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Estimation of the Proton Position and the Energy of O-H..O Bridges in Crystals from X-ray Diffraction Data.

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Abstract. A model based on the bond number conservation rule is proposed leading to the evaluation of the proton position for a given O...O interatomic distance and consequently the H-bond energy for such system. Application of the model to the Lippincott - Schroeder potential gave results showing a good agreement between the calculated energy and the energy determined from the neutron diffraction geometry of H-bridges for a sample of 126 precisely determined systems. Such an approach is very useful for X-ray diffraction molecular geometries of H-bonded systems for which the position of proton is ill defined. © 1998 Elsevier Science Ltd. All rights reserved.

Introduction

Information on the position of the proton in a H-bridge is of fundamental importance. The most widely used method in structural studies - the X-ray diffraction technique - fails in this respect since the X-rays are scattered by electrons and hence the position of the proton (H-atoms in covalently bonded systems too) is not reliably determined from electron density maps.[1,2] There are two sources of error in measuring position of proton: (i) a systematic one - bonded X-H distances are underestimated because the centre of electron density is displaced towards the atom X; (ii) a random one which arises largely because H atoms have only one electron and therefore contribute much less to the diffraction pattern than other atoms. In the crystalline state, only the neutron diffraction gives the precise positions of protons.[1] The main source of crystallographic data of organic compounds is the Cambridge Structural Database[2] but neutron studies constitute less than 1% of structure determinations. A similar situation exists for the inorganic data base in respect to the systems with H-bonds.[3] As a

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consequence of this situation, X-ray data must often be used in statistical investigations. For X-ray diffraction crystal structures X-H distances are observed too short and hence H..A (A denotes an acceptor) distances in hydrogen bonds are too long. That is why different methods have been proposed to define the H-atom positions. For example, it was pointed out that the H-atoms in crystalline hydrates may be determined by using an electrostatic model.[4] The most frequently used method is the normalisation suggested by Jeffrey and Lewis [5] where the H-atom is moved along the X-H bond to the standard position typical of the respective X-atom. However, in such treatments the elongation of the X-H bond as a result of H-bond formation is not taken into account and is justified only when the X-H bonds are not strongly influenced by environmental effects.[6,7]

For many purposes not only the structural characterisation of a hydrogen bond is required but also the determination of its energy. Many empirical and semi-empirical models of the hydrogen bond allow us to calculate such energy if the positions of the atoms constituting the H-bond are known. For example, the model of Lippincott and Schroeder [8] (hereafter referred to as the L-S model) first proposed for the O-H..O systems, was later applied to other types of hydrogen bonds.[9] Alternative approaches were suggested by Moulton and Kromhout[10] who included an angular dependence within the model, and by Sokolov; [11] Scheraga and co-workers applied their model to biological molecules;[12] the model of Caillet and Claverie was first applied to the study of the arrangement of molecules in adenine crystals;[13] the model based on the idea of the bond number [14] was used to describe inter- and intramolecular H-bonds.[15]

The L-S model seems to be the most general treatment since it was modified by Reid [16] for the strongest hydrogen bonds. A discussion of weak and strong hydrogen bonds within the L-S model was presented by Spencer and co-workers [17] who analysed HX_2^- ions (X denotes F, Cl, Br or I atoms) and systems with C-H bond as a proton donor (C-H..Y systems). As another example of the application of the L-S model we can mention here the calculations concerning the crystal structures of carboxylic acids [18] or, more recently, the analysis of the covalent nature of the strong homonuclear hydrogen bond.[19]

The aim of this work is to present a model permitting the determination of the H-atom positions within H-bonds taken from X-ray structures which, in consequence, make it possible to estimate the H-bond energies from X-ray data.

