

The authors thank Mr Cs. Kertész and Miss F. Kálmán (Budapest) for their assistance.

This joint research was sponsored financially in Hungary by the Hungarian Research Fund, grant No. OTKA 1806, and in Yugoslavia by the Research Foundation of the Autonomous Province Vojvodina.

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Geometric Analysis of Non-Ionic O—H...O Hydrogen Bonds and Non-Bonding Arrangements in Neutron Diffraction Studies of Carbohydrates

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(Received 30 December 1991; accepted 15 April 1992)

Abstract

The geometry of chemically related O—H...O hydrogen bonds in strictly non-ionic surroundings is analyzed using neutron diffraction data derived from carbohydrates. Correlations between the hydrogen-bond parameters $d_{\text{H}\cdots\text{O}}$, $d_{\text{O}\cdots\text{O}}$ and $\alpha_{\text{O}\cdots\text{H}\cdots\text{O}}$ are studied in scatterplots, which are extended far beyond the normally accepted hydrogen-bonded region to the limits $d_{\text{H}\cdots\text{O}} < 5.0 \text{ \AA}$ and $0 < \alpha_{\text{O}\cdots\text{H}\cdots\text{O}} < 180^\circ$. The restriction to non-ionic arrangements produces scatterplots that differ considerably from those obtained from chemically heterogeneous data samples. Minor components of three-center and four-center hydrogen bonds frequently differ with respect to the major components and produce significant outliers compared with correlation plots obtained from major components alone. The hydrogen-bonded regions merge with regions of non-bonding arrangements, as

$\alpha_{\text{O}\cdots\text{H}\cdots\text{O}}$ decreases below 90° and $d_{\text{H}\cdots\text{O}}$ increases above $\sim 3.0 \text{ \AA}$, and no clear separation between these regions can be observed. It is shown that the scatterplots of $\alpha_{\text{O}\cdots\text{H}\cdots\text{O}}$ against $d_{\text{H}\cdots\text{O}}$ and $d_{\text{O}\cdots\text{O}}$ are equivalent if variations of the covalent bond length d_{OH} are neglected.

Introduction

The geometry of O—H...O hydrogen bonds has repeatedly been analyzed based on accurate neutron crystallographic data, see Olovsson & Jönsson (1976); Ceccarelli, Jeffrey & Taylor (1981); Taylor & Kennard (1984); Savage (1986); Jeffrey & Saenger (1991). The hydrogen bonds are usually described by the distances O—H, H...O, O...O (d_{OH} , $d_{\text{H}\cdots\text{O}}$, $d_{\text{O}\cdots\text{O}}$) and the angle O—H...O ($\alpha_{\text{O}\cdots\text{H}\cdots\text{O}}$), Fig. 1. As a rule of thumb, an O—H...O interaction was formerly called a hydrogen bond, if the H...O separation was significantly shorter than the sum of the van der Waals

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radii ~ 2.6 Å (Olovsson & Jönsson, 1976). As weak hydrogen bonds are primarily due to long-range electrostatic attraction, it is now more common to use the criterion $d_{\text{H}\cdots\text{O}} < 3.0$ Å and $\alpha_{\text{OH}\cdots\text{O}} > 90^\circ$, or even more permissive criteria, for the geometrical identification of hydrogen bonds. If more than one acceptor atom satisfies the criterion, the hydrogen bond is of the 'three-center type' (two acceptor atoms) or 'four-center type' (three acceptor atoms). A three-center hydrogen bond is rarely symmetric with both components $d_{\text{H}\cdots\text{O}}$ having roughly the same length; if they have different lengths, it is called 'unsymmetric' with the shorter bond $d_{\text{H}\cdots\text{O}}$ called the 'major' and the longer bond the 'minor component'. In crystal structures containing a large number of hydrogen-bond donors and acceptors, such as the carbohydrates, the hydrogen bonds form complex spatial networks, see Fig. 2.

Because hydrogen bonds are 'soft', the parameters described in Fig. 1 cover wide ranges. Correlations between these parameters have repeatedly been described. If $\alpha_{\text{OH}\cdots\text{O}}$ is plotted *versus* $d_{\text{H}\cdots\text{O}}$ for water donors only (Savage & Finney, 1986), the scatterplot in Fig. 3(a) is obtained. It shows that short hydrogen bonds are almost linear, while increasing $d_{\text{H}\cdots\text{O}}$ allows

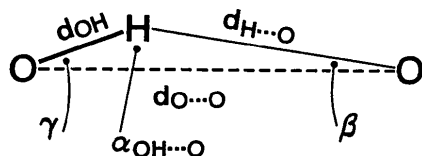


Fig. 1. Schematic illustration of the hydrogen-bond parameters d_{OH} , $d_{\text{H}\cdots\text{O}}$, $d_{\text{O}\cdots\text{O}}$ and $\alpha_{\text{OH}\cdots\text{O}}$. Due to trigonometrical relations only three of these four parameters are independent; if d_{OH} is regarded as constant ~ 0.97 Å, only two independent parameters remain. The angles β and γ are auxiliary parameters used in the text.

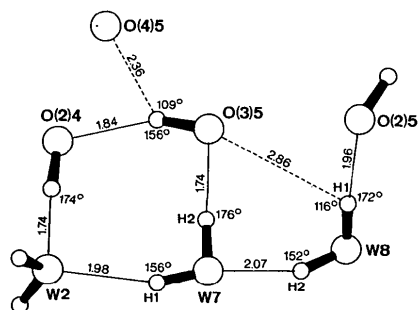


Fig. 2. Part of the hydrogen-bond network in β -cyclodextrin ethanol octahydrate at $T = 15$ K (Steiner, Mason & Saenger, 1990). Water molecules are labelled as W , hydroxyl groups as $O(m)n$, where n is the number of the glucose residue in the cyclodextrin molecule and m is the number of the hydroxyl group in the given residue. $O(4)5$ is a glycosidic oxygen atom. Distances are given in Å.

