



QTAIMC study of the X–H/H···O bond order indices (X = O, N, C) in molecular systems

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ABSTRACT

The O–H/H···O bond order indices are evaluated at the B3LYP level using the Quantum Theory of Atoms in Molecules and Crystals (QTAIMC). The parameters of bond critical points, such as electron density, principal electron-density curvatures, kinetic and potential energy densities, are calculated for 32 molecular systems comprising of 40 covalent O–H bonds and 69 hydrogen H···O bonds of different strength. Different models for the bond order index are tested using the Cioslowski–Mixon approach as a standard. A uniform description of the bond order indices for the covalent and H-bonds in the O–H···O fragment, ranging from 0.97 to 2.91 Å, is achieved using the electron density and electronic kinetic energy density features. The model describing the H-bond indices of the X–H···O fragment (X = O, N and C) in terms of electron density and potential energy density is also suggested.

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1. Introduction

The interest to the quantitative characterization of intermolecular interactions [1–6] is permanently supported by new theoretical and experimental results [7–9]. It especially concerns description of hydrogen bonds (H-bonds) in molecular complexes and crystals. The geometrical and energy characteristics in molecular systems with H-bonds have been described in the literature using various concepts and approaches. In particular, the great attention has been paid to the classification of the H-bonds formed by organic molecules in gas phase and condensed state [10–17]. Some of these studies deal with atomic interactions within X–H···Y fragments (X = O, N, C and Y = O, N) in terms of Quantum Topological Theory of Atoms in Molecules and Crystals (QTAIMC) [18]. The distance dependent variations of electron density (ED), ρ_b , at the H-bonds critical points (CP) have been described [19–22], the regions of closed shells atomic interactions with a significant covalent component have been identified [23–25], and the transition region separating these two limited cases has been determined [26,27]. Various correlations between the observed IR characteristics of H-bonded systems and the X–H/H···O or O···O distances of the X–H···O (X = O, N, C) fragment have also been suggested [28–30]. The link between the ED properties at the bond CP and interatomic distance for the different kinds of H···X interactions (X = C, N, O, F, S, Cl, π) have been studied in detail [31].

It is significant that the ED features allow one to consider uniformly the covalent and H-bonds using both quantum-chemical computations and high-resolution X-ray diffraction data [32–37]. This approach was recently applied to derive the covalent X–Y (X, Y = C, N, O) bond order indices, n_{topo} , via the ED at the bond CP, ρ_b [38–40] and the combination of the ED curvatures at the bond CP perpendicular to the bond line, λ_1 , λ_2 , and along the bond line, λ_3 [41–45]. As a result, the empirical equations with coefficients obtained from quantum-chemical calculations have been suggested for estimation of the n_{topo} values. These quantities have then been applied to calculate the covalent C–H, N–H, O–H bond order indices in some organic molecular crystals from an experimental (X-ray) ED.

The aim of the present work is to describe the hydrogen bond order indices in terms of QTAIMC. In addition, we will investigate the possibility to reach a uniform description of the hydrogen H···O and covalent X–H bond order indices in organic molecular crystals with the X–H···O (X = O, N and C) fragments. Then, we search for the model equations providing the best description of the H-bond order indices in terms of the QTAIMC. Finally, we compare the models for calculating O···H hydrogen bond and O–H covalent bond order indices.

2. Methodology

2.1. Sampling the O–H/H···O bonds based on the analysis of interatomic distances

The sample for the analysis of bond order indices has been formed by the selection of O–H/H···O bond set which evenly (i.e.

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without significant gaps) fill the range of interatomic distances from typical covalent and hydrogen bonds to weak intermolecular contacts in crystals. Using the Cambridge Structural Database CSD V5.30 [46,47] we selected the set of compounds, which form the intermolecular bonds by means of two adjacent carboxyl groups or by these groups and the water molecules. It has generated a wide range of interatomic distances with a relatively small number of the crystallographic structures: N-oxides of 2-pyridine and 2-quinoline carboxylic acids, perfluoroadipinic, pyrazinetetracarboxylic and oxalic acid hydrates and 4-hydroxycoumarin. The shortest H···O distances are observed in monoanions of dicarboxylic acids, e.g. 4,5-dichlorohydrophthalate-ion (1.19 Å) and hydromaleate-ion (1.21 Å).

