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On Hydrogen Bonds in Crystalline Hydrates

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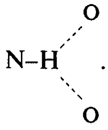
According to the results of recent neutron and X-ray diffraction studies of crystalline hydrates linear hydrogen bonds are not as common in these compounds as has been hitherto assumed. Bent and bifurcated hydrogen bonds, as well as hydrogen atoms in positions in which they do not form hydrogen bonds, have been found to occur even in cases where arrangements with more linear hydrogen bonds would have been geometrically possible. These observations are at variance with the notion that the coordination number of the hydrogen atom in a hydrogen bond is necessarily two. It seems that the orientation of the water molecules, and hence the geometry of the hydrogen bonds, is determined by the electrostatic interactions between the water molecules and the surrounding atoms. This view is supported by the good agreement found in several hydrates between the positions of the hydrogen atoms (*a*) as determined experimentally and (*b*) as calculated theoretically to have the least electrostatic energy. The calculation of the electrostatic energy was done for different orientations of the water molecule until the position with the extreme value of the electrostatic energy was found. The shape of the molecule and the position of the water oxygen atom were held fixed throughout the calculations.

Introduction

Hydrogen bonds are formed between the most electronegative elements like F, O, N, Cl and S. Usually the hydrogen atom is connected more closely with one of the atoms, the donor atom X(*d*), and is at a larger distance from the second atom, the acceptor atom Y(*a*) of the hydrogen bond: X(*d*)–H · · · Y(*a*). Until the advent of neutron diffraction methods this arrangement was believed to be more or less linear, the angle X(*d*)–H · · · Y(*a*) being close to 180°. According to Pauling (1960) the hydrogen bond is largely ionic in character, since the hydrogen atom with its one stable orbital is capable of forming one covalent bond only (to the donor atom). Coulson & Danielsson (1954) estimated the relative magnitudes of the ionic and covalent contributions to the hydrogen bond. They concluded that the electrostatic contribution seems to be dominant, and is the more so the longer the hydrogen bond is. Pimentel & McClellan (1960) emphasized the difficulties in reconciling the electrostatic description of the hydrogen bond with some of its properties and stressed the importance of the covalent contribution to the hydrogen bond. It is generally accepted that the coordination number of a hydrogen atom in a hydrogen bond is two. There are a few exceptions to this rule; one of these is glycine (Albrecht & Corey, 1939; Marsh, 1957; Burns & Levy, 1958), where a hydrogen atom from the $-NH_3^+$ group has the coordination number three:  $N\!-\!H\begin{smallmatrix}\cdots O\\ \cdots O\end{smallmatrix}$. Such an arrangement is called a bifurcated hydrogen bond.

Since C. A. Beevers, H. Lipson and coworkers in the early 1930's determined the crystal structures of several salt hydrates it is known that the oxygen atoms of the water molecules, O(*w*), in these structures can act as

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Table 1. *Geometry of some hydrogen bonds as determined by neutron diffraction in crystalline hydrates*

The numbering of the atoms is the same as in the original papers. TH refers to the calculated positions of the hydrogen atoms (see Tables 3 through 8).

Compounds	Hydrogen bonds	Distances				Angles			
		$O(w)–Y(a)$	$O(w)–H$	$H\cdots Y(a)$	$TH\cdots Y(a)$	$O(w)–H\cdots Y(a)$	$O(w)–TH\cdots Y(a)$	$Y(a)–O(w)–Y(a)$	$H–O(w)–H$
	$H(1)\cdots O(1)$	2·82 Å	1·00 Å	1·82 Å	—	178°	—		
$CaSO_4 . 2H_2O$ (Atoji&Rundle, 1958)	$O(w)$								106°
	$H(2)\cdots O(1)$	2·82	0·98	1·84	—	178	—	106°	
	$H(54)\cdots O(4)$	2·83	0·94	1·91	1·88 Å	168	166°		
$CuSO_4 . 5H_2O$ (Bacon&Curry, 1962)	$O(w5)$								111
	$H(59)\cdots O(w9)$	2·76	0·96	1·81	1·81	171	165	121	
	$H(1)\cdots O(1)$	2·84	0·98	1·87	1·88	167	169		
$Na_2Al_2Si_3O_{10} . 2H_2O$ (Torrie, Brown & Petch 1964)	$O(w)$								108
	$H(2)\cdots O(5)$	3·01	0·94	2·13	2·10	154	154	134	
	$H(1)\cdots O(1)$	2·87	0·93	2·01	1·97	152	153		
$Li_2SO_4 . H_2O$ (Smith *et al.*, 1961)	$O(w)$								111
	$H(2)\cdots O(w)$	2·96	0·97	2·08	2·07	151	151	146	
	$H(3a)\cdots O(4)$	2·86	0·95	2·06	1·98	140	149		
$MgSO_4 . 4H_2O$ (Bauer, 1964*a*)	$O(w3)$								109
	$H(3b)\cdots O(1)$	2·83	0·99	1·85	1·88	174	166	137	
	$D(w1)\cdots O(4)$	2·76	0·97	1·82	1·83	162	159		
Violuric acid monohydrate (Craven & Takei, 1964)	$O(w)$ $O(5)$	2·97		2·11	2·05	150	157	115	106
	$D(w2)$		0·94						
	$O(6)$	2·79		2·07	2·13	131	124	60	

