

Opening and Narrowing of the Water H—O—H Angle by Hydrogen-Bonding Effects: Re-inspection of Neutron Diffraction Data

THOMAS STEINER

Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-14195 Berlin, Germany.

E-mail: steiner@chemie.fu-berlin.de

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Abstract

For 71 water molecules donating two $O_w-H\cdots O$ hydrogen bonds, the correlation of the covalent H—O—H angle and the $O\cdots O_w\cdots O$ angle is inspected from 49 well refined organic and organometallic neutron diffraction crystal structures. Compared to sample average, the water angle is opened for large and narrowed for small $O\cdots O_w\cdots O$ angles. Notably, the H—O—H angle is widened compared with the gas phase value even for small $O\cdots O_w\cdots O$. Related behavior is observed for chloride anion acceptors. The correlation exhibits a considerable scatter which should not be interpreted as experimental inaccuracies, but as secondary effects. Possible secondary effects are multi-center hydrogen bonding and effects of coordination to the water O atom. In a comparative test, low-temperature X-ray diffraction data were shown to be completely unsuitable for this type of analysis. The dependence of the C—O—H angle on the C—O \cdots O angle in hydrogen bonds donated by hydroxyl groups in carbohydrates is also shown.

1. Introduction

It is well known that hydrogen bonding affects the covalent geometry of the donor and, to a smaller extent, also of the acceptor groups (Jeffrey & Saenger, 1991; Gilli *et al.*, 1994). The strongest effect is on the donor X—H bond length, which is elongated compared with free X—H groups, and correlated with the hydrogen-bond distance $H\cdots Y$ (Nakamoto *et al.*, 1955; Olovsson & Jönsson, 1976; Steiner & Saenger, 1994; Steiner, 1995*a,b*). Characterization of this effect requires exact knowledge of the H-atom position and must, therefore, be based on neutron diffraction data, whereas X-ray data is unsuitable.

Much less is known about the effects of hydrogen bonding on covalent bond angles. In their comprehensive analysis of water molecules in crystalline hydrates, Chiari & Ferraris (1982) reported, based on neutron diffraction data, that the water H—O—H angle is correlated with the $A\cdots O_w\cdots A$ angle (A = hydrogen bond acceptor). The correlation shown, however, is extremely soft and smeared out. Presumably because of

this softness, the effect has not attracted much attention. Since the data quantity and quality has increased in the last 15 years and since water interactions are of eminent importance in structural chemistry and biology, it seems about time to take up this matter again and reinspect the published neutron diffraction data.

2. Database analysis

In contrast to the work of Chiari & Ferraris (1982), who analyzed mainly inorganic hydrates, the present study is based on the organic and organometallic crystal structures archived in the Cambridge Structural Database (CSD; Allen & Kennard, 1993). Only ordered and error-free single-crystal neutron diffraction data of hydrates with $R < 0.07$ were considered. The intermolecular surrounding of each water molecule was individually

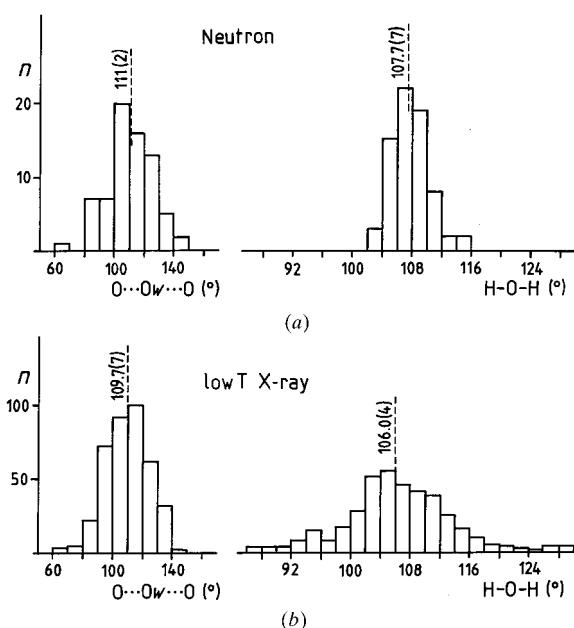


Fig. 1. (a) Distribution of $O\cdots O_w\cdots O$ and H—O—H angles of water molecules which donate two O—H \cdots O hydrogen bonds with $H\cdots O < 2.2$ Å, analyzed from neutron diffraction data. Note the different angle scales. (b) As above, for low-temperature X-ray data.