The Lippincott - Schroeder model and its modifications

In the model of Lippincott and Schroeder the hydrogen bond potential energy, V_{HB}, is the sum of four terms:

$$V_{HB} = V_1 + V_2 + V_3\,(\text{repulsion}) + V_4\,(\text{electrostatic}) \qquad (1)$$

O-H and H..O interaction energies can be described by Morse-like functions (V_1 and V_2), V_3 and V_4 refer to O..O interaction.[20]

A detailed disscusion of this model and its applications and limitations has been given by Gilli and coworkers.[19] The authors claimed that the constant g (see ref.20) strongly affects the calculated values of the covalent part of the hydrogen bond ($V_1 + V_2$). This happens especially for short H-bridges for which O..O distances tend to have a value of 2.5 Å or even less. For such short H-bridges, the electrostatic part of the H-bond energy (the term V_4) should tend to zero. According to Novak,[21] the O..O distance is correlated with the strength of appropriate H-bond, which means the shorter the distance the stronger the H-bond. Recent investigations of Jeffrey and Saenger[22] suggest that there is no direct experimental evidence for the existence of such a relationship. However, measurements of pulsed electron-beam mass spectrometry in the gas phase have shown that for compounds with short O..O distances the association enthalpies are in the range from -30 to - 36 kcal/mol.[23,24]

The original version of the Lippincott - Schroeder model[8,9] is not in agreement with the experimental results because it gives positive values of H-bond energy for such H-bridges (with very short O..O distances). The appropriate modifications for short donor-acceptor distances were first proposed by Reid[16] and later discussed by Gilli and coworkers.[19] The V_2 and V_4 terms change: the constant g tends towards unity and B approaches zero for shorter O..O distances because the covalent nature increases and the electrostatic nature decreases for such systems.[25] The key information necessary to calculate the H-bond energy is the position of the proton in the O-H..O bridge.

A model for determination of the position of H-atom in O-H..O bridges

It is impossible to estimate the H-bond energy if the position of H-atom for O-H..O system is not known or is determined inaccurately. Such situations are often encountered in the case of X-ray crystallographic data of the crystal structures.

In order to solve this problem the concept of bond number is used. It had been introduced by Pauling[14] and was later used successfully in many chemical problems.[1,14,26-31] It is particularly useful for the systems which fall between the typical covalent bonds and nonbonded contacts.[1] The bond number n_i is defined by the relation:

$$r_i - r_o = \Delta r_i = - c \log n_i \qquad (2)$$

where: r_i is the length of the bond or of the atom-atom nonbonded contact, r_o is the length of the reference single bond, c is a constant which may be determined from the last equation if we know the value of n_i for a given length of the bond or contact r_i. The length of the contact is usually known for the value of n_i equal to 0.5.

The definition of the bond number may be obtained from the Morse function which describes the energy of the bond.[1,28] The concept of the bond number has a more general meaning since the other functions describing the atom-atom interactions, e.g. Varshni, Buckingham and Rydberg potentials also lead to a similar definition as that for the bond number.[27]

The bond number concept was widely used in organic and inorganic structural chemistry. [14,15,26-31] The idea of the bond number conservation introduced by Johnston[32,1] may be applied to O-H..O bridges:

$$10^{-\Delta r_i/c} + 10^{-\Delta r_j/c} = 1 \qquad (3)$$

where $\Delta r_i = r_i - r_o$ is the difference between the O-H bond length (r_i) and the length of the single reference O-H bond (r_o usually equals to 0.957 Å as for water molecules in gaseous state). $\Delta r_j = r_j - r_o$ is the difference between the length of H..O contact (r_j) and r_o. The constant value c was determined from the relation (2) applied to fractional O-H bond - $r_{1/2}$:

$$r_{1/2} - r_o = - c \log 1/2 \qquad (4)$$

$r_{1/2}$ = 1.22 A is based on the averaged data of Speakman[33]. In the present paper the value taken from the paper of Gilli and coworkers[19] was used (1.2 Å from the O..O distance of 2.4 Å as the shortest one occurring when the proton is centered). This choice determines the location of the minimum in the plot of Fig.1 and parameters presented in ref.25.

