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Bond Valence *vs* Bond Length in O···O Hydrogen Bonds

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Abstract

The total valence of the bonds between acceptors and the H atoms bonded to a water molecule (s_d) is taken equal to the bond valence (s_r) received by the donor O atom from coordination bonds. For an OH$^-$ group, $s_d = s_r - 1$. Plots of the bond valence s for H···O bonds as functions of O···O, H···O and O–H distances are fitted with the function $s = (R/R_0)^{-b} + k$. The most reliable fitting is obtained for s *vs* O···O; a minimum value of O···O $\simeq 2{\cdot}55$ Å for the hydrogen bonds donated by a water molecule is predicted. Similar curves from the literature are compared and discussed.

Introduction

In recent years, Pauling's (1929) definition of a bond strength (p), which depends only on the valence and the coordination number of the cations, has been modified to take into account the length R of the bond. This modified bond strength is usually called bond valence (s) and lists of empirical values of R_1 and N to calculate the function

$$s = (R/R_1)^{-N} \qquad (1)$$

have been published (*e.g.* Brown & Wu, 1976; Brown, 1981).

Except for studies based on neutron diffraction data, the location of protons in crystalline structures is unsatisfactory; this fact hinders the calculation of s values from donor–proton or proton–acceptor distances. At least for the oxygen–oxygen hydrogen bond, curves of s *vs* the donor–acceptor distance have been proposed on the basis of various considerations (Brown, 1976*a,b*; Brown & Altermatt, 1985).

In general, the total valence of the bonds between acceptors and the H atoms bonded to a water molecule (s_d) is equal to the bond valence received (s_r) by the donor O atom from coordination bonds, including accepted hydrogen bonds. If $(s_r)_i$ is the bond valence received from each coordination bond and $(s_d)_i$ is the bond valence transferred through each donated hydrogen bond, we can write

$$\textstyle\sum_i (s_r)_i = s_r = \sum_i (s_d)_i = s_d. \qquad (2)$$

For a water molecule donating two hydrogen bonds of comparable length, the bond valence transferred to a single acceptor is $s \simeq s_d/2 = s_r/2$. For OH$^-$ groups the exact relation $s = s_d = s_r - 1$ holds.

Some correlations between Pauling's bond strength p and the O···O distance in hydrogen bonds can be found in the literature. Examples are correlations of O···O with (i) the difference Δp between the bond strengths of the donor and of the acceptor (Baur, 1970); (ii) the average p value received by the donors belonging to oxoanions (Ferraris & Ivaldi, 1984); (iii) the average p values received by water molecules grouped according to their type of coordination (Ferraris, Fuess & Joswig, 1986).

In this paper, curves of the bond valence as a function of the O···O, H···O and O–H distances in hydrogen bonds are obtained by fitting the values of s calculated from s_r; a comparison with similar curves from the literature is made.

Results

The data concerning O···O hydrogen bonds have been extracted from structures with the following characteristics.

(*a*) Hydrated and/or protonated oxysalts and hydroxides.

(*b*) The required bond lengths can be obtained from the Inorganic Crystal Structure Database (Bergerhoff, Hundt, Sieves & Brown, 1983) or are reported in the original paper.

(*c*) Absence of positional and substitutional disorder, at least for the atoms involved in the required bonds.

(*d*) The donor of a hydrogen bond does not accept hydrogen bonds, except the symmetrical ones.

(*e*) Each proton is involved in only one hydrogen bond.

(*f*) The two hydrogen bonds donated by a water molecule have O···O distances differing by less than 0·1 Å if both O···O $\leq$ 2·8 Å and less than 0·2 Å if both O···O > 2·8 Å.

(*g*) Parameters R_1 and N are available for the calculation of (1).

(*h*) Cations show a smooth variation of bond lengths. For cations, like Cu, which can have longer and shorter coordination bonds, Brown & Wu's (1976) parameters can yield unreliable s values for long bonds.

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Following these criteria, 157 structures were selected;* 63 of them are based on neutron diffraction work. These structures contain 232 water molecules and 96 OH^- groups (81 from protonated oxoanions) which donate O···O hydrogen bonds in agreement with the selection criteria; a few values were not included in the fitting procedure, as shown in Figs. 1, 2 and 3. The values of s obtained from values s_r calculated with Brown & Wu's (1976) parameters are reported in Figs. 1, 2 and 3, as a function of O···O, H···O and O—H distances, respectively. For the water molecules the mean of the two corresponding bond lengths was taken.

