With the exception of those dimensions which have already been discussed, the remaining features of the molecules agree well with literature values for similar bond types. Examinations of the crystal-packing arrangements of (III) and (V) reveal O–H···O hydrogen bonding in both cases. For (III), a helix of hydrogen-bonded molecules [O···O 2·83 Å, O···H 1·98 Å, angle O–H···O 173°] extends in the **b** direction, while for (V) there are two independent and unlinked helices [O···O 2·87 Å. O···H 1·99 Å, angle O–H···O 169°] extending in the **a** direction.

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The Geometry of Hydrogen Bonds from Donor Water Molecules

By Bjørn Pedersen

Kjemisk institutt, Universitetet i Oslo, Blindern, Oslo 3, *Norway**

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Analysis of the observed geometry of about 190 hydrogen bonds where the water molecule act as donor shows that the equilibrium configuration of the bond is linear and that the bending of the bond is isotropic.

The most direct and accurate information on the geometry of the hydrogen bond has been derived from neutron-diffraction studies of crystals. However, each crystal structure is a compromise between many competing interactions, and the observed geometry is therefore expected to be distorted from the inherent equilibrium configuration. To determine the equilibrium configuration, distortions from other interactions have to be corrected for or removed. It is generally assumed that the hydrogen bond is linear, but recently *ab initio* calculations by Kistenmacher, Popkie & Clementi (1973) on water molecule–anion complexes show that the configuration of maximal stability is non-linear.

We shall study in this paper the geometry of the hydrogen bonds formed by water molecules when the water molecule acts as a hydrogen-bond donor: H–O–H···A. We shall also obtain information on the equilibrium configuration from analysis of the approximately 190 bonds of this type presently known. Our basic assumption will be that the variations in geometry from one structure to another will be random. We therefore expect the averaged quantities to be representative for the equilibrium configuration and that the random character of the distortions will result in Gaussian distributions.

There are interactions that cannot be removed in this way. It is expected that the hydrogen-bond length will be shortened in molecular solids owing to compression from the long-range attractive forces making the observed distances systematically too small. We shall therefore concentrate on characterizing the shape of the hydrogen bond.

To describe the shape we shall use the two angles defined in Fig. 1, θ and φ, where θ is the angle between the O–H vector and the H···A vector, and φ is the angle between the projection of the H···A vector in the *xy* plane and the plane of the water molecule. The data we will use have been taken from the survey by Ferraris & Franchini-Angela (1972). A similar review has recently been published by Falk & Knop (1973).

Fig. 2 is a histogram showing the number of bonds grouped according to the deviation from linearity. In this histogram bifurcated bonds are also included as separate bonds. It is seen that the most probable value for θ is not in the region 0–5°, but in the region 5–10°. The deviation from linearity can be very large. Hamilton & Ibers (1968) concluded from a similar plot that

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* Also at the Central Institute for Industrial Research, Oslo 3, Norway.

linearity appears to be more an exception than the rule for hydrogen bonds in crystals.

Fig. 3 shows the deviation from linearity plotted as a function of the hydrogen–acceptor distance, R. It can be seen that the deviation from linearity increases with increasing R. It is tempting to conclude from Figs. 2 and 3 that the equilibrium configuration for the hydrogen bond is not linear, at least for the longer bonds, supporting the results of the calculation by Kistenmacher *et al.* (1973). However, we will show that this interpretation is not correct.

The θ-distribution shown in Fig. 2 is a distribution averaged over all values of φ. The interpretation of the θ-distribution will depend on the φ-distribution.

The φ-distribution is shown in Fig. 4. The angle φ was not used by Ferraris & Franchini-Angela (1972) who used instead the angle between the H···A vector and the plane of the water molecule, γ. It is easy to show that

$$\sin\varphi = \frac{\sin\gamma}{\sin\theta}\,. \qquad (1)$$

Equation (1) implies that $\gamma \le \theta$ and some of the correlations noted by Ferraris & Franchini-Angela (1972) follow from this limitation. We have used equation (1) to calculate φ for the hydrates surveyed by them.

Somewhat surprisingly the φ-distribution in Fig. 4 does not show any preference for the acceptor atom to be in the donor plane. Furthermore, as shown in Fig. 5, there is no correlation between φ and the hydrogen–acceptor distance. Apparently, the energy required to bend a hydrogen bond by an angle θ changes only slightly with φ, and is not sufficient to be a factor of importance in a solid.