Agglomerates formed by the neighboring molecules in a crystal were considered. They exhibit hydrogen bonds of several types, in addition to the O–H···O bonds naturally formed. For example, 8% of H-bonds in the sample were N–H···O bonds, represented by interactions in the cyclic dimers with carbonyl-amide interaction of neighboring molecules in a crystal. That is typical for acetamide, 2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid, etc. The C–H···O bonds (17% the sample) with the carbon atom mainly belonging to an aromatic or heteroaromatic ring were also included in consideration. The average interatomic distances for the observed C–H···O contacts in the crystals was 2.63 ± 0.23 Å, which is much more than the sum of the Van der Waals radii of oxygen and hydrogen atoms (1.72 Å according to the Bondi scale [48]).

The one-third of all considered bonds was the covalent O–H bonds. Carboxylic groups have formed 33% of covalent bonds; water molecules gave 25% of such bonds, while the rest bonds were formed by the hydroxyl groups in the alcohol and phenol fragments of molecules.

It should be stressed that application of the QTAIMC for calculation of bonding characteristics without explicit account for forces acting on nuclei implies the equilibrium geometry of a system. However the molecular structures obtained by X-ray diffraction do not correspond to an equilibrium state unless atomic positions are fixed by symmetry. In general, these are time-averaged structures. Moreover, the geometry of three-dimensional ordered crystal structure is different from the equilibrium geometry of a fragment (cluster) taken from the same crystal. In particular, significant conformational and intermolecular bond-length changes are observed in the H-bonded molecular cluster at the equilibrium as compared with a crystal. For example, the equilibrium-geometry cluster consisting of six water molecules surrounding the oxalic acid molecule (Fig. 1) shows the average O–H bond

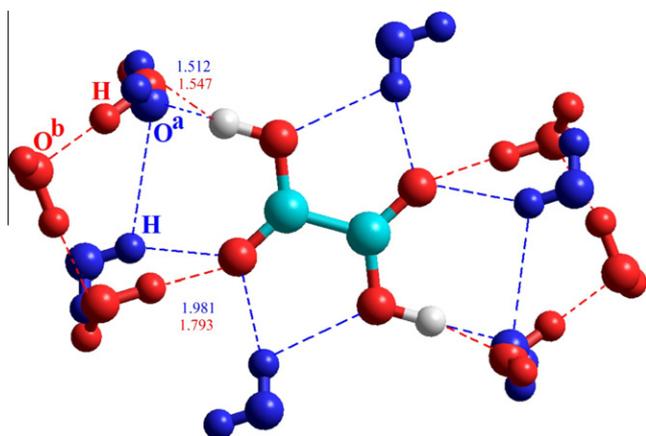


Fig. 1. O–H/H···O distances in oxalic acid dihydrate: X-ray diffraction data are given by red, B3LYP/6-31G(d,p) data are by blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

length elongation in the water molecules of 0.12 Å comparing with a crystal. The elongation of O–H bond in carboxylic acid group is relatively small (0.035 Å). In addition, the O atom of the carbonyl group forms different number of H-bonds in the cluster and crystal (Fig. 1).

Thus, the interatomic $d_{\text{H}\cdots\text{O}}$ distances obtained experimentally for molecular crystals and calculated for the isolated H-bonded systems at the equilibrium geometry, are different. It will lead to a difference in the corresponding ρ_b values. Taking that into account, we have considered those systems only which exhibit small change in the structural characteristics after extraction of the molecular cluster from a crystal. We have assumed that the probability of the interatomic distance deviation from its expectation value by amount larger than $3S = \sqrt{\sum_i (\Delta d_i)^2 / N}$ is nearly equal to zero. Here $\Delta d_i = d_{\text{O-H/H}\cdots\text{O}} - d_{\text{O-H/O}\cdots\text{H}}^{\text{CSD}}$ and $d_{\text{O-H/O}\cdots\text{H}}^{\text{CSD}}$ are interatomic distances for the structures taken from the Cambridge Structural Database, and N is the number of bonds in the sample. We have found that $3S = 1.31$ Å for our sample. The bond elongations did not exceed this value (Fig. 2); the appearance of $|\Delta d| > 3S$ values results from rearrangement of the system and changes of the set of interatomic contacts involved in the hydrogen bond. Therefore contacts with $|\Delta d| > 3S$ have been discarded.

As a result, our sample used for determination of the bond order indices contained 109 covalent O–H and hydrogen H···O bonds, with interatomic distances $d_{\text{O-H/H}\cdots\text{O}}$ ranging from 0.97 to 2.91 Å without significant gaps. The complete list of the compounds considered in this work is listed in Table S1.