an increasingly bent angle $\alpha_{\text{OH}\cdots\text{O}}$. A plot of $\alpha_{\text{OH}\cdots\text{O}}$ *versus* $d_{\text{O}\cdots\text{O}}$ shows a similar picture, Fig. 3(b). These correlations have formerly been described by regression lines (Olovsson & Jönsson, 1976), but the characterization by curves for minimal allowed values and corresponding 'forbidden regions' is more appropriate (Savage & Finney, 1986). For water donors, and for the special case of $\text{N}-\text{H}\cdots\text{O}=\text{C}$ in proteins, curves for minimal allowed values have been parametrized in linear approximations and included in a protein crystal structure refinement program as 'repulsive restraints' (Cheng & Schoenborn, 1990, 1991). In addition, it is found that the covalent $\text{O}-\text{H}$ bond is lengthened for either short $d_{\text{H}\cdots\text{O}}$ or $d_{\text{O}\cdots\text{O}}$ (Nakamoto, Margoshes &

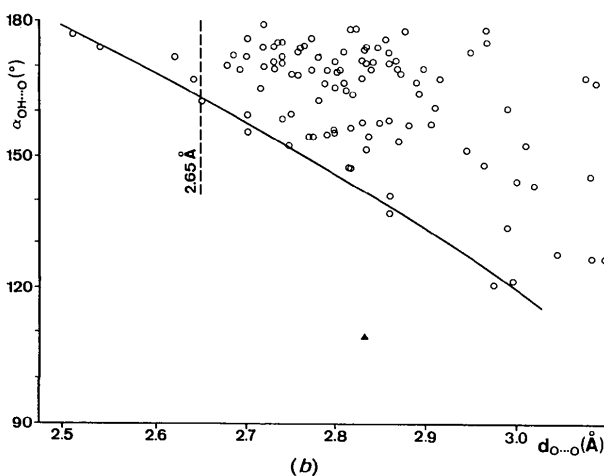
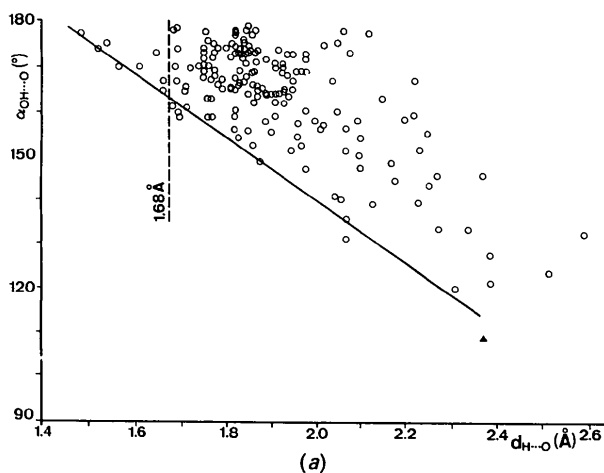


Fig. 3. (a) Plot of $\alpha_{\text{OH}\cdots\text{O}}$ *versus* $d_{\text{H}\cdots\text{O}}$ for water donors. (b) Plot of $\alpha_{\text{OH}\cdots\text{O}}$ *versus* $d_{\text{O}\cdots\text{O}}$ for water donors. Both plots redrawn from Savage (1986); (a) was first published by Savage & Finney (1986). Curves drawn with full lines represent minimum allowed values, the dashed lines were included for this work to show the limiting values for non-ionic hydrogen bonds. The triangle \blacktriangle represents the minor hydrogen-bond component $\text{O}(3)5-\text{H}\cdots\text{O}(4)5$ of Fig. 2.

Rundle, 1955; Olovsson & Jönsson, 1976). On average, d_{OH} is ~ 0.025 Å longer for hydrogen bonds with $d_{\text{H}\cdots\text{O}} \approx 1.7$ Å than for those with $d_{\text{OH}} > 2.0$ Å; this effect is more significant for very short hydrogen bonds with $d_{\text{H}\cdots\text{O}} < 1.7$ Å, which are not considered here.

In the present study, we extend these analyses for the following reasons:

(1) The correlations between $\alpha_{\text{OH}\cdots\text{O}}$ and $d_{\text{H}\cdots\text{O}}$, $d_{\text{O}\cdots\text{O}}$ have been empirically described, but the background of these correlations has, to our knowledge, not been discussed analytically.

(2) Minor components of three-center hydrogen bonds have been included in only very few of these studies (Jeffrey & Maluszynska, 1990), and were not systematically analyzed. For many of the minor components, the limiting lines in Figs. 3(a) and 3(b) do not hold, as is shown by the triangles representing the bond O(3)5—H \cdots O(4)5 of Fig. 2.

(3) Figs. 3(a) and 3(b), and many other shown in the cited studies, represent data from hydrogen bonds in which ions may be involved or not. It is known for 'non-ionic' O—H \cdots O hydrogen bonds that the O \cdots O distances are rigidly limited to values $d_{\text{O}\cdots\text{O}} > 2.65$ Å, and the H \cdots O distances to values $d_{\text{H}\cdots\text{O}} > 1.68$ Å (Ceccarelli, Jeffrey & Taylor, 1981). We have drawn these limits as horizontal boundary lines in Figs. 3(a) and 3(b); all data points to the left of these lines correspond to hydrogen bonds involving ions. If the latter are excluded, the analysis is considerably simplified.

The data set analyzed

In our study, we use only data for chemically related O—H \cdots O hydrogen bonds in a strictly non-ionic surrounding. The atomic coordinates of 15 neutron crystal structures of carbohydrates which contain no ions and display quality factors $R < 0.06$ were extracted from the Cambridge Structural Database (1990) (Allen *et al.*, 1979); in the code of this database, these structures are: ABINOS01, FRUCTO02, GLUCA01, LYXOSE01, MALTOS11, MBDGAL02, MDRIBP02, MEMANP11, MGALPY01, MGLUCP11, RHAMAH12, SORBOL01, SUCROS04, XYLOBM01 and XYLOSE01. These data were combined with those of two high-resolution neutron crystal structures of hydrated β -cyclodextrin (β -CD) complexes [β -CD.11.6D₂O, $T = 120$ K, $R = 0.049$ (Zabel, Saenger & Mason, 1986) and β -CD.ethanol.8D₂O, $T = 15$ K, $R = 0.041$ (Steiner, Mason & Saenger, 1990)]. Partially occupied or orientationally disordered donor and acceptor groups, and two water molecules with poor covalent geometry ($W6$ and $W13$ in β -CD.11.6D₂O) were excluded from the analysis. The remaining structural data set contains 110 hydroxyl groups, 53 ether-type

oxygen atoms and 16 water molecules as potential O—H \cdots O hydrogen-bond donors and acceptors. Covalent O—H bond lengths are not corrected for thermal motion; in consequence the values of d_{OH} are systematically too short by ~ 0.01 to 0.02 Å for the room-temperature structures.

