Applications

The criteria for locating hydrogen bonds and hydrogen atom positions can be illustrated most clearly by using, as examples, recently reported crystal-structure determinations. The hydrogen atom positions calculated

Table 4. $KH_5(PO_4)_2$, *calculated* P–O *distances, based on the assumption that* (O1)–O(7) *is a symmetrical hydrogen bond, and the observed* P–O *distances*

	p_O	Δp	d_{calc}	d_{obs}	$\lvert\Delta d_{oc}\rvert$
P(1)–O(1)	1·86 v.u.	−0·12 v.u.	1·517 Å	1·512 (4) Å	0·005 Å
P(1)–O(2)	2·19	0·21	1·553	1·549 (4)	0·004
P(1)–O(3)	2·19	0·21	1·553	1·560 (4)	0·007
P(1)–O(4)	1·69	−0·29	1·498	1·502 (4)	0·004
Mean	1·98				
P(2)–O(5)	2·19	0·18	1·550	1·559 (4)	0·009
P(2)–O(6)	2·19	0·18	1·550	1·550 (5)	0·000
P(2)–O(7)	1·97	−0·04	1·526	1·515 (4)	0·011
P(2)–O(8)	1·69	−0·32	1·495	1·490 (4)	0·005
Mean	2·01			1·530	0·006

with *CALHPO* for these structures (listed in Table 3) are considered to be more reliable than the experimentally derived positions given in the original papers.

The symmetric hydrogen bond in $KH_5(PO_4)_2$

The crystal structure of $KH_5(PO_4)_2$ has been determined by X-ray diffraction with high accuracy (Philipott & Lindquist, 1971). Because of short O···O contacts between oxygen atoms belonging to different phosphate groups, the authors assume that $O(1) \rightarrow O(7)$ (2·405 Å), $O(2) \rightarrow O(4)$ (2·585 Å), $O(3) \rightarrow O(8)$ (2·636 Å), $O(5) \rightarrow O(4)$ (2·587 Å), and $O(6) \rightarrow O(8)$ (2·596 Å) are hydrogen bonds. They support this assumption by a qualitative consideration of the P–O bond lengths, and by hydrogen atom positions based on a difference synthesis, according to which $O(1) \rightarrow O(7)$ should be an asymmetric hydrogen bond with O(1) as the donor atom. However, the authors recognize that $O(1) \rightarrow O(7)$ might be a symmetric hydrogen bond, but do not see how this could be proved short of performing a neutron diffraction analysis. The results of applying equation (2) to the P–O bond length in $KH_5(PO_4)_2$ are shown in Table 4, assuming that O(1) and O(7) are connected by a symmetrical hydrogen bond, so that each receives a bond strength of 0·5 v.u. from the central hydrogen atom; $d(\text{P–O})_{\text{mean}}$ is taken as 1·530 Å, as observed in $KH_5(PO_4)_2$, and b is taken as 0·109/v.u. (Baur, 1970*a*). The average deviation Δd_{oc} between observed and calculated P–O bond lengths is 0·006 Å, which compares favorably with the estimated standard deviations of the bond lengths. If O(1)–O(7) were an asymmetric hydrogen bond, P(1)–O(1) and P(2)–O(7) should have a greater difference in their observed bond lengths. Since they are approximately equal, the O(1)–O(7) bond should be essentially symmetrical. Any asymmetry in this bond should amount to only a few hundreths of one Å, and the hydrogen atom might possibly be shifted in the direction of oxygen atom O(1), because it is receiving a slightly smaller p_O than O(7). The geometrically calculated hydrogen atom positions (Table 3) are based on strict symmetry for this bond, and on an O–H distance of 0·98 Å for the other hydrogen bonds. $KH_5(PO_4)_2$ should be studied by neutron diffraction, nevertheless, because it is one of the rare instances where a symmetrical hydrogen bond is present in the absence of a symmetry element.

