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Golden ratio and bond-valence parameters of hydrogen bonds of hydrated borates

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Abstract

A quantitative understanding of microscopic characteristics of hydrogen bonds in various compounds is quite important for the deep study of structure-property relationships of functional crystals. The present work skillfully applies the well-known Golden ratio in the quantitative analysis of bond lengths of O–H···O hydrogen bonds. On the basis of the bond valence sum model, the bond-valence parameters d_0 of the stronger O–H and weaker H···O bonds are respectively calculated from the bond length data of hydrogen bonds in hydrated borates, which are available in the Inorganic Crystal Structure Database (2004). Two linear functions directly relating d_0 value to the respective bond length are recommended here, which provide us a powerful tool to structurally design new types of hydrated borate crystals by employing hydrogen bonds in the crystallographic frame.

Keywords: Golden ratio; Hydrogen bonds; Bond-valence parameters; Hydrated borates

1. Introduction

The Golden ratio [1], also called as the Divine ratio, Golden section or Golden mean, has been well known since the time of Euclid, which is the number phi ($\phi = 1.618$, precisely half the sum of 1 and the square root of 5). The ratio is often encountered when taking the ratios of distances in simple geometric figures such as the pentagram, decagon and dodecagon. Mathematically, the Golden ratio divides a segment into two parts so that the length of the smaller part (C) is to the length of the larger part (B) as the length of the larger part is to the length of the entire segment (A), i.e., [1,2]

$$A/B = B/C = \phi, \tag{1a}$$

$$1/A = 1/C - 1/B, \tag{1b}$$

$$\phi = 1 + 1/\phi = \phi^2 - 1 = (1 + 5^{1/2})/2 = 1.618; \quad 1/\phi = 0.618 \text{ and } \phi^2 = 2.618. \tag{1c}$$

This innocent-looking line division, which reflects harmonic connection of parts and the whole, is widely presented in numerous natural phenomena ranging from the leaf and seed arrangements of plants to the crystal structures of some aluminium alloys, and even from arts to the stock market.

Recently, Heyrovska [2] found that the Golden ratio also plays a unique significant role in atomic physics. It governs the Bohr radius, the covalent and ionic radii of atoms and enables one to quantitatively account for many bond lengths between atoms and ions and the partial ionic character of some. Therefore, we here apply the Golden ratio in the study of microscopic characteristics of hydrogen bonds by the analysis of bond lengths of hydrogen bonds. It is beneficial to catch on the idea that hydrogen bonds are of particular interest in the study of various structure-property relationships of functional crystal materials, especially for nonlinear optical (NLO) crystals, which has been confirmed in our previous studies [3–5].

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Table 1
Some suggested expressions of the bond-valence parameters d_0 and B available in literature

d_0(Å)	B (Å)	H–O distance (Å)	Reference
0.882	0.37	–	[6]
0.914	0.404	–	[7]
0.928	0.393	–	[8]
0.907	0.28	<1.05	[9]
0.569	0.94	1.05–1.70	[9]
0.99	0.59	>1.70	[9]

As the parameters bridging the bond valence and bond length, d_0 and B are crucial to predict bond lengths of inorganic crystals and to evaluate the final result of a crystal structure analysis on the basis of the bond valence sum (BVS) model [6]. For hydrogen bonds, some suggested expressions have been reported [7–9], which are summarized in Table 1. From Table 1 it can be seen that the limitation exists in the application of BVS model to a quantitative analysis of hydrogen bonds. In the present work, we firstly apply the Golden ratio in the stronger O–H and weaker H···O bonds of hydrogen bonds, respectively, the respective ionic radii $d_{(H+)}$ and $d_{(O-)}$ can be obtained. Then, taking the distribution of the only one valence electron of the hydrogen cation into consideration, the leverage equilibrium is used for calculating the bond valences of constituent hydrogen bonds. Finally, d_0 values of both O–H and H···O bonds of hydrogen bonds are reported, which are calculated from BVS model via a survey of crystal structures of hydrated borates in the Inorganic Crystal Structure Database (ICSD) (2004) [10]. The parameter d_0 is fitted with the linear function against the corresponding bond length of hydrogen bond, which effectively proves that the Golden ratio provides us a powerful tool in the structure design of NLO hydrated borate crystals utilizing hydrogen bonds.