$BaCl_2 . 2H_2O$ (Padmanabhan *et al.*, 1963)	H(3) · · · Cl(1)	3·18	0·97	2·22	2·23	171	167		
	O(*w*2) Cl(1)	3·30		2·66	2·66	125	124	99	103
	H(4)		0·95						
	Cl(2)	3·24		2·49	2·50	135	132	76	
$MgSO_4 . 4H_2O$ (Baur, 1964*a*)	H(2*a*) · · · O(4)	2·84	0·97	1·95	1·91	151	158		
	O(*w*2) O(2)	3·04		2·39	2·48	127	117	147	111
	H(2*b*)		0·93						
	O(2)	3·28		2·59	2·50	132	137	92	

both donor and acceptor atoms of hydrogen bonds. The hydrogen bonds of water molecules in hydrates are usually of the longer, weaker type, the distances O(*d*)–O(*a*) from the water oxygen atoms to the acceptor atoms being between 2·6 and 3·0 Å, whereas hydrogen bonds originating from hydroxyl groups may have O(*d*)–O(*a*) distances in the 2·4 to 2·6 Å range.

Review of experimental results

In the earlier neutron diffraction studies of hydrates (see the review paper by Hamilton, 1962) it was found that all the hydrogen atoms of the water molecules participated in hydrogen bonds, the angle O(*w*)–H · · · Y(*a*) however being in some cases different from 180°. The largest deviation so far was found in $Li_2SO_4 . H_2O$ (Smith, Peterson & Levy, 1961) where O(*w*)–H · · · O(*a*) is 151°. In a number of more recent neutron diffraction investigations of crystalline hydrates it has been shown:

(*a*) That hydrogen bonds in hydrates can be even more severely bent. O(*w*)–H · · · O(*a*) is 140° for one of the hydrogen bonds in $MgSO_4 . 4H_2O$ (Baur, 1964*a*).

(*b*) That bifurcated hydrogen bonds are possible in hydrates: they have been described in violuric acid monohydrate (5-hydroxyiminobarbituric acid monohydrate; Craven & Takei, 1964) and in $BaCl_2 . 2H_2O$ (Padmanabhan, Busing & Levy, 1963).

(*c*) That sometimes a hydrogen atom of a water molecule does not participate in a hydrogen bond at all, as it is the case for one of the hydrogen atoms in $MgSO_4 . 4H_2O$.

In Table 1 there are shown the distances and angles describing the geometry of some hydrogen bond arrangements. They have been selected in order to demonstrate that there are no sharp limits between the geometrically different types of hydrogen bond. Rather there seem to occur all intermediate stages from a linear hydrogen bond, through the bent hydrogen bond and the bifurcated one, to a configuration without any hydrogen bonding. Furthermore it is evident that in some cases it would have been geometrically possible to form hydrogen bonds which would have been less 'abnormal'. Atom H(2*b*) in $MgSO_4 . 4H_2O$ might form a hydrogen bond to the oxygen atom O(2) at a distance of 3·04 Å from O(*w*2). The H · · · O(2) distance would be then about 2·2 Å and since the angle O(4)–O(*w*)–O(2) is 147°, the arrangement would be similar to the bonding of the water molecule in $Li_2SO_4 . H_2O$. Instead H(2*b*) was found experimentally to occupy a site which according to the usual criteria cannot be called a hydrogen bonding position. In the case of violuric acid monohydrate rather normal hydrogen bonds involving an angle O(4)–O(*w*)–O(5) of 115° are conceivable, but instead one of the hydrogen atoms was found experimentally to form a bifurcated hydrogen bond. On purely geometrical grounds the bent angle O(*w*3)–H(3*a*) · · · O(4) in $MgSO_4 . 4H_2O$ need not occur, and the bending might as well have been equally distributed between the two hydrogen bonds originating from O(*w*3). The examples quoted here cannot be dismissed as exceptions. So far 14 crystal structures of hydrates have been investigated by neutron diffraction. In these 14 structures there are 24 crystallographically different water molecules of which 9 are reported as being involved in 'abnormal' configurations: one has a hydrogen atom which does not form a hydrogen bond, two have hydrogen atoms forming bifurcated bonds, six form considerably bent bonds, meaning they have angles O(*w*)–H · · · Y(*a*) smaller than 160°.