$Si_3O_8(OH)_2$ *groups in kinoite*

Laughon (1971) has determined the crystal structure of the mineral kinoite and he formulates it as $Cu_2Ca_2Si_3O_{10}.2H_2O$ (about 2000 observed intensities $R=0·037$). One of the hydrogen atoms was indicated by a density of 1·3 e.Å^{-3}. The shape of the water molecule is almost as expected, with O(*W*)–H distances of 1·15 and 1·32 Å, and an angle, H–O(*W*)–H, of 114°. The author cautions that the hydrogen atom positions must be considered as being questionable. Actually, however, it is obvious that the position of H(2) must be completely wrong, because the distance H(2)–Cu(2) is 1·73 Å, H(2)–Ca is 1·98 Å, and the implied hydrogen bond $O(W) \rightarrow O(1)$ is in the edges of the Cu(2) and Ca coordination polyhedra. Moreover, a calculation of the electrostatic bond strengths shows that the water oxygen atom (which is bonded to two copper atoms, one calcium atom, and two hydrogen atoms) is receiving a total p_O of 2·90 v.u., while one of the silicate oxygen atoms, O(6), is receiving a p_O of 1·33 v.u. from one Si atom and one Ca atom. A bond length calculation analogous to the one for $KH_5(PO_4)_2$ shows that the Si(1)–O(6) distance would be 1·58 Å, if Laughon's assumption is correct, while the observed value is 1·646 (4) Å. On the other hand, all the cation–O(*W*) distances should be long to compensate for the p_O of 2·90 v.u. The conclusion from this is that Laughon's assignment is wrong and that instead, atoms O(6) and O(*W*) are both hydroxide groups. Based on this assumption O(6) receives a bond strength of 2·17 v.u. and O(*W*) receives a bond strength of 2·07 v.u. Oxygen atom O(6) forms a short hydrogen bond of 2·68 Å to O(3), while for O(*W*) the next atom that could possibly be a hydrogen bond acceptor is O(5), at a distance of 3·13 Å.

This reinterpretation of the crystal structure of kinoite means that its chemical formula should be written as $Cu_2Ca_2(OH)_2[Si_3O_8(OH)_2]$. The isolated triple tetrahedral unit, $Si_3O_8(OH)_2$, has two hydroxide groups directly attached to the two terminal silicate tetrahedra. A similar unit has been described by Maksimov, Uljuchin & Belov (1968) in $K_3Y[Si_3O_8(OH)_2]$.

Bifurcated hydrogen bond in $Na_2CO_3.H_2O$

Dickens, Mauer & Brown (1970) have deduced in their refinement of $Na_2CO_3.H_2O$ the hydrogen atom positions from a difference synthesis. They took as best positions, however, those calculated on the basis that the two assumed hydrogen bonds (one of which [O(*W*4)–O(1)] is in the edge of the Na(2) coordination polyhedron) are as linear as possible. The two sets of positions are in general agreement. However, the H(1)–Na(2) distance is 2·42 Å, while the angle H(1)–O(*W*4)–Na(2) is 63°; thus it is implied that the hydrogen atom H(1) belongs to the coordination polyhedron around Na(2) [the average Na(2)–O distance is 2·53 Å]. A more likely hydrogen atom arrangement can be visualized, if we consider that atom O(3) is twice at approximately hydrogen bonding distance from O(*W*4): at 2·684 and 3·174 Å [∠O(3)–O(*W*4)–O(3) = 60°]. A geometrical calculation, assuming that both hydrogen atoms are in the O(3)–O(*W*4)–O(3) plane and removed as far as possible from the Na(1) and Na(2) atoms gives coordinates (Table 3) that result in the following distances and angles around H(1) and H(2): H(1)–Na, 2·66 to 2·84 Å; H(2)–Na, 2·79 to 2·98 Å; H(1)–O(1), 2·25 Å; H(1)–O(3), 2·34 Å; H(2)–O(3), 1·77 Å; ∠O(*W*4)–H(1)–O(1), 124°; ∠O(*W*4)–H(1)–O(3) 144°; ∠O(*W*4)–H(2)–O(3) 157°; ∠H(1)–O(*W*4)–Na, 95 to 130°. Thus it appears that H(1) is involved in a bifurcated bond to

