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Hydrogen Bonding in Solids. Part II. The Strength of the O–H Bond and of the H..O Interaction for the O–H..O Systems*

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Correlations between the values of bond number and bond energy were found. The H–bond strength was investigated by using potential curves obtained for different positions of H–atom.

1. Bond Number as Strength of the Bond

The idea of bond number (n) has been introduced by Pauling.^{1,2}

$$n = 10^{-\frac{r-r_0}{c}} \quad (1)$$

where: r – the length of the bond, r_0 – the length of the single reference bond, c – the constant.

It has been shown that the bond number definition may be derived from the Morse function³ as well as from other functions describing atom–atom interactions.^{4,5}

Bond numbers have been calculated for triatomic systems,³ among them π –electron systems.⁶ It has been postulated that for triatomic O–H..O bridge we may write:⁷

$$n_1 + n_2 = 1, \quad (2)$$

where n_1, n_2 are bond numbers for O–H and H..O, respectively.

* Part I. The Hydrogen Bonding Model for the O–H..O Systems in Crystals of Carboxylic Acids. S. J. Grabowski, *Croat. Chem. Acta*, 61 (1988) 805.

The unity — the right side of eq. 2 may be interpreted as a pair of electrons of the bond; so $n_1 = 1$ for free O—H bond not embedded in H—bond. The bond number decreases by increasing the length of O—H bond in O—H..O system. The correlation n_1 .vs. V_{OH} (energy of O—H bond) supports this idea. (Figure 1). V_{OH}

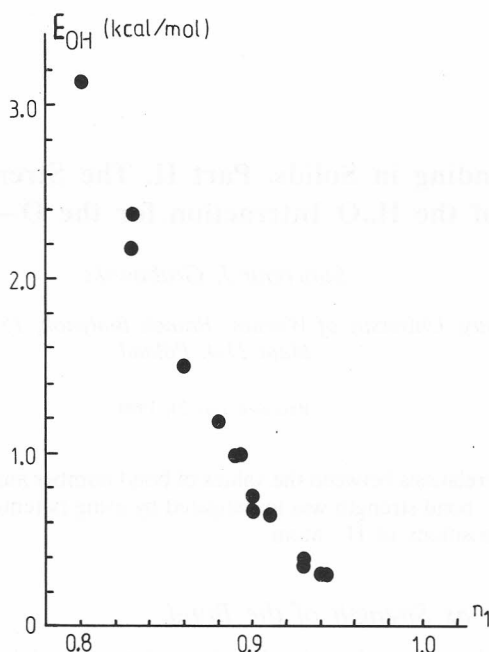


Figure 1. Relation between the value of the bond number (n_1) and energy of O—H bond (V_{OH})

has been taken from the Derissen and Smit model of H—bond⁸ as a contribution to H—bond energy (V_{HB}):

$$V_{HB} = V_{OH} + V_{H..O} + V_{O..O} - V_{OH}^{\circ} \quad (3)$$

where V_{OH}° is the reference energy of O—H bond not involved in H..O interaction, $V_{H..O}$ and $V_{O..O}$ are energies of the H..O contact and that between oxygen atoms, respectively.

Figure 2 shows that for a greater n_2 bond number the H..O interaction is stronger. Figures 1 and 2 have been obtained from the neutron diffraction data of carboxylic groups forming H—bonds ($R \leq 5\%$, e.s.d.' $s \leq 0.003 \text{ \AA}$, data have been taken from Cambridge Crystal Data Base — Table I).

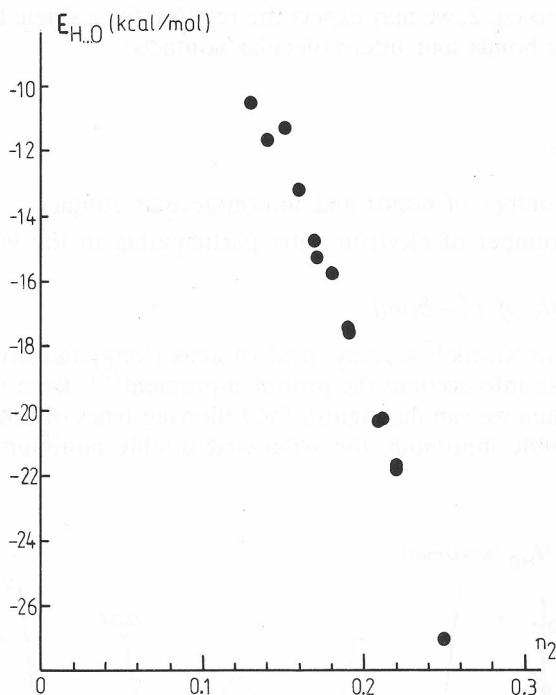


Figure 2. Relation between the value of bond number (n_2) and energy of H..O intermolecular contact ($V_{H..O}$)

TABLE I

The geometries of O—H..O bridges of crystal carboxylic acids, r_{OH} , $r_{H..O}$ and $R_{O..O}$ — the lengths of the O—H bond, H..O contact and of the O..O distance, respectively (all distances in Å)

	r_{OH}	$r_{H..O}$	$R_{O..O}$	ref.	compound
1	1.039	1.457	2.496	9	anthranilic acid
2.	0.996	1.636	2.632	10	ferrocene—1,1'—dicarboxylic acid
3.	1.008	1.593	2.600	10	— " —
4.	1.005	1.601	2.606	10	— " —
5.	0.997	1.663	2.660	10	— " —
6.	1.024	1.568	2.581	11	<i>L</i> —glutamic acid
7.	1.018	1.609	2.619	12	<i>L</i> —Tyrosine hydrochloride
8.	1.036	1.513	2.549	13	<i>N</i> —Acetyl— <i>L</i> —cysteine
9.	1.036	1.531	2.566	14	Sodium hydrogen oxalate monohydrate
10.	1.014	1.566	2.570	15	5-Nitro-1- β -D-Ribosyluronic acid/uracil monohydrate
11.	0.994	1.688	2.678	16	Succinic acid
12..	1.006	1.670	2.673	16	— " —

We may say that the value of $n_{i=[1,2]}$ shows the strength of the bond or of the intermolecular contact.