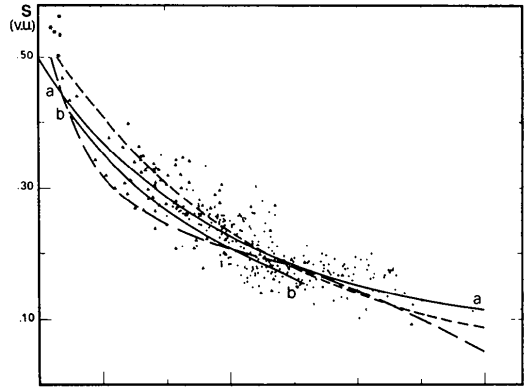

Fig. 1. Bond valence s for the H···O bond *vs* O···O distance for O···O hydrogen bonds. The experimental points correspond to s values obtained from the bond valence s_r received by the donor O atom from its coordination bonds as follows: $s = s_r/2$ for water molecules (dots); $s = s_r - 1$ for OH^- groups from oxysalts (triangles) and hydroxides (crosses). Stars show points not included in the fitting. The equation of the fitting curve (full line *a–a*) is $s = [(O\cdots O)/2{\cdot}17]^{-8{\cdot}2} + 0{\cdot}06$. Curves from Brown (1976*a*) (short-dash line), Brown & Altermatt (1985) (long-dash line) and Brown (1976*b*) (full line *b–b*) are also shown.

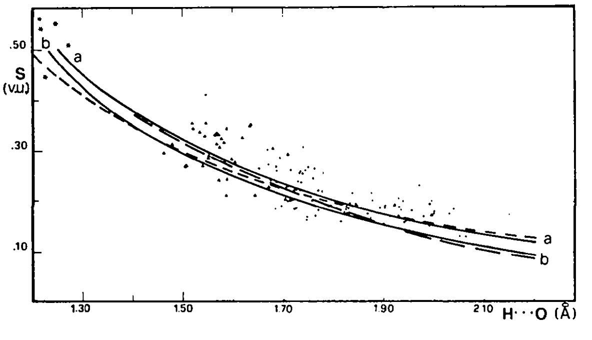

Fig. 2. Bond valence s for the H···O bond *vs* H···O distance for O···O hydrogen bonds. Neutron diffraction data only. Meaning of the experimental points as in Fig. 1. The equation of the fitting curve (full line *a–a*) is $s = [(H\cdots O)/0{\cdot}93]^{-2{\cdot}1} - 0{\cdot}04$. Curves from Brown & Altermatt (1985) (long-dash line), Brown & Wu (1976) (short-dash line) and Brown (1987) (full line *b–b*) are also shown.

The analytical form of the fitting function is ($a = R_0{}^b$)

$$s = (R/R_0)^{-b} + k \quad \text{or} \quad \ln(s - k) = \ln a - b\ln R \quad (3)$$

for R = O···O (Fig. 1) and R = H···O (Fig. 2), and

$$s = 1 - (R/R_0)^{-b} \quad \text{or} \quad \ln(1 - s) = \ln a - b\ln \mathrm{R} \quad (4)$$

for R = O—H (Fig. 3). The boundary condition $s = 0{\cdot}5$ v.u. (v.u. = valence unit) for a reasonable value of R (R_{bnd}, Table 1) was used to constrain a; the best value of the unknown b was then obtained by minimizing the sum of the squared residuals $(s_{\text{calc}} - s_{\text{obs}})^2$ with R_{bnd} and k as parameters; final values are shown in Table 1. Even if the values of R_{bnd} are close to the minimum (O···O and H···O) or the maximum (O—H) experimental values of the relevant distances, they are not to be taken as theoretical limits. The suitability of the chosen functions in fitting the experimental points is supported by a difference smaller than $\sigma(b)$ between the values of b calculated for different ranges of R. The values of b obtained from the single experimental s values tend to be normally distributed around the fitting value.

Discussion

The fitting

Scattering of the experimental points in the plots may be due to several causes.

(*a*) Bond valence values calculated from (1) account only for the first sphere of coordination; individual errors of 5%, or larger, can be expected, according to experience. Longer bonds might be missed in the case of cations (like Na^+, K^+, Cs^+, Ca^{2+}) with irregular

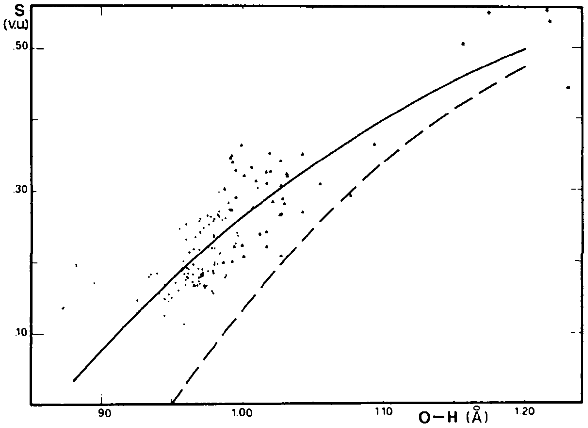

Fig. 3. Bond valence s for the H···O bond *vs* O—H distance for O···O hydrogen bonds. Neutron diffraction data only. Meaning of the experimental points as in Fig. 1. The equation of the fitting curve is $s = 1 - [(O{-}H)/0{\cdot}87]^{-2{\cdot}1}$ (full line). The broken line is from Brown (1987).