We can now return to the θ-distribution in Fig. 2. As pointed out above, this distribution is averaged over all values of φ and we have found that the φ-distribution is isotropic.* Therefore, whatever the true configuration may be we must first correct the distribution for the pure geometric factor that the θ-distribution is not formed by counting number of bonds in equal intervals of solid angle, but in equal intervals of θ. This geometric factor for the ith column in the histogram in Fig. 2 is the area of the surface of the spherical segment between the limits θ_{i-1} and θ_i, A_i. In Fig. 6 is plotted this corrected distribution, g_i:

$$g_i = \frac{\Delta N_i}{A_i} \quad \text{where} \quad A_i = 2\pi(\cos\theta_{i-1} - \cos\theta_i)\,. \qquad (2)$$

ΔN_i is the number of bonds in the interval θ_{i-1}, θ_i given in Fig. 2.

It can be seen that the distribution shown in Fig. 6 has a maximum for θ in the interval 0–5°. The distribution for $\theta < 20°$ is approximately Gaussian, showing the random character of the distribution.

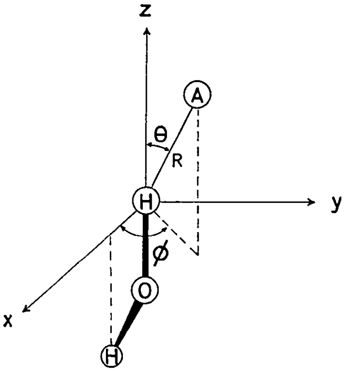

Fig. 1. Coordinates used in the description of the geometry of the hydrogen bond from a donor water molecule, HOH, to an acceptor atom, A. The water molecule is located in the xz plane.

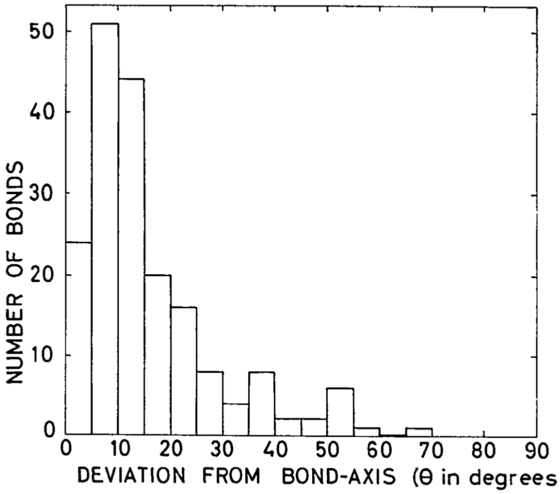

Fig. 2. Histogram showing the number of hydrogen bonds from donor water molecules as a function of the observed angle between the H···A vector and the O–H vector in a OH···A bond in steps of 5°. [Data from Ferraris & Franchini-Angela (1972).]

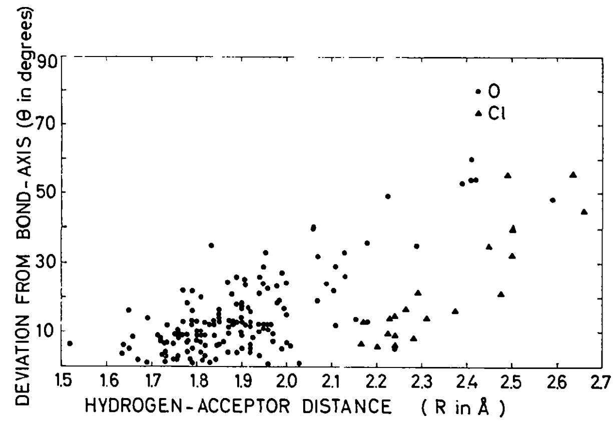

Fig. 3. The observed angle between the H···A vector and the O–H vector in a OH···A bond as a function of hydrogen atom-acceptor atom distance. When the acceptor atom is an oxygen atom the point is a filled circle and when the acceptor atom is a Cl^- ion the point is a filled triangle. [Data from Ferraris & Franchini-Angela (1972).]

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* A two-dimensional θ,φ-histogram has also been prepared. The statistics are then not so good, but the histogram does not reveal any correlation between θ and φ.

