the donor–acceptor distances behave as expected.

4. Conclusions

Shallow, corner-cutting tunneling is very wide spread in hydrogen transfer reactions. It is intrinsic to quantum mechanisms, just as zero-point energy is.[37] In the present and previous[3,14] calculations its effect on hydrogen transfer rate constants for temperatures around 300 K have usually been only a factor of about 10 and never as high as 10^2. If these calculations approximate reality, as we believe they do,[14] tunneling only changes the Gibbs free energy of activtaion by 5–10%. Nevertheless, it usually accounts for around half of the primary hydrogen isotope effect.

The exponent of the Swain–Schaad relation cannot give information about the importance of tunneling in systems with only one isotopically sensitive hydrogen. The exponent is usually within the 1.33–1.55 range even though the tunneling correction is significant. In addition to this, the variational effect can lead to a larger value of the exponent than 1.55 without tunneling. In fact, the tunneling effect has a tendency to bring the exponent of the Swain–Schaad relation back within the expected range when the variational effect makes it large. The Swain–Schaad relation seems to be a reliable way to approximate a tritium isotope effect from the corresponding deuterium isotope effect, and vice versa.

On the basis of rate constants measured around 300 K, values of $E_a(D) - E_a(H)$ greater than 1.20 kcal mol^{-1} will usually signal tunneling as will values of $A_H/A_D < 1.0$ for hydrogen transfer between massive, polyatomic donors and acceptors. When both characteristics are present they are strong evidence of tunneling, but they cannot be described as completely definitive.

A particular pattern of the variation of k_H/k_D with changes in donor and acceptor structures and K_{eq}, described previously and above, can sometimes provide very strong evidence of shallow, corner-cutting tunneling.

There probably is no completely unambiguous way to demonstrate shallow, corner-cutting tunneling for reactions carried out around 300 K. Such evidence is only available at much lower temperatures, where deep tunneling becomes prevalent and rate constants for hydrogen transfer reactions approach temperature independence. However, models incorporating tunneling will generally provide a more accurate understanding of experimental observations than those which do not.

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Covalent Bond Lengthening in Hydroxyl Groups Involved in Three-Center and in Cooperative Hydrogen Bonds. Analysis of Low-Temperature Neutron Diffraction Data

Thomas Steiner and Wolfram Saenger*

Contribution from the Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, W-1000 Berlin 33, Germany. *Received December 6, 1991*

Abstract: The lengthening of the covalent O–D bond d_{O-D} in O–D···O hydrogen-bonding hydroxyl groups is studied from low-temperature, high-resolution neutron diffraction data of two β-cyclodextrin complexes (all O–D groups deuterated). The focus is primarily on the long-distance region of the hydrogen bond length D···O ($d_{D\cdots O}$). The slope of the regression line d_{O-D} versus $d_{D\cdots O}$ does not become 0, and an asymptotic value of d_{O-D} for an unperturbed hydroxyl group is not reached even for long distances of $d_{D\cdots O} \sim 2.1$ Å. This may be taken as an experimental indication for the long-range interaction of the hydrogen bond, which decreases very smoothly. An influence of three-center hydrogen bonding and of cooperativity on the O–D bond length is clearly observed. In three-center bonds, the formation of a minor hydrogen bond component < 2.4 Å lengthens the O–D bond by ~0.01 Å in addition to the lengthening by the major component. In chains of hydrogen-bonded O–D groups, the cooperative effect lengthens the O–D bond also by ~0.01 Å if the D···O distance is <1.8 Å.

Introduction

It was recognized early from neutron diffraction experiments that in O–H···O hydrogen bonds (H-bonds), the covalent O–H bond (d_{OH}) is lengthened with shortening H-bond distance $d_{H\cdots O}$ (or $d_{O\cdots O}$),[1] correlation plots of d_{OH} versus $d_{O\cdots O}$ and $d_{H\cdots O}$ derived from neutron diffraction data have repeatedly been shown.[2-6] General interest has focused primarily on short hydrogen bonds with $d_{H\cdots O} < 1.7$ Å, for which the lengthening of d_{OH} is considerable; in the extreme case, the H atom may be placed exactly between two O atoms ("*symmetric*" hydrogen bonds with $d_{O\cdots O} \sim 2.4$ Å and $d_{OH} \sim 1.2$ Å). Short distances $d_{H\cdots O} < 1.7$ Å are, however, only observed if the donor or the acceptor group is an ion, and in intramolecular H-bonds with sterically constrained, short O···O separations.[6] For longer H-bonds with $d_{H\cdots O} > 1.7$ Å, the lengthening of d_{OH} has not been explored as extensively. For the special case of water donors, a correlation plot between d_{OH} and $d_{H\cdots O}$ for the region 1.6 Å $< d_{H\cdots O} <$ 2.2 Å shows that d_{OH} decreases with increasing $d_{H\cdots O}$ even for the longest H···O separations considered.[5] This suggests that d_{OH} should be slightly