2. Theoretical basis

If the appropriate d_0 is available, BVS model [6] can be precisely used to analyze the crystal structure, chemical bonding and oxidation state of constituent atoms in solids. In BVS model, all atoms are considered to be cations or anions according to the sign of the oxidation state. All neighboring cation–anion distances (i.e., bond lengths) are considered to be chemical bonds although not all are of equal strength. Each bond between atoms i and j is associated with the bond valence (or bond strength), S_{ij}, which may be related to the length d_{ij} of a given chemical bond (over the limited distance ranges observed for most bonds) by the function form of an inverse exponential or negative power,

$$S_{ij} = \exp[(d_0 - d_{ij})/B], \tag{2}$$

where the parameters d_0 and B are constants fitted empirically. B varies very little from one atom pair to another, which lies between 0.32 and 0.42 Å for many bonds. Thus, it is convenient to fix its value at 0.37 Å for all bond types [6]. Using the same value of B for all bond types makes the determination of d_0 much simpler since only one parameter now needs to be fitted [9]. In the current work, we use the value of B as 0.37 Å throughout. Based on the above expression, the oxidation state contributions are quantitatively apportioned between the atom centers according to the BVS values. The sum of the nearest integers to each BVS value for a structure is equal to the total of the atom oxidation states, V_i, i.e.

$$V_i = \sum_j S_{ij}. \tag{3}$$

The oxidation state or ionic charge, and bond valence are measured in valence units, v.u., which formally correspond to units of electronic charge, although the actual charges may be smaller. Eq. (3) necessarily holds for sums around both the anions and the cations.

In hydrogen bonds, the donor is bonded to one or more acceptor atoms, each of these bonds has its own valence, the BVS value surrounding H is equal to the oxidation state 1 v.u.. In particular, for H^+ cation of a triatomic O–H···O hydrogen bond, Eq. (3) can be simply written as,

$$S_{O-H} + S_{H\cdots O} = 1, \tag{4}$$

where S_{O-H} and $S_{H\cdots O}$ are the bond valences of the stronger O–H and weaker H···O bonds of hydrogen bonds, respectively. Evidently, if the corresponding bond valences can be obtained, the different parameters d_0 of the stronger O–H and weaker H···O bonds can be calculated from the bond length data of hydrogen bonds. Herein, the Golden ratio is used to analyze the bond lengths of constituent bonds of hydrogen bonds. For the stronger O–H bond, the bond length d_{O-H} is divided into two parts, the larger anionic radius $d_{(O-)}$ and the smaller cationic radius $d_{(H+)}$, i.e.

$$d_{O-H} = d^S_{(H+)} + d^S_{(O-)}, \tag{5a}$$

$$d^S_{(H+)} = d_{O-H}/\phi^2, \tag{5b}$$

$$d^S_{(O-)} = d_{O-H}/\phi. \tag{5c}$$

Similarly, the bond length $d_{H\cdots O}$ of the weaker H···O bond is also interpreted as the sum of the cationic and anionic radii,

$$d_{H\cdots O} = d^W_{(H+)} + d^W_{(O-)}, \tag{6a}$$

$$d^W_{(H+)} = d_{H\cdots O}/\phi^2, \tag{6b}$$

$$d^W_{(O-)} = d_{H\cdots O}/\phi. \tag{6c}$$

The superscripts S and W represent the stronger O–H and weaker H···O bonds of hydrogen bond, respectively.

Taking the hydrogen atom of hydrogen bond as a focus of attention, the following expression can be obtained for the diameter of the hydrogen atom when