Similar results have been obtained in recent years in very accurate X-ray diffraction studies of hydrates. For $Ce_2Mg_3(NO_3)_{12}\,.\,24H_2O$ (Zalkin, Forrester & Templeton, 1963), $Ca(VO_3)_2\,.\,4H_2O$ (Ahmed & Barnes, 1963), $BF_3\,.\,2H_2O$ (Bang & Carpenter, 1964), $HgSO_4\,.\,H_2O$ (Templeton, Templeton & Zalkin, 1963), $MnCl_2\,.\,4H_2O$ (Zalkin, Forrester & Templeton, 1964) and for $FeSO_4\,.\,7H_2O$ (Baur, 1964*b*) the respective authors report that some of the hydrogen atoms are involved in severely bent or even in bifurcated hydrogen bonds, and that some of the hydrogen atoms do not participate in hydrogen bonding at all (for details see the original papers). Hydrate structures like $MgSO_4\,.\,6H_2O$ (Zalkin, Ruben & Templeton, 1964) and $MgSO_4\,.\,7H_2O$ (Baur, 1964*c*) in which all the hydrogen atoms seem to be involved in approximately linear hydrogen bonds are more the exception than the rule.

In view of this evidence it is difficult to avoid the conclusion that the coordination number of hydrogen atoms of water molecules in hydrates is not necessarily two. Rather it seems that the orientation of the water molecules is governed by the electrostatic interactions between the water molecule dipole and the surrounding positive and negative ions, even if this involves a departure from the linear hydrogen bond (compare the discussion of the hydrogen atom positions in $MgSO_4\,.\,4H_2O$, Baur, 1964*a*). For more or less straight hydrogen bonds it is obvious that the electrostatically most favorable position of the hydrogen atoms must be close to the line joining the donor with the acceptor atoms. But in these cases the hydrogen bonds might as well be interpreted as directed bonds. This interpretation is not feasible for bifurcated hydrogen bonds. Pimentel & McClellan (1960), who favor the covalent description of the hydrogen bond, fail even to mention in their book the bifurcated hydrogen bond. When one accepts Pauling's (1960) and Coulson's (1961) viewpoint that the hydrogen bonds are essentially electrostatic in nature, there seems to be no difficulty in going one step further and postulating that there is no qualitative difference between a straight hydrogen bond as in $CaSO_4\,.\,2H_2O$ and the position of a hydrogen atom which does not form a hydrogen bond, like H(2*b*) in $MgSO_4\,.\,4H_2O$. 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. Common to all these geometrically different cases would be that the positions of the hydrogen atoms and hence the geometry of the hydrogen bonds depend largely upon the orientation of the water molecule dipole in the electrostatic field of the surrounding ions.

Calculation of positions of least electrostatic energy

To what extent this last statement is valid can be tested by calculating the electrostatically most favorable positions of water molecules in hydrates and by comparing them with the results of neutron diffraction experiments. This has been done for six crystalline hydrates: $BaCl_2\,.\,2H_2O$, $MgSO_4\,.\,4H_2O$, $Li_2SO_4\,.\,H_2O$, violuric acid monohydrate, $Na_2Al_2Si_3O_{10}\,.\,2H_2O$ and $CuSO_4\,.\,5H_2O$. For these compounds the orientation of each crystallographically different water molecule was varied in turn and for each orientation the electrostatic energy was calculated until the configuration of least energy, *i.e.* with the maximum value of the 'Madelung constant', was reached. Varying the orientation of the water molecules involved only changes in the positions of the hydrogen atoms, while the positions of the water oxygen atoms themselves and of all the other atoms in the structure were kept constant. The shape of the water molecules was held fixed throughout the variations of the orientation with the values: H–O(*w*)–H = 109·5° and O(*w*)–H = 0·97 Å. The actual dimensions of the water molecules determined experimentally in these crystals varied for H–O(*w*)–H from 103 to 114°, for O(*w*)–H from 0·93 to 1·00 Å. In most cases the deviation from the values accepted here is not significant. The electrostatic energies were calculated by Ewald's (1921) method, employing a program written by the author in FORTRAN II for the IBM 7090 computer (see Appendix).