For the linear H-bonded systems with fixed O..O distances eq. (3) permits one to estimate the position of the H atom. For the general case we should consider nonlinear O-H..O bridges.[34] For linear O-H..O bridges the rule of bond number conservation allows us to determine only one position of the H-atom. For non-linear systems many positions of the H-atom are allowed for a given fixed O..O distance depending on the OH..O angle. Hence an extra condition is necessary to determine the H-bridge geometry. For this purpose the condition of the minimal energy of the system was chosen and the calculations were performed with the use of the Lippincott-Schroeder model modified for short O..O distances of the H-bridge. The lowest energy of O-H..O bridge obtained in such a way is -29.1 kcal/mol for the O..O distance of 2.4 Å. There is some disagreement with the energies estimated by pulsed electron-beam mass spectrometry in the gas phase,[23,24] which for some systems are lower than -30 kcal/mol. This effect may be attributed to the crystal lattice which may influence the energy of the H-bond [35] since the systems considered here are taken from crystallographic data. For the H-bond models the energies are usually considered as if they depended only on the positions of three atoms; the geometry of the remaining parts of the molecules is not taken into account. The same is in force for the procedure presented here, where the calculated energy does not depend directly on the lattice forces or on the remaining parts of the molecules.

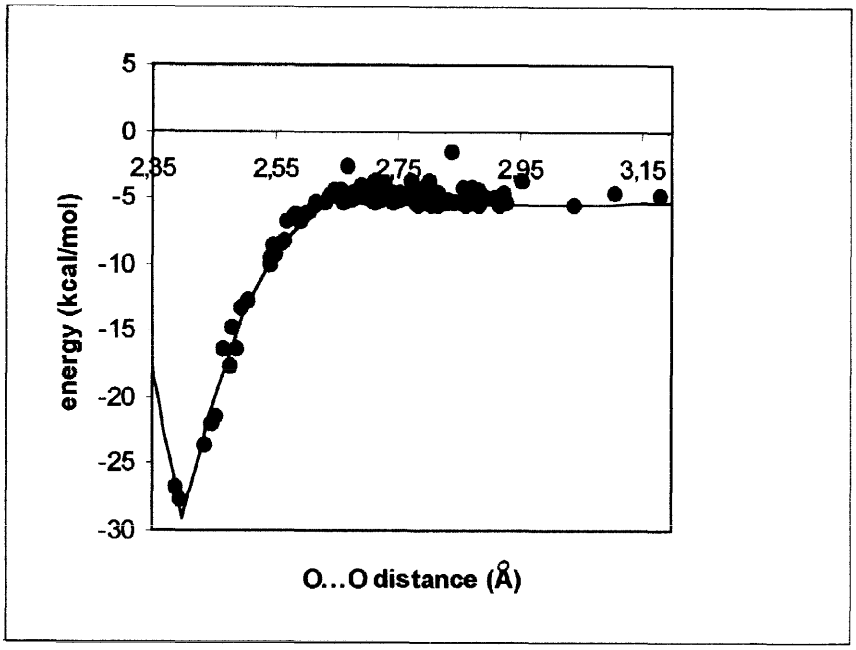

Fig 1. Plot of the lowest energies of H-bridges for fixed O..O distances calculated by the method presented in this paper (the continuous curve); H-bond energies for the data taken from CSD versus O..O distances (circles).

The continuous curve in Fig 1 stands for the calculated H-bond energies for the given O..O distances within the model presented above whereas circles represent energies calculated by the L-S model from experimental neutron diffraction geometries. The agreement is suprisingly good. Hence the fitted polynomial [36] may be used to estimate the H-bond energy if only the O...O interatomic distance is known, as is usually the case with the X-ray diffraction molecular geometry.

