This research was supported by grants from the NIH (No. GM40706) and from NASA (No. NAG8-804).

References

DICKERSON, R. E. (1980). *Sci. Am.* **242**, 136-153.

HAMPSEY, D. M., DAS, G. & SHERMAN, F. (1986). *J. Biol. Chem.* **261**, 3259-3271.

LOUIE, G. V., HUTCHEON, W. L. B. & BRAYER, G. D. (1988). *J. Mol. Biol.* **199**, 295-314.

MCPHERSON, A. (1990). *Eur. J. Biochem.* **189**, 1-23.

MATTHEWS, B. W. (1968). *J. Mol. Biol.* **33**, 491-497.

Acta Cryst. (1991). B47, 1022-1023

H···H van der Waals distance in cooperative O—H···O—H···O hydrogen bonds determined from neutron diffraction data.

By TH. STEINER and W. SAENGER, *Institut für Kristallographie, Freie Universität Berlin, Takustraße 6, D-1000 Berlin 33, Germany*

(*Received* 9 *February* 1991; *accepted* 15 *May* 1991)

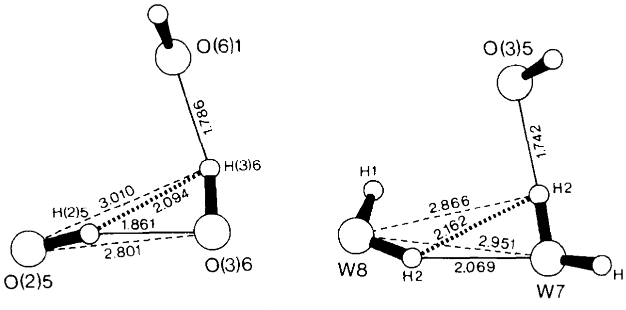
Abstract

The shortest possible H···H distance in hydrogen bonds of the cooperative type O—H···O—H···O has been determined from 23 neutron diffraction crystal structures of carbohydrates. The value of $d_{\rm HH,min}$ ~2·05 Å is the same for all combinations of hydroxyl and water donors and acceptors and for all hydrogen-bonding geometries observed, and significantly shorter than the 2·4 Å based on classical van der Waals radii.

Indroduction

In classical and still widely accepted concepts, the shape of a bonded hydrogen atom is that of a sphere with radius r = 1·2 Å, see, for example, Bondi (1964). This, however, implies that in crystal structures, the shortest possible non-bonding H···H distance $d_{\rm HH,min}$ is ~2·4 Å. Actually, considerably shorter H···H distances are observed. Recently, Nyburg, Faerman & Prasad (1987) have determined the effective van der Waals shape of hydrogen atoms bonded to sp^3- and sp^2-hybridized carbon atoms by examining a large number of short C—H···H—C contacts. They find a *head-on* radius r_h = 1·01 Å and a *side-on* radius r_s = 1·26 Å' for C(sp^3)—H (based on data for 500 H···H contacts in 78 structures) and r_h = 0·94, r_s = 1·32 Å for C(sp^2)—H (from 418 H···H contacts in 88 structures) ('*polar flattening*'). As a consequence, $d_{\rm HH,min}$ depends on the orientation of the C—H groups: for C(sp^3)—H it is about 2·0 Å for head-to-head and over 2·5 Å for side-to-side contacts. The method for data evaluation is described in Nyburg & Faerman (1985). More recently, Ikuta, Ishikawa, Katada & Sano (1990) have theoretically studied the polar flattening of the H atom in several small molecules using Hartree Fock-type methods. They predict a linear relation of r_h and r_s with the Mulliken partial charge on the H atom: if the partial (positive) charge increases, both radii decrease and the 'flattening' $r_s - r_h$ increases. For the extreme case of H—F, theoretical values of r_h = 0·75 and r_s = 1·08 Å were determined.