Discussion of the geometrical background

The parameters d_{OH} , $d_{\text{H}\cdots\text{O}}$, $d_{\text{O}\cdots\text{O}}$ and $\alpha_{\text{OH}\cdots\text{O}}$ (Fig. 1) are not independent; if any three of them are given, the fourth is determined by trigonometric relations.

In non-ionic hydrogen bonds, the lengthening of the covalent O—H bond is small, and the values for d_{OH} vary in a much narrower range than those for $d_{\text{H}\cdots\text{O}}$ and $d_{\text{O}\cdots\text{O}}$. In a first (and rough) approximation one may therefore regard d_{OH} as constant, $d_{\text{OH}} \approx 0.97$ Å, and only two independent parameters remain. Then, for any given distance $d_{\text{O}\cdots\text{O}}$ (for example), $d_{\text{H}\cdots\text{O}}$ is a function of $\alpha_{\text{OH}\cdots\text{O}}$, *i.e.* the hydrogen-bond angle *precisely* determines the bond distance $d_{\text{H}\cdots\text{O}}$ (and *vice versa*). This is also illustrated by Fig. 1: for any given $d_{\text{O}\cdots\text{O}}$, the O—H group may in principle rotate around the donor oxygen atom. This leads to various hydrogen-bonded geometries, each of which is characterized by a certain angle $\alpha_{\text{OH}\cdots\text{O}}$ and a *corresponding* distance $d_{\text{H}\cdots\text{O}}$.

The angle $\alpha_{\text{OH}\cdots\text{O}}$ may vary between 180° for linear hydrogen bonds and 0° for linear non-bonding arrangements, and correspondingly $d_{\text{H}\cdots\text{O}}$ may vary between $(d_{\text{O}\cdots\text{O}} - d_{\text{OH}})$ and $(d_{\text{O}\cdots\text{O}} + d_{\text{OH}})$. If $\alpha_{\text{OH}\cdots\text{O}}$ is plotted against $d_{\text{H}\cdots\text{O}}$, as in Fig. 3(a), the data points for given values of $d_{\text{O}\cdots\text{O}}$ must follow curves described by the function $d_{\text{H}\cdots\text{O}} = f(\alpha_{\text{OH}\cdots\text{O}}, d_{\text{O}\cdots\text{O}} = \text{const}, d_{\text{OH}} = \text{const})$, which is given by $d_{\text{H}\cdots\text{O}} = d_{\text{O}\cdots\text{O}} \sin \gamma / \sin \alpha_{\text{OH}\cdots\text{O}}$ with $\gamma = (180^\circ - \alpha_{\text{OH}\cdots\text{O}} - \beta)$, and $\sin \beta = d_{\text{OH}} \sin \alpha_{\text{OH}\cdots\text{O}} / d_{\text{O}\cdots\text{O}}$. In practice, this otherwise stringent relation is 'softened' by variation of d_{OH} : in the systems under study, d_{OH} may have values $\sim 0.97 \pm 0.02$ Å (Ceccarelli, Jeffrey & Taylor, 1981), leading to a certain scatter of the data points around the calculated curves. In Fig. 4 we show the curves for discrete values of $d_{\text{O}\cdots\text{O}}$ together with the data points of the structural data set described above. To illustrate an example, in Fig. 4 we have shaded the data points corresponding to hydrogen bonds with $d_{\text{O}\cdots\text{O}}$ experimentally determined between 2.80 and 2.90 Å.

The position of each data point in the plot of $\alpha_{\text{OH}\cdots\text{O}}$ against $d_{\text{H}\cdots\text{O}}$ permits calculation of the position of the corresponding data point in the plot of $\alpha_{\text{OH}\cdots\text{O}}$ against $d_{\text{O}\cdots\text{O}}$ (neglecting variation of d_{OH}). The basic information supplied by these two scatterplots is therefore equivalent. Consequently, any empirically observed 'minimum value for $\alpha_{\text{OH}\cdots\text{O}}$ ' must *equivalently* be present in both scatterplots, see

Figs. 3(a) and 3(b). If it is determined and conveniently parametrized in one of the plots, it can easily be transferred to the other one; and if it is included as a constraint in a refinement program (Cheng & Schoenborn, 1990, 1991), it is unnecessary to determine the limits from both plots and to use them as independent constraints.

In principle, the systematic increase of d_{OH} with shortening $d_{\text{H}\cdots\text{O}}$ may be included in these considerations: if the empirical correlation $d_{\text{OH}} = f(d_{\text{H}\cdots\text{O}})$ [or $d_{\text{OH}} = f(d_{\text{O}\cdots\text{O}})$] given for short $d_{\text{H}\cdots\text{O}}$ by Olovsson & Jönsson (1976) and for long $d_{\text{H}\cdots\text{O}}$ by Chiari & Ferraris (1982) and Steiner & Saenger (1992) is suitably parametrized, it readily replaces the mean value $d_{\text{OH}} \approx 0.97 \text{ \AA}$ used throughout this work.

Extended scatterplots for hydroxyl and water donors

In Fig. 4, the data points clustered in the high-angle and short-distance region correspond to two-center and to major components of three-center hydrogen bonds, whereas those in the low-angle and long-distance region correspond to minor components of three- and four-center hydrogen bonds. Because of the very small number of symmetrical three-center bonds in the carbohydrates, the two regions are clearly separated. The region of the minor components seems to be somewhat arbitrarily cut off by the limits of the plot imposed by the hydrogen-bond criterion $d_{\text{H}\cdots\text{O}} < 3.0 \text{ \AA}$ and $\alpha_{\text{OH}\cdots\text{O}} > 90^\circ$; this suggests that the plot should be extended beyond these hydrogen-bond cut-off limits.