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Table I. Mean Values[a] of Several Hydrogen Bond Parameters[b,c] for the Total Set of 36 OD Groups, for the Two Individual Structures, and for the Two Types of Hydroxyl Groups

	n^d	$\langle d_{O-D} \rangle$	$\langle d_{D\cdots O} \rangle$	$\langle d_{O\cdots O} \rangle$
all OD groups	36	0.975 (2)	1.88 (2)	2.83 (2)
β-CD·11.6D_2O; T = 120 K[11]	18	0.974 (3)	1.90 (2)	2.86 (2)
β-CD·EtOD·8D_2O; T = 15 K[12]	18	0.976 (3)	1.86 (3)	2.81 (2)
primary OD groups[e]	12	0.974 (3)	1.88 (2)	2.83 (2)
secondary OD groups[e]	24	0.976 (3)	1.89 (3)	2.84 (3)

[a] Arithmetic mean of the published[11,12] individual values. [b] Distances in angstroms. [c] Estimated standard deviations in parentheses, esd $(\langle d \rangle) = [\sum_i(\langle d \rangle - d_i)^2/n(n-1)]^{1/2}$. [d] Number of OD groups. [e] Averaged over both structures.

lengthened also by weak hydrogen bonds with $d_{H\cdots O} > 2.2$ Å.

It is obvious that d_{OH} must extrapolate toward the value of the "free" molecule (gas phase: d_{OH} = 0.958 Å for water,[7] 0.971 Å for ethanol[7]) with increasing $d_{H\cdots O}$. Due to the apparent bond length reduction by thermal vibrations,[8,9] which is notoriously observed in crystallography, the numeric asymptotic value of d_{OH} for room temperature data will be some 0.01 Å smaller than the gas-phase values. This is well illustrated by the published data,[5] where O–H distances significantly shorter than 0.94 Å are observed. For hydrogen-bonding O–H groups, the established methods for bond length correction can give only rough approximations even at low temperatures. It is therefore *not* possible to predict with good reliability which apparent d_{OH} should be observed by crystallography for "relaxed" O–H groups at a given temperature, and it is not feasible to draw a horizontal asymptotic line for d_{OH} in plots of d_{OH} against $d_{H\cdots O}$.

The correlation between d_{OH} and $d_{H\cdots O}$ is "soft" with a considerable scatter around the regression line. For H_2O, for example, the published values of d_{OH} vary by over ±0.03 Å for any given $d_{H\cdots O}$.[5] As this scatter cannot be explained by experimental errors alone, it was associated with the different chemical natures of the donor groups R–O–H and acceptor O atoms and with the widely differing environments of the hydrogen bonds studied.[4]

Due to "environmental" effects aside from the distance $d_{H\cdots O}$, a certain covalent bond length d_{OH} will depend (for example) on the possibility that this OH group donates three-center hydrogen bonds or engages in cooperatively interacting chains of OH groups. To specify the influence of the most evident of these effects on d_{OH}, it is reasonable to minimize the influence of chemical heterogeneity by analyzing d_{OH} in a suitable simple model system. Such a system is provided by the β-cyclodextrin complexes, which contain a large number of chemically related O–H···O hydrogen bonds, and for which high-resolution neutron diffraction data are available. Due to the influence of thermal vibrations on d_{OH}, it is necessary to restrict such a study to low-temperature data.

