

diffraction data is more seriously compromised by the use of protonated rather than deuterated samples.

This work was supported by the Gaduiertenkolleg 'Synthese und Strukturaufklärung niedermolekularer Verbindungen'. One of us (AL) is grateful to Professor M. B. Hursthouse, Cardiff, for being a most friendly host while part of this work was carried out. Beam-time allocation by ISIS under RB/2472 is gratefully acknowledged.

#### References

- COPPENS, P., DAM, J., HARKEMA, S., FEIL, D., FELD, R., LEHMANN, M. S., GODDARD, R., KRÜGER, C., HELLNER, E., JOHANSEN, H., LARSEN, F. K., KOETZLE, T. F., McMULLAN, R. K., MASLEN, E. N. & STEVENS, E. D. (1984). *Acta Cryst.* **A40**, 184–195.
- COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. J. & YANG, Y. W. (1979). *Acta Cryst.* **A35**, 63–72.
- COPPENS, P. & SABINE, T. M. (1969). *Acta Cryst.* **B25**, 2442–2451.
- COPPENS, P., SABINE, T. M., DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2451–2458.
- DAVID, W. I. F. & IBBERSON, R. M. (1992). *Acta Cryst.* **C48**, 301–303.
- DAVID, W. I. F., IBBERSON, R. M., JEFFREY, G. A. & RUBBLE, J. R. (1992). *Physica B*, **180/181**, 597–600.
- DAVID, W. I. F., IBBERSON, R. M. & MATTHEWMAN, J. C. (1992). Report RAL-92-032. Rutherford Appleton Laboratory, Chilton, Didcot, England.
- DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2423–2437.
- FELD, R. (1980). Thesis, Phillips-Universität, Marburg/Lahn, Germany.
- HAUSER, J. & BÜRGI, H.-B. (1991). *PEANUT*. Universität Bern, Switzerland.
- HENDRIKSEN, K., LARSEN, F. K. & RASMUSSEN, S. E. (1986). *J. Appl. Cryst.* **19**, 350–354.
- HUMMEL, W., HAUSER, J. & BÜRGI, H.-B. (1990). *J. Mol. Graphics*, pp. 214–220.
- HUMMEL, W., RASELLI, A. & BÜRGI, H.-B. (1990). *Acta Cryst.* **B46**, 683–692.
- IBBERSON, R. M., DAVID, W. I. F. & KNIGHT, K. S. (1992). Report RAL-92-031. Rutherford Appleton Laboratory, Chilton, Didcot, England.
- IBBERSON, R. M., DAVID, W. I. F. & PRAGER, M. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1438–1439.
- JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KLOOSTER, W. T., SWAMINATHAN, S., NANNI, R. & CRAVEN, B. M. (1992). *Acta Cryst.* **B48**, 217–227.
- LUGER, P., ANDRE, C., RUDERT, R., ZOBEL, D., KNÖCHEL, A. & KRAUSE, A. (1992). *Acta Cryst.* **B48**, 33–37.
- RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
- SABINE, T. M., COX, G. W. & CRAVEN, B. M. (1969). *Acta Cryst.* **B25**, 2437–2441.
- ZOBEL, D., LUGER, P., DREISSIG, W. & KORITSANSZKY, T. (1992). *Acta Cryst.* **B48**, 837–848.

*Acta Cryst.* (1994). **B50**, 348–357

## Lengthening of the Covalent O—H Bond in O—H···O Hydrogen Bonds Re-examined from Low-Temperature Neutron Diffraction Data of Organic Compounds

BY TH. STEINER AND W. SAENGER

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

(Received 11 May 1993; accepted 27 October 1993)

#### Abstract

The lengthening of the covalent O—H bond in O—H···O hydrogen bonds is re-examined from high-precision low-temperature neutron diffraction studies of organic molecules (32 crystal structures, 136 hydrogen bonds,  $T < 130$  K,  $R < 0.06$ , H atoms on symmetry elements excluded). Accuracies are around or better than 0.002 Å. The dependencies of the covalent O—H bond length on the H···O and O···O separations are smooth with no sign of discontinuities. For all types of O—H and O—D hydrogen-bond donors and in combination with all types of O acceptors, the O—H bond length follows the same function of the H···O separation (within the experimental accuracy). For angles at H  $> 150^\circ$ , no depen-

dency of the O—H bond length on the hydrogen-bond angle can be detected for constant H···O. The bond-valence concept that is established in inorganic chemistry also proves to be a good model for O—H···O hydrogen bonds in organic compounds.

#### Introduction

It is well known that in  $X-H\cdots Y$  hydrogen bonds, the covalent  $X-H$  bond is lengthened because of the  $H\cdots Y$  interaction, and that the lengthening increases with shortening hydrogen-bond distances  $X\cdots Y$  and  $H\cdots Y$ . A quantitative empirical description of the relevant relations requires neutron diffraction data,

Table 1. *The data sample*

Entry (CSD): entry number and reference code in the Cambridge Structural Database (CSD).

Substance	<i>T</i> (K)	Donors	Entry (CSD)	Reference
Putrescine diphosphate	85	P—OH	26767 PUTRDP11	Takusagawa & Koetzle (1979a)
Quinolinic acid (deuterated)	35	COOD	26139 DQOLAC20	Takusagawa & Koetzle (1979b)
Quinolinic acid (deuterated)	80	COOD	26136 DQOLAC02	Takusagawa & Koetzle (1979b)
Quinolinic acid (deuterated)	100	COOD	28556 DQOLAC01	Takusagawa & Koetzle (1979b)
1,1'-Ferrocenedicarboxylic acid (triclinic)	78	COOH	27407 FEROCA12	Takusagawa & Koetzle (1979c)
NRURAM*	80	C—OH*, H <sub>2</sub> O	26606 NRURAM11	Takusagawa <i>et al.</i> (1979)
$\beta$ -L-Arabinopyranose (partially deuterated)†	123	C(sp <sup>3</sup> )—OD	37149 YYYYYA	Jeffrey <i>et al.</i> (1980)
$\alpha$ -L-Xylopyranose (partially deuterated)†	123	C(sp <sup>3</sup> )—OD	37152 YYYYYF	Jeffrey <i>et al.</i> (1980)
Urea:hydrogen peroxide (1:1)	81	H <sub>2</sub> O <sub>2</sub>	33457 UREXPO11	Fritchie & McMullan (1981)
<i>N</i> -Acetyl-L-cysteine	16	COOH	34731 NALCYS02	Takusagawa <i>et al.</i> (1981)
Succinic acid	77	COOH	36061 SUCACB03	Leviel <i>et al.</i> (1981)
Sodium hydrogen maleate.3H <sub>2</sub> O	120	COOH, H <sub>2</sub> O	49120 NAHMAL01	Olovsson <i>et al.</i> (1984)
Phosphorylethanolamine	122	P—OH	49194 AEPHOS02	Weber <i>et al.</i> (1984)
Sodium hydrogen oxalate.H <sub>2</sub> O	120	COOH, H <sub>2</sub> O	51120 NHOXAL14	Delaplane <i>et al.</i> (1984)
$\beta$ -DL-Arabinose	75	C(sp <sup>3</sup> )—OH	51184 ABINOR04	Longchambon <i>et al.</i> (1985)
Lithium hydrogen phthalate.H <sub>2</sub> O	15	COOH, H <sub>2</sub> O	57227 LIHPAL01	Küppers <i>et al.</i> (1985)
Lithium hydrogen phthalate.H <sub>2</sub> O	100	COOH, H <sub>2</sub> O	57228 LIHPAL02	Küppers <i>et al.</i> (1985)
Naphthazarin C	60	C(sp <sup>3</sup> )—OH	57607 DHNAPH17	Herbstein <i>et al.</i> (1985)
$\beta$ -Cyclodextrin.11.6D <sub>2</sub> O	120	C(sp <sup>3</sup> )—OD, D <sub>2</sub> O	60579 CUXCON01	Zabel <i>et al.</i> (1986)
(-)-(2 <i>R</i> )-Succinic-2- <i>d</i> acid	100	COOH	79757 KACBEV01	Yuan <i>et al.</i> (1988)
VUYYUJ‡	30	C(sp <sup>3</sup> )—OH	84189 VUYYUJ	Fenn <i>et al.</i> (1989)
( <i>S</i> )-Asparagine.H <sub>2</sub> O	15	H <sub>2</sub> O	71808 ASPARM06	Weisinger-Lewin <i>et al.</i> (1989)
Sodium oxalate monoperhydrate	123	H <sub>2</sub> O <sub>2</sub>	86459 NAOXAP11	Pedersen & Kvicik (1989)
Potassium oxalate monoperhydrate	123	H <sub>2</sub> O <sub>2</sub>	86453 KOXPHY11	Pedersen & Kvicik (1990)
Phosphonic acid§	15	P—OH	—	Becker <i>et al.</i> (1990)
Phosphonic acid (deuterated)¶	15	P—OD	—	Becker <i>et al.</i> (1990)
$\beta$ -Cyclodextrin-ethanol.8D <sub>2</sub> O	15	C(sp <sup>3</sup> )—OD, D <sub>2</sub> O	—	Steiner <i>et al.</i> (1990)
Urea:oxalic acid (2:1)	100	COOH	—	van Hummel & Helmholdt (1991)
Adenosine	123	C(sp <sup>3</sup> )—OH	—	Klooster <i>et al.</i> (1991)
Mellite	15	H <sub>2</sub> O	—	Robl & Kuhs (1991)
Beryllium acetylenedicarboxylate.4H <sub>2</sub> O	15	H <sub>2</sub> O	—	Robl <i>et al.</i> (1992)
20-Methylpregnene-3,20-diol methanolate	123	C(sp <sup>3</sup> )—OH	—	McMullan <i>et al.</i> (1992)