The scatterplot $\alpha_{\text{OH}\cdots\text{O}}$ against $d_{\text{H}\cdots\text{O}}$

Fig. 5 shows the plot of $\alpha_{\text{OH}\cdots\text{O}}$ against $d_{\text{H}\cdots\text{O}}$ for all arrangements O—H \cdots O in the data set (hydroxyl and water donors) with $d_{\text{H}\cdots\text{O}} < 5.0 \text{ \AA}$, no matter whether these arrangements are hydrogen bonds or not. As the only exception, a few non-hydrogen-bonding intramolecular arrangements were excluded where the oxygen atoms are separated by only one carbon atom (H—O—C—O—C). The dotted theoretical lines represent hydrogen bonds with discrete values of $d_{\text{O}\cdots\text{O}}$ ($d_{\text{OH}} = 0.97 \text{ \AA}$), the solid limiting line corresponds to $d_{\text{O}\cdots\text{O}} = 2.65 \text{ \AA}$, which is the shortest O \cdots O separation that occurs in the data set. In Fig. 5, several distinct regions are observed:

(1) The well known region of two-center and major components of three-center hydrogen bonds. Except for short $d_{\text{H}\cdots\text{O}}$, the minimum allowed $\alpha_{\text{OH}\cdots\text{O}}$ given by Savage & Finney (1986) for water donors holds rather well. No hydrogen bonds with $d_{\text{H}\cdots\text{O}}$ shorter than 1.69 \AA are observed, corresponding to a shortest $d_{\text{O}\cdots\text{O}}$ slightly greater than $\sim 2.65 \text{ \AA}$, see also Fig. 4.

(2) The extended region of minor components of three-center hydrogen bonds. Most of the data points that represent short, but strongly bent minor components, such as O(3)5—H \cdots O(4)5 in Fig. 2 ($d_{\text{H}\cdots\text{O}} = 2.36 \text{ \AA}$, $\alpha_{\text{OH}\cdots\text{O}} = 108.6^\circ$) correspond to intramolecular minor components donated to glycosidic oxygen atoms, which are separated from the donor by two carbon atoms (H—O—C—C—O—C); they are an important feature of hydrogen bonding in cyclodextrins (Steiner, Mason & Saenger, 1991).

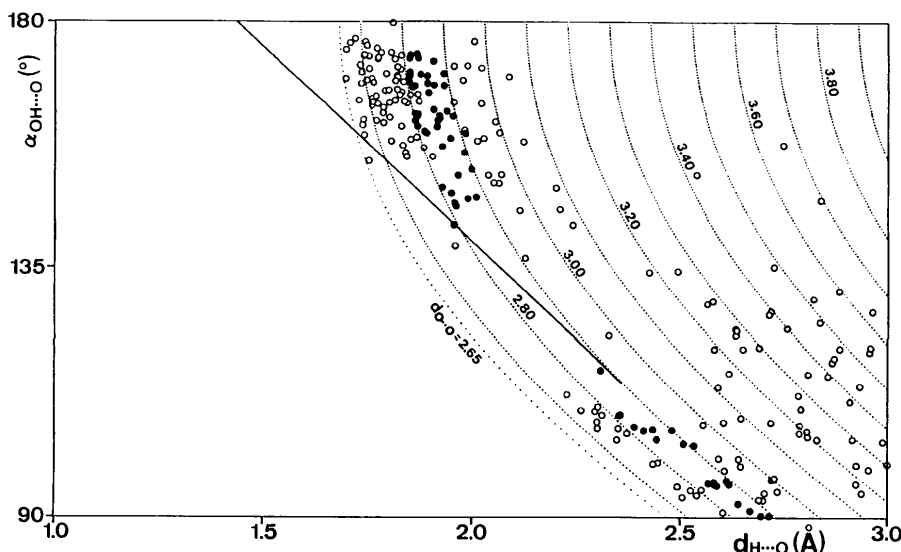


Fig. 4. Scatterplot of $\alpha_{\text{OH}\cdots\text{O}}$ versus $d_{\text{H}\cdots\text{O}}$ for hydroxyl and water hydrogen-bond donors in carbohydrate crystal structures. The inclined solid line is the limiting line for water donors from Fig. 3(a), the dotted theoretical lines correspond to discrete values of $d_{\text{O}\cdots\text{O}}$ based on an O—H bond length of 0.97 \AA . Data points for experimentally determined $d_{\text{O}\cdots\text{O}}$ between 2.80 and 2.90 \AA are drawn filled.

As $\alpha_{\text{OH}\cdots\text{O}}$ decreases below 90° or $d_{\text{H}\cdots\text{O}}$ increases above 3.0 \AA , the region of minor hydrogen-bond components continuously merges with the regions (3) and (4) of non-bonding arrangements.

(3) An elongated cluster of data points for angles $\alpha_{\text{OH}\cdots\text{O}} < 90^\circ$ between the lines for $d_{\text{O}\cdots\text{O}} = 2.65$ and 3.0 \AA . These points represent arrangements $\text{H}-\text{O}\cdots\text{O}$ where the hydrogen atom points away from the 'acceptor atom', whereas another hydrogen atom forms a hydrogen bond between the two oxygen atoms (see inset in Fig. 5); some examples in Fig. 2 are: $\text{O}(2)4-\text{H}\cdots\text{O}(3)5$ ($d_{\text{H}\cdots\text{O}} = 3.02 \text{ \AA}$, $\alpha_{\text{OH}\cdots\text{O}} = 65.7^\circ$), $\text{OW}7-\text{H}1\cdots\text{OW}8$ ($d_{\text{H}\cdots\text{O}} = 3.83 \text{ \AA}$, $\alpha_{\text{OH}\cdots\text{O}} = 18.8^\circ$), $\text{OW}7-\text{H}2\cdots\text{OW}8$ ($d_{\text{H}\cdots\text{O}} = 2.87 \text{ \AA}$, $\alpha_{\text{OH}\cdots\text{O}} = 85.2^\circ$) and $\text{OW}8-\text{H}1\cdots\text{OW}7$ ($d_{\text{H}\cdots\text{O}} = 2.99 \text{ \AA}$, $\alpha_{\text{OH}\cdots\text{O}} = 78.7^\circ$). These arrangements frequently involve short $\text{H}\cdots\text{H}$ van der Waals contacts, such as $\text{H}2(\text{W}7)\cdots\text{H}2(\text{W}8)$, $d_{\text{HH}} = 2.16 \text{ \AA}$ (Steiner & Saenger, 1991). Region (3) also contains data points from intramolecular arrangements with short $\text{O}\cdots\text{O}$ separations $< 3.0 \text{ \AA}$, where no hydrogen bond is formed.

