

Bond-valence parameters for characterizing O–H···O hydrogen bonds in hydrated borates

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Abstract

The bond-valence parameters d_0 of homonuclear O–H···O hydrogen bonds in hydrated borates are investigated on the basis of the crystallographic data available in the Inorganic Crystal Structure Database (2004 release). Using two different approaches (based on Coulomb's law and Golden ratio, respectively), our present work can strongly support the conclusion that bond-valence parameters d_0 are linearly correlated to the corresponding bond lengths of hydrogen bonds. A design route for inorganic crystals is suggested when comparing and analyzing these two methods, which may be of some benefit to understanding the important role of the bond-valence parameter d_0 in structurally designing crystals with hydrogen bonds.

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1. Introduction

Crystal engineering is the understanding of intermolecular interactions in the context of crystal packing and in the utilization of such understanding in the design of new solids with desired physical and chemical properties [1]. From this viewpoint, distance dependence and directionality are basic criteria for the classification of intermolecular interactions. Hydrogen bonds appear to be unique in their nature due to their considerable direction and stoichiometry, which are known to have specific effects upon crystal packing. Recent investigations [2,3] demonstrated that hydrogen bonds not only create and stabilize noncentrosymmetric structures, but also contribute to the enhancement of hyperpolarisabilities of hydrogen-bonded molecular systems or to the enhancement of second-order susceptibilities of crystals. Our previous studies of the structure–property relationship in nonlinear optical (NLO) crystals also confirm that each type of constituent chemical bonds has certain contributions to the total nonlinearity of the whole crystal, and hydrogen bonds in inorganic NLO crystals

often possess dominant NLO contributions to the total nonlinearity [4–6]. In the process of materials designing, excellent NLO crystals may be obtained with optimizing the geometry of hydrogen bonds in crystals to the optimum space direction. Therefore, the study of microscopic structure characteristics of hydrogen bonds is essential to correlate structural properties to NLO responses with the ultimate goal of allowing ‘tuning’ of the structure to enhance NLO properties of crystals.

The bond valence sum (BVS) model [7] is well known and can be used as a guide for predicting bond lengths from a given bond valence, checking the structure solution correctness, analyzing the geometric strains in crystals, and estimating the oxidation state of atoms. The bond-valence parameters d_0 , which relate bond valences to bond lengths, are extremely useful for structural chemists, even for general chemists. Therefore, our research is focused on the parameter d_0 of hydrogen bonds, which may be applicable to the evaluation of the crystal structure with hydrogen bonds.

Due to the unique configuration of O–H···O hydrogen bonds, a special treatment is needed to determine the bond-valence parameters d_0 . It can be said that, up to now, no satisfactory analytical expression has ever been found. Therefore, we firstly review the bond-valence parameters of hydrogen bonds in Section 2, and then give the theoretical basis for the calculation of parameters d_0 in Section 3. On the

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basis of the crystallographic data retrieval of O–H···O hydrogen bonds in Section 4, the bond-valence parameters d_0 of hydrogen bonds are directly related to the corresponding bond lengths in the form of linear functions in Section 5, though two different approaches are employed in the calculation of d_0 values. Finally, a design route is proposed for hydrated borates holding together by hydrogen bonds. Our conclusions are summarized in Section 6.

2. Bond-valence parameters of hydrogen bonds

Brown and Altermatt [7] gave the value of parameters d_0 and B of H–O bonds, respectively, as 0.882 and 0.37 Å through the statistical analysis of vast compounds obtained from the Inorganic Crystal Structure Database (ICSD) (1983). After that, Brese and O’Keeffe [8] suggested that there was a strong linear correlation between the parameters for bonds from cations to pairs of anions, and obtained the estimation values of d_0 for 969 pairs of atoms by extrapolation, which were considered as the supplement of Brown and Altermatt’s compilation. The recommended d_0 value of O–H bonds is 0.95 Å with regarding B as the constant 0.37 Å. Some suggested expressions have also been reported successively. Alig et al. [9] fitted H–O bonds with the parameters $d_0 = 0.914$ Å and $B = 0.404$ Å, determined from the bond valence sums around H^+ cations. Although these values give good valence sums around the H^+ ion, the valence sums around O^{2-} were not checked. In the same year, Steiner and Saenger [10] found that using $d_0 = 0.928$ Å and $B = 0.393$ Å, which were obtained from 80 low-temperature data of two-centered hydrogen bonds, reproduced the geometry of two-centered O–H···O hydrogen bonds reasonably well except for very strong and very weak bonds. Similarly, they obtained practically the same values as for two-centered hydrogen bonds, $d_0 = 0.927$ Å and $B = 0.395$ Å, for all investigated 136 hydrogen bonds involving the multi-centered cases. Compared with these results, the d_0 value given by Alig et al. is even shorter, this could be due to apparent shortening of the covalent O–H bond as a result of thermal vibrations in the analyzed room temperature crystal structures. Gilli et al. [11] reported that the shortest O–H distance in the absence of hydrogen bonds was 0.957 Å, however, the value $d_0 = 0.925$ Å was proposed instead of it when taking into account the electrostatic interaction. Bertolasi et al. [12] also referred $d_0 = 0.925$ Å and $B = 0.397$ Å for 80 low-temperature data regardless of the number of acceptor oxygen atoms. Subsequently, Steiner [13] found that the parameters d_0 and B were to some degree sample-dependent, who not only summarized several published values of d_0 and B , but also provided new parameters $d_0 = 0.934$ Å and $B = 0.388$ Å for 69 low-temperature crystal structure data of $O_{\text{Hydroxy}}\text{--}H\cdots O$ bonds.