According to eq. 2, we may expect the relation for a single atom connected with other atoms by bonds and intermolecular contacts:

$$\sum_i^N n_i = M, \quad (4)$$

where: N – number of bonds and intermolecular contacts,

M – number of electron pairs participating in the bonds.

2. The Strength of H–bond

According to Novak,¹⁷ we may speak of weak (long) and strong (short) hydrogen bonds. If we take into account the proton movement^{18,19} from proton donor to proton acceptor, then we can distinguish the following types of potential barriers:¹⁷ the asymmetric double minimum, the symmetric double minimum and the symmetric

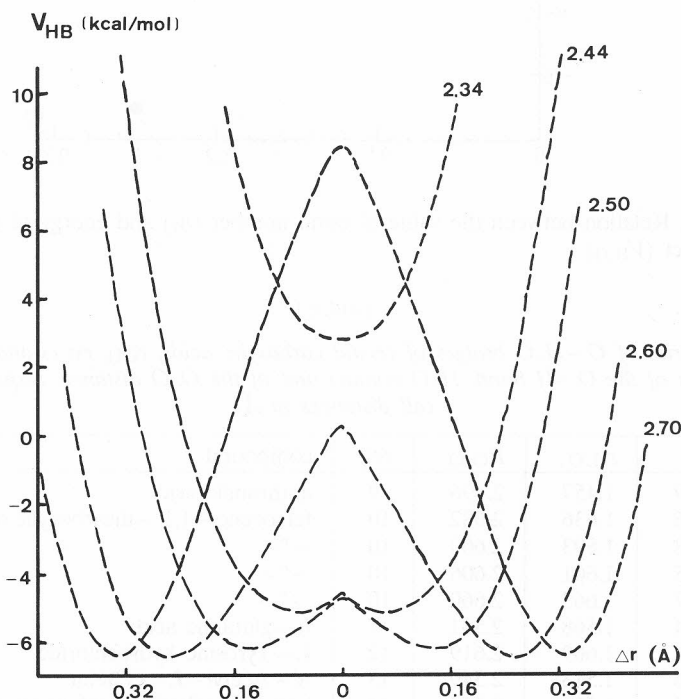


Figure 3. H–bond energies for different fixed values of $R_{O...O}$ distances; each curve presents the values of E_{HB} for different positions of H–atom ($\Delta r=0$ for H–atom in the middle of O–H...O bridge)

single minimum. The last case exists for short (strong) hydrogen bonds.¹⁷ Thus, strictly speaking, if we have strong (short) hydrogen bonds, then a single minimum exists for the potential well of proton movement along the O..O line and we have a double minimum for weak (long) and intermediate hydrogen bonds.

Let us consider the O–H..O bridges. Figure 3. presents the values of the H–bridge energy (V_{HB}) for different positions of the hydrogen atom for a few fixed values of the O..O distance ($R_{O..O}$). The curves of Figure 3. have been obtained in the following way. For the fixed value of the O..O distance we have changed the O–H and H..O distances (we have assumed that O–H..O bridge is linear). So for the given curve the proton position is variable ($\Delta r = 0$ for the proton position in the middle of the O..O distance).

We have obtained one single minimum for the O..O distances smaller than 2.44 Å and the most stable configurations have a double minimum (Figure 3). It is well known that for strong H–bonds, like for example (F..H..F)[–], for the great value of F..F distance we have two minima of energy which are closer after a decrease of the length of F..F distance as long as the single minimum of the lower energy appears and after that for the decrease of F..F distance we have a single minimum but of greater energy.²⁰

Thus, if a single potential well exists for the curve for which we have the least energy of H–bond like for (F..H..F)[–], then we have a symmetrical strong H–bond; otherwise, like in the case presented in Figure 3 we have a weak or intermediate H–bond. For O–H..O systems, the most stable are those which have a double minimum. This is in agreement with experimental data because the structures of crystal carboxylic acid show that intermediate O–H..O bridges are not symmetrical and that they have a double minimum.

It should be pointed out that Figure 3 supports the idea of the bond number. Eq. 2 for $n_1 = n_2 = 0.5$ is satisfied for the O..O distance equal to 2.44 Å ($n = 0.5$ for $r_{H..O} = r_{OH} = 1.22$ Å) and Figure 3. shows that a single potential well appears for the O..O distances smaller than 2.44 Å.

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SAŽETAK

Vodikova veza u čvrstom stanju. II. Jakost veza O—H i međudjelovanje H...O u sustavima O—H...O

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Za niz sustava s vodikovom vezom utvrđena je korelacija između vrijednosti broja veza i energije veze. Jakost vodikove veze ispitana je primjenom potencijalskih krivulja, koje su određene za različite položaje atoma vodika.