O(1) and O(3), and that all O(*W*4)–H – O angles deviate significantly from linearity. This arrangement appears more reasonable than the one favored by Dickens *et al.* (1970), because the hydrogen atom H(1) is further removed from Na(2). Even this proposal, however, contains an oddity: the bifurcated bond involves atom O(1), which means that the O(*W*4)–O(1) edge of the coordination polyhedron around Na(2) contains half a bifurcated hydrogen bond. This arrangement might be made possible by the peculiar bonding geometry around the water molecule: the Na(2)–O(*W*4) distance is very long (2·936 Å) and, furthermore, O(*W*4) is one of the rare cases of a five-coordinated water oxygen atom (three times to Na, twice to H). The crystal structure of $Na_2CO_3.H_2O$ should be studied by neutron diffraction in order to obtain further information on this interesting hydrogen bonding geometry.

Hydrogen bonding in α-$Al(OH)_3$

The crystal structure of α-$Al(OH)_3$ (bayerite) was refined from X-ray powder data by Rothbauer, Zigan & O'Daniel (1967). The structure consists of layers similar to those found in gibbsite, in which the Al atoms occupy two thirds of the available octahedral coordination sites between the hydroxide groups. The authors discuss potential hydrogen atom locations, and give coordinates for deuterium atoms based on the refinement of neutron powder diffraction data. According to these authors, only one of the three deuterium atoms is placed between the $Al(OH)_3$ layers. Two are placed within the oxygen layers; one of these [D(6)] is in the edge of the coordination polyhedron around the Al atom [D(6)–Al = 1·79 Å]. Because of the strong electrostatic repulsion between hydrogen atoms and Al atoms, the positions proposed by Rothbauer *et al.* are highly unlikely. The positions calculated here are based on the assumptions that all hydrogen atoms must be between the layers so that they can contribute to the cohesion of the structure, that no H–H distance is shorter than 2·0 Å and finally that the distance O(3)–O(4) of 2·92 Å corresponds to an essentially straight hydrogen bond between the layers. The distance O(2)–O(2), of 3·01 Å, also between the layers and discussed by Rothbauer *et al.* as a possible hydrogen bond, was excluded from the considerations because the two O(2) atoms are related by an inversion center. Two choices must be considered since both O(3) and O(4) are potential hydrogen bond donors. This results in two sets of hydrogen atom positions, which are symmetrical with regard to the H(3) and H(4) atoms. Both sets appear equally likely, and it is possible that the hydrogen atoms are disordered over both sets of positions. This may have contributed to the difficulties encountered by Rothbauer *et al.* in their attempts to interpret the neutron powder pattern.

Short H–H *contacts in* $Na_2S_2O_3.5H_2O$

Padmanabhan, Yadava, Navarro, Garcia, Karsono, Il-Hwan Suh & Lin Shi Chien (1971) refined the crystal structure of $Na_2S_2O_3.5H_2O$ from two-dimensional neutron diffraction data. They confirmed, largely, the hydrogen bonding scheme as proposed by Taylor & Beevers (1952) based on an X-ray determination, and by El Saffar (1968) based on an n.m.r. study. An exception is hydrogen atom H(9), which according to the earlier workers should hydrogen-bond to S(1), but according to Padmanabhan *et al.* does not participate in any hydrogen bonding. Based on the positional coordinates supplied by Padmanabhan *et al.*, the H(9)–H(8)

Table 5. *Short experimental hydrogen–cation distances from recent precise X-ray diffraction determinations*

In some cases, the authors assumed the hydrogen bond to be located in the edge of a coordination polyhedron (*p.e*). The positions of the hydrogen atoms should be considered as doubtful until verified by neutron diffraction.