(4) The region for long non-hydrogen-bonding distances between $\text{O}-\text{H}$ and the second next or even further separated 'acceptor' oxygen atoms shows 'random' scatter. This is expected, since both groups do not interact directly, and may adopt any mutual orientation. Some examples in Fig. 2 are: $\text{O}(3)5-\text{H}\cdots\text{OW}2$ ($d_{\text{H}\cdots\text{O}} = 3.54 \text{ \AA}$, $\alpha_{\text{OH}\cdots\text{O}} = 107.2^\circ$), $\text{OW}8-\text{H}2\cdots\text{OW}2$ ($d_{\text{H}\cdots\text{O}} = 4.70 \text{ \AA}$, $\alpha_{\text{OH}\cdots\text{O}} = 154.1^\circ$) and $\text{OW}7-\text{H}1\cdots\text{O}(2)5$ ($d_{\text{H}\cdots\text{O}} = 4.70 \text{ \AA}$, $\alpha_{\text{OH}\cdots\text{O}} = 26.9^\circ$).

There appears to be, however, some faint structuring in the density of the scattered points, which is not the subject of the present study.

(5) An almost unpopulated region to the right of the two-center and major three-center hydrogen-bond components corresponds to linear, but long hydrogen bonds. These are in no way forbidden, and may occur in crystal structures where the density of acceptor atoms is low; but in carbohydrates there are so many acceptors that every donor can find a partner for a short and nearly linear hydrogen bond, or it finds even two acceptor atoms to form three-center interactions with longer $\text{H}\cdots\text{O}$ distances and more acute angles $\alpha_{\text{OH}\cdots\text{O}}$.

(6) The large 'forbidden' region left of the solid curve. It should be stressed that the region is not forbidden by any repulsive forces on the hydrogen atom, but by mere limitation of the oxygen-oxygen approach.

The scatterplot $\alpha_{\text{OH}\cdots\text{O}}$ against $d_{\text{O}\cdots\text{O}}$

Fig. 6 shows the plot of $\alpha_{\text{OH}\cdots\text{O}}$ against $d_{\text{O}\cdots\text{O}}$. The dotted lines represent hydrogen bonds with constant $d_{\text{H}\cdots\text{O}}$ ($d_{\text{OH}} = 0.97 \text{ \AA}$); they are given by the function $d_{\text{O}\cdots\text{O}} = (d_{\text{OH}}^2 + d_{\text{H}\cdots\text{O}}^2 - 2d_{\text{OH}}d_{\text{H}\cdots\text{O}}\cos\alpha_{\text{OH}\cdots\text{O}})^{1/2}$. The distinct regions that are observed correspond to the ones described above for the plot of $\alpha_{\text{OH}\cdots\text{O}}$ versus $d_{\text{H}\cdots\text{O}}$. Note that minor components of three-center hydrogen bonds are observed from $d_{\text{O}\cdots\text{O}} = 2.75 \text{ \AA}$ onwards.

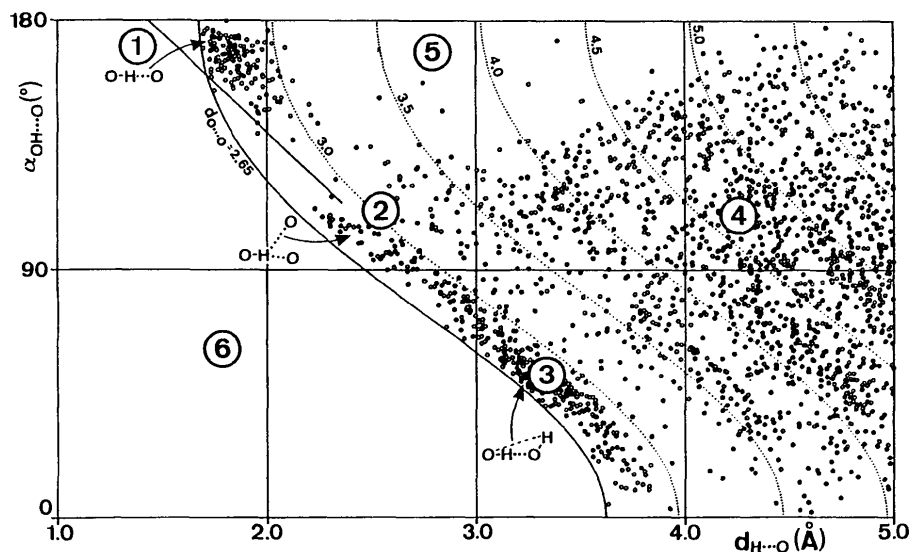


Fig. 5. Extended scatterplot of $\alpha_{\text{OH}\cdots\text{O}}$ versus $d_{\text{H}\cdots\text{O}}$ for hydroxyl and water donors in carbohydrate crystal structures. The inclined solid line is the limiting line for water donors from Fig. 3(a), the dotted theoretical lines correspond to discrete values of $d_{\text{O}\cdots\text{O}}$ based on an $\text{O}-\text{H}$ bond length of 0.97 \AA , which are indicated at the lines. Note that the solid curve representing $d_{\text{O}\cdots\text{O}} = 2.65 \text{ \AA}$ is a good approximation to the data limit in the regions $\alpha_{\text{OH}\cdots\text{O}} > 155^\circ$ and $\alpha_{\text{OH}\cdots\text{O}} < 75^\circ$. Circled numbers indicate regions of (1) two-center and major components of three-center bonds, (2) minor components of three-center (and four-center) bonds, (3) non-bonding next-neighbors, (4) non-bonding second-next neighbors (random scatter of the data points), (5) weakly populated region corresponding to near-linear lengthened bonds, (6) stereochemically forbidden region due to limited $\text{O}\cdots\text{O}$ approach.

The limit of lowest possible $\alpha_{\text{OH}\cdots\text{O}}$ in the scatterplots

In Fig. 6, the sharp limit $d_{\text{O}\cdots\text{O}} \geq 2.65 \text{ \AA}$ is independent of $\alpha_{\text{OH}\cdots\text{O}}$ in surprisingly large regions of the plot, that is $\alpha_{\text{OH}\cdots\text{O}} > 155^\circ$ and $\alpha_{\text{OH}\cdots\text{O}} < 75^\circ$. Hydrogen-bond angles between ~ 155 and $\sim 75^\circ$ are only found for somewhat larger $\text{O}\cdots\text{O}$ separations. The limit derived exclusively from major hydrogen-bond components is completely inappropriate for the minor components of three-center bonds. As a result of an insufficient number of data points in the critical region we did not draw a global line that would indicate limiting values.