Table 1. *The data sets on hydrates*

System	$n\text{H}_2\text{O}$ (n Structure)	$A\cdots\text{O}_w\cdots A$ ($^\circ$) mean	$\sigma(A\cdots\text{O}\cdots A)$ ($^\circ$)	$\text{H}-\text{O}-\text{H}$ ($^\circ$) mean	$\sigma(\text{H}-\text{O}-\text{H})$ ($^\circ$)
Neutron data					
$\text{O}\cdots\text{O}_w\cdots\text{O}$	71 (49)	110.8 (19)	15.8	107.7 (3)	2.6
$\text{O}\cdots\text{O}_w\cdots\text{Cl}^-$	6 (4)	111 (4)	11	105.4 (14)	3.5
$\text{Cl}^-\cdots\text{O}_w\cdots\text{Cl}^-$	7 (4)	104 (4)	11	105.0 (8)	2.1
Low-temperature X-ray data					
$\text{O}\cdots\text{O}_w\cdots\text{O}$	387 (219)	109.7 (7)	14.1	106.0 (4)	7.8

inspected on a graphics display. No distinction is made between H and D.

For §3.3 of this study, ordered and error-free carbohydrate neutron diffraction crystal structures with $R < 0.07$ were used. $\text{C}-\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with $\text{H}\cdots\text{O} < 2.4 \text{ \AA}$ were retrieved and analyzed further.

For §3.4, ordered and error-free low-temperature X-ray crystal structures of hydrates with $R < 0.05$ were used. Only conventional $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with $\text{H}\cdots\text{O} < 2.2 \text{ \AA}$ were considered (for formalized H-atom positions). Owing to the large data quantity, the search was in this case performed automatically without individual inspection of the hits.

3. Results

3.1. Water molecules donating two $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds

For water molecules which donate two $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with $\text{H}\cdots\text{O}$ distances $< 2.2 \text{ \AA}$, the distributions of $\text{O}\cdots\text{O}_w\cdots\text{O}$ and $\text{H}-\text{O}-\text{H}$ angles are shown in Fig. 1, top, and numerical data are given in Table 1. Note the different angle scales of the two distributions. The $\text{O}\cdots\text{O}_w\cdots\text{O}$ angles exhibit a very broad distribution ranging from 69 to 147° with a mean value of $111 (2)^\circ$. This is a range of almost 80° , but the peak position in the interval 100 – 110° shows that a

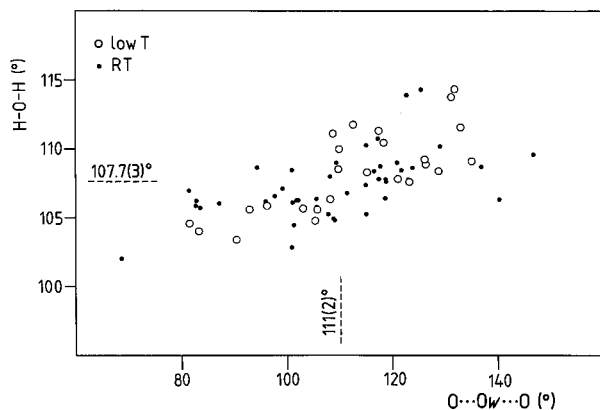
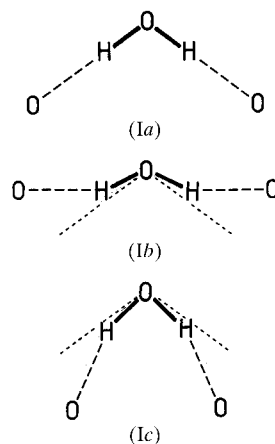


Fig. 2. Correlation of $\text{O}\cdots\text{O}_w\cdots\text{O}$ angles and covalent $\text{H}-\text{O}-\text{H}$ angles of water molecules donating two $\text{O}_w-\text{H}\cdots\text{O}$ hydrogen bonds (neutron diffraction data). Mean values are indicated.

roughly tetrahedral angle is preferred. The $\text{H}-\text{O}-\text{H}$ angles have a distribution ranging from 102.0 to 114.6° and a mean value of $107.7 (7)^\circ$.