The calculations were begun on $BaCl_2\,.\,2H_2O$, assuming that in this compound the barium and chlorine atoms are fully ionized. The calculations were repeated five times, changing on each run the assumed electric charge on the hydrogen atoms from +0·7e in steps of 0·1e to +0·3e. For each assumed charge distribution the orientations of the water molecules were varied until the extreme value of the electrostatic energy was found. The distances between experimental positions and theoretical positions of least energy for corresponding hydrogen atoms are listed in Table 2. It can be seen that the calculated positions are not extremely sensitive to the changes in the assumed electric charges on the water molecule. The best agreement is found for model III which places −1·0e on the water oxygen atom and +0·5e each on the hydrogen atoms (actually the minimum of the square of the deviations is at 0·49e for the hydrogen atom). This is essentially the same distribution which Bernal & Fowler (1933) have used for their point charge model of the water molecule. For this model the average distance between experimental and calculated positions of the hydrogen

Table 2. *Distances* (*d*) *between corresponding experimental and calculated positions of hydrogen atoms in* $BaCl_2 . 2H_2O$, *assuming varying effective charges on the water molecules*

			d		
	I	II	III	IV	V
O(*w*):	−1·4e	−1·2e	−1·0e	−0·8e	−0·6e
H:	0·7e	0·6e	0·5e	0·4e	0·3e
Atom					
H(1)	0·048 Å	0·040 Å	0·037 Å	0·039 Å	0·050 Å
H(2)	0·088	0·070	0·057	0·050	0·049
H(3)	0·081	0·064	0·050	0·031	0·015
H(4)	0·043	0·058	0·072	0·090	0·107
Σd^2	$185 \cdot 10^{-4}$Å^2	$140 \cdot 10^{-4}$Å^2	$123 \cdot 10^{-4}$Å^2	$131 \cdot 10^{-4}$Å^2	$166 \cdot 10^{-4}$Å^2

atoms is found to be 0·05 Å. Even atom H(4), which is involved in a bifurcated hydrogen bond to Cl(1) and Cl(2) is found to have its position of least energy close to the experimentally determined position. The overall agreement is surprisingly good considering the simplicity of the underlying concept. Parameters of the experimental and theoretical positions of the hydrogen atoms are listed in Table 3.

Table 3. $BaCl_2 . 2H_2O$ (*Padmanabhan et al.*, 1963): $a=6·738$, $b=10·860$, $c=7·136$ Å, $\beta=90°\ 57'$, $Z=4$, $P2_1/n$. *Comparison of experimental* (H) *and calculated* (TH) *parameters of the hydrogen atoms*

In this table, as well as in the following ones, all data pertinent to the calculations have been given: cell constants, cell contents, space group, positional parameters of all the atoms, assumed effective charges on the atoms and the distances (*d*) between the calculated and the experimental hydrogen atom positions.

Atom	Charge	*x*	*y*	*z*
Ba	2·0e	0·0412	0·2166	0·1461
Cl(1)	−1·0	0·8626	0·0812	0·7944
Cl(2)	−1·0	0·6420	0·1050	0·3017
O(*w*1)	−1·0	0·3776	0·1406	0·9410
O(*w*2)	−1·0	0·2006	0·1475	0·5057
H(1)	0·5	0·3534	0·0616	0·8824
H(2)	0·5	0·4756	0·1255	0·0402
H(3)	0·5	0·0977	0·1368	0·5967
H(4)	0·5	0·2466	0·0654	0·4877
	d			
TH(1)	0·037 Å	0·357	0·062	0·878
TH(2)	0·057	0·473	0·130	0·043
TH(3)	0·050	0·096	0·141	0·597
TH(4)	0·072	0·256	0·066	0·483