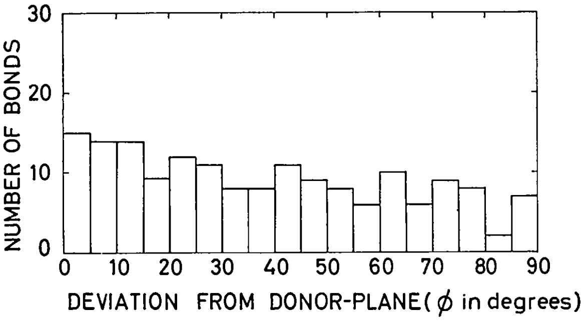

Fig. 4. A Histogram giving the number of hydrogen bonds from donor water molecules as a function of the observed angle of deviation from the donor-plane, φ (see Fig. 2), in steps of 5°. (The same data base as used in constructing Fig. 2.)

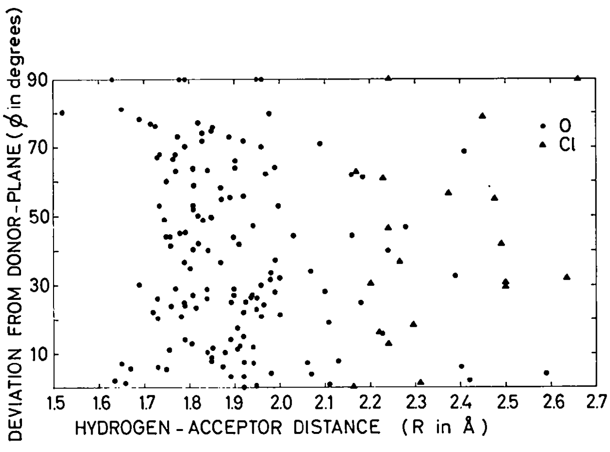

Fig. 5. The observed angle of deviation between the projection of the H···A vector in the xy plane and the donor plane and the distance from the hydrogen atom to the acceptor atoms. When the acceptor distance is an oxygen atom the point is a filled circle and when the acceptor atom is a Cl^- ion the point is a filled triangle. (The same data base as used in constructing Fig. 3.)

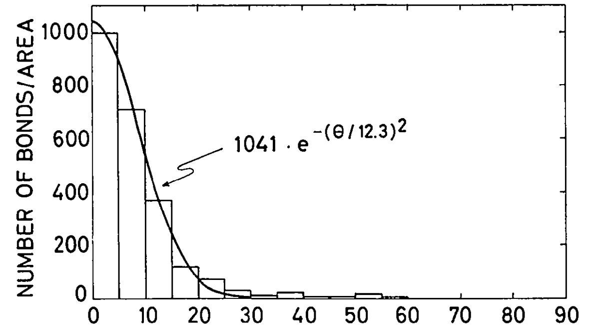

Fig. 6. Histogram showing the number of hydrogen bonds per unit solid angle as a function of the observed angle between the H···A vector and the O–H vector in a O–H···A bond in steps of 5°.

We conclude that the equilibrium configuration for the hydrogen bond from a donor water molecule is linear and that the bending of the bond is isotropic. Each water molecule forms two hydrogen bonds and some molecules have close contacts with more than two neighbouring atoms. The isotropic bending found above indicates that the bonds do not interfere with each other. This is also supported by the fact that there is no tendency for the acceptor atoms to be located *trans* to the plane of the donor molecule. In the survey by Ferraris & Franchini-Angela (1972) there are 49 cases where the acceptors are in the *cis* configuration and 44 cases in the *trans* configuration.

Kistenmacher *et al.* (1973) have calculated the energy of the H_2O–X complex where $X = F^-$ and Cl^-. The calculated configuration of maximum stability is:

Acceptor	F^-	Cl^-
φ	0°	0°
θ	7·4	20·4
R	1·52 Å	2·39 Å .

They find that the energy surface is very flat in the region $0 \le \theta \le 105°$, $\varphi = 0$. Hence, according to this calculation the hydrogen bond should be very easy to bend. This is not in accordance with the distribution shown in Fig. 6 and also not in agreement with the semi-empirical potential proposed by Chidambaram & Sikka (1968) and discussed in detail by Chidambaram (1968). The values of R obtained are also somewhat surprising. The calculated $Cl^- \cdots H$ distance is longer than those usually observed in solids (see Fig. 3) and also somewhat longer than the distance found in aqueous LiCl solution by Narten, Vaslow & Levy (1973). On the other hand, the calculated $F^- \cdots H$ distance is shorter than those observed in solids (Pimentel & McClellan, 1971). The difference between the two calculated A···H distances, 0·87 Å, is almost twice the difference in van der Waals radii between Cl^- and F^-, 0·45 Å.

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