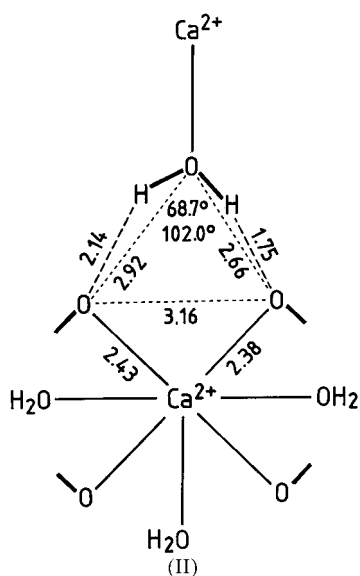
The scatterplot of $\text{H}-\text{O}-\text{H}$ drawn against $\text{O}\cdots\text{O}_w\cdots\text{O}$ shows an obvious positive correlation (Fig. 2), confirming the results of Chiari & Ferraris (1982). This is good evidence that the covalent $\text{H}-\text{O}-\text{H}$ angle is opened for large, and compressed for small, $\text{O}\cdots\text{O}_w\cdots\text{O}$ angles, compared with the sample average, see (I).



A possible (and simplified) explanation for this behavior is that only for $\text{O}\cdots\text{O}_w\cdots\text{O}$ angles close to the $\text{H}-\text{O}-\text{H}$ angle, close to linear hydrogen bonds, can be formed (Ia). This is the optimal case. For large or small $\text{O}\cdots\text{O}_w\cdots\text{O}$ angles, the hydrogen bonds are necessarily nonlinear, (Ib) and (Ic). This leads to force vectors that try to improve hydrogen-bond linearity and thereby open or narrow $\text{H}-\text{O}-\text{H}$ (until they are balanced by the force that tries to restore optimal $\text{H}-\text{O}-\text{H}$ geometry). This mechanism must reflect in a correlation between $\text{O}\cdots\text{O}_w\cdots\text{O}$ and the $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bond angles. In fact, the scatterplot of $\text{O}-\text{H}\cdots\text{O}$ versus $\text{O}\cdots\text{O}_w\cdots\text{O}$ shows that on average hydrogen bonds become more nonlinear as $\text{O}\cdots\text{O}_w\cdots\text{O}$ deviates from 110° , Fig. 3. Corresponding numerical values are given in Table 2.

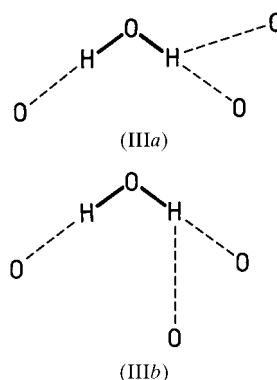
The correlation in Fig. 2 has a somewhat nonlinear appearance and, actually, it must be expected to be nonlinear for hydrogen-bond potentials of general shapes.

Therefore, linear regression analysis is not attempted here, no linear correlation coefficient is calculated and no regression line is drawn in Fig. 2. Owing to the relatively small data quantity and the large scatter of data points, only a semi-quantitative numerical analysis can be performed: mean H—O—H angles in 10° intervals of $O \cdots Ow \cdots O$ are given in Table 2. The typical opening compared to the average H—O—H angle is by $\sim 4^\circ$ for the largest $O \cdots Ow \cdots O$ angles $< 130^\circ$, and the compression is $\sim 2^\circ$ for small angles in the range $80\text{--}90^\circ$. The extreme case in the data sample is a water molecule in the crystal structure of $Ca^{2+}[C_6(C_2H_5)_2O_4]^{2-} \cdot 3H_2O$ (Robl & Kuhs, 1989; ref. code FUSPIS10, with the dianion of 3,6-diethyl-2,5-dihydroxy-*p*-benzoquinone). This water molecule, which is coordinated to a Ca^{2+} ion, donates two hydrogen bonds with an $O \cdots Ow \cdots O$ angle of only 68.7° and O—H \cdots O angles of 142.6 (9) and 159.1 (8) $^\circ$, respectively. As a consequence, the H—O—H angle is compressed to 102.0 (9) $^\circ$, 5.7° below the sample average. This remarkable water configuration is shown roughly to scale in (II).