\* 5-Nitro-1-( $\beta$ -D-ribosyluronic acid)uracil.H<sub>2</sub>O; donors: C(sp<sup>3</sup>)—OH, COOH, H<sub>2</sub>O.

† Degree of deuteration ~80%.

‡ 5-Hydroxy-7,10-dimethyltetracyclo[4.4.0.0<sup>3,9</sup>.0<sup>4,8</sup>]decan-2-one.§ Crystal 2(*N*),  $\lambda = 1.042$  Å, anisotropic refinement.¶ Crystal 3(*N*),  $\lambda = 1.317$  Å, isotropic refinement.

because only these supply accurately determined H positions. The correlation of the X—H bond length with the hydrogen-bond distances was repeatedly shown for the systems O—H $\cdots$ O (for example Nakamoto, Margoshes & Rundle, 1955; Olovsson & Jönsson, 1976; Chiari & Ferraris, 1982) and N—H $\cdots$ O (for example Olovsson & Jönsson, 1976; Koetzle & Lehmann, 1976). These earlier works, however, are mainly based on neutron diffraction data measured at room temperature. This results in relatively large experimental errors, primarily due to thermal smearing of the H-atom positions. In particular, in the long H $\cdots$ X distance regions of the relations, the experimental errors exceeded the true variations of the X—H bond length.

In recent years, low-temperature neutron diffraction data has become available, which is of superior accuracy compared with room-temperature studies. This prompted us to re-examine the bond lengthening of O—H in O—H $\cdots$ O interactions, for which the largest quantity of high-precision data is available. In a first study, the influence of minor components of three-center hydrogen bonds on CO—D bond lengths in  $\beta$ -cyclodextrin complexes was specified

(Steiner & Saenger, 1992a). In that study, the restriction to  $\beta$ -cyclodextrin complexes, in which no atoms other than C, O, H/D and no ions are present, was in order to exclude effects from chemical heterogeneity; in consequence, the results are strictly valid only for the C(sp<sup>3</sup>)—O—D donor type, and no data for very short hydrogen bonds is included. In the present (purely empirical) study, the aim is to describe the O—H bond lengthening in H $\cdots$ O ranges as wide as possible and to check for different behaviour of chemically different types of O—H (and O—D) donors and O acceptors.

### The structure data set

Single-crystal neutron diffraction studies at temperatures  $T < 130$  K, with  $R < 0.06$  and crystallographic resolutions  $\lambda/2 \sin \theta_{\max} < 1.0$  Å, were extracted from the Cambridge Structural Database (Allen *et al.*, 1979) July 1991 release, and more recent literature. Within these crystal structures, only hydrogen bonds were considered in which the H and both O positions are ordered, and in which the H atom is not placed on a symmetry element; this is because apparently

Table 2. *Types of hydrogen bonds in the data set*

Structures: number of crystal structures containing the specified donor type; some structures contain more than one donor type. Hydrogen bonds *etc.*: number of symmetry-independent hydrogen bonds with  $H\cdots O < 3.0 \text{ \AA}$  and angle at H  $> 90^\circ$ .

Donor	Structures	Hydrogen bonds (total)	Two-center	Three-center	Four-center
C—OH	16	31	23	7	1
C—OD*	7	47	17	28	2
P—OH	3	7	6	1	—
P—OD	1	4	3	1	—
H <sub>2</sub> O	8	30	21	5	4
D <sub>2</sub> O†	2	14	11	3	—
H <sub>2</sub> O‡	3	3	2	1	—
Sum		136	83	46	7

\* Including the 80% deuterated structures YYYAA and YYYAF, see Table 1; dominated by 38 C—OD groups from  $\beta$ -cyclodextrin complexes.

† All data originate from  $\beta$ -cyclodextrin complexes, see Table 1.

‡ Originating from three H<sub>2</sub>O<sub>2</sub> molecules with their midpoints placed on symmetry elements, see Table 1.

symmetric hydrogen bonds O···H···O with twofold or mirror crystallographic symmetry are usually associated with disorder O— $\frac{1}{2}$ H··· $\frac{1}{2}$ H—O with half occupied H-atom sites separated by a few 0.1 Å, and must be excluded (see Thomas & Liminga, 1978). For  $\beta$ -cyclodextrin inclusion compounds, the complexed guest molecules were excluded from the data set, because their atomic positions are generally less accurately determined than those of the host and the interstitial water molecules. The resulting data set contains 32 crystal structures (Table 1), most of which are not contained in the earlier studies.

The data set is chemically highly heterogeneous (Tables 1 and 2). It contains numerous types of O—H and O—D hydrogen-bond donors and O acceptors. There is, however, no example of an H<sub>3</sub>O<sup>+</sup> or an OH<sup>-</sup> ion in the sample, and no crystal structure of any of the ice phases satisfies the quality criteria. All compounds are organic, except for phosphonic acid.

The data sample was screened for O—H···O hydrogen bonds with  $H\cdots O < 3.0 \text{ \AA}$ , angle  $\theta$  at H  $> 90^\circ$  ( $\theta = \text{angle O—H}\cdots\text{O}$ ), and no acceptor type other than O satisfying these criteria simultaneously (for the arbitrary nature of any such cutoff criterion, see, for example, Steiner & Saenger, 1992b; Steiner & Saenger, 1993a). Of the 136 O—H···O hydrogen bonds in the data set, Table 2, 83 (=61%) are of the 'two-center' type, *i.e.* the H atom contacts only one acceptor atom, 46 (=34%) are of the three-center type and seven (=5%) of the four-center types (two and three acceptor O atoms, respectively; Jeffrey & Maluszynska, 1982). For reasons of completeness, the scatterplots of the hydrogen-bond angle  $\theta$  against  $H\cdots O$  and  $O\cdots O$  separations are shown in Fig. 1; details are discussed in the figure legend (compare

with results obtained from different samples and drawn to different limits: Olovsson & Jönsson, 1976; Savage & Finney, 1986; Jeffrey & Maluszynska, 1990; Steiner & Saenger, 1992b).

Experimental accuracies vary from structure to structure. Refinement e.s.d.'s are in the range between 0.001 and 0.008 Å for distances and between ~0.05 and 0.7 Å for angles involving H atoms.