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* A list of the structural papers utilized has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44739 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Values of the parameters in equations* (3) *and* (4) *together with the number of observations* (n), *the mean-square error* $\alpha^2 = \sum(s_{calc}-s_{obs})^2/(n-1)$, *and the value of* $R = R_{bnd}$ *for which* $s = 0{\cdot}5$ *v.u.*

The e.s.d.'s of the optimized parameter b are shown in parentheses.

	b	R_o (Å)	k (v.u.)	n	α^2 [(v.u.)^2]	$R_{\rm bnd}$ (Å)
O···O	8·2 (1·7)	2·17	0·06	323	0·0009	2·40
H···O	2·1 (4)	0·93	−0·04	117	0·0011	1·25
O—H	2·1 (3)	0·87	—	125	0·0019	1·20

coordination and without a definite gap between first and second spheres of coordination.

(*b*) Under the plausible hypothesis of a constant average percent error, the absolute error increases with s.

(*c*) The majority of bonds with O···O > 2·6 Å (small s) belong to water molecules, where the use of mean bond lengths introduces a further approximation for the s values.

While the number and the chemical nature of coordinated cations can be correlated with the length of the hydrogen bond [*cf.* Ferraris *et al.* (1986) for water molecules], the spread of s values for a given R value does not appear biased by the type of coordination.*

Scarcity of experimental values at the extremities of the R range is mainly due to the Gaussian distribution of the relevant bond lengths (Chiari & Ferraris, 1982; Ferraris & Franchini-Angela, 1972). Further, long O···O hydrogen bonds can either be polyfurcated or the small s_r value involved with them is often provided by accepted weak hydrogen bonds; because of the selection criteria, such cases have been rejected. On the other hand, several strong hydrogen bonds are affected by disorder and they too have been rejected.

According to the values of the mean-square error (Table 1), the best fitting is obtained for s *vs* O···O. In particular, this curve gives $s = 0{\cdot}33$ v.u. for O···O = 2·55 Å, confirming the hypothesis that such a distance represents the minimum bond length for the two hydrogen bonds donated by a water molecule (Ferraris *et al.*, 1986). In fact, for O···O < 2·55 Å, $s > 0{\cdot}33$ v.u. is obtained from Fig. 1; in this case the bond valence of the O—H bond, [$s_{\rm O-H} = (1-s) < 0{\cdot}67$ v.u.] would be smaller than the bond valence s_r which the water O atom must receive from coordination bonds ($s_r = 2s$).

The fitting of s *vs* O—H is definitely worse. More than to the degree of insensitiveness to s, this behaviour should be related to a lower reliability of the O—H distance because of the substantially different thermal motion which usually affects the proton and its covalently bonded O atom. Another reason for preferring s *vs* O···O (or H···O) curves is the rapidly increasing slope of the correlation between O—H and O···O and the scatter of points for short O···O hydrogen bonds (Ishikawa, 1978; Joswig, Fuess & Ferraris, 1982). In other words, O···O and H···O distances are smoother indicators of the bond strength.

Comparison with published curves

The fitting curve of s *vs* O···O (Fig. 1, full line) shows the largest discrepancies (> 0·05 v.u.) with the curves proposed by Brown (1976*a,b*) and Brown & Altermatt (1985) in the regions of shorter and longer bonds. In particular, the long-dash curve of Fig. 1 tends to lie below the experimental points. On the other hand, the curves of s *vs* O···O proposed by Brown and co-workers are not based on fitting of experimental values, but on s *vs* O—H curves suppplemented with the concept of 'minimum non-bonded O···O distance' (Brown, 1976*a*) or by taking into account the bending of the hydrogen bond (Brown & Altermatt, 1985). Instead, the curve of s *vs* O···O of Brown (1976*b*) (Fig. 1, full line *b*–*b*) has been optimized to give better valence sums around oxonium ions and water molecules.

For s *vs* H···O curves (Fig. 2), good agreement is observed between the present fitting curve (full line *a*–*a*) and that (short-dash line) obtained from (1) with $R_1 = 0{\cdot}87$ and $N = 2{\cdot}2$ (Brown & Wu, 1976), apart from the stronger bonds, where the curves are sensitive to the boundary conditions and suffer from the scarcity of experimental values. The curve proposed in this work for s of the H···O bond *vs* O—H (Fig. 3) is practically coincident with that calculated from (1) with Brown & Wu's (1976) parameters (not reported in the figure).