Testing the model

The data from the Cambridge Structural Database (CSD)[2] have been used to verify the model presented in the previous section. The accurate data of neutron diffraction have been used (with e.s.d's ≤ 0.005 Å and R ≤ 5%); 52 such crystal structures have been found for which 126 independent O-H..O bridges exist. Only the H-bonds with O-H interatomic distance >0.957 Å [37] (i.e. OH in water molecule in the gasoeus state) were taken into account. For all 126 O-H..O bridges the H-bonds energies were calculated within the Lippincott-Schroeder model presented in the previous section and plotted versus O..O distances denoted as circles in Fig. 1.

Comparison of neutron diffraction H-bond geometries with the geometries obtained from the model

Fig. 2 shows the differences (in Å) between the predicted geometries (for the lowest energies for fixed O..O distances) and the geometries taken from crystal data (for the sample of neutron diffraction data analysed in this paper).

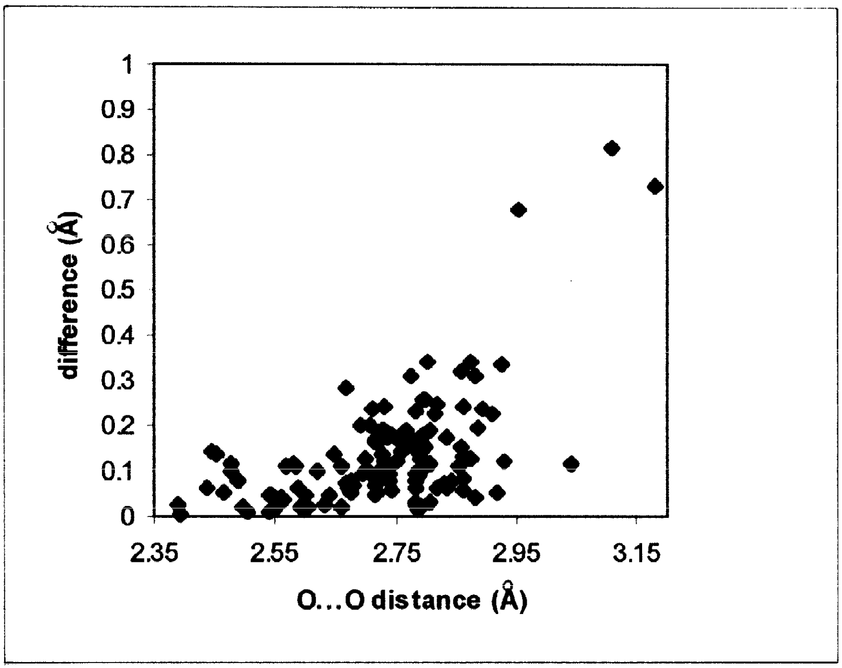

Fig 2. The difference between the predicted positions of H-atoms and those taken from CSD versus O..O distance

The difference means the distance between the position of the H-atom for a given H-bridge taken from CSD and the position predicted by the procedure described by the model for the same O..O distance. One can see that the differences are greater for longer O..O distances. So the strong H-bond interaction for short O..O distances has the effect that the proton in the bridge may not move freely.[38] The results presented in Fig. 2 may be connected with the effect of thermal vibrations. It is well known that the X-H bond lengths observed in the crystal structures are systematically shortened because of thermal vibrations, the shortening increases with increasing vibration amplitudes.[39] In O-H..O hydrogen bonds, the vibration amplitude of the H-atom decreases with reducing H-bond length. This may be the reason why for greater O..O distances the differences presented in Fig.2 are greater. For strong (O..O distance <2.6 Å) and medium H-bonds (O..O distance 2.60 - 2.8 Å) such differences are 0.06 and 0.17 Å, respectively. This is undoubtedly a better information than low or unknown precision of the H position from X-ray data.

Table 1. O-H..O systems in data set (distances in Å, angles in degrees).