Mean *d* 0·05 Å

The charge distribution for the water molecule found to give the best results in $BaCl_2 . 2H_2O$ was adopted for the subsequent calculations on the other compounds. The data employed and the results obtained are listed in Tables 4 through 8. The average deviation of the calculated and experimental hydrogen positions was found to be 0·12 Å in $Li_2SO_4 . H_2O$, when the charges on the sulfur atom and on the sulfate oxygen atoms were assumed to be +2·0e and −1·0e respectively. The agreement was improved considerably when the computation was repeated with the charge distribution given in Table 5. The calculated positions of the hydrogen atoms in $Li_2SO_4 . H_2O$ are very sensitive to the relative charges assumed on the water and the sulfate oxygen atoms, since one of the hydrogen bonds of the water molecule goes to a sulfate oxygen atom and the other to the water oxygen atom. The calculations for $MgSO_4 . 4H_2O$ were already completed when it became clear that the first choice of the assumed charges on the sulfate group was not the best possible one. Therefore the calculation on $MgSO_4 . 4H_2O$ was repeated for one of the four water molecules, for O(*w*3). The resulting improvement in the distances between experimental and calculated hydrogen positions was insignificant however. It seems that here the calculated hydrogen atom positions were not so sensitive to assumptions about the charge distribution in the sulfate group because both hydrogen atoms were directed towards the same kind of atoms, the sulfate oxygens. In $Li_2SO_4 . H_2O$ the effect was more pronounced since the two hydrogen atoms of the water molecule were

Table 4. $MgSO_4 . 4H_2O$ (*Baur*, 1964*a*): $a=5·922$, $b=13·604$, $c=7·905$ Å, $\beta=90°\ 51'$, $Z=4$, $P2_1/n$. *Comparison of calculated* (TH) *and experimental* (H) *parameters of the hydrogen atoms*

Atom	Charge	*x*	*y*	*z*
Mg	2·0e	0·0691	0·1030	0·2216
S	2·0	0·1957	0·1070	0·8263
O(1)	−1·0	0·0074	0·0460	0·7601
O(2)	−1·0	0·2482	0·0774	0·0011
O(3)	−1·0	0·3975	0·0913	0·7218
O(4)	−1·0	0·1290	0·2106	0·8148
O(*w*1)	−1·0	0·3583	0·0740	0·3589
O(*w*2)	−1·0	0·7716	0·1395	0·0914
O(*w*3)	−1·0	0·8914	0·1282	0·4412
O(*w*4)	−1·0	0·1752	0·2482	0·2222
H(1*a*)	0·5	0·3726	0·0851	0·4797
H(1*b*)	0·5	0·4580	0·0232	0·3246
H(2*a*)	0·5	0·6802	0·1904	0·1417
H(2*b*)	0·5	0·6819	0·0943	0·0330
H(3*a*)	0·5	0·8018	0·1855	0·4560
H(3*b*)	0·5	0·9207	0·0980	0·5533
H(4*a*)	0·5	0·3167	0·2645	0·2753
H(4*b*)	0·5	0·5771	0·1938	0·7249
	d			
TH(1*a*)	0·129 Å	0·393	0·088	0·477
TH(1*b*)	0·065	0·451	0·020	0·321
TH(2*a*)	0·085	0·689	0·190	0·150
TH(2*b*)	0·136	0·667	0·100	0·024
TH(3*a*)	0·187	0·782	0·181	0·439
TH(3*b*)	0·108	0·905	0·102	0·555
TH(4*a*)	0·083	0·324	0·264	0·267
TH(4*b*)	0·074	0·084	0·308	0·218

Mean *d* 0·11 Å

directed towards different acceptor atoms. None of the water molecules in $MgSO_4 . 4H_2O$ is in such position: consequently the calculation was not repeated for the other water molecules of $MgSO_4 . 4H_2O$. An electric charge of −0·5e on the sulfate oxygens is reasonable in terms of (*a*) the electro-negativity differences between sulfur and oxygen and (*b*) the double bond character of the S–O bonds in the sulfate group (Pauling, 1960). The effective charges on the atoms in the violuric acid molecule and in the aluminosilicate framework of natrolite were therefore chosen proportional to the amount of ionic character resulting from the application of these principles.