The Data Set Studied

β-Cyclodextrin (β-CD), $(C_6H_{10}O_5)_7$, is a cyclic oligosaccharide consisting of seven D-glucose moieties linked by α(1–4) interglucose bonds. The molecule has 21 hydroxyl groups (7 primary CH_2–OH and 14 secondary CH–OH) and 14 ether-like (C–O–C) oxygen atoms. All atoms are uncharged. β-CD readily forms inclusion complexes with suitable guest molecules, which always cocrystallize with several water molecules. Due to the large number of O–H···O hydrogen bonds formed, these inclusion complexes are used as model systems for general studies of hydrogen bonding (see ref 10 and references therein). A characteristic feature of cyclodextrin complexes is the unusually large number of three-center hydrogen bonds.[10] Low-temperature, high-resolution neutron diffraction studies are available for two of these complexes: β-CD·11.6D_2O[11] (T = 120 K, crystallographic quality factor R = 0.049) and β-CD·EtOD·8D_2O[12] (T = 15 K, R = 0.041); all C–OH and H_2O are deuterated.

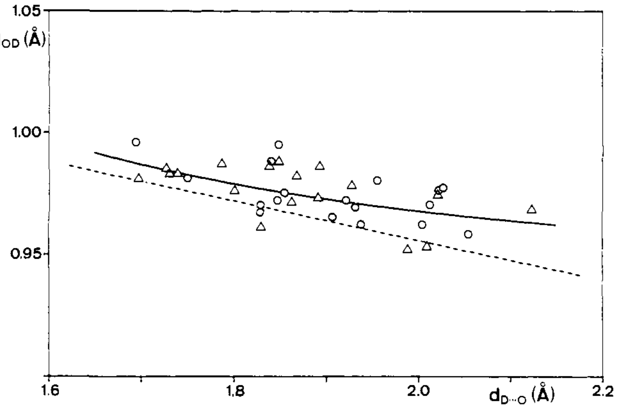

Figure 1. Plot of d_{OD} versus $d_{D\cdots O}$ for hydroxyl groups in complexes of β-cyclodextrin as determined by neutron diffraction at low temperatures,[11,12] d_{OD} not corrected for thermal motion. Circles: data from β-CD·11.6D_2O, T = 120 K. Triangles: β-CD·EtOD·8D_2O at T = 15 K. Dashed line: linear approximation for $d_{OH} = f(d_{H\cdots O})$ for water donors[5] (the line was taken directly from the plot in ref 5). The root mean square deviation of the data points with respect to the regression line, which measures the "width" of the scatter, is 0.009 Å (definition used: rms dev = $[\sum_i(d_{\text{regress.}} - d_i)^2/(n-1)]^{1/2}$).

Individual hydrogen bond geometries (including OD bond lengths) are listed in the original papers,[11,12] where, however, the very restrictive van der Waals cutoff criterion $d_{H\cdots O} \leq 2.6$ (or 2.7) Å for minor components of three-center bonds has been used. More complete hydrogen bond listings for $d_{H\cdots O} < 3.0$ Å are in the supplementary material of this paper. Disordered β-CD OD groups and water molecules were excluded from the present analysis. The remaining 36 OD groups (18 from each structure) form O–D···O hydrogen bonds with $d_{D\cdots O}$ between 1.69 and 2.12 Å, the range generally observed in carbohydrates.[13] The mean values of d_{OD}, $d_{D\cdots O}$ and $d_{O\cdots O}$ are listed in Table I for the two structures (and temperatures) and for the two types of hydroxyl groups. The differences in the various $\langle d_{OH} \rangle$ are marginal and do not justify a separate analysis of the two structures or the two types of OD groups. In the following we therefore analyze all 36 OD groups as a set of chemically closely related hydrogen bond donors.

Results

The correlation plot of d_{OD} versus $d_{D\cdots O}$ (Figure 1, data points for the two structures are indicated differently) is similar to that reported in the earlier works,[4,5] with d_{OD} increasing smoothly changing by over 0.025 Å from the longest to the shortest H-bonds. Due to the limited number of data, the curved empirical regression line can only be taken as an estimate, and therefore it is not suitable for any extrapolations. Nevertheless it is obvious that its slope does not become 0 even for the longest H-bonds, i.e., an asymptotic value of d_{OD} for relaxed OD groups is not yet reached for $d_{D\cdots O}$ = 2.1 Å. This clearly shows the long-range nature of the hydrogen bond. For comparison, the linear approximation of d_{OH} as a function of $d_{H\cdots O}$ for water donors[5] is shown as a dashed line; because it is based primarily on room temperature data, it is systematically lower by ~ 0.01 Å than the regression line. As to be expected, the scatter of the data points is less pronounced compared with chemically heterogeneous data samples[4,5] (which also contain, for example, data from inorganic salts). A closer look at the data reveals an influence of two multiatom interactions. These interactions are three-center H-bonding and the "cooperative effect".