Although the correlation in Fig. 2 is much clearer than that in the previous study of Chiari & Ferraris (1982), the data scatter is still considerable. The first thought is to assume large experimental errors for part of the sample and to restrict the study to high-precision low-temperature data. However, room- and low-temperature data are scattered almost the same way (circles and dots in Fig. 2), indicating that the scatter is not merely due to experimental inaccuracy, but caused by secondary effects which open or close the H—O—H angle *in addition* to the primary effect shown in (Ia) and (Ib). Several attempts were made to specify such secondary mechanisms by dividing the data into suitable subsets and to see if they behave differently. One

possible reason for the scatter is multi-center hydrogen bonding (Jeffrey & Saenger, 1991): many water O—H donors interact with more than one acceptor, typically with one short and dominant ‘major hydrogen bond’ and one or two additional weak ‘minor hydrogen bonds’ with long H \cdots O separations > 2.2 Å. In the present data sample, 44 out of the 71 water molecules donate at least one minor hydrogen bond with H \cdots O in the range $2.2\text{--}3.0$ Å, in addition to the hydrogen bonds with H \cdots O < 2.2 Å. For the very simple case of a water molecule forming one two-center and one three-center hydrogen bond, there are two different configurations: in one the additional bond must slightly widen and in the other it must slightly compress the H—O—H angle, in addition to the effect caused by the major bonds (III).



In realistic data samples the situation is much more complex: both O—H bonds of the water molecules may form two-, three- and four-center hydrogen bonds, leading to a multitude of possible configurations (Jeffrey & Maluszynska, 1990; Steiner & Saenger, 1993), and all should have different characteristics concerning widening or narrowing of the H—O—H angle. These

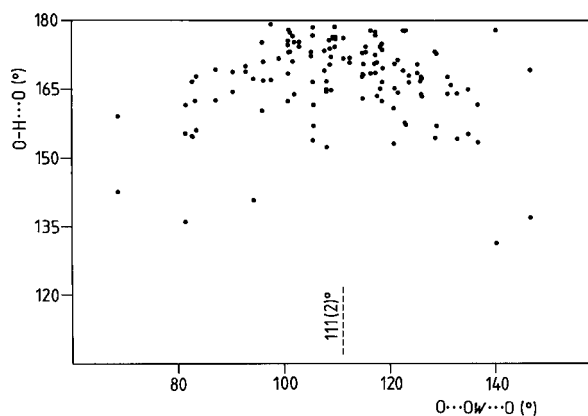


Fig. 3. Plot of the hydrogen-bond angle *versus* the $O \cdots Ow \cdots O$ angle for water molecules donating two $Ow\text{--}H \cdots O$ hydrogen bonds. Hydrogen bonds have the strongest tendency for linearity for $O \cdots Ow \cdots O$ angles around 110° .

Table 2. Results on water molecules

Correlation of H—O—H and Ow—H...O angles with O...Ow...O angles: mean H—O—H and O—H...O values are given in intervals of O...Ow...O. Intervals < 80° and > 140° contain less than three data points and are therefore unsuitable statistically.

O...Ow...O (°) range	n(H ₂ O)	O...Ow...O (°) mean	H—O—H (°) mean	Ow—H...O (°) mean
80–90	7	83.2 (7)	105.6 (4)	160 (2)
90–100	7	95.2 (11)	106.2 (6)	167 (2)
100–110	20	105.6 (8)	106.5 (5)	171.0 (11)
110–120	16	116.3 (5)	108.6 (5)	170.4 (7)
120–130	13	124.5 (7)	109.5 (6)	166.6 (13)
130–140	5	133.6 (11)	111.5 (12)	161.7 (17)
Whole range	71	110.8 (19)	107.7 (3)	167.2 (7)

secondary effects are certainly much smaller than the primary effect shown in (Ib) and (Ic) and, therefore, more difficult to quantify. Attempts to characterize the effect of multi-center hydrogen bonds in Fig. 2 unfortunately lead to very small subsets for the many different configurations, preventing analysis of statistical significance.

Chiari & Ferraris (1982) assumed that the coordination of the water lone pairs influences the H—O—H angle, in particular if metal ions are involved. This reasonable assumption could not be tested here for the same reason as for the multi-center hydrogen bonding. In a stringent analysis one would have to divide the water molecules into different classes considering their donor and acceptor configurations (e.g. single acceptor–double donor, single acceptor–triple donor, double acceptor–double donor *etc.*, for different donor and acceptor types and for different geometries). Owing to the small number of neutron crystal structures published, this is not a realistic enterprise either today or in the near future. In essence, one can therefore only conclude that the correlation in Fig. 2 is smeared out by a considerable number of secondary effects operating at the same time.