The positions of altogether 28 different hydrogen atoms of water molecules have been calculated. The average deviation from the theoretical to the experimental positions was found to be 0·1 Å. These deviations do include the error arising from the fact that for all calculations the same idealized shape of the water molecule was used, while the experimentally determined dimensions of the water molecules differed

Table 5. $Li_2SO_4 . H_2O$ (*Larson*, 1965; *Smith et al.*, 1961): $a=5·454$, $b=4·857$, $c=8·173$ Å, $\beta=107°\ 22'$, $Z=2$, $P2_1$. *Comparison of calculated* (TH) *and experimental* (H) *positions of the hydrogen atoms*

Atom	Charge	*x*	*y*	*z*
Li(1)	1·0e	0·3053	0·4949	0·9938
Li(2)	1·0	0·5619	0·4878	0·3950
S	0·0	0·2938	0	0·2084
O(1)	−0·5	0·0217	0·0701	0·1694
O(2)	−0·5	0·4355	0·1129	0·3787
O(3)	−0·5	0·4010	0·1230	0·0789
O(4)	−0·5	0·3298	0·7008	0·2102
O(*w*)	−1·0	0·9112	0·4718	0·3950
H(1)	0·5	0·9668	0·393	0·3082
H(2)	0·5	0·0060	0·638	0·4379
	d			
TH(1)	0·113 Å	0·985	0·382	0·315
TH(2)	0·025	0·009	0·636	0·441

Mean *d* 0·07 Å

Table 6. *Violuric acid monohydrate*, $C_4D_3N_3O_4 . D_2O$ (*Craven & Takei*, 1964): $a=6·217$, $b=14·373$, $c=7·516$ Å, $Z=2$, $Cmc2_1$. *Comparison of calculated* (TD) *and experimental* (D) *positions of the water hydrogen atoms*

x is zero for all the atoms.

Atom	Charge	*y*	*z*
C(2)	0·4e	0·4282	0
C(4)	0·4	0·2847	0·1774
C(5)	0·1	0·2302	0·0121
C(6)	0·4	0·2803	−0·1639
N(1)	−0·2	0·3755	−0·1506
N(3)	−0·2	0·3801	0·1588
N(5)	−0·3	0·1422	0·0333
O(2)	−0·4	0·5134	0·0008
O(4)	−0·4	0·2508	0·3251
O(5)	−0·4	0·0890	−0·1112
O(6)	−0·4	0·2432	−0·3034
O(*w*)	−1·0	0·0805	0·4945
D(1)	0·2	0·4112	−0·274
D(3)	0·2	0·4179	0·266
D(5)	0·6	0·0224	−0·063
D(*w*1)	0·5	0·1327	0·413
D(*w*2)	0·5	0·1063	0·610
	d		
TD(*w*1)	0·032 Å	0·134	0·416
TD(*w*2)	0·092	0·101	0·617

Mean *d* 0·06 Å

Table 7. *Natrolite*, $Na_2Al_2Si_3O_{10} . 2H_2O$ (*Torrie et al.*, 1964): $a=18·30$, $b=18·63$, $c=6·60$ Å, $Z=8$, *Fdd*2. *Comparison of calculated* (TH) *and experimental* (H) *positions of the hydrogen atoms*

Atom	Charge	*x*	*y*	*z*
Na	1·0e	0·2216	0·0311	0·6158
Si(1)	2·0	0	0	0
Si(2)	2·0	0·1542	0·2111	0·6220
Al	1·0	0·0373	0·0944	0·6120
O(1)	−1·0	0·0230	0·0683	0·8595
O(2)	−1·0	0·0703	0·1821	0·5954
O(3)	−1·0	0·0980	0·0351	0·4967
O(4)	−1·0	0·2066	0·1530	0·7219
O(5)	−1·0	0·1804	0·2275	0·3828
O(*w*)	−1·0	0·0562	0·1894	0·1045
H(1)	0·5	0·0513	0·1443	0·0282
H(2)	0·5	0·1012	0·1883	0·1740
	d			
TH(1)	0·060 Å	0·052	0·147	0·022
TH(2)	0·036	0·102	0·188	0·179

Mean *d* 0·05 Å

Table 8. $CuSO_4 . 5H_2O$ (*Bacon & Curry*, 1962): $a=6·141$, $b=10·736$, $c=5·986$ Å, $\alpha=82°\ 16'$, $\beta=107°\ 26'$, $\gamma=102°\ 40'$, $Z=2$, $P\bar{1}$. *Comparison of calculated* (TH) *and experimental* (H) *positions of the hydrogen atoms*