Three-Center Hydrogen Bonds. A three-center (four-center) hydrogen bond is the interaction of an H atom with *two* (*three*) acceptor atoms. Usually the two (three) H···O separations differ; the shorter is called the "major" component, the longer the "minor" component. Such arrangements are frequently observed in cy-

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Table II. Mean Values of H-Bond Distances and Angles[a,b] for the Sets of Three-Center Hydrogen Bonds

OD groups donating minor H-bond comp	n^c	$\langle d_{\mathrm{D\cdots O,major}}\rangle$	$\langle d_{\mathrm{D\cdots O minor}}\rangle$	$\langle \alpha_{\mathrm{OD\cdots O,major}}\rangle$	$\langle \alpha_{\mathrm{OD\cdots O,minor}}\rangle$
$d_{\mathrm{D\cdots O,minor}} < 2.4$ Å	10	1.93 (3)	2.31 (1)	160 (1)	108 (1)
2.4 Å $\leq d_{\mathrm{D\cdots O,minor}} < 2.7$ Å	10	1.89 (3)	2.55 (3)	169 (2)	101 (2)
2.7 Å $\leq d_{\mathrm{D\cdots O,minor}} < 3.0$ Å	7	1.88 (4)	2.81 (4)	164 (3)	104 (5)
no $d_{\mathrm{D\cdots O,minor}} < 3.0$ Å	9	1.83 (4)		168 (2)	

[a] Distances in angstroms, angles in degrees. [b] Estimated standard deviations in parentheses, esd $(\langle d\rangle) = [\sum_i(\langle d\rangle - d_i)^2/n(n-1)]^{1/2}$. [c] Number of OD groups.

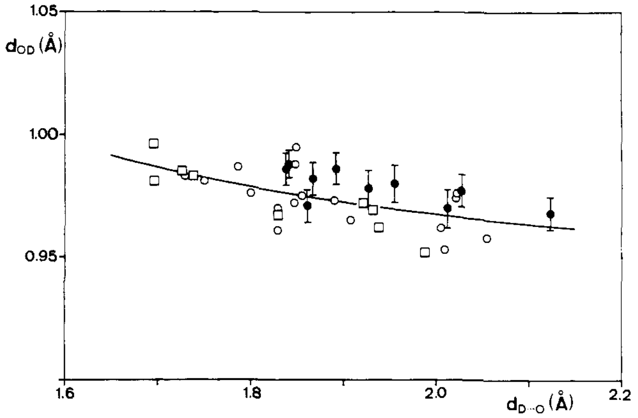

Figure 2. Data as in Figure 1. Filled circles with error bars (esd between 0.006 and 0.009 Å): OD donating three-center H-bonds with a minor component $d_{\mathrm{D\cdots O,minor}} < 2.4$ Å. Open circles: OD donating minor components 2.4 Å $\leq d_{\mathrm{D\cdots O,minor}} < 3.0$ Å (esd between 0.007 and 0.009 Å, error bars omitted for clarity). Open squares: OD donating two-center H-bonds or three-center bonds with weak minor components ≥ 3.0 Å (esd between 0.007 and 0.009 Å, error bars omitted for clarity).

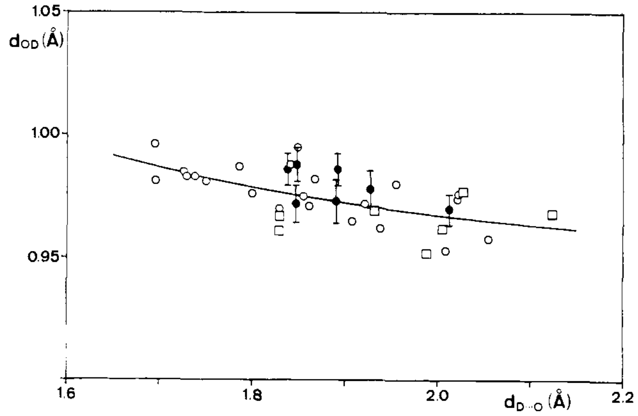

Figure 3. Data as in Figure 1. Filled circles (with error bars): OD accepting an H-bond $d_{\mathrm{D\cdots O,accepted}} < 1.8$ Å. Open circles: OD accepting an H-bond 1.8 Å $\leq d_{\mathrm{D\cdots O,accepted}} < 2.0$ Å. Open squares: OD *not* accepting an H-bond with $d_{\mathrm{D\cdots O}} < 2.0$ Å.