	H–*M*		*D*–*A*	
$K_2[B_5O_8(OH)].2H_2O$ Marezio, 1969	H(1)–K(2) H(2)–K(1)	2·52 Å 2·76	O(8)→ O(5) O(10)→O(1)	2·74 Å *p.e.* 2·81 *p.e.*
$Ca_3Na_2Cl(SO)_4)_2B_5O_8(OH)_2$ Burzlaff, 1967	H–Na	2·48	O(25)→Cl	3·18
$Na_4P_2O_7.10H_2O$ McDonald & Cruickshank, 1967	H(12)–Na(2) H(22)–Na(1)	2·20 2·19	O(*W*1)→O(2) O(*W*2)→O(4)	2·81 *p.e.* 2·74
$Zn_2Mn(OH)_2SiO_4$ Rentzeperis, 1963	H(1)–Zn(2) H(2)–Mn	1·91 2·02	O(5)—O(2)	2·91
$Ca_2NaHSi_3O_9$ Prewitt, 1967	H–Na	2·34	O(3)→O(4)	2·48 *p.e.*
$CaNa_2(CO_3)_2.5H_2O$ Dickens & Brown, 1969	H(2)–Na	2·22	O(5)→O(2)	2·85 *p.e.*
$Na_5P_3O_8.14H_2O$ Mootz & Altenburg, 1969	H(41)—Na(1) H(42)—Na(2) H(51)—Na(2) H(52)—Na(2) H(102)-Na(4)	2·41 2·55 2·29 2·36 1·83	O(*W*4)→ O(31) O(*W*4)→ O(32) O(*W*5)→ O(13) O(*W*5)→ O(12) O(*W*10)→O(*W*1)	2·73 2·81 *p.e.* 2·78 2·73 3·15 *p.e.*

distance is 1·49 (3) Å, a shorter distance than either H(9)–H(10) or H(8)–H(7), which are both distances within the water molecules. On the other hand, the positions of H(9) derived by El Saffar (1968) and by geometrical calculation (Table 3) are at a reasonable distance from the surrounding hydrogen atoms. It appears that Padmanabhan *et al.* misplaced atom H(9), because it is poorly resolved in all three projections for which they collected data. It seems, therefore, that H(9) is bonding to S(1) as originally assumed by Taylor & Beevers. A new neutron diffraction refinement of $Na_2S_2O_3.5H_2O$ might be necessary, since, in addition, some other distances [H(2)–H(5) = 1·95 (4) Å] appear to be too short.

Can hydrogen atoms be coordinated to cations?

Kerr & Williams (1969) determined by X-ray diffraction, with high accuracy, the crystal structure of the zeolite yugawaralite, $Ca_2Al_4Si_{12}O_{32}.8H_2O$. The four crystallographically independent water molecules are all bonded to the Ca atom. Kerr & Williams proposed a hydrogen bonding scheme which assumed $O(W) \rightarrow O(A)$ distances of 2·85 to 3·04 Å. Five of these distances are edges in the coordination polyhedron around the Ca atom, and the angles Ca–O(*W*)–O(*A*) average 55°. A much more likely hydrogen bonding arrangement can be easily constructed by choosing some longer distances, which are not polyhedral edges, to be hydrogen bonds. The average $O(W) \rightarrow O(A)$ distance is then 3·11 Å. Nevertheless, this assignment appears reasonable because the Δp for all these bonds is in the range of 0·0 to −0·33 v.u., and the bonds should therefore be longer than usual. Also, the angles O(*A*)–O(*W*)–O(*A*) are all close to the tetrahedral angle.