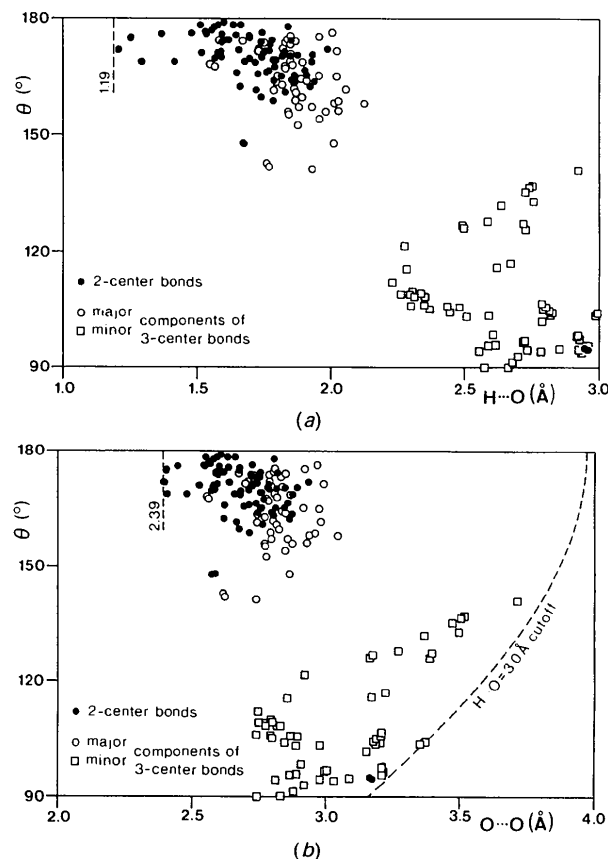


Fig. 1. Scatterplots of the hydrogen-bond angle  $\theta$  against (a) the  $H\cdots O$  separation and (b) the  $O\cdots O$  separation. Two-center hydrogen bonds, and major and minor components of three-center and four-center hydrogen bonds are indicated differently. The dashed lines at 1.19 and 2.39 Å, respectively, indicate rough estimates for the shortest possible  $H\cdots O$  and  $O\cdots O$  distances. The limits of the plots correspond to the arbitrary cutoff definition of hydrogen bonds:  $H\cdots O < 3.0 \text{ \AA}$  and  $\theta > 90^\circ$ ; for similar plots drawn to different limits, see Olovsson & Jönsson (1976), Savage & Finney (1986), Steiner & Saenger (1992b). The data sample accidentally contains no 'symmetric' three-center hydrogen bonds with geometrically similar major and minor components; therefore, the clusters of data points for major and minor components of multi-center hydrogen bonds appear to be clearly separated. In larger data samples, the apparent gap between these clusters does not exist (Jeffrey & Maluszynska, 1990; Steiner & Saenger, 1992b). Note also that at the shortest possible  $H\cdots O$  and  $O\cdots O$  separations,  $\theta$  may still be significantly nonlinear (the extreme example is  $H\cdots O = 1.195$ ,  $O\cdots O = 2.394 \text{ \AA}$ ,  $\theta = 171.9^\circ$  in lithium hydrogen phthalate monohydrate at 15 K; Küppers, Takusagawa & Koetzle, 1985).

**O—H (and O—D) bond lengths for all data**

In Figs. 2(a) and 2(b), the covalent O—H bond length is plotted against the H···O and O···O distances (H and D are not distinguished at this stage). For multi-center interactions, only the shortest H···O separation ('major component') is considered. The restriction to low-temperature data considerably reduces the scatter of data points compared with earlier studies of the same relations (Olovsson & Jönsson, 1976; Chiari & Ferraris, 1982); unlike with room-temperature data, no bond lengths are significantly shorter than the gas-phase values of relaxed O—H bonds [O—H = 0.945 (3) Å for methanol, Lees & Baker, 1968; O—H = 0.957 Å for H<sub>2</sub>O, Benedict, Gailar & Plyler, 1956]. Still, the data exhibit a broader scatter than would be expected from experimental inaccuracy alone.

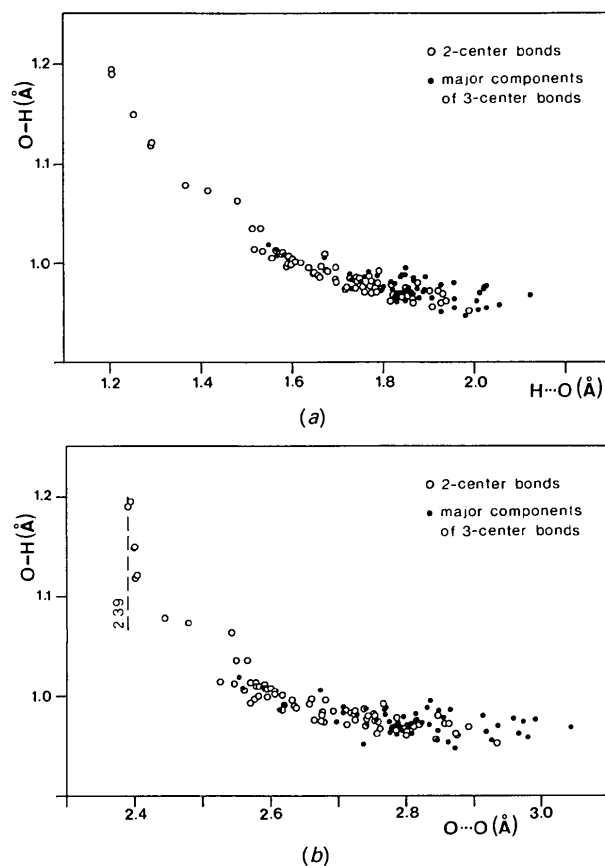


Fig. 2. Lengthening of the covalent O—H bond because of the hydrogen-bond interactions: (a) O—H plotted against the H···O distance; (b) O—H plotted against the O···O distance. For three-center and four-center hydrogen bonds, the shortest H···O separation ('major component') is regarded. The dependencies are smooth, as reported earlier by Olovsson & Jönsson (1976). There is no indication of sudden changes of the slope or even of inflection points that were reported based on data of lower quality (Ichikawa, 1978; Joswig, Fuess & Ferraris, 1982).

It has been shown for cyclodextrin complexes that the residual scatter is partly caused by effects due to multi-center interactions (Steiner & Saenger, 1992a). This is illustrated in Fig. 2, where circles represent two-center hydrogen bonds and dots represent the major components of three-center (and four-center) hydrogen bonds. As in multi-center interactions where the minor component(s) lengthen(s) the O—H bond in addition to the lengthening by the major component, the dots are, on average, slightly scattered above the circles. This is most obvious for relatively long major components (H···O > 1.8 Å), which dominate the O—H bond lengthening less prominently than short and strong major components. In principle, this data allows the quantification of the additional lengthening by the minor components. The data for the three-center hydrogen bonds, however, are so strongly dominated by the cyclodextrin complexes (which, for example, contribute ten of the 13 bonds with very short minor components < 2.4 Å) that no additional information is obtained compared with the earlier study.

**O—H bond lengths in two-center O—H···O hydrogen bonds**

In the following, effects from multi-center interactions will be avoided by studying only hydrogen bonds without minor components shorter than H···O = 3.0 Å. Two anomalous long-distance bonds (Fig. 1 and figure legend) are also excluded; the remaining data set consists of 81 two-center hydrogen bonds.

*Dependence of the O—H bond length on the H···O distance*

For the 81 two-center hydrogen bonds, the plot of O—H against H···O is shown in Fig. 3. It is of interest to see whether different behavior can be detected for specific subsets [e.g. for different donors like H<sub>2</sub>O, C(sp<sup>3</sup>)—OH *etc.*]. Such an analysis is most easily performed by comparison of specified subsets with a common regression line. The search for and the determination of the regression line drawn in Fig. 3 (which is purely empirical, *i.e.* not based on any theoretical models, and must not be extrapolated) is outlined in *Appendix 2*. Also, some relations to the bond-valence concept of the hydrogen bond (Brown, 1992) are discussed in *Appendix 2*. One data point is classified as an outlier and excluded from the analysis, but drawn in all figures (see *Appendix 2* and the legend of Fig. 3).

The scatter of the data points around this regression line is narrow: the r.m.s. deviation for all 80 data is only 0.0065 Å, Table 3, which is already the magnitude of the individual refinement e.s.d.'s. This

reflects the good quality of the data set, but it also foretells that only small differences will be found between any subsets.