It is of interest that the average H—O—H angle is widened compared with the gas-phase value for free

water molecules, 104.5° (Callomon *et al.*, 1976) even for small O...Ow...O angles. This circumstance has already puzzled Chiari & Ferraris (1982) and cannot be explained satisfactorily here either. An effect that is responsible at least in part is the apparent H—O—H opening due to thermal vibrations (*i.e.* an experimental artifact related to the better known apparent O—H shortening), which is calculated to be around 1–2° (Eriksson *et al.*, 1979).

For reasons of completeness, and in order to characterize the data set used, the correlation of Ow—H bond lengths with H...O hydrogen distances is shown in Fig. 4. The lengthening of the O—H bond due to hydrogen bonding can be clearly seen. The scatter is reduced compared with the related figure shown by Chiari & Ferraris (1982), but is much larger than observed if only two-center hydrogen bonds in very accurate low-temperature neutron crystal structures are considered (Steiner & Saenger, 1994).

3.2. Water molecules donating one or two O—H...Cl⁻ hydrogen bonds

The effects on the H—O—H angle shown in (I) should also be observed for hydrogen bonds with different acceptors than oxygen. Unfortunately, for most other acceptors the quantity of neutron data is much too small for reasonable analysis. Only for chloride ions does the available data allow at least a rough analysis similar to that for oxygen acceptors. The correlation of H—O—H angles with A...Ow...A angles is shown in Fig. 5(a) for water molecules which donate hydrogen bonds to two chloride ions and in Fig. 5(b) for those which donate hydrogen bonds to one O atom and one Cl⁻ ion. To show the typical experimental accuracy, standard errors are indicated here. Numerical data are given in Table 1. The general behavior is the same as for oxygen acceptors.

3.3. Hydroxyl groups donating O—H...O hydrogen bonds

An interesting comparison is that with hydrogen-bonding hydroxyl groups. Here, an analogous effect

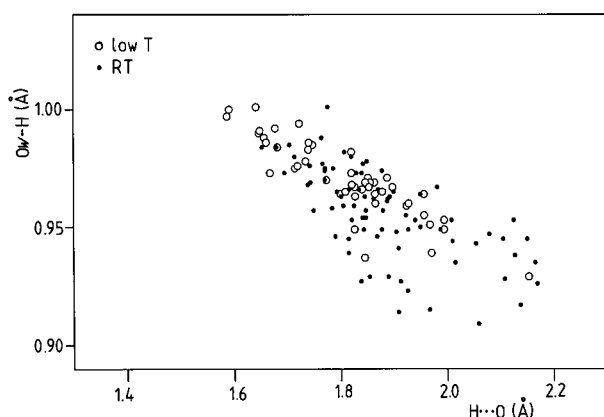


Fig. 4. Lengthening of the covalent Ow—H bond, owing to the O—H...O hydrogen-bond interaction. Data as in Fig. 1(a).

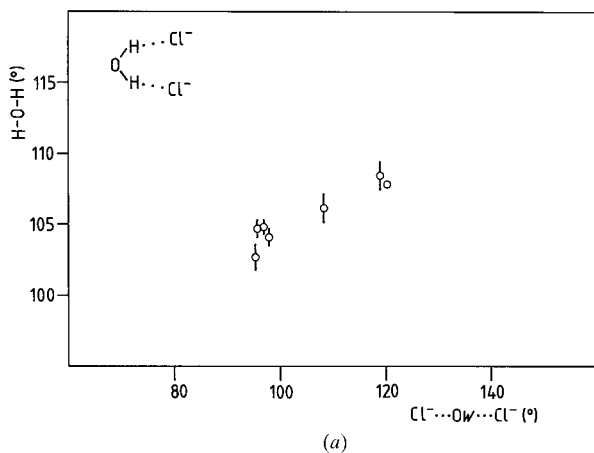
Table 3. Results on hydroxyl groups in carbohydrates

Correlation of C—O—H and C—H...O angles, and of H...O distances with C—O...O angles: mean values are given in intervals of C—O...O.