REFCODE [a]	O-H	O..H	O-H..O	O..O	Temp [b]
1 ACAMCL01	1.213	1.213	180.0	2.426	120
2 ADENOS01	0.980	1.787	164.0	2.743	123
3 AEPHOS02	1.013	1.535	176.1	2.546	122
4 AMBACO07	1.039	1.457	179.1	2.496	295
5 ARGIND11	0.974	1.770	172.1	2.739	295
6 CUHOPT04	0.973	1.694	170.5	2.658	295
7 DETSBR01	1.046	1.421	176.2	2.465	295
8 DIALAC02	1.012	1.583	169.8	2.585	295
9 DLASPA02	1.035	1.508	179.4	2.542	295
10 DOBJIN01	0.965	1.822	178.4	2.787	295
11 EDATAR01	0.976	1.784	163.0	2.732	295
12 FAHCAS01	0.974	1.877	163.9	2.826	295
13 FAHCAS01	0.977	1.766	175.3	2.741	295
14 FAHCAS01	0.970	1.770	153.4	2.673	295
15 FAHCAS01	0.970	1.846	161.6	2.783	295
16 FAHCAS01	0.975	1.786	178.5	2.761	295
17 FAHCAS01	0.959	1.825	153.9	2.718	295
18 FEROCA12	0.996	1.636	178.4	2.632	78
19 FEROCA12	1.008	1.593	176.0	2.600	78
20 FEROCA12	1.005	1.601	179.1	2.606	78
21 FEROCA12	0.997	1.663	178.4	2.660	78
22 FIJBOP01	0.990	1.726	162.7	2.688	295
23 FRUCTO02	0.972	1.965	152.0	2.859	295
24 FRUCTO02	0.979	1.750	154.6	2.668	295
25 FRUCTO02	0.964	1.977	169.3	2.930	295
26 FRUCTO02	0.964	2.593	113.6	3.107	295
27 FRUCTO02	0.963	1.869	163.2	2.805	295
28 FUSPIS10	0.973	1.829	168.7	2.790	295
29 FUSPIS10	0.973	1.839	153.2	2.742	295
30 HDRZHO11	1.227	1.227	180.0	2.454	295
31 HOPROL12	0.971	1.843	164.9	2.791	295
32 KAOXYA01	1.151	1.328	174.3	2.476	295
33 KDGLUM01	0.977	1.985	150.4	2.875	295
34 KDGLUM01	0.974	1.667	177.3	2.640	295
35 KDGLUM01	0.963	1.834	165.2	2.776	295
36 KDGLUM01	0.958	1.784	168.0	2.728	295
37 KDGLUM02	0.963	1.974	159.1	2.894	295

38 KDGLUM02	0.975	1.809	178.0	2.783	295
39 KDGLUM02	0.971	1.914	176.2	2.884	295
40 KDGLUM02	0.964	1.805	164.2	2.745	295
41 KDGLUM02	0.961	2.317	123.3	2.955	295
42 KDGLUM02	0.961	1.887	173.1	2.844	295
43 KDGLUM02	0.966	1.816	178.0	2.782	295
44 KHCROT01	1.141	1.348	178.0	2.488	295
45 KIDREU01	0.990	1.646	175.7	2.635	15
46 KIDREU01	0.991	1.648	166.0	2.620	15
47 KOXALM10	0.963	1.801	169.7	2.754	295
48 LGLUAC03	1.024	1.568	169.3	2.581	295
49 LIHPAL01	1.122	1.294	168.9	2.404	15
50 LIHPAL01	0.964	1.864	163.5	2.801	15
51 LIHPAL01	0.967	1.826	167.5	2.778	15
52 LIHPAL01	1.205	1.195	171.9	2.394	15
53 LIHPAL01	0.970	1.837	174.7	2.804	15
54 LIHPAL01	0.970	2.495	126.9	3.173	15
55 LIHPHM01	1.205	1.195	171.3	2.393	295
56 LIHPHM01	1.226	1.173	169.3	2.388	295
57 LIHPHM01	0.960	1.876	174.7	2.834	295
58 LIHPHM01	0.972	1.813	174.6	2.782	295
59 LSERMH10	0.957	1.843	166.9	2.784	295
60 LTYRHC10	1.018	1.609	170.7	2.619	295
61 LTYROS11	0.981	1.689	173.8	2.667	295
62 MALTOS11	0.974	1.799	167.6	2.758	295
63 MALTOS11	0.962	1.927	149.8	2.801	295
64 MALTOS11	0.971	1.846	169.8	2.807	295
65 MALTOS11	0.975	1.814	165.7	2.769	295
66 MALTOS11	0.967	1.850	166.7	2.800	295
67 MALTOS11	0.962	1.825	166.7	2.769	295
68 MALTOS11	0.981	1.762	167.0	2.732	295
69 MALTOS11	0.966	1.870	173.4	2.832	295
70 MALTOS11	0.966	1.834	169.1	2.789	295
71 MDRIBP02	0.965	2.568	96.2	2.839	295
72 MDRIBP02	0.960	1.947	158.8	2.863	295
73 MEMANP11	0.957	1.998	153.1	2.884	295
74 MEMANP11	0.976	1.809	179.8	2.785	295
75 MEMANP11	0.959	2.051	150.6	2.925	295
76 MGLUCP11	0.985	1.737	162.2	2.692	295
77 MGLUCP11	0.969	1.769	162.0	2.708	295
78 MGLUCP11	0.966	1.772	165.1	2.717	295