### Temperature effect on the O—H bond lengths

X—H bond lengths are notoriously affected by thermal vibrations, and this may (but need not) be significant even at liquid-nitrogen temperatures: in neutron crystal structures, the (observed) C—H bond length in C—CH<sub>3</sub> at ~100 K is on average ~0.006 Å shorter than at  $T < 30$  K (Steiner & Saenger, 1993b). An effect of this magnitude would be clearly observable with the present data: systematic bond shortening at the higher temperatures ~100 K would cause systematic scattering of these data below the regression line. Consequently, the 80 data were divided into three temperature ranges; none of these groupings, however, shows mean deviations from the regression line greater than the standard error of the mean (s.e.m.) of ~0.001 Å, Table 3. This negative result, which reflects that H in a hydrogen bond has less vibrational freedom than in a methyl group, justifies the analysis of the data determined at liquid-nitrogen and liquid-helium temperatures in a common data set.

### O—H bond lengthening for different donor and acceptor types

If subsets of different donor types are formed [COOH, C(sp<sup>3</sup>)—OH, C(sp<sup>2</sup>)—OH, P—OH, H<sub>2</sub>O

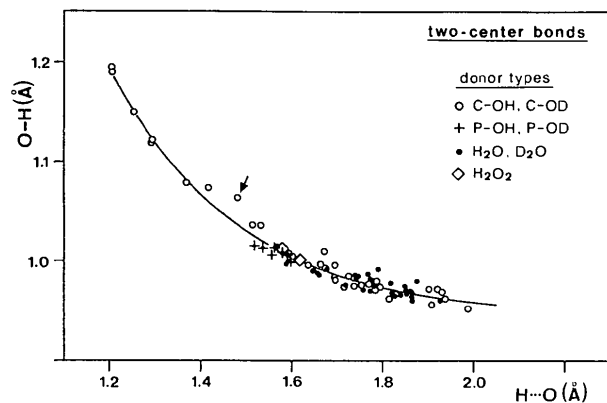


Fig. 3. Lengthening of the covalent O—H bond in 81 two-center hydrogen bonds: the donor types C—OH/D, P—OH/D, H<sub>2</sub>O/D<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> are indicated differently, cf. Table 3. At the longest H...O separations ~2.0 Å, an asymptotic value  $d_o$  for relaxed O—H groups is not yet reached. The solid curve represents the empirical regression function  $O—H = d_o + k_1 \exp(-k_2 r)$ ; the parameters  $d_o = 0.944$ ,  $k_1 = 17.7$  Å and  $k_2 = 3.55$  Å<sup>-1</sup> were obtained by least-squares fit to the data (see Appendix 2). The point marked by an arrow corresponds to H...O = 1.480, O—H = 1.064 Å in KACBEV01, Table 1, and is a severe outlier which was excluded from all numerical calculations.

Table 3. Dependence of  $d_{OH}$  on H...O in two-center hydrogen bonds: mean deviations  $\langle \Delta d_{OH} \rangle$  of specific data subsets from the empirical regression function

Regression function (see Appendix 2):  $d_{OH}(r) = d_o + k_1 \exp(-k_2 r)$  with  $r = H...O$  separation,  $d_o = 0.944$  Å,  $k_1 = 17.7$  Å, and  $k_2 = 3.55$  Å<sup>-1</sup>. For each data point:  $\Delta d_{OH} = d_{OH,obs}(r) - d_{OH,regress}(r)$ . For any data subset: mean deviation from the regression line  $\langle \Delta d_{OH} \rangle = \sum \Delta d_{OH} / n$ ; standard error of the mean deviation: s.e.m. =  $[\sum (\Delta d_{OH} - \langle \Delta d_{OH} \rangle)^2 / (n-1)]^{1/2}$  given in parentheses.\* r.m.s. dev.\* = root-mean-square deviation from the regression line =  $[\sum (\Delta d_{OH} - \langle \Delta d_{OH} \rangle)^2 / (n-1)]^{1/2}$ .

Type	<i>n</i>	$\langle \Delta d_{OH} \rangle$	r.m.s. dev.
All	80	0.0000 (7)	0.0065
Temperature effect			
80 ≤ <i>T</i> < 130 K	36	0.000 (1)	0.007
30 ≤ <i>T</i> < 80 K	11	+0.002 (2)	0.007
<i>T</i> < 30 K	24	-0.001 (1)	0.006
Donor types			
C—OH, C—OD (all)	39	+0.001 (1)	0.007
COOH/D	16	+0.002 (2)	0.006
C(sp <sup>3</sup> )—OH/D	21	-0.001 (1)	0.006
C(sp <sup>2</sup> )—OH†	2	+0.011‡ (—*)	—*
P—OH/D	9	-0.003 (2)	0.005
H <sub>2</sub> O, D <sub>2</sub> O	30	0.000 (1)	0.007
H <sub>2</sub> O <sub>2</sub>	2	+0.002 (—*)	—*
Acceptor types			
C—OH/D	22	0.000 (1)	0.006
C=O, COO	36	0.000 (1)	0.007
C—O—C	3	-0.002 (—*)	—*
P=O	9	-0.003 (2)	0.005
H <sub>2</sub> O, D <sub>2</sub> O	10	+0.003 (2)	0.007
Deuteration effect§ (donors)			
C(sp <sup>3</sup> )—H	7	0.000 (2)	0.006
C(sp <sup>3</sup> )—D	14	-0.001 (2)	0.006
H <sub>2</sub> O	19	-0.003 (1)	0.004
D <sub>2</sub> O	11	+0.004 (2)	0.008
Hydrogen-bond angle $\theta$			
170° < $\theta$	46	-0.0004 (8)	0.006
160° < $\theta$ < 170°	30	0.000 (1)	0.007
$\theta$ < 160°	4	+0.003 (6)	0.011
Cooperative effect			
Hydrogen bond $d^{\ddagger} < 1.7$ Å accepted	8	+0.002 (3)	0.007
Hydrogen bond $1.7 < d^{\ddagger} < 2.0$ Å accepted	20	+0.001 (2)	0.007
Metal ion coordinated	18	-0.002 (1)	0.006
No hydrogen bond < 2.0 Å; no ion	34	0.000 (1)	0.007

\* Only given if  $n > 3$ .

† C bonded to two other C atoms.

‡ The high value of  $\langle \Delta d_{OH} \rangle$  is caused by a single long O—H bond in naphthazarin C.

§ For COOH/D and P—OH/D donors, there are only O—D groups from one publication each (Table 1), making a comparison of  $d_{OH}$  and  $d_{OD}$  statistically irrelevant.

¶ H...O distance.

and H<sub>2</sub>O<sub>2</sub>], the picture shown in Figs. 3 and 4, and Table 3 is obtained. Figs. 3 and 4 reflect the well known circumstance that different X—OH groups have different 'donor strengths', i.e. that they form hydrogen bonds with different H...O ranges (the description of these ranges does not require low-temperature data and is performed better with larger quantities of room-temperature data, e.g. Jeffrey & Saenger, 1991). The important observation is that all donor types follow the same function  $O—H = f(H...O)$  in their H...O ranges; for all donor types, the mean deviations  $\langle \Delta d_{OH} \rangle$  are smaller than 2 s.e.m.,

hence statistically insignificant (Table 3). (Note that the standard errors are only 0.001–0.002 Å.) This is most obvious in the region  $H\cdots O \approx 1.6$  Å, where all data subsets neatly overlap (Fig. 3).

For the important case of the donor  $H_3O^+$ , for which no example is contained in the data set, it can be shown with reduced accuracy from room-temperature data that  $O-H$  also follows the same function of  $H\cdots O$ , see *Appendix 1*.

As for the subsets of different donors, subsets of five different acceptor types now show significant deviations from the common regression line, Table 3 (standard errors 0.001–0.002 Å). This implies that for different donor-acceptor combinations, such as  $O_w-H\cdots O=C$ ,  $O_w-H\cdots O-C$ ,  $C-O-H\cdots O_w$  etc., only the  $O\cdots O$  and  $H\cdots O$  ranges are different, but the function  $O-H = f(H\cdots O)$  is always the same: different donor-acceptor combinations populate different regions of the common relation shown in Fig. 3.