When the results of this work were presented at the XIV International Congress of Crystallography (Ferraris & Ivaldi, 1987), we became aware of the following equation submitted for publication by Brown (1987):

$$s = B/(R - R') - C \qquad (5)$$

with $B = 0{\cdot}41$, $C = 0{\cdot}16$ and $R' = 0{\cdot}60$ for the H···O (and O—H) bond. The curve calculated from (5) tends to lie below the experimental points in the range of the H···O bond (Fig. 2, full line *b*–*b*) and the results are quite inadequate for the O—H bond (Fig. 3, broken line).

Because of the boundary conditions, extrapolation of the present fitting curves is meaningless for O···O and

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* With respect to the classification of water molecules studied by neutron diffraction proposed by Ferraris & Franchini-Angela (1972) and expanded by Chiari & Ferraris (1982), the following four further configurations of coordination bonds have been detected during this investigation: (1) one coordination bond from M^+ and one from M^{3+} in $CsAl(SO_4)_2.12H_2O$, $KAl_2F(PO_4)_2.4H_2O$ and $K_5Fe_3O(SO_4)_6.10H_2O$; (2) one coordination bond from M^{2+} and one from M^{3+} in $Ca_2NaAl_2F_4OH(PO_4)_2.2H_2O$; (3) two coordination bonds from M^+ and one from M^{2+} in $KHCO_3.MgCO_3.4H_2O$ and in $K_2Mg(CO_3)_2.4H_2O$; (4) four coordination bonds from M^+ in $Rb_3VO_4.4H_2O$. Except for the first one, all these structures have been studied by X-rays.

H···O $< R_{\mathrm{bnd}}$ and O—H $> R_{\mathrm{bnd}}$; some moderate extrapolation could, perhaps, be done at the other end of this range.

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The Incommensurately Modulated Structure of an Andesine (An_{38})

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Dedicated to Professor Dr Theo Hahn on the occasion of his 60*th birthday*

Abstract

The modulated structure of the intermediate plagioclase $Ca_{0.38}Na_{0.62}Al_{1.38}Si_{2.62}O_8$ has been determined by single-crystal X-ray methods. The structure has been refined using general sinusoidal density and displacement waves because only main reflections and first-order satellites were observable. Crystal data: $M_r = 268{\cdot}4$, superspace group $P^{P\bar{1}}_{\bar{1}}$ [0·080 (9), 0·031 (8), −0·261 (10)] with additional centering translations, $a = 8{\cdot}151\ (3)$, $b = 12{\cdot}829\ (5)$, $c = 14{\cdot}206\ (7)$ Å, $\alpha = 93{\cdot}62\ (3)$, $\beta = 116{\cdot}21\ (2)$, $\gamma = 89{\cdot}70\ (2)°$, $V = 1329{\cdot}7$ Å^3, $Z = 8$, $D_x = 2{\cdot}68$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}03$ mm^{-1}, $F(000) = 980{\cdot}9$, half-period of the modulation wave $T = 26{\cdot}7\ (3)$ Å, $wR = 0{\cdot}047$ for all reflections, 0·044 for 1176 main reflections and 0·151 for 2343 satellite reflections. The analysis of the mean *T*—O bond lengths reveals nearly complete Al/Si ordering on the *T* sites. The displacive modulation of the extra framework cations is strongly correlated with the periodic distortion of the framework structure. There is no Ca/Na substitutional modulation. The long-range order of the modulated structure can be characterized by the sequence ...An...An*... where An and An* represent regions with *I*-anorthite-like structure having antiphase relation to each other. The disordered boundary zones ... correspond to the average structure of the andesine. The absence of *f* reflections even in strongly overexposed X-ray diffraction photographs excludes any long-range order of anorthite- and albite-like lamellae as can be found in Ca-rich intermediate plagioclases.

Introduction

The diffraction patterns of intermediate plagioclases are characterized by numerous diffuse and/or sharp satellite reflections and diffuse scattering phenomena (Jagodzinski, 1984). They reflect complicated structures resulting from complex ordering and/or exsolution processes dependent on chemical composition and conditions of formation. Their most prominent feature besides the main reflections are the *e* and, in Ca-rich plagioclases, the *f* reflections. They can be interpreted as first- and second-order satellites caused by Al/Si and Ca/Na ordering (*a* or main reflections *hkl*0: $h + k = 2n$, $l = 2n$; *e* satellites *hklm*: $h + k = 2n + 1$, $l = 2n + 1$, $m = \pm 1$; *f* satellites *hklm*: $h + k = 2n$, $l = 2n$, $m = \pm 2$). Electron diffraction patterns, with their enhancement of weak satellite reflections resulting from dynamical scattering, even show third-order satellites [for An_{52} see Nakajima, Morimoto & Kitamura (1977)] indicating a rather high coherence

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