clodextrin,[10-12] carbohydrate,[13] and amino acid[14,15] crystal structures. In the present data set, 10 out of 36 H-bonds (~28%) have a strong additional minor component $d_{\mathrm{H\cdots O}} < 2.4$ Å (this is an unusually high fraction), and only nine (~25%) have no minor component < 3.0 Å. Most of the short minor components are intramolecular bonds to ether-type O atoms.

A minor H-bond component must lengthen d_{OH} *in addition* to the major component, i.e., in the plot of d_{OH} versus $d_{\mathrm{H\cdots O}}$, corresponding data points should be scattered *above* the regression line. To test this assumption, the data were divided into three sets of OD groups that donate three-center H-bonds with a minor component $d_{\mathrm{D\cdots O}} < 2.4$ Å, 2.4 Å $\leq d_{\mathrm{D\cdots O}} < 2.7$ Å, and 2.7 Å $\leq d_{\mathrm{D\cdots O}} < 3.0$ Å and a fourth set with the OD groups that donate *no* minor component < 3.0 Å. The mean values of the corresponding H-bond parameters, Table II, show that in three-center bonds the major components tend to be longer and angles $\alpha_{\mathrm{OD\cdots O}}$ are more strongly bent than in two-center bonds (as expected).

In Figure 2, data points for the first and fourth sets are drawn as filled circles and as open squares, respectively; they clearly show the anticipated effect: nine out of 10 data points for the OD groups donating $d_{\mathrm{D\cdots O,minor}} < 2.4$ Å are above the regression line, and eight out of nine data points for two-center bonds are on or below this line. The mean deviations $\langle \Delta d_{\mathrm{OD}}\rangle$ from the regression line are listed for all data sets in Table III; comparison of these deviations shows that donation of a minor hydrogen bond component with $d_{\mathrm{H\cdots O}} < 2.4$ Å lengthens the (observed) d_{OD} by 0.012 (3) Å on the average with respect to two-center bonds (or three-center bonds with very long $d_{\mathrm{D\cdots O}} \geq 3.0$ Å). For the data sets with longer minor components $d_{\mathrm{H\cdots O}} \geq 2.4$ Å, the observed lengthening of d_{OD} does not exceed the estimated standard deviation of 0.004 Å.

To perform a more rigorous analysis, one should not study the deviations from a regression line that is based on all OD groups, but compare directly three-center and two-center bonds. This requires individual regression lines for each data set (which will *not* have identical slopes at any given $d_{\mathrm{D\cdots O}}$); the limited quantity of data, however, does not allow such a study.

Table III. The Effect of Three-Center Hydrogen Bonding. Mean Deviations $\langle \Delta d_{\mathrm{OD}}\rangle^a$ of d_{OD} from the Regression Line[b] for the Four Sets of OD Groups Donating Three-Center Bonds and Two-Center Bonds, and Difference[c] from the Set of Two-Center Bonds

	uncorrected[d]	corrected lower bound[16]	corrected riding motion[16]
$\langle \Delta d_{\mathrm{OD}}\rangle$ from the regression line			
$d_{\mathrm{D\cdots O,minor}} < 2.4$ Å	+0.007 (2)	+0.006 (3)	+0.005 (2)
2.4 Å $\leqslant d_{\mathrm{D\cdots O,minor}} < 2.7$ Å	−0.001 (3)	−0.001 (3)	−0.001 (3)
2.7 Å $\leqslant d_{\mathrm{D\cdots O,minor}} < 3.0$ Å	−0.002 (3)	−0.001 (3)	+0.001 (2)
no $d_{\mathrm{D\cdots O,minor}} < 3.0$ Å	−0.005 (2)	−0.004 (2)	−0.004 (3)
difference from two-center bonds			
$d_{\mathrm{D\cdots O,minor}} < 2.4$ Å	+0.012 (3)	+0.010 (4)	+0.009 (4)
2.4 Å $\leqslant d_{\mathrm{D\cdots O,minor}} < 2.7$ Å	+0.004 (4)	+0.003 (4)	+0.003 (3)
2.7 Å $\leqslant d_{\mathrm{D\cdots O,minor}} < 3.0$ Å	+0.003 (4)	+0.003 (4)	+0.005 (4)