These findings are not self-evident, as for  $C-H$  bond lengths, low-temperature neutron diffraction differences of  $\sim 0.02$  Å are observed between different chemical types of C, and of more than 0.01 Å between different types of  $C(sp^3)-H$  (Steiner & Saenger, 1993b); this is about ten times the standard error of the present study. Also, for  $N(sp^2)-H$  and  $N(sp^3)-H$ , different dependencies of  $N-H$  on  $H\cdots O$  were reported (Koetzle & Lehmann, 1976).

#### Deuteration effect on the $O-H$ bond lengthening

The effects of deuteration on hydrogen-bond geometries are still only poorly known. To obtain an insight into this problem, one must compare crystal structures of protonated and of deuterated, but otherwise identical, molecules. The present data set contains no suitable pair of crystal structures, so that such an analysis is not possible (the structures of

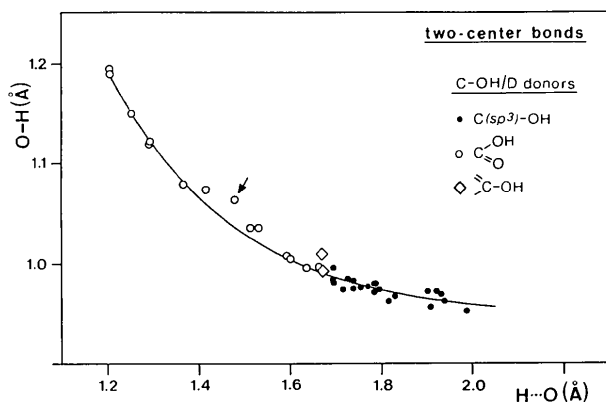


Fig. 4. Lengthening of the covalent  $O-H$  bond for different types of  $C-OH$  donors ( $H$  and  $D$  not distinguished). Regression line as in Fig. 3, cf. Table 3.

protonated and deuterated phosphonic acid were determined under very different conditions, Table 1, Becker *et al.* 1990). As a crude analysis, the behavior of  $C(sp^3)-D$  and  $D_2O$  donors in Fig. 3 was compared to that of the protonated counterparts, Table 3. The difference between  $C(sp^3)-H$  and  $C(sp^3)-D$  is insignificant. The difference between  $H_2O$  and  $D_2O$  is apparently larger; as it is not observed with the more reliably refined hydroxyl groups, however, it should be better interpreted as insignificant because of the small number of data.

#### Is there a dependence of $O-H$ on the hydrogen-bond angle $\theta$ ?

One can assume that  $O-H$  should not only be dependent on the  $H\cdots O$  (or  $O\cdots O$ ) separation, but also on the hydrogen-bond angle  $\theta$ . In fact, however, and maybe surprisingly, linear and bent two-center hydrogen bonds show no difference in the correlation of  $O-H$  against  $H\cdots O$  within statistical accuracy (standard errors of 0.001 Å for  $\theta > 160^\circ$ ), Fig. 5 and Table 3. As there are only four data points with  $\theta \leq 160^\circ$ , the statistical significance of this statement is weaker for strongly bent angles, Table 3.

The observation that in organic crystal structures,  $O-H$  is a function of  $H\cdots O$ , but not (or only marginally) of  $\theta$  (for  $\theta \geq 150^\circ$ ), directs attention towards the bond-valence concept of the hydrogen bond, which has been established for inorganic compounds and predicts exactly this behavior (*e.g.* Brown, 1992). According to this concept, the only really relevant parameters in a hydrogen bond are the  $O-H$  and  $H\cdots O$  separations. The bond-valence concept is not in the focus of the present study; some consequences, however, will be discussed in *Appendix 2*.

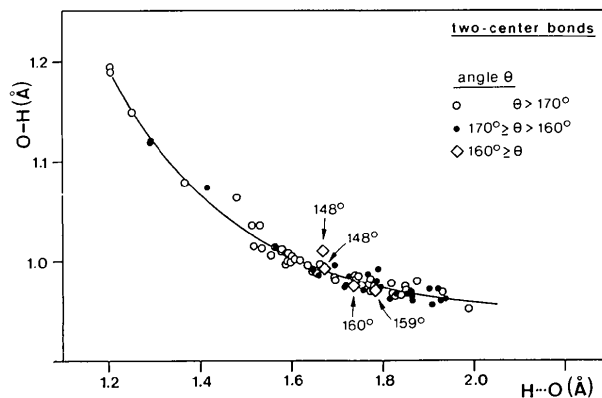


Fig. 5. Lengthening of the covalent  $O-H$  bond in 81 two-center hydrogen bonds with different angles  $\theta$  are indicated differently. Regression line as in Fig. 3. Within the given statistical accuracy, no influence of the hydrogen-bond angle can be observed, cf. Table 3.

As a result of a referee's comment, we note that Fig. 5 shows that O—H does not (or only marginally) depend on  $\theta$  for constant H...O. For trigonometric reasons, bending of  $\theta$  with constant H...O is accompanied with an approach of donor and acceptor, *i.e.* with a reduction of O...O. Therefore, one can argue (if there is desire) that the 'weakening' of the hydrogen bond as a result of bending is compensated by 'strengthening' due to closer O...O approach, and O—H remains more or less unaffected. If variation of  $\theta$  is considered for constant O...O, bending of the hydrogen bond moves H away from the acceptor, H...O increases and, according to Fig. 3, O—H slightly reduces (as is predicted, for example, by Duijneveldt-van de Rijdt *et al.*, 1984).

#### The cooperative effect

It is well known that the polarization of an O—H group is enhanced if it accepts a hydrogen bond, leading to strengthening of hydrogen bonds that form chains or rings ('cooperative effect'). Structurally, this is reflected by considerably shorter O...O and H...O separations compared with isolated hydrogen bonds (see Jeffrey & Saenger, 1991, and references therein). To see if this influences the function  $O-H = f(H...O)$ , the data were divided into four sets with donors that accept hydrogen bonds with  $H...O < 1.7$  Å, between 1.7 and 2.0 Å, metal-ion contacts and neither hydrogen bonds shorter than 2.0 Å nor ion contacts (a finer subdivision would be appreciable, but is not possible with the limited number of data; there are, for example, five kinds of metal ions in the data set). The result is negative, Table 3 (s.e.m. between 0.001 and 0.003 Å).

This implies the following picture of the cooperative effect: as the O...O and H...O separations are shortened, the O—H bond length increases according to the same function  $O-H = f(H...O)$  that is also valid for isolated hydrogen bonds, *i.e.* the H atom moves to the left along the curve shown in Fig. 3. [This corrects the earlier study that was based on a smaller quantity of data, Steiner & Saenger (1992a).]

#### O—H and H...O drawn on the same axis

O—H and H...O separations can be regarded as parameters that measure the same type of quantity, that is the separation of an H atom from an O atom. This suggests drawing O—H and H...O distances in diagrams on a common axis. The plot of O—H against H...O for two-center hydrogen bonds (which then is necessarily symmetric) shows a perfectly smooth curve, with no trace of any exceptional behavior at the midpoint which corresponds to 'symmetric' O...H...O bonds, Fig. 6. It was proposed that

in proton-transfer processes between two O atoms, the H atom should follow this curve (Bürgi & Dunitz, 1983). The plot of O—H and H...O against O...O for two-center hydrogen bonds, Fig. 7, also shows a continuous relation which smoothly changes its direction at the O...O separation corresponding to symmetric bonds,  $\sim 2.39$  Å.

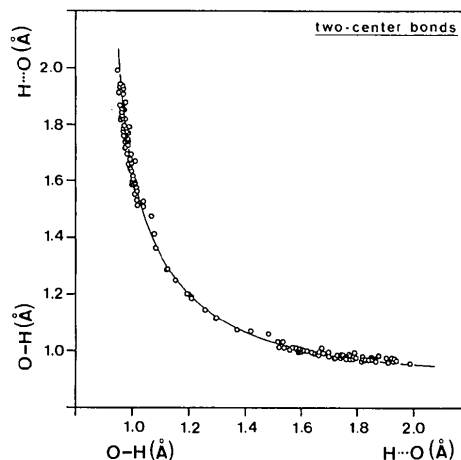


Fig. 6. Lengthening of the covalent O—H bond in 81 two-center hydrogen bonds: following Bürgi & Dunitz (1983), the O—H and H...O separations are drawn on a common axis. Note the perfectly smooth behavior at the 'midpoint' of the symmetric picture. The theoretical curve is a semi-quantitative approximation for  $O-H = f(r)$  derived from the bond-valence concept, see Appendix 2:  $r_1 = r_0 - b \ln|1 - \exp[(r_0 - r_2)/b]|$ , with  $r_0 = 0.928$  and  $b = 0.393$  Å; drawn on a larger scale, it becomes obvious that the curve falls too steeply at longer H...O separations  $\geq 1.8$  Å (not shown).