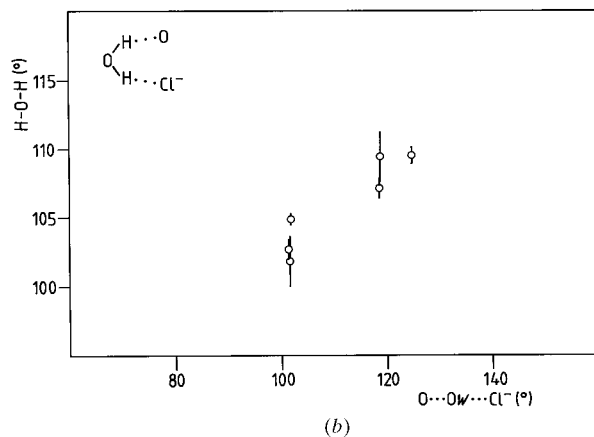
C—O...O (°) range	n(C—OH)	C—O...O (°) mean	C—O—H (°) mean	C—H...O (°) mean	H...O (Å) mean
80–100	18	94.5 (11)	106.9 (3)	158 (2)	1.87 (3)
100–110	37	105.1 (6)	108.6 (1)	168.9 (9)	1.83 (2)
110–120	31	115.1 (5)	110.1 (2)	168 (1)	1.84 (2)
120–130	20	123.8 (6)	111.5 (3)	159 (1)	1.86 (2)
130–150	6	138 (2)	111.5 (4)	135 (5)	2.15 (6)
Whole range	112	111.3 (12)	109.4 (2)	163 (2)	1.86 (1)

should exist, *i.e.* in C—O—H...O hydrogen bonds the covalent C—O—H angle should be correlated with the C—O...O angle. To obtain relevant data, O—H...O hydrogen bonds with H...O < 2.4 Å were retrieved from the carbohydrate neutron diffraction subset of the CSD (112 data from 26 crystal structures). For these the correlation of C—O—H with C—O...O is shown in Fig.

6, numerical data are given in Table 3. The results are fully in line with those for water molecules and show that the C—O—H angle is narrowed compared with the sample average for small C—O...O angles and widened for large C—O...O angles. Furthermore, the data in Table 3 show that hydrogen bonds with close to tetrahedral C—O...O angles (intervals 100–120°) are on average shorter and more linear than those with very small or large C—O...O angles.



(a)



(b)

Fig. 5. (a) Correlation of Cl⁻...Ow...Cl⁻ angles and covalent H—O—H angles of water molecules donating two Ow—H...Cl⁻ hydrogen bonds (neutron diffraction data). (b) Correlation of O...Ow...Cl⁻ angles and covalent H—O—H angles of water molecules donating one Ow—H...O and one Ow—H...Cl⁻ hydrogen bond (neutron diffraction data).

3.4. The failure of X-ray diffraction

In X-ray crystal structures, X—H bond lengths are systematically shortened because of the unequal distribution of the bonding electrons between X and H (Allen, 1986). Y—X—H bond angles, on the other hand, are unaffected on average. Since the effect discussed in §3.1 and §3.2 involves only the H—O—H angle and not the O—H bond distances, one might suppose that it is also detectable from X-ray diffraction data. Therefore, a database analysis was performed on the X-ray crystal structures of organic and organometallic hydrates. The large data quantity allowed the use of restrictive quality criteria: only ordered low-temperature crystal structures with *R* values < 0.05 were used.

For water molecules donating hydrogen bonds to two oxygen acceptors (H...O < 2.2 Å), the distributions of

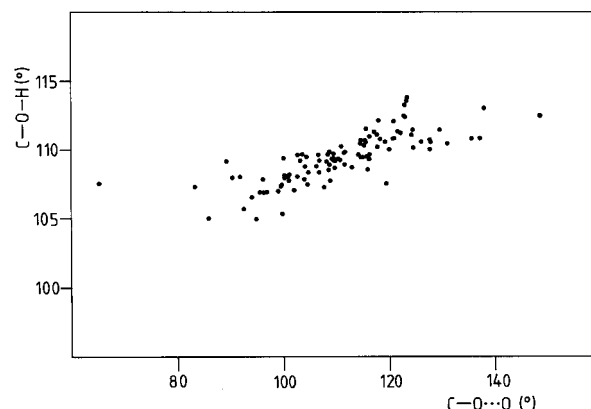


Fig. 6. Correlation of C—O...O angles and covalent C—O—H angles of hydroxyl groups in carbohydrates which donate O—H...O hydrogen bonds (neutron diffraction data).