Extended scatterplots for water donors

The data presented above comprise a substantial fraction of intramolecular hydrogen bonds, which are an integral part of hydrogen bonding in carbohydrates. In cyclodextrins, for example, over 50% of the hydroxyl groups donate at least minor three-center intramolecular hydrogen-bond components (Steiner, Mason & Saenger, 1991). Since in intramolecular arrangements severe stereochemical restrictions are imposed on the participating groups, it is of interest to study hydrogen bonds with water as donor, where no such restrictions occur. As our structural data set contains only 16 water molecules, the statistical significance is inferior to that of the results shown above.

In Figs. 7(a) and 7(b), the scatterplots of $\alpha_{\text{OH}\cdots\text{O}}$ versus $d_{\text{H}\cdots\text{O}}$ and $\alpha_{\text{OH}\cdots\text{O}}$ versus $d_{\text{O}\cdots\text{O}}$ are shown for

water donors (and water, C—O—H and C—O—C acceptors). The most obvious difference to Figs. 5 and 6 is that the 'cluster' of short, but strongly bent minor hydrogen-bond components is missing. In consequence, strongly bent hydrogen bonds with $110 > \alpha_{\text{OH}\cdots\text{O}} > 90^\circ$ are observed only for relatively long $\text{O}\cdots\text{O}$ separations $\geq 2.95 \text{ \AA}$.

In Fig. 7(b), the shortest $\text{O}\cdots\text{O}$ separations are $\sim 2.70 \text{ \AA}$ in region (1), where water molecules donate short hydrogen bonds, but $\sim 2.65 \text{ \AA}$ in region (3), which represents $\text{H}\cdots\text{O}$ contacts to groups (water or hydroxyl) from which the water molecule *accepts* a hydrogen bond (see inset in Fig. 5). This reflects the well known observation that water is a strong hydrogen-bond acceptor, but a relatively weak donor (Jeffrey & Maluszynska, 1990).

Surprisingly, a limiting line for shortest $d_{\text{O}\cdots\text{O}}$ depending on $\alpha_{\text{OH}\cdots\text{O}}$ seems to be better defined than in Fig. 6. In Fig. 7(b) we (preliminarily) suggest such an empirical limiting line for water donors, the equivalent limiting line in the plot of $\alpha_{\text{OH}\cdots\text{O}}$ against $d_{\text{H}\cdots\text{O}}$ is shown in Fig. 7(a). As the lines do not follow simple mathematical functions, and due to the moderate number of data points, we refrain from parametrizations.

Conclusions and discussion

(1) If O—H \cdots O hydrogen bonds are studied, arrangements with ionic and non-ionic molecules should be treated separately. This is obvious from Figs. 3(a) and 4: Fig. 4 represents only hydrogen

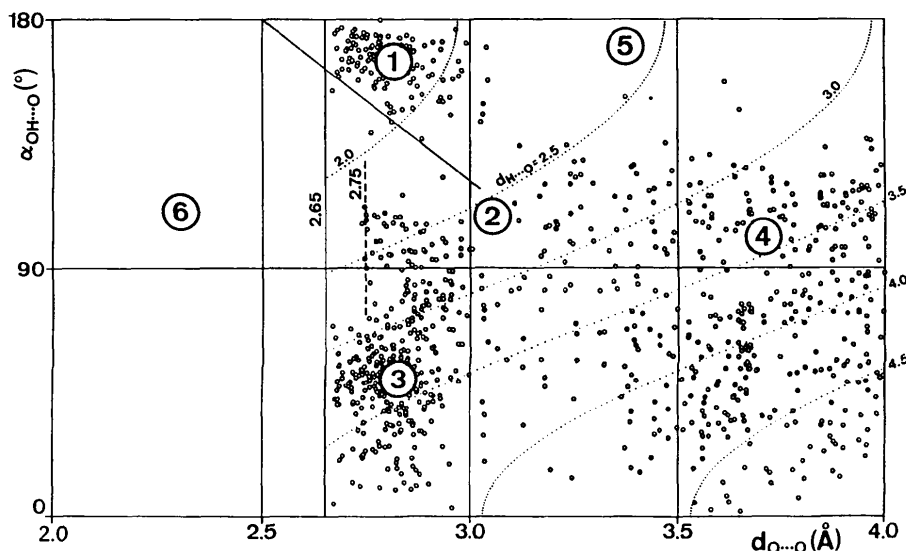


Fig. 6. Extended scatterplot of $\alpha_{\text{OH}\cdots\text{O}}$ versus $d_{\text{O}\cdots\text{O}}$ for hydroxyl and water donors in carbohydrate crystal structures. The inclined solid line is the limiting line for water donors from Fig. 3(b), the dotted theoretical lines correspond to discrete values of $d_{\text{H}\cdots\text{O}}$ based on an O—H bond length of 0.97 \AA , which are indicated at the lines. Circled numbers indicate regions as in Fig. 5. Note that no hydrogen bonds with $d_{\text{O}\cdots\text{O}} < 2.65 \text{ \AA}$ are observed.

bonds in a non-ionic environment, while in Fig. 3(a) ionic acceptors are also included. Differences are observed primarily in the low-distance region corresponding to very strong hydrogen bonds and lead to significantly different interpretations in terms of 'limits of lowest possible values'.

(2) In studies of the relations between hydrogen-bond parameters, minor components of three-center and four-center hydrogen bonds should be explicitly included; any 'extrapolations' of results obtained from major components only need to be valid. As an

example, Fig. 8 shows minor hydrogen-bond components donated by a water molecule [*W*10 to O(3)5] which represent substantial outliers in Fig. 3(b) (where only major components are considered).

(3) If variation of d_{OH} is neglected, the scatterplots of $\alpha_{OH\cdots O}$ versus $d_{H\cdots O}$ and $d_{O\cdots O}$ are equivalent.

(4) To show general properties of the data-point distribution, such scatterplots should be extended far beyond the hydrogen-bond region, preferably to the complete range of $0 < \alpha_{OH\cdots O} < 180^\circ$, see Figs. 4 and 5.