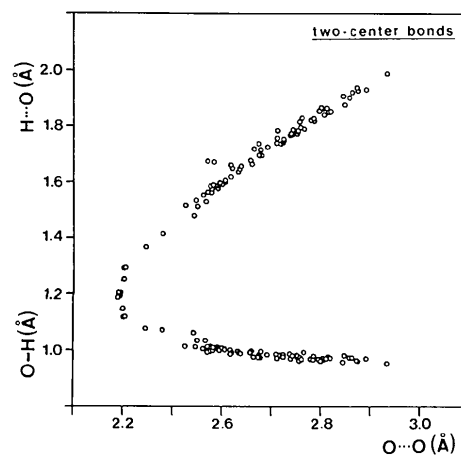


Fig. 7. Lengthening of the covalent O—H bond in 81 two-center hydrogen bonds: plot of the O—H and H...O separations against O...O. Note how smoothly the relation reverses its direction at O...O  $\sim 2.39$  Å, corresponding to symmetric O...H...O hydrogen bonds.

Table 4. Neutron crystal structures containing  $\text{H}_3\text{O}^+$  ions; all determined at room temperature

Entry (CSD): entry number and reference code in the Cambridge Structural Database (CSD). Structures with disorder or with H on symmetry elements were disregarded.

Substance	R value	Entry (CSD)	Reference
<i>p</i> -Toluenesulfonic acid monohydrate	0.061	21241 TOLSAM12	Lundgren & Williams (1973)
Picrylsulfonic acid tetrahydrate	0.052	17550 PICSUL01	Lundgren & Tellgren (1974)
<i>o</i> -Sulfobenzoic acid trihydrate	0.083	19323 SLBZAC01	Attig & Williams (1976)
Oxonium trifluoromethanesulfonate	0.078	23086 TFMSUL02	Lundgren <i>et al.</i> (1978)
2-Nitro-1,3-indandione dihydrate	0.050	31541 NINDOD01	Selenius & Lundgren (1980)

### Summary and discussion

For  $\text{O—H}\cdots\text{O}$  hydrogen bonds, the lengthening of the covalent  $\text{O—H}$  bond was re-examined from high-precision low-temperature neutron diffraction data. The data set contains 136 hydrogen bonds in 32 crystal structures ( $T < 130$  K,  $R < 0.06$ ). The main part of the analysis was restricted to two-center hydrogen bonds. For these, the dependencies of  $\text{O—H}$  on  $\text{H}\cdots\text{O}$  and  $\text{O}\cdots\text{O}$  are perfectly smooth, confirming the views of Olovsson & Jönsson (1976) and disproving several reports of less regular behavior.

Within the statistical standard error of  $\sim 0.001$ – $0.002$  Å, all  $\text{O—H}$  and  $\text{O—D}$  donor types (including  $\text{H}_3\text{O}^+$ ) follow the same general relation  $\text{O—H} = f(\text{H}\cdots\text{O})$ . Different donor-acceptor combinations have different  $\text{O}\cdots\text{O}$  and  $\text{H}\cdots\text{O}$ , and consequently also  $\text{O—H}$  ranges (*e.g.* Jeffrey & Saenger, 1991); the function  $\text{O—H} = f(\text{H}\cdots\text{O})$ , however, is always the same: different donor-acceptor combinations populate different regions of a common relation  $\text{O—H} = f(\text{H}\cdots\text{O})$  (Fig. 3).

For about  $\theta > 150^\circ$ , no dependency of  $\text{O—H}$  on the hydrogen-bond angle  $\theta$  can be detected for constant  $\text{H}\cdots\text{O}$ . This directs attention to the bond-valence model of the hydrogen bond, which is discussed in *Appendix 2*.

This study was supported by the Bundesministerium für Forschung und Technologie, FKZ 03 SA3 FUB, and by the Fonds der Chemischen Industrie.

### APPENDIX 1

#### Dependence of the $\text{O—H}$ bond length on $\text{H}\cdots\text{O}$ for oxonium ions ( $\text{H}_3\text{O}^+$ )

The present low-temperature data set contains no  $\text{H}_3\text{O}^+$  (oxonium) ions. As this is a chemically very important ion, we test briefly (albeit with reduced accuracy) for the available room-temperature data whether or not the covalent  $\text{O—H}$  bond length shows the same dependency on  $\text{H}\cdots\text{O}$  as in the other types of  $R\text{—OH}$ . Crystal structures with disordered  $\text{H}_3\text{O}^+$  ions or with relevant H nuclei on symmetry elements were excluded. For the remaining five oxonium ions (Table 4), the 15  $\text{O—H}$  bond lengths are

plotted against  $\text{H}\cdots\text{O}$  in Fig. 8. It is obvious that the hydrogen-bond distances are on the average much shorter for  $\text{H}_3\text{O}^+$  ( $\text{H}\cdots\text{O}$  between 1.2 and  $\sim 1.7$  Å) than for  $\text{H}_2\text{O}$ , but  $\text{O—H}$  follows the same dependency on  $\text{H}\cdots\text{O}$  as all other  $\text{O—H}$  donors.

### APPENDIX 2

#### The empirical regression function in the plot of $\text{O—H}$ against $\text{H}\cdots\text{O}$

In Figs. 3–5, a regression line is drawn in the plot of  $\text{O—H}$  against  $\text{H}\cdots\text{O}$ . In principle, such a function  $\text{O—H}_{\text{calc}} = f(\text{H}\cdots\text{O})$  should follow three basic properties of the data scatter: (1) for large  $\text{H}\cdots\text{O}$ , it should extrapolate to a reasonable value for relaxed  $\text{O—H}$  groups; (2) the function must remain identical if  $\text{O—H}$  and  $\text{H}\cdots\text{O}$  are interchanged, Fig. 6; (3) the function must be smooth at the midpoint, Fig. 6. One cannot expect that any simple analytical function with these properties perfectly fits the data over the whole range of  $\text{O—H}$ , and actually no such function could be found. As a further difficulty, the 'true' bond length for relaxed  $R\text{—OH}$  is not precisely known, as the appropriate gas-phase data are

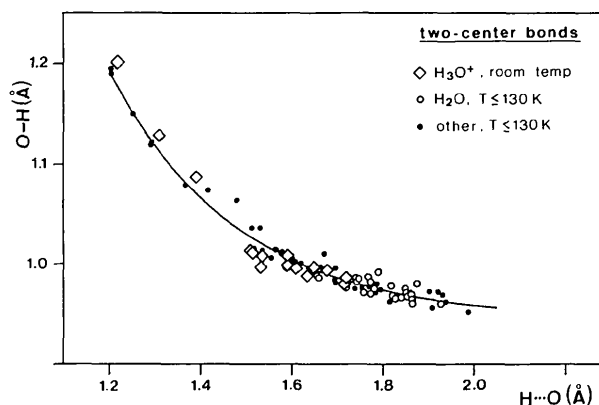


Fig. 8. Lengthening of the covalent  $\text{O—H}$  bond in 15 two-center hydrogen bonds donated by five oxonium ( $\text{H}_3\text{O}^+$ ) ions compared with other  $R\text{—OH}$  donor types. All data on  $\text{H}_3\text{O}^+$  are from room-temperature crystal structures (Table 4). Regarding the slightly reduced accuracy of the room-temperature data, the dependency of  $\text{O—H}$  on  $\text{H}\cdots\text{O}$  is the same for  $\text{H}_3\text{O}^+$  as for the other donor types. Regression line as in Fig. 3.



not unambiguous; furthermore, different values could be expected for different chemical types of relaxed R—O—H (compare the spectroscopic results compiled by Callomon *et al.*, 1976).