$O\cdots Ow\cdots O$ and $H-O-H$ angles are shown in Fig. 1, bottom, and numerical data are given in Table 1. Since the $O\cdots Ow\cdots O$ angle does not involve H-atom positions, a close similarity in neutron- and X-ray-based results is expected, and the two distributions are very similar indeed. For the $H-O-H$ angles, the mean values for neutron and X-ray data are also similar, but the distribution of the X-ray results is broader by a factor of three (the sample standard deviations σ are 2.6 and 7.8° for neutron and X-ray data, respectively). The $\sigma = 2.6^\circ$ scatter of the neutron-determined $H-O-H$ angles is largely 'true', *i.e.* it represents actual variations of $H-O-H$ angles in different crystal environments. For X-ray determined $H-O-H$ angles, the observed scatter exceeds by far the true variations, *i.e.* it is dominated by experimental uncertainty.

The correlation plot of $H-O-H$ versus $O\cdots Ow\cdots O$ angles is shown for low-temperature X-ray data in Fig. 7 on the same scale as for neutron data in Fig. 2. The correlation is completely smeared out and would not show a dependence of $H-O-H$ on $O\cdots Ow\cdots O$. Although the $H-O-H$ angles are not systematically affected in X-ray data, the pure statistical scatter prevents analysis on the level required here.

4. Conclusions

It is shown conclusively from neutron diffraction data that for water molecules which donate two $Ow-H\cdots O$ hydrogen bonds, the covalent $H-O-H$ angle is correlated with the $O\cdots Ow\cdots O$ angle. For small $O\cdots Ow\cdots O$ angles the $H-O-H$ angle is compressed and for large $O\cdots Ow\cdots O$ angles it is widened compared with the sample average. The circumstance has been observed before qualitatively, but is now far better established. Similar observations are made for water molecules hydrogen bonded to chloride ions and

hydroxyl groups forming $O-H\cdots O$ hydrogen bonds (not published before).

The correlations observed exhibit a considerable scatter, which is very similar for room-temperature data and the much more accurate low-temperature data. This indicates that the scatter is not only due to experimental errors, but also due to secondary effects that cause some opening or narrowing of $H-O-H$ in addition to the primary effect. Possible secondary effects are multi-center hydrogen bonding and effects of coordination to the lone pairs of Ow (accepted hydrogen bonds or/and metal contacts). It must be expected that several secondary effects operate at the same time. Attempts to specify such effects in detail were unsuccessful because of the small data sample and the complexity of the problem.

An attempt to show the correlation of the $O\cdots Ow\cdots O$ angle and the covalent $H-O-H$ angle from X-ray diffraction data was a complete failure, even though only low-temperature X-ray data of crystal structures with $R < 0.05$ were used. This shows that the neutron diffraction technique is indispensable when hydrogen-bond phenomena are to be investigated in depth.

It is unfortunate that 15 years after the work of Chiari & Ferraris (1982) the published neutron diffraction data is still far too small in quantity to allow quantitative analysis of the discussed effects. Owing to the small number of neutron diffraction crystal structures being published per year, no greater improvement can be expected in the near future.

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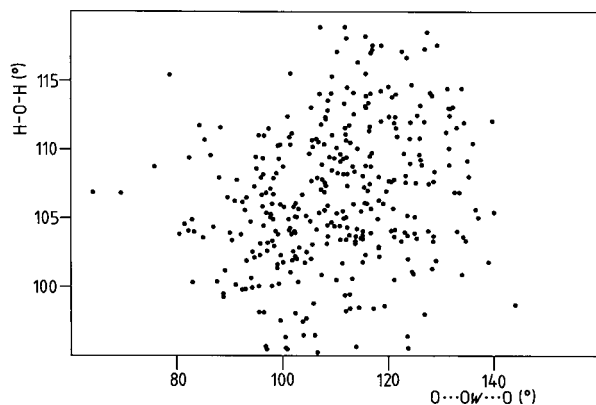


Fig. 7. Correlation of $O\cdots Ow\cdots O$ angles and covalent $H-O-H$ angles of water molecules donating two $Ow-H\cdots O$ hydrogen bonds (low-temperature X-ray diffraction data). The correlation that is obvious in Fig. 2 is completely blurred here.

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