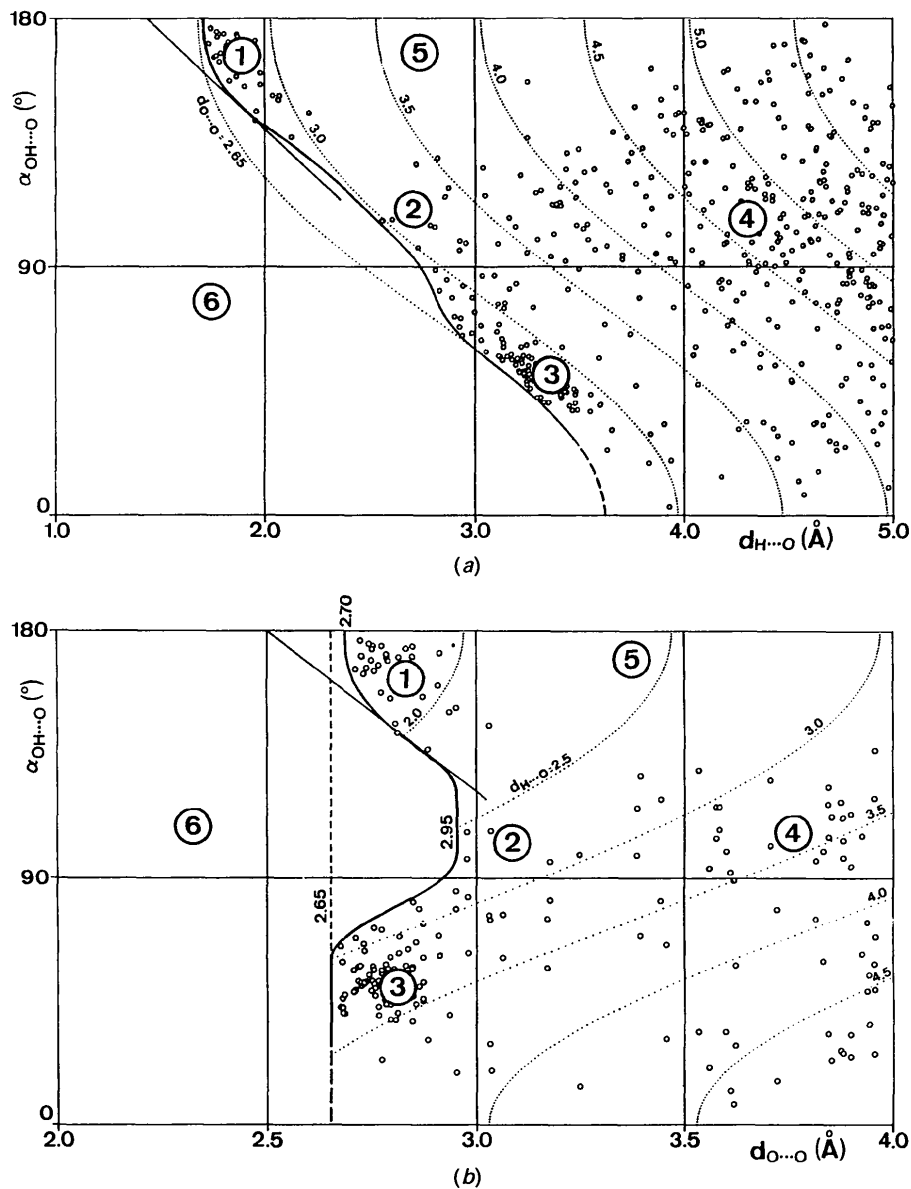


Fig. 7. (a) Scatterplot of $\alpha_{OH\cdots O}$ versus $d_{H\cdots O}$ for water donors only (water, hydroxyl and glycosidic acceptors). The empirical solid line suggests a limit of minimal allowed $\alpha_{OH\cdots O}$; it is equivalent to the limiting line in (b). Circled numbers indicate regions as in Fig. 5. (b) Scatterplot of $\alpha_{OH\cdots O}$ versus $d_{O\cdots O}$ for water donors only. The solid limiting line is purely empirical.

(5) It is obvious from Fig. 6 that for hydroxyl and water donors the minimum possible O...O approach is very sharply limited to a value slightly above 2.65 Å for $180 > \alpha_{\text{OH}\cdots\text{O}} > 155^\circ$, independent of $\alpha_{\text{OH}\cdots\text{O}}$. More strongly bent hydrogen bonds are found only for longer O...O separations. In carbohydrates, minor intramolecular components of three-center hydrogen bonds are associated with a minimum O...O separation of $d_{\text{O}\cdots\text{O}} \sim 2.75$ Å. If only water donors are included to avoid intramolecular effects (Fig. 7b), this value increases to 2.95 Å. A linear approximation for the limit of $d_{\text{O}\cdots\text{O}}$ as a function of $\alpha_{\text{OH}\cdots\text{O}}$ (Savage & Finney, 1986) is valid only in an intermediate range of $125 < \alpha_{\text{OH}\cdots\text{O}} < 155^\circ$.

(6) Because of stereochemical restrictions, intramolecular hydrogen bonds may have geometries that are not observed for intermolecular bonds. Examples are the numerous intramolecular minor hydrogen-bond components in carbohydrates, in which the acceptor oxygen is separated from the donor by two carbon atoms, see Fig. 9. These (and related) intramolecular hydrogen bonds produce the cluster of data points at $90 < \alpha_{\text{OH}\cdots\text{O}} < 120^\circ$ and left of the 3.0 Å line in Fig. 6 that is missing in Fig. 7(b). This observation shows that results obtained from studies of only intermolecular bonds, or only water donors, need not be valid for intramolecular hydrogen bonds. It also suggests that studies based on crystal structures of different substances or substance classes with different types of intramolecular hydrogen bonds can only be compared with great care.

(7) For short $d_{\text{O}\cdots\text{O}} < 3.0$ Å, the region of minor hydrogen-bond components of three-center bonds (2) continuously merges with the non-bonding arrangements (3) as $\alpha_{\text{OH}\cdots\text{O}}$ decreases below 90° , see Fig. 5. This implies that all possible orientations of a donor with respect to a neighboring potential acceptor atom are not only possible in principle, but do actually occur in crystal structures. The widely accepted hydrogen-bond criterion $\alpha_{\text{OH}\cdots\text{O}} > 90^\circ$, which demands that in a hydrogen bond the donor must point in the direction of the acceptor atom, is not basically affected by this observation.