In the main part of the analysis, the regression line should only serve as a reference for comparisons of different data subsets, and the only requirement is an optimal fit to the data in the range  $1.2 < \text{H}\cdots\text{O} < 2.1 \text{ \AA}$ . Consequently, and very pragmatically, the symmetry requirements were abandoned, and the simple function  $\text{O—H} = d_o + k_1 \exp(-k_2 r)$  was used. In a least-squares fit with the data for the 81 two-center hydrogen bonds, the three parameters  $d_o$ ,  $k_1$  and  $k_2$  were independently varied [quantity minimized:  $\sum(d_{\text{OH,obs}} - d_{\text{OH,calc}})^2$ ]. The data scatter around the resulting function was r.m.s. = 0.0071 Å; one data point, however, had a deviation of almost 4 r.m.s. (O2—H1...O4 in KACBEV01,  $\text{H}\cdots\text{O} = 1.480$ ,  $\text{O—H} = 1.064 \text{ \AA}$ ). After exclusion of this data point, which is marked by an arrow in Fig. 3, the fit was repeated, leading to values of  $d_o = 0.944 \text{ \AA}$ ,  $k_1 = 17.7 \text{ \AA}$ ,  $k_2 = 3.55 \text{ \AA}^{-1}$  and an r.m.s. deviation from  $\text{O—H}_{\text{calc}}$  of only 0.0065 Å for 80 data.

The derived function fits the data excellently in the whole experimental  $\text{H}\cdots\text{O}$  range and therefore serves its purpose. Even though the fitted value  $d_o = 0.944 \text{ \AA}$  for relaxed  $\text{O—H}$  is very reasonable, we explicitly warn from extrapolations (and do not draw asymptotic lines in Figs. 3–8).

### The bond-valence model of the hydrogen bond

In inorganic chemistry, the 'bond-valence' model is well established (Brown, 1992, and references therein). In this concept, a strict bond-length–bond-valence relation is assumed. For  $\text{O—H}\cdots\text{O}$  hydrogen bonds, the valences  $s$  of the covalent  $\text{O—H}$  bond and all  $\text{H}\cdots\text{O}$  interactions are a function of only the  $\text{H}\cdots\text{O}$  separations, irrespective of any  $\text{O}\cdots\text{H}\cdots\text{O}$  (and  $\text{O—H}\cdots\text{O}$ ) angles, and the sum of the valences at H is 1.0. For two-center hydrogen bonds, obviously  $s_{\text{OH}} + s_{\text{H}\cdots\text{O}} = 1.0$ . In the present study it was actually observed that, at least for  $\theta > 150^\circ$ ,  $\text{O—H}$  is a function of only  $\text{H}\cdots\text{O}$ , and not of  $\theta$ . This led us to examine the relevance of the model for organic systems in more detail.

The dependence of the valence  $s$  on the bond distance  $r$  certainly does not follow a simple function, but several approximations have been proposed. The best known is

$$s_r = \exp[(r_o - r)/b], \quad (1)$$

[or equivalent forms such as  $s_r = \exp(p - qr)$ ]; for most  $X—Y$  bonds,  $b$  has values around 0.37 Å (Brown, 1992). For two-center hydrogen bonds, this allows the derivation of an approximate function which correlates  $\text{O—H}$  with  $\text{H}\cdots\text{O}$ : if  $\text{O—H}$  is  $r_1$  and

$\text{H}\cdots\text{O}$  is  $r_2$ , and  $s(r_1) + s(r_2) = 1$ , it can be shown that

$$r_1 = r_o - b \ln\{1 - \exp[(r_o - r_2)/b]\}. \quad (2)$$

In this equation,  $r_1$  and  $r_2$  can be interchanged. The function contains only two variable parameters,  $r_o$  and  $b$ , and therefore has little flexibility in a fitting procedure. In a least-squares fit of the 80 above mentioned two-center hydrogen bonds, values of  $r_o = 0.928 \text{ \AA}$  and  $b = 0.393 \text{ \AA}$  are obtained {quantity minimized  $\sum[1 - (s_1 + s_2)]^2$ , mean discrepancy  $\sum|1 - (s_1 + s_2)|/n = 0.012$ }. The value of  $r_o$  is somewhat short compared with the gas-phase values of  $\text{O—H}$  0.945 Å in methanol (Lees & Baker, 1968) and 0.957 Å in  $\text{H}_2\text{O}$  (Benedict, Gailar & Plyler, 1956), and in a plot such as in Fig. 3, the curve falls too steeply for longer hydrogen bonds with  $\text{H}\cdots\text{O} > 1.8 \text{ \AA}$ . Also, for symmetric  $\text{O}\cdots\text{H}\cdots\text{O}$  bonds, the  $r_1 = r_2 = 1.201$  value obtained is slightly too long (experimental  $\approx 1.195 \text{ \AA}$ ). In consequence, this approximation is unsuitable for the quantitative analysis performed in the main text. Nevertheless, the overall fit is surprisingly good: in Fig. 6, the curve is drawn on a large scale, and the systematic deviation at long distances and around the midpoint are barely apparent.

A further popular approximation of  $s$  on  $r$  is

$$s = (r/r_o)^{-N} \quad (3)$$

(*e.g.* Brown, 1976; Ferraris & Ivaldi, 1988). This approximation, however, yielded fits of lesser quality than in (1) and will not be discussed here any further.

For multi-center hydrogen bonds, the long-distance interactions must be included, and the valences of all components are summed in  $\sum s = 1.0$ . Using the approximation (1) for the functions  $s = f(r)$ , the quantity  $\sum(1 - \sum s)^2$  was minimized in a least-squares fitting procedure for all 136 hydrogen bonds in the data set, Table 2, yielding practically the same values as for two-center hydrogen bonds:  $r_o = 0.927$ ,  $b = 0.395$ , mean discrepancy = 0.014 Å. We attribute only a semi-quantitative meaning to these results. If used with reservation, however, the numeric values of  $s = f(r)$  listed in Table 5 may serve as rough estimates for the 'valences' of hydrogen-bond components. Also, it must be stressed that the bond valence is not a direct measure for bond strengths or energies (see Brown, 1992).

In a more rigorous application of the bond-valence concept, all distance and angle cutoff criteria must be abandoned. This was recently performed for 93 H atoms in inorganic crystal structures by Alig, Lösel & Trömel (1994), yielding  $r_o = 0.911$  and  $b = 0.403 \text{ \AA}$  for the approximation (1) of  $s = f(r)$ . The value for  $r_o$  is even shorter than ours; this could be because of apparent shortening of the covalent  $\text{O—H}$  bond as a result of thermal vibrations in the analyzed room-temperature crystal structures.

Table 5. The 'valences' of hydrogen-bond components, estimated by  $s(r) = \exp[(r_o - r)/b]$ , with values  $r_o = 0.927$  and  $b = 0.395$  Å determined from 136 hydrogen bonds (Appendix 2)

These data can only be taken as guiding values, in particular for long distances  $>2.0$  Å, and must not be interpreted as a direct measure for bond 'strengths' or energies (see Brown, 1992).