79 NAHMAL01	0.971	1.887	164.5	2.834	120
80 NAHMAL01	0.960	1.927	168.8	2.875	120
81 NAHMAL01	0.970	1.773	173.2	2.739	120
82 NAHMAL01	0.973	1.820	172.3	2.788	120
83 NAHMAL01	0.964	1.956	175.3	2.918	120
84 NAHMAL01	0.971	1.851	174.3	2.819	120
85 NALCYS02	1.036	1.513	178.4	2.549	16
86 NINDOD01	1.008	1.589	160.9	2.563	295
87 NINDOD01	1.008	2.462	113.7	3.011	295
88 NINDOD01	0.997	1.648	177.2	2.643	295
89 NINDOD01	0.997	2.408	116.2	2.985	295
90 NINDOD01	1.087	1.390	179.2	2.477	295
91 NINDOD01	0.969	1.743	177.9	2.712	295
92 NRURAM11	0.974	1.874	152.6	2.775	80
93 NRURAM11	1.014	1.566	169.8	2.570	80
94 NRURAM11	0.967	1.853	164.1	2.796	80
95 PYOTCA01	1.148	1.284	174.9	2.430	120
96 RBHOXY01	1.225	1.225	174.5	2.446	295
97 RESORA13	0.984	1.732	175.9	2.714	295
98 RESORA13	0.981	1.756	165.6	2.718	295
99 RHAMAH12	0.979	1.740	174.0	2.715	295
100 RHAMAH12	0.974	1.814	173.2	2.784	295
101 RHAMAH12	0.968	1.820	171.8	2.781	295
102 RHAMAH12	0.967	1.981	160.3	2.909	295
103 RHAMAH12	0.975	1.771	175.2	2.744	295
104 SGLACU01	0.964	1.964	172.4	2.923	130
105 SGLACU01	1.008	1.611	174.6	2.616	130
106 SGLACU01	0.964	1.946	167.0	2.894	130
107 SOGGEA	0.986	1.660	162.5	2.617	15
108 SOGGEA	1.000	1.591	170.0	2.582	15
109 SOGGEA	0.992	1.677	168.9	2.657	15
110 SOGGEA	0.997	1.587	170.8	2.576	15
111 SOGGEA	0.988	1.656	171.9	2.638	15
112 SOGGEA	0.976	1.719	161.6	2.664	15
113 SOGGEA	0.986	1.740	167.0	2.710	15
114 SOGGEA	0.985	1.747	171.0	2.724	15
115 SUBRAC01	1.009	1.631	176.0	2.638	18
116 SUCACB02	0.994	1.688	173.7	2.678	295
117 UREAOH12	0.994	1.669	167.6	2.648	295
118 UROXAL01	1.074	1.416	168.9	2.479	100
119 VUYYUJ	0.972	1.902	166.6	2.857	30