These studies are restricted to H atoms *not* involved in hydrogen bonding. As van der Waals radii are an important factor in the characterization of a hydrogen bond, the effective shape of H atoms in hydrogen-bonded functional O—H, N—H or S—H groups are of interest. Very short H···H contacts around $d_{\rm HH}$ ~2·1 Å in hydrogen-bonding systems have repeatedly been reported, but, to our knowledge, they were not systematically analyzed. Since a sufficient number of accurate neutron diffraction studies on crystal structures with O—H···O—H···O hydrogen bonds are available, we have analyzed their geometries to derive $d_{\rm HH,min}$ and find a value of ~2·05 Å.



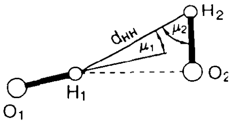


Fig. 1. Two examples of short H···H contacts (Å) in cooperative O—H···O—H···O hydrogen bonds, both in β-cyclodextrin–ethanol octahydrate, neutron diffraction at T = 15 K, Steiner *et al.* (1990). Water molecules are labelled as *W*, hydroxyl groups as O(*m*)*n*, H(*m*)*n*, where *n* is the number of the glucose residue in the cyclodextrin molecule and *m* the number of the hydroxyl group in the given residue. Standard deviations are between 0·006 and 0·009 Å.

Method

21 neutron crystal structures of carbohydrates with quality factors $R < 0{\cdot}06$ were extracted from the Cambridge Database (references in the deposited material*), and combined with two high-precision neutron crystal structures of cyclodextrin (CD) complexes [β-CD.11D$_2$O, $T = 120$ K, 0·80 Å resolution, $R = 0{\cdot}049$ (Zabel, Saenger & Mason, 1986) and β-CD.ethanol.8D$_2$O, $T = 15$ K, 0·93 Å resolution, $R = 0{\cdot}041$ (Steiner, Mason & Saenger, 1990)]. In the CD structures, hydroxyl groups and water molecules are deuterated. Hydrogen bonds, where the donor or the acceptor group is disordered, were excluded from the analysis. Following Nyburg & Faerman (1985), we analyzed the parameters described in Fig. 1 for cooperative arrangements O—H···O—H···O where *both* H atoms are involved in hydrogen bonding. O—H can be hydroxyl groups and water molecules in any combination (for examples see Fig. 1). For the 186 ordered contacts of this type in 23 structures, $d_{\rm HH}$ was plotted *versus* the polar angle μ_1, Fig. 2.

Results

Fig. 2 shows a well defined shortest value for $d_{\rm HH}$, which is independent of μ_1 except for small μ_1 (see Fig. 1). If μ_1 is small, the acceptor group is oriented 'away' from the donor, and the H···H distance exceeds the van der Waals contact. If $d_{\rm HH}$ is plotted against the hydrogen-bond angle α(O—H···O), a similar scatterplot is obtained, showing the shortest $d_{\rm HH}$ to be independent of α. The values for carbohydrate and cyclodextrin structures are scattered the same way and no significant difference is observed between hydroxyl and water donors and acceptors and between D and H. We agree with Nyburg & Faerman (1985) that the determination of $d_{\rm HH,min}$ from such a plot is somewhat subjective, but the value certainly lies between 2·05 and 2·10 Å. The dashed line $d_{\rm HH} = 2{\cdot}05$ Å is our lower estimate. In systems O—H···O—H···O the angles μ_1 and μ_2 vary only in a certain range and all short H···H contacts are of the head-to-side type, see Fig. 1. Our value of $d_{\rm HH,min}$ holds only for this special type of arrangement.