H...O (Å)	s	H...O (Å)	s	H...O (Å)	s
1.2	0.50	1.7	0.14	2.2	0.039
1.3	0.39	1.8	0.11	2.4	0.024
1.4	0.30	1.9	0.084	2.6	0.014
1.5	0.23	2.0	0.065	2.8	0.009
1.6	0.18	2.1	0.051	3.0	0.005

## References

- ALIG, H., LÖSEL, J. & TRÖMEL, M. (1994). *Z. Kristallogr.* **209**, 18–21.
- ALLEN, F. H., BELLARD, S., BRICE, M. D., CARTWRIGHT, B. A., DOUBLEDAY, A., HIGGS, H., HUMMELINK, T., HUMMELINK-PETERS, B. G., KENNARD, O., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1979). *Acta Cryst.* **B35**, 2331–2339.
- ATTIG, R. & WILLIAMS, J. M. (1976). *Inorg. Chem.* **15**, 3057–3061.
- BECKER, G., HAUSEN, H.-D., MUNDT, O., SCHWARZ, W., WAGNER, C. T. & VOGT, T. (1990). *Z. Anorg. Allg. Chem.* **591**, 17–31.
- BENEDICT, W. S., GAILAR, N. & PLYLER, E. K. (1956). *J. Chem. Phys.* **24**, 1139–1165.
- BROWN, I. D. (1976). *Acta Cryst.* **A32**, 24–31.
- BROWN, I. D. (1992). *Acta Cryst.* **B48**, 553–572.
- BÜRGI, H. B. & DUNITZ, J. D. (1983). *Acc. Chem. Res.* **16**, 153–161.
- CALLOMON, J. H., HIROTA, E., KUCHITSU, K., LAFFERTY, W. J., MAKI, A. G. & POTE, C. S. (1976). *Structure Data of Free Polyatomic Molecules. Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology*, New Series, Group II, Vol. 7. Berlin: Springer-Verlag.
- CHIARI, G. & FERRARIS, G. (1982). *Acta Cryst.* **B38**, 2331–2341.
- DELAPLANE, R. G., TELLGREN, R. & OLOVSSON, I. (1984). *Acta Cryst.* **C40**, 1800–1803.
- DUIJNEVELDT-VAN DE RIJDT, J. G. C. M. VAN, DUIJNEVELDT, F. B. VAN, KANTERS, J. A. & WILLIAMS, D. R. (1984). *J. Mol. Struct.* **109**, 351–366.
- FENN, R. H., LEHMANN, M. S., MILLS, O. S., WATT, C. I. F. & WHITWORTH, S. (1989). *Acta Cryst.* **C45**, 412–428.
- FERRARIS, G. & IVALDI, G. (1988). *Acta Cryst.* **B44**, 341–344.
- FRITCHIE, C. J. JR & McMULLAN (1981). *Acta Cryst.* **B37**, 1086–1091.
- HERBSTSTEIN, F. H., KAPON, M., REISNER, G. M., LEHMANN, M. S., KRESS, R. B., WILSON, R. B., SHIAU, W.-I., DUESLER, E. N., PAUL, I. C. & CURTIN, D. Y. (1985). *Proc. R. Soc. London Ser. A*, **399**, 295–319.
- HUMMEL, G. J. VAN & HELMHOLDT, R. B. (1991). *Acta Cryst.* **C47**, 213–215.
- ICHIKAWA, M. (1978). *Acta Cryst.* **B34**, 2074–2080.
- JEFFREY, G. A. & MALUSZYNSKA, H. (1982). *Int. J. Biol. Macromol.* **4**, 173–185.
- JEFFREY, G. A. & MALUSZYNSKA, H. (1990). *Acta Cryst.* **B46**, 546–549.
- JEFFREY, G. A., ROBBINS, A., McMULLAN, R. K. & TAKAGI, S. (1980). *Acta Cryst.* **B36**, 373–377.
- JEFFREY, G. A. & SAENGER, W. (1991). *Hydrogen Bonding in Biological Structures*. Berlin: Springer.
- JOSWIG, W., FUESS, H. & FERRARIS, G. (1982). *Acta Cryst.* **B38**, 2798–2801.
- KLOOSTER, W. T., RUBLE, J. R., CRAVEN, B. M. & McMULLAN, R. K. (1991). *Acta Cryst.* **B47**, 376–383.
- KOETZLE, T. F. & LEHMANN, M. S. (1976). *The Hydrogen Bond, Recent Developments in Theory and Experiments*, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, pp. 457–469. Amsterdam: North-Holland.
- KÜPPERS, H., TAKUSAGAWA, F. & KOETZLE, T. F. (1985). *J. Chem. Phys.* **82**, 5636–5647.
- LEES, R. M. & BAKER, J. G. (1968). *J. Chem. Phys.* **48**, 5299–5318.
- LEVIEL, J.-L., AUVERT, G. & SAVARIAULT, J.-M. (1981). *Acta Cryst.* **B37**, 2185–2189.
- LONGCHAMBO, F., GILLIER-PANDRAUD, H., WIEST, R., REES, B., MITSCHLER, A., FELD, R., LEHMANN, M. & BECKER, P. (1985). *Acta Cryst.* **B41**, 47–56.
- LUNDGREN, J.-O. & TELLGREN, R. (1974). *Acta Cryst.* **B30**, 1937–1947.
- LUNDGREN, J.-O., TELLGREN, R. & OLOVSSON, I. (1978). *Acta Cryst.* **B34**, 2945–2947.
- LUNDGREN, J.-O. & WILLIAMS, J. M. (1973). *J. Chem. Phys.* **58**, 788–796.
- McMULLAN, R. K., KOETZLE, T. F. & FRONCKOWIAK, M. D. (1992). *Acta Cryst.* **C48**, 1509–1512.
- NAKAMOTO, K., MARGOSHES, M. & RUNDLE, R. E. (1955). *J. Am. Chem. Soc.* **77**, 6480–6486.
- OLOVSSON, I. & JÖNSSON, P.-G. (1976). *The Hydrogen Bond, Recent Developments in Theory and Experiments*, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, pp. 393–455. Amsterdam: North-Holland.
- OLOVSSON, G., OLOVSSON, I. & LEHMANN, M. S. (1984). *Acta Cryst.* **C40**, 1521–1526.
- PEDERSEN, B. F. & KVICK, Å. (1989). *Acta Cryst.* **C45**, 1724–1727.
- PEDERSEN, B. F. & KVICK, Å. (1990). *Acta Cryst.* **C46**, 21–23.
- ROBL, C., HENTSCHEL, S. & MCINTYRE, G. J. (1992). *J. Solid State Chem.* **96**, 318–323.
- ROBL, C. & KUHS, W. F. (1991). *J. Solid State Chem.* **92**, 101–109.
- SAVAGE, H. F. J. & FINNEY, J. L. (1986). *Nature (London)*, **322**, 717–720.
- SELENIUS, C.-O. & LUNDGREN, J.-O. (1980). *Acta Cryst.* **B36**, 3172–3175.
- STEINER, TH., MASON, S. A. & SAENGER, W. (1990). *J. Am. Chem. Soc.* **112**, 6184–6190.
- STEINER, TH. & SAENGER, W. (1992a). *J. Am. Chem. Soc.* **114**, 7123–7126.
- STEINER, TH. & SAENGER, W. (1992b). *Acta Cryst.* **B48**, 819–827.
- STEINER, TH. & SAENGER, W. (1993a). *J. Am. Chem. Soc.* **115**, 4540–4547.
- STEINER, TH. & SAENGER, W. (1993b). *Acta Cryst.* **A49**, 379–384.
- TAKUSAGAWA, F. & KOETZLE, T. F. (1979a). *Acta Cryst.* **B35**, 867–877.
- TAKUSAGAWA, F. & KOETZLE, T. F. (1979b). *Acta Cryst.* **B35**, 2126–2135.
- TAKUSAGAWA, F. & KOETZLE, T. F. (1979c). *Acta Cryst.* **B35**, 2888–2896.
- TAKUSAGAWA, F., KOETZLE, T. F., KOU, W. W. H. & PARTHASARATHY, R. (1981). *Acta Cryst.* **B37**, 1591–1596.
- TAKUSAGAWA, F., KOETZLE, T. F., SRIKRISHNAN, T. & PARTHASARATHY, R. (1979). *Acta Cryst.* **B35**, 1388–1394.
- THOMAS, J. O. & LIMINGA, R. (1978). *Acta Cryst.* **B34**, 3686–3690.
- WEBER, H.-P., McMULLAN, R. K., SWAMINATHAN, S. & CRAVEN, B. M. (1984). *Acta Cryst.* **B40**, 506–511.
- WEISINGER-LEWIN, Y., FROLOW, F., McMULLAN, R. K., KOETZLE, T. F., LAHAV, M. & LEISEROWITZ, L. (1989). *J. Am. Chem. Soc.* **111**, 1035–1040.
- YUAN, H. S. H., STEVENS, R. C., FUJITA, S., WATKINS, M. I., KOETZLE, T. F. & BAU, R. (1988). *Proc. Natl Acad. Sci. USA*, **85**, 2889–2893.
- ZABEL, V., SAENGER, W. & MASON, S. A. (1986). *J. Am. Chem. Soc.* **108**, 3664–3673.