[a] $\Delta d_{\mathrm{OD}} = d_{\mathrm{OD,obsd}} - d_{\mathrm{OD,regress}}$; $\langle \Delta d_{\mathrm{OD}}\rangle = \sum \Delta d_{\mathrm{OD}}/n$; estimated standard deviation (esd) in parentheses: esd $(\langle \Delta d_{\mathrm{OD}}\rangle) = [\sum(\langle \Delta d_{\mathrm{OD}}\rangle - \Delta d_{\mathrm{OD}})^2/n(n-1)]^{1/2}$. [b] In angstroms. [c] esd (diff) $= (\mathrm{esd}_1{}^2 + \mathrm{esd}_2{}^2)^{1/2}$. [d] Values of d_{OD} as published.[11,12]

It is tempting to study an assumed influence of the hydrogen bond angle $\alpha_{\mathrm{OD\cdots O}}$ on d_{OD} (as was suggested by a referee): for any given $d_{\mathrm{H\cdots O}}$, an H-bond should become weaker with increasingly bent $\alpha_{\mathrm{OH\cdots O}}$. Consequently, d_{OH} should be slightly shorter in bent than in more linear H-bonds, and data from strongly bent H-bonds should be scattered below the regression line in Figure 2. Actually, however, strongly bent H-bonds are highly correlated with the formation of a short minor H-bond component: in the present data set, of the eight H-bonds with $\alpha_{\mathrm{OD\cdots O}} < 160°$, six are major components of three-center bonds with minor components $d_{\mathrm{D\cdots O}} < 2.4$ Å. Consequently, d_{OD} experiences additional lengthening by the short minor component that far more than compensates any effect due to bending of $\alpha_{\mathrm{OD\cdots O}}$: the data points for $\alpha_{\mathrm{OD\cdots O}} < 160°$ are scattered above the regression line by $\langle \Delta d_{\mathrm{OD}}\rangle = +0.007$ (3) Å. If an influence of $\alpha_{\mathrm{OH\cdots O}}$ on d_{OH} should be studied, a different data set with pure two-center H-bonds has to be analyzed.

The Cooperative Effect. The "cooperative effect" is the mutual polarization of hydrogen-bonding groups, which are interconnected to form larger arrangements.[16] It strengthens an H-bond if the donor *accepts* an H-bond from another donor. As a consequence,

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Table IV. The Effect of Cooperativity. Mean Deviations $\langle \Delta d_{OD} \rangle^a$ of d_{OD} from the Regression Line[a] for OD Groups That Accept an H-Bond $d_{D\cdots O}$ < 1.8 Å and That Do Not Accept an H-Bond $d_{D\cdots O}$ < 2.0 Å

	uncorrected[a]	corrected lower bound[16]	corrected riding motion[16]
$\langle \Delta d_{OD} \rangle$ from the regression line			
$d_{D\cdots O,accepted}$ < 1.8 Å	+0.005 (2)	+0.005 (3)	+0.003 (3)
no $d_{D\cdots O,accepted}$ < 2.0 Å	−0.006 (4)	−0.005 (4)	−0.005 (4)
difference[a] between these sets	+0.011 (4)	+0.010 (5)	+0.008 (5)

[a] For definitions, see footnotes of Table III.

for H-bonds with a given $d_{H\cdots O}$, d_{OH} should increase if the donor accepts a strong H-bond; in the plot of d_{OH} versus $d_{H\cdots O}$, corresponding data points should be scattered above the regression line. This is actually observed, as shown in Figure 3: filled circles show OD groups that accept an H-bond with $d_{D\cdots O}$ < 1.8 Å (seven out of 36, ~19%), and squares show those that do *not* accept an H-bond with $d_{D\cdots O}$ < 2.0 Å (seven out of 36, ~19%). The deviations $\langle \Delta d_{OD} \rangle$ with respect to the regression line are given in Table IV; the difference between $\langle \Delta d_{OD} \rangle$ of the two sets is 0.011 (4) Å.