(8) For long $d_{\text{H}\cdots\text{O}}$, the region of minor hydrogen-bond components (2) merges with the non-bonding arrangements (4). There is *no* limit of $d_{\text{H}\cdots\text{O}}$ or $d_{\text{O}\cdots\text{O}}$ that separates these regions: as $d_{\text{H}\cdots\text{O}}$ exceeds ~ 2.9 Å, non-bonding arrangements are observed in increasing numbers that represent H...H van der Waals contacts rather than hydrogen bonds (an example is shown in Fig. 10), whereas minor hydrogen-bond components as shown in Fig. 2 are also found for $d_{\text{H}\cdots\text{O}} > 3.0$ Å.

(9) For practical reasons, it would be highly desirable to have specific, qualitative, simple and reliable criteria for the identification of hydrogen

bonds based only on geometrical parameters; this problem has not been solved so far. No qualitative justification for any geometrical hydrogen-bond criterion can be derived from plots like Figs. 5 to 7 owing to the continuous transition between the hydrogen-bond regions and non-bonding arrangements.

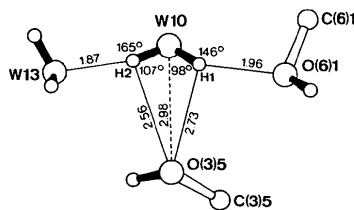


Fig. 8. Three-center hydrogen bonds donated by a water molecule in β -CD.11.6D₂O at $T = 120$ K (coordinates from Zabel, Saenger & Mason, 1986). The minor components OW10—H...O(3)5 produce outliers in Fig. 3(b) which was derived only from major hydrogen-bond components [values of $d_{\text{O}\cdots\text{O}}$ that are not indicated: OW10...O(6)1 = 2.81 Å, OW10...OW13 = 2.75 Å]. Arrangements of this type are frequently found in the hydrate structures of cyclodextrin complexes (Steiner & Saenger, unpublished results). Distances are given in Å.

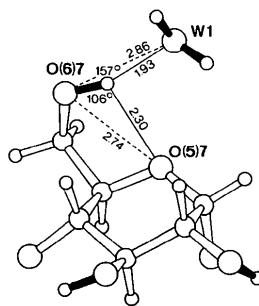


Fig. 9. Typical example of a three-center hydrogen bond with an intramolecular minor component in β -CD.EtOD.8D₂O at $T = 15$ K (Steiner, Mason & Saenger, 1990); glucose residue (7) of the β -CD molecule is shown. Due to stereochemical restrictions, the minor component has a short O...O separation, and strongly bent angle $\alpha_{\text{OH}\cdots\text{O}}$. Such O(6)—H...O(5) interactions are an important feature of hydrogen bonding in cyclodextrins. Similarly short and strongly bent *intermolecular* hydrogen bonds are not observed. Distances are given in Å.

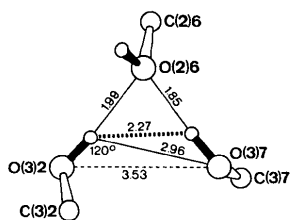


Fig. 10. Typical example of a non-bonding arrangement of two hydroxyl groups that represents a van der Waals contact between the two H atoms (in β -CD.EtOD.8D₂O at $T = 15$ K, Steiner, Mason & Saenger, 1990). Such arrangements are observed for $d_{\text{H}\cdots\text{O}} \geq 2.9$ Å. Distances are given in Å.

This study was supported by the Bundesministerium für Forschung und Technologie, FKZ 03 SA1 FUB 6.

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Complexation with Diol Host Compounds. 8. Structures and Thermal Analysis of 1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol with Selected Ketones

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(Received 5 March 1991; accepted 29 April 1992)

Abstract

The structures of three inclusion compounds of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol with methyl ethyl ketone (1), diethyl ketone (2) and acetophenone (3) have been determined and their thermal decomposition investigated by thermogravimetry and differential scanning calorimetry. Crystal data are: (1), $C_{30}H_{22}O_2 \cdot 2C_4H_8O$, $M_r = 558.72$, monoclinic, $P2_1/n$, $a = 8.321$ (3), $b = 11.845$ (3), $c = 17.153$ (4) Å, $\beta = 100.35$ (2)°, $V = 1663$ (1) Å³, $Z = 2$, $D_m = 1.09$ (3), $D_x = 1.12$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.39$ cm⁻¹, $F(000) = 596$, $T = 294$ K, final $R = 0.073$ ($wR = 0.084$) for 1494 independent reflections. (2), $C_{30}H_{22}O_2 \cdot 2C_5H_{10}O$, $M_r = 586.77$, monoclinic, $P2_1/n$, $a = 10.108$ (2), $b = 8.579$ (1), $c = 20.536$ (2) Å, $\beta = 102.45$ (1)°, $V = 1738.9$ (4) Å³, $Z = 2$, $D_m = 1.10$ (2), $D_x = 1.12$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.33$ cm⁻¹, $F(000) = 628$, $T = 294$ K, final $R = 0.081$ ($wR = 0.090$) for 1818 independent reflections. (3), $C_{30}H_{22}O_2 \cdot 2C_8H_8O$, $M_r = 654.80$, triclinic, $P\bar{1}$,

$a = 11.204$ (4), $b = 11.856$ (6), $c = 16.236$ (6) Å, $\alpha = 69.50$ (4), $\beta = 79.32$ (3), $\gamma = 62.98$ (4), $V = 1799$ (2) Å³, $Z = 2$, $D_m = 1.20$ (1), $D_x = 1.21$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.41$ cm⁻¹, $F(000) = 692$, $T = 294$ K, final $R = 0.096$ ($wR = 0.102$) for 2106 independent reflections.

Introduction

A large number of organic compounds can act as hosts in the formation of inclusion compounds. Some can be classified as clathrates because the host-guest aggregate is stabilized by steric factors alone. However, when there is hydrogen bonding between host and guest, the compounds are better classified as coordinato clathrates (Weber & Josel, 1983). Diol host compounds are particularly versatile hosts and their uses with respect to the isolation and optical resolution of racemates, as well as their role in controlling guest reactions in clathrates have been