Atom	Charge	*x*	*y*	*z*
Cu(1)	2·0e	0	0	0
Cu(2)	2·0	0·5	0·5	0
S	0·0	0·011	0·287	0·624
O(1)	−0·5	0·907	0·152	0·675
O(2)	−0·5	0·243	0·318	0·797
O(3)	−0·5	0·859	0·373	0·635
O(4)	−0·5	0·045	0·300	0·384
O(*w*5)	−1·0	0·817	0·074	0·154
O(*w*6)	−1·0	0·290	0·118	0·149
O(*w*7)	−1·0	0·465	0·406	0·299
O(*w*8)	−1·0	0·756	0·416	0·019
O(*w*9)	−1·0	0·434	0·125	0·630
H(54)	0·5	0·897	0·141	0·250
H(59)	0·5	0·719	0·011	0·229
H(62)	0·5	0·300	0·202	0·067
H(69)	0·5	0·335	0·128	0·322
H(74)	0·5	0·320	0·378	0·342
H(73)	0·5	0·603	0·394	0·425
H(83)	0·5	0·805	0·400	0·888
H(84)	0·5	0·853	0·384	0·159
H(91)	0·5	0·601	0·132	0·670
H(92)	0·5	0·410	0·196	0·697
	d			
TH(54)	0·181 Å	0·874	0·150	0·242
TH(59)	0·072	0·709	0·013	0·223
TH(62)	0·150	0·324	0·201	0·068
TH(69)	0·192	0·361	0·123	0·316
TH(73)	0·051	0·603	0·390	0·421
TH(74)	0·103	0·331	0·378	0·359
TH(83)	0·033	0·810	0·399	0·891
TH(84)	0·061	0·855	0·387	0·167
TH(91)	0·185	0·601	0·149	0·658
TH(92)	0·214	0·376	0·193	0·672

Mean *d*=0·12 Å

slightly from compound to compound. $MgSO_4 . 4H_2O$ (Baur, 1962, 1964*a*) is the only one of the structures discussed here for which the parameters of the hydrogen atoms have been determined both by X-ray and neutron diffraction. The agreement between the calculated positions of the hydrogen atoms and the positions determined by neutron diffraction is better (average $d=0{\cdot}11$ Å) than that between the positions determined respectively by X-ray and by neutron diffraction (average $d=0{\cdot}24$ Å). The good fit between theory and experiment can be seen from the comparison of the $H \cdots X(a)$ with the $TH \cdots X(a)$ distances and the $O(w)–H \cdots X(a)$ with the $O(w)–TH \cdots X(a)$ angles for the hydrogen bonds listed in Table 1.

Coulson (1957) has estimated the various contributions to the energy of one separate hydrogen bond in ice. He arrives at the following values: electrostatic energy, $+6{\cdot}0$ kcal.mole^{-1}; delocalization energy, $+8{\cdot}0$ kcal.mole^{-1}; repulsive energy, $-8{\cdot}4$ kcal.mole^{-1}; dispersion energy, $+3{\cdot}0$ kcal.; total theoretical energy, $+8{\cdot}6$ kcal.mole^{-1}, whereas the experimental value is $+6{\cdot}1$ kcal.mole^{-1}. According to Coulson the individual contributions may be in error by as much as 50%. This estimate may be taken as typical of a long hydrogen bond in a crystalline hydrate. Of these four different contributions only the electrostatic energy has a wide range, being proportional to the inverse of the distance. The other energies, when described by an inverse power law $1/r^n$, have values of n up to 9 (compare Fowler, 1936) and hence fall off with the distance r much more rapidly than the electrostatic contribution. Therefore neighbouring atoms which are not directly involved in the bond $X(d)–H \cdots Y(a)$ may well influence the hydrogen bond electrostatically, while they cannot contribute to the other energy terms. Furthermore when we consider Coulson's estimate of the energy contributions to the bond $O(d)–H \cdots O(a)$ it seems sensible to assume that the non-electrostatic terms cancel each other approximately, leaving the electrostatic energy as the only one determining the positions of the hydrogen atoms.