Corrections for Thermal Motion. Crystallographically determined bond lengths are affected by thermal motion of the individual atoms[8,9] and of the molecule as a whole.[17] At low temperatures (120 and 15 K in the present study), this is more significant for bonds involving H atoms; and even for these, it is not a major effect. For O–D, the lowest estimate for the apparent bond length reduction by harmonic vibrations of O and D is given by the "lower-bound" distance,[8] and a more appropriate correction is given by the model of "riding motion"[8] of the D on the O atom. These simple corrections, which are based only on the anisotropic thermal parameters of O and D, are of course only rough approximations for the more complex system O–D···O. Both corrections were performed (program PARST[18]), leading to shifts of d_{OD} between +0.001 and +0.005 Å, mean shift +0.0025 Å, for the lower-bound model; and between +0.009 and +0.022 Å, mean shift 0.015 Å, for the riding motion model. Apart from a collective shift, the data points on average move slightly toward the regression line: the root mean square deviation of d_{OD} with respect to the regression line (see caption to Figure 1) is 0.009 Å for the uncorrected data; it reduces to 0.008 Å for lower bound and to 0.007 Å for riding motion corrections. This is as to be expected. For the various data sets, the values of $\langle \Delta d_{OD} \rangle$ decrease on the same scale, Tables III and IV. The riding motion model reduces the estimated additional OD bond lengthening by a minor H-bond component $d_{D\cdots O}$ < 2.4 Å from 0.012 (3) to 0.009 (4) Å (Table III).

Corrections for bond lengthening by anharmonic oscillations are less well established. For C–H, an estimate has been suggested that is based on Morse potential functions obtained from the gas phase and on the harmonic mean square amplitudes along the bond.[19] We refrain from such calculations for the present system O–D···O, as no corresponding data on the potential is available. We note, however, that at low temperatures the lengthening by anharmonic vibration tends to *compensate* the reduction by harmonic oscillations, as actually observed for several small molecules.[20,21] For the present data, the marginal difference of the mean d_{OD} at $T = 15$ K and at $T = 120$ K indicates a compensation of these two effects, suggesting that the uncorrected values in Tables III and IV are already the relevant results.

Discussion

In the correlation plot of d_{OD} versus $d_{D\cdots O}$ (Figure 1), the slope of the regression line does not become 0, and an asymptotic value of d_{OD} for unperturbed hydroxyl groups is not observed even for long distances $d_{D\cdots O}$ ~ 2.1 Å. This directly shows that the hydrogen bond is a long-range interaction and decreases only slowly with increasing distance $d_{H\cdots O}$. Actually, quantum chemical calculations have indicated that long hydrogen bonds are primarily electrostatic interactions with a slowly diminishing strength.[22,23]

By analyzing a model system that contains chemically related H-bond donors and acceptors (and no ions), we are able to specify in a semiquantitative manner two major "environmental" effects on the O–D bond length in H-bonding hydroxyl groups. Due to the small number of data used, the numerical results have to be regarded with care, but the general trends are obvious. In three-center H-bonds, a strong minor component $d_{D\cdots O}$ < 2.4 Å lengthens the covalent O–D bond by ~0.01 Å. This is in addition to lengthening by the major component and shows the significance of such an interaction. For weaker minor components 2.4 Å < $d_{D\cdots O}$ < 3.0 Å, only marginal lengthening is observed, close to the standard deviation.

An influence of the cooperative effect on d_{OD} is also observed; for a given $d_{D\cdots O}$, the d_{OD} is ~0.01 Å longer in OD groups that accept an H-bond with $d_{D\cdots O}$ < 1.8 Å than in those that accept only H-bond components > 2.0 Å. In chemically more complex systems, the number of (competing) environmental effects on d_{OH} certainly is larger and they will be more difficult to separate.

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Registry No. β-CD·11.6D_2O, 139300-24-6; β-CD·EtOD·8D_2O, 128660-73-1.

Supplementary Material Available: Listings of hydrogen bond parameters for the two analyzed neutron crystal structures, β-CD·11.6D_2O and β-CD·EtOD·8D_2O (4 pages). Ordering information is given on any current masthead page.

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