120	XYLOBM01	0.962	2.088	170.0	3.040	295
121	XYLOBM01	0.969	1.885	160.1	2.816	295
122	XYLOBM01	0.969	1.785	163.4	2.728	295
123	XYLOSE01	0.971	1.805	158.3	2.730	295
124	XYLOSE01	0.974	1.751	171.5	2.719	295
125	XYLOSE01	0.981	1.732	168.8	2.701	295
126	ZZZFQQ02	0.985	1.691	169.1	2.664	15

[a] The REFCODE refers to the reference for data retrieval on the Cambridge Structural Database

[b] The temperature of the determination of the structure (in K); the corrections for libration were not incorporated within the sample under consideration

Acknowledgements

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20. According to the assumptions of the model:

$V_1 = D\,[\,1 - \exp(-n\,\Delta r^2/2r)\,],\quad \Delta r = r - r_o,$

$V_2 = -D^*\{\exp[-n^*(R - r - r_o^*)^2/2(R - r)]\},$

$V_3 = A\exp(-b\,R),$

$V_4 = -B/R^m,$

where: R is the O..O distance, r - the length of O-H bond, D is the dissociation energy of O-H bond, r_o is the length of the reference single O-H bond not involved in H-bond, m is the constant which is usually 1 or 6 (in our case it amounts to 1), n, A, B and b are other constants.

Lippincott and Schroeder have suggested the assumptions: $n^* = g\,n$ (g=1.45), $D^* = D/g$, and $r_o = r_o^*$.

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25. The following linear relations proposed in this paper fulfil the above assumptions:

$g = 1 + 1.8\,(R - 2.40)$ for $R \in <2.40; 2.65>$

$B = 72.8\,(R - 2.40)$ for $R \in <2.40; 2.65>$.

For R > 2.65 Å, B is equal to 18.2 and g to 1.45 as it was originally given by Lippincott and Schroeder; for R <2.40 Å B is equal to zero and g to 1. We do not know the accurate values of g and B to be used for shorter O..O distances so the relations given above may be changed in the case when a specific class of compounds is used or if the extra appropriate, experimental data are given. The remaining constant values used in the Lippincott-Schroeder model are as follows: D = 118.0 kcal/mol, n = 9.18, A = 43.00 x 10^5, b = 4.815, r_o = 0.957 Å (the length of O-H bond for water molecule in the gas phase).

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31. The bond valence (BV) model introduced and studied extensively by Brown has a similar meaning as the bond number. Additionally the BV model was used for the investigation of acidity and basicity of functional groups and of terminal atoms within hydrogen bonds, see for example; Brown, I.D. *Acta Cryst.*, **1976**, A32, 24.
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34. For the linear bridges the H..O distances were calculated as a difference between the distances of O..O and O-H. But in general the H..O distance should be given by the relation:

    $r_{H..O} = (r_{OH}^2 + R_{O..O}^2 - 2 R_{O..O} r_{OH} \cos\alpha)^{1/2}$,

    where α is the angle between O..O distance and O-H bond. If we put this equation into the relation of the bond number conservation then it is possible to calculate the α angle. Thus for the given values of $R_{O..O}$ and r_{OH} it is possible to calculate the α angle. This means that the relation of the bond number conservation allows us to determine many H-atom positions for fixed O..O distance (with different O-H bonds and different α angles).
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36. $V_{HB} = - 438.861 R^4 + 5152.31 R^3 - 22594.3 R^2 + 43962.8 R - 32028.9$; for $R > 2.4$ Å;

    $V_{HB} = 541.071 R^2 - 2794.23 R + 3560.49$, for $R \leq 2.4$ Å, V_{HB} in kcal/mol
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