Conclusions

It has been shown that the positions of the hydrogen atoms in hydrogen bonds of water molecules in crystalline hydrates can be predicted using an electrostatic model. Evidence in support of this conclusion is:

(*a*) A qualitative consideration of the geometry of hydrogen bonds as determined by neutron diffraction shows that 'abnormal' hydrogen bonds are formed even where more 'normal' bonds would have been geometrically possible;

(*b*) A good agreement was found between calculated and experimental hydrogen atom positions in $BaCl_2 . 2H_2O$ and other hydrates.

It was especially interesting to note that Bernal & Fowler's (1933) point charge model of the water molecule was confirmed essentially by the results of the calculations on $BaCl_2 . 2H_2O$. The outcome of the calculations on the other hydrates is less conclusive, because it depends partly on the assumptions made about the effective charges on the individual atoms. Nevertheless these calculations are interesting in their own right, since they might be used (assuming the validity of the approach) as a check on the assumptions made about the charge distributions. For instance from the calculations on $Li_2SO_4 . H_2O$ it can be concluded that the effective charges on the water oxygen and the sulfate oxygen atoms must be slightly different.

It has to be stressed that the discussion in this paper relates only to the long hydrogen bonds formed by water molecules as donors. The extent to which it is possible to generalize these results remains to be studied. For instance it may be that the same principles are not applicable to hydrogen bonds originating from covalently bonded hydroxyl groups. In this case the positions of the hydrogen atoms might be determined by the valence angle subtended at the hydroxyl oxygen atom. Evidence for the stability of this valence angle is the rather constant value of the angle $H–O(w)–H$ in the water molecule; it is found to deviate in widely different crystalline environments by only ±6° from its mean value of 109°.

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APPENDIX

The calculations were performed on the IBM 7090 computer of the Computation Center of the University of Pittsburgh. The program used can compute the electrostatic energy for crystals of any symmetry, as well as repulsion (inverse power) and van der Waals terms needed in lattice energy calculations. It contains a set of subroutines for performing solid analytic geometry; these were used for the systematic variation of the orientation of the water molecules.

Bertaut (1952) gave Ewald's (1921) formula for the calculation of the electrostatic energy of crystals a slightly different form, which however is more advantageous for machine computation than the original form, since the separate evaluation of the potentials of each different ion is not necessary here:

$$W=\{(2\pi V)^{-1}[\sum_{hkl}|F_{hkl}|^2 . d^2_{hkl} . \exp(-\pi . K^{-2} . d^{-2}_{hkl})] -K\sum_{j} q_j^2\}+0{\cdot}5\sum_{i\neq j} q_i . q_j . r_{ij}^{-1}\,\mathrm{ERFC}(\sqrt{\pi} . K . r_{ij})$$

where

W = electrostatic energy per unit cell ($e^2 . Å^{-1}$)

V = volume of the unit cell ($Å^3$)

F_{hkl} = electrostatic structure factor

d_{hkl} = interplanar spacing (Å)
K = constant (Å^{-1})
q_j = charge on the jth ion
r_{ij} = distance from the ith to the jth ion (Å)
ERFC = complement of the error function

The magnitude of the arbitrary constant K determines the relative convergences of the two parts of the formula. The larger the numerical value chosen for K the worse is the convergence of the first sum, and the better is the convergence of the second sum, and *vice versa*. In practice one has to choose a value of K which makes the combined number of terms in both sums a minimum. In order to check the results for their accuracy and for possible errors the same calculation can be repeated with different values of K. Such check runs showed that the rounding errors and the neglected outer terms of the sums never accumulated to more than 1 unit of the sixth digit, *i.e.* the error was 10^{-6} at most.

The program can be requested from the author by interested persons.

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On the Curves in the Greninger and Leonhardt Nets

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The algebraic equations for the lines in both the Greninger and Leonhardt charts are derived, in order to complete or correct the statements found in the current literature. The meridians are conics and the parallels are quartics. Also, parametric equations are given for computational purposes.

In the X-ray orientation of single crystals, two charts are widely used: The Greninger chart (Greninger, 1935) for the back-reflection Laue method and the Leonhardt chart (Leonhardt, 1924; Dunn & Martin, 1949) for the transmission Laue method. The meaning and the use of both nets are quite well explained in the standard X-ray books, but, especially in the case of the Greninger net, some incomplete (Barrett, 1952; Guinier, 1956; Wood, 1963) or even wrong (Terpstra & Codd, 1961; Cullity, 1956; *International Tables for X-Ray Crystallography*, 1959) statements on the geometrical nature of the curves of the chart are frequently made. The pur-

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