Many crystal structures, in recent years, have been determined with high accuracy by X-ray diffraction, in which the investigators interpreted difference densities as being due to hydrogen atoms. In many cases the hydrogen atom positions found in this way are reasonable, as judged by the eight criteria discussed above, and in some cases they have been subsequently confirmed by neutron diffraction studies. However, there are some instances (Table 5) in which the positions arrived at by X-ray diffraction disagree with the criteria and, therefore, must be considered doubtful until validated by accurate neutron diffraction studies. In no neutron diffraction investigation has a hydrogen atom (which is covalently bonded to an electronegative atom and is therefore a potential hydrogen bond donor) been found to be at the same time coordinated to a cation, *i.e.* to have a cation–hydrogen distance approximately equal to, or smaller than, the average cation–anion distance. This, of course, is no proof that it could not be found in the future. The compounds listed in Table 5 are, therefore, good candidates for starting a search this direction. Such a search might result in a revision of the criteria for the geometry of hydrogen bonds set forth in this paper.

Conclusion

The application of the eight criteria for predicting hydrogen bonds and hydrogen atom positions can be a guide in judging whether or not a proposed hydrogen atom position is reasonable. Extreme caution should be exercised in accepting electron densities in difference maps as proof for a hydrogen atom location, when second (or higher) row elements are present in a crystal structure. Even without any direct experimental evidence it should be possible, in most cases, to arrive at a likely hydrogen atom distribution from a knowledge of the heavy-atom positions and distances. The identification of oxygen atoms as hydroxide groups, water molecules, *etc.* is a by-product of such considerations.

For purely practical reasons, the discussion in this paper has been limited to inorganic crystal structures. Most of the criteria are valid for hydrogen bonds in organic structures as well. For instance, there is no evidence to make us believe that a hydrogen atom in the salt of an organic molecule could be coordinated to a cation. Consequently, *CALHPO* can be, and has been, applied to the calculation of hydrogen atom positions in organic crystal structures. For more details, the reader is referred to the very useful reviews of hydrogen bonding in organic structures which have been given by Clark (1963) and by Donohue (1968).

The eight criteria discussed in this paper are of different origins and orginality and have many sources. Doubtlessly, most of these criteria have been applied before, even if they have not been explicitly formulated in print. The basis of the whole discussion is of course Chapter 12 in Pauling (1960). An early article which expressly mentions the unlikelihood of hydrogen bonds in polyhedral edges was written by Templeton (1960). For further literature, see the book by Hamilton & Ibers (1968), and the reviews and discussions by Baur (1961), Hamilton (1962), Clark (1963), Baur (1965*a*), Donohue (1968), Hamilton (1968) and Baur (1970*a*, *b*). It may be appropriate to point out that the criteria 1, 4, and 8 are based on a new inspection of all neutron diffraction studies (about 60 crystal structure determinations) known to the author as of July, 1971. Since the original papers usually do not state explicitly all the bond distances and angles needed, it was necessary to calculate these from the parameters supplied, using a bond distance and angle computer program (*SADIAN* 69, Baur & Wenninger, unpublished program). Thus, the criteria and Table 2 are based on more extensive statistical material than any previous reviews. Because of space limitations, the voluminous tables of distances and angles and the references to them have not been included in this paper. The reader is again referred to the above-mentioned reviews, which cover the literature up to about 1967.

A listing of *CALHPO* is available on request. I thank the Computer Center of the University of Illinois at Chicago for time provided on the computer, and Dr

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Note added in proof: The litterature on neutron diffraction and infrared studies of crystalline stoichiometric hydrates is treated in a forthcoming comprehensive review article by Falk & Knop (1972). The authors take the view that the angle *M*-*D*-H could be as small as 70°; this means it could be appreciably smaller than the 90° angle proposed in criterion 1. An example of a crystal structure in which the angle *M*-*D*-H must be smaller than 90° because of the geometry and symmetry of the OH-group environment is $Sr(OH)_2$ (Grueninger & Bärnighausen, 1969). This case is also supported by preliminary neutron powder diffraction results (personal communication by Grueninger & Bärnighausen· Such data may point to the possibility of relaxing criteria 1 and 3 for cases where the hydrogen bond donor is coordinated to a cation with small charge and/or high coordination number. Because of this possibility it would be interesting to study by single-crystal neutron diffraction some of the compounds listed in Tables 5 and 3. It may be significant that several of the short H-*M* distances listed in Table 5 involve Na atoms.

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