All these parameters are widely adopted in the subsequent researches. Lutz et al. [14] established for the first time the correlation curve of the bond valences of intramolecular O–H bonds and the wavenumbers of OD stretching modes (S_{O-H} vs. V_{OD}) of water molecules in condensed materials, in which the bond valences were calculated with $d_0 = 0.914$ Å and $B =$

0.404 Å. Grabowski [15] showed that the relations between O–H and H···O bond lengths of O–H···O systems (which were obtained from BVS model with $d_0 = 0.925$ Å) were in agreement with those obtained from the neutron diffraction results. Steiner [16] calculated bond orders S for O–H and H···O bonds with $d_0 = 0.927$ Å and $B = 0.395$ Å, which provided a good fit for O–H···O hydrogen bonds over the whole distance range.

However, the contributions of weaker H···O bonds to the total bond valence of H^+ cations of O–H···O hydrogen bonds have not yet been revealed. The problem was also worked by providing three sets of values for d_0 and B , respectively, 0.907 and 0.28 Å for H–O distances smaller than 1.05 Å, 0.569 and 0.94 Å for H–O distances between 1.05 and 1.70 Å, and 0.99 and 0.59 Å for H–O distances larger than 1.70 Å [17]. Brown further suggested that it is best to assign valences to H–O bonds

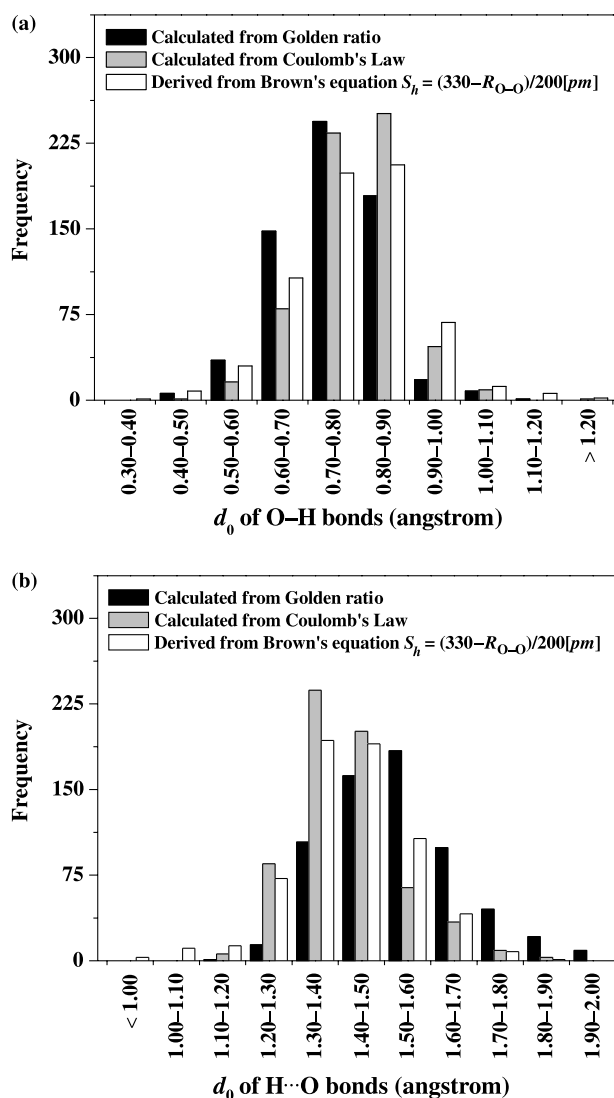


Fig. 1. Distribution histograms of the bond-valence parameters d_0 of O–H···O hydrogen bonds of hydrated borates, respectively, calculated from two diverse approaches, which are compared with those derived from Brown’s empirical equation $S_h = (330 - R_{O-O})/200$ [pm]. (a) For the stronger O–H bonds, (b) for the weaker H···O bonds.

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