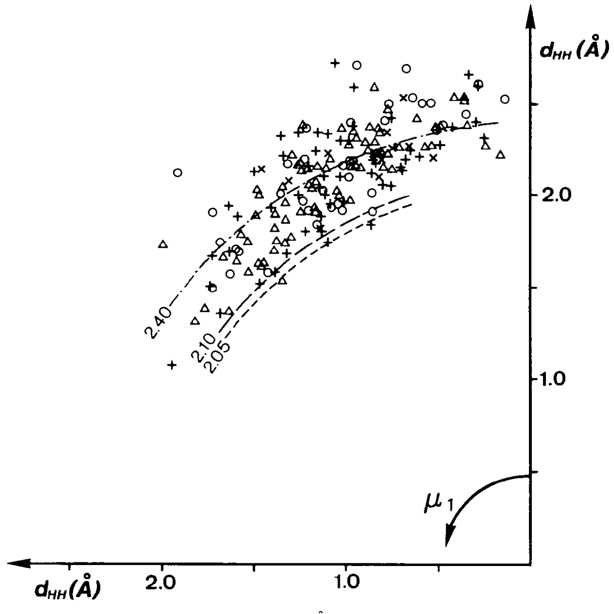


Fig. 2. Polar scatterplot of $d_{\rm HH}$ (Å) versus μ_1 (measured counterclockwise from the vertical). ○ and +: hydroxyl and water acceptors, respectively, in deuterated cyclodextrin crystal structures. △ and ×: hydroxyl and water acceptors in small carbohydrates. The dashed lines correspond to $d_{\rm HH} = 2{\cdot}10$ and 2·05 Å, the dashed-dotted line to $d_{\rm HH,min}$ for the classical van der Waals radius of 1·2 Å.

Discussion

(1) In cooperative O—H···O—H···O hydrogen bonds, H atoms may approach each other to a well-defined minimal distance $d_{\rm HH,min} \sim 2{\cdot}05$ Å. This value is the same, or at least very similar, for hydroxyl and water donors and acceptors, and is independent of the hydrogen-bond geometry. In crystal structures, H positions with distances $d_{\rm HH}$ significantly $< 2{\cdot}0$ Å cannot be occupied simultaneously and consequently indicate disorder or refinement artefacts.

(2) The shape of the H atom in O—H certainly is polar flattened, as in the C—H groups. Our study gives no information on the effective shape, r_h or r_s, as the data are only for the special case of head-to-side contacts. If, however, the 'mean radius' for a spherical approximation is required, for O—H a value close to 1·0 Å is more realistic than the classical van der Waals radius of 1·2 Å.

(3) Savage & Finney (1986) empirically found that the non-bonding distance H$_2$···O$_1$ is limited to values ≥ 3·0 Å. This can be explained exclusively by H$_1$···H$_2$ van der Waals repulsions, as these also determine a shortest possible H$_2$···O$_1$ distance. Any further approach of H(3)6 to O(2)5 in Fig. 1 (left), for example, would have to reduce $d_{\rm HH}$, which is only 2·09 Å, or to push away H(2)5. Trigonometrical considerations show that the shortest possible distance H$_2$···O$_1$ is longer for hydrogen bonds with low μ_1 as in Fig. 1, left, than in those with large μ_1 such as in Fig. 1, right.

This study was supported by the Bundesministerium für Forschung und Technologie, FKZ 02 SA1 FUB6.

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Ikuta, S., Ishikawa, M., Katada, M. & Sano, H. (1990). *Acta Cryst.* B**46**, 23–27.

Nyburg, S. C. & Faerman, C. H. (1985). *Acta Cryst.* B**41**, 274–279.

Nyburg, S. C., Faerman, C. H. & Prasad, L. (1987). *Acta Cryst.* B**43**, 106–110.

Savage, F. J. & Finney, J. L. (1986). *Nature (London)*, **322**, 717–720.

Steiner, Th., Mason, S. A. & Saenger, W. (1990). *J. Am. Chem. Soc.* **112**, 6184–6190.

Zabel, V., Saenger, W. & Mason, S. A. (1986). *J. Am. Chem. Soc.* **108**, 3664–3673.

---

* Lists of substance names, crystallographic R values and references of the 23 neutron crystal structures analyzed have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54241 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.