2.2. Computations

Computations of the wave functions and harmonic frequencies for compounds listed in Table S1 have been carried out by the Kohn–Sham method in the B3LYP/6-31+G(d,p) approximation. The software package Firefly, version 7.1.G [49] has been used. It has already been demonstrated [50–54] that the B3LYP functional provides a satisfactory description of the exchange and electron correlation both in the gas-phase H-bonded systems consisting of more than 20 atoms with $2 \leq Z \leq 9$ and in molecular crystals. Also, the 6-31+G(d,p) basis set is suitable for the calculation of the structure and vibration frequencies of molecular systems with H-bonds [55,56]. The minimum-energy states of the molecular complexes have been confirmed by calculating the harmonic frequencies. Wave functions obtained have been used to perform the QTAIMC

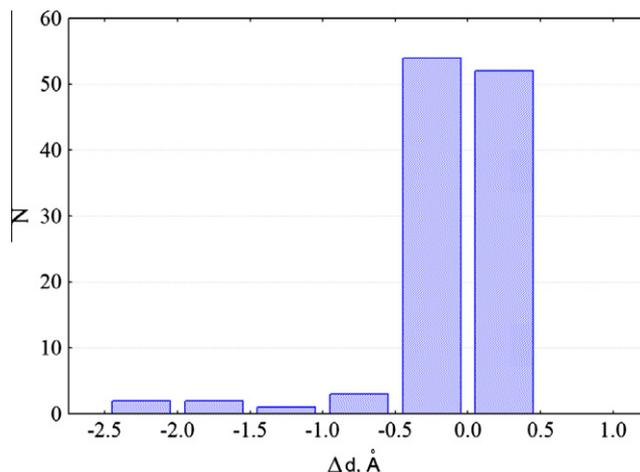


Fig. 2. The distribution of the Δd values, $\Delta d_i = d_{\text{O-H/H}\cdots\text{O}} - d_{\text{O-H/O}\cdots\text{H}}^{\text{CSD}}$, where $d_{\text{O-H/H}\cdots\text{O}}$ are interatomic distances computed using the B3LYP/6-31+G(d,p) approximation and $d_{\text{O-H/O}\cdots\text{H}}^{\text{CSD}}$ the corresponding distances taken from the Cambridge Structural Database.

analysis of the ED at the bond critical points of covalent and hydrogen bonds. The quantities ρ_b , $\nabla^2\rho_b$, λ_1 , λ_2 , λ_3 as well as the densities of potential energy, v_b , and kinetic energy, g_g , of electrons have been calculated using the AIMPACK and AIMALL software [57,58].

First, it is necessary to determine the quantitative expressions for H bond order indices. As a standard in the determination of a «quantum topological» bond order index, n_{topo} , we have used the Cioslowski–Mixon bond order values, n_{CM} [43]. In this method, the elements of the overlap matrix are computed for each atom A:

$$\langle \phi_i | \phi_j \rangle_A = \int_{\Omega_A} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r}$$

where ϕ_i are the localized molecular orbitals determined from the principle of maximum electron occupancy. Integration is carried out over an atomic basin A, Ω_A , restricted by the surface of a zero-flux ED gradient. This surface is determined by the condition $\nabla\rho(\mathbf{r}) \cdot \mathbf{n} = 0$, where \mathbf{n} is a unit vector which is normal to the surface. For the end atoms, the surface boundary was taken at $\rho = 0.002$ a.u. For a pair of atoms A and B, the products of corresponding diagonal elements of the overlap matrix are calculated and summed:

$$n_{CM} = \sum_k n_k^2 \langle \phi_k | \phi_k \rangle_A \langle \phi_k | \phi_k \rangle_B. \quad (1)$$

The electron populations of the orbitals, n_k , can be determined in different ways [59]. We took the overlap occupancy equal to two; that corresponds to the maximum electron population of bonding σ -MO.

To determine the QTAIMC bond order indices, n_{topo} , we followed the works [44–47]: n_{CM} values have been approximated by n_{topo} (ρ_b , $\nabla^2\rho_b$, λ_1 , λ_2 , λ_3 , v_b , g_g). The specific equations for n_{topo} are given and discussed below.

3. Results and discussion

3.1. The electron density at the H-bond critical points

For weak and intermediate H-bonds the bond critical points are characterized by the ED values of $0.004 < \rho_b < 0.105$ a.u. and positive values of the Laplacian of ED. H-bonds in carboxylic acid dimer are characterized by relatively high values of $\rho_b = 0.065 \pm 0.020$ a.u. On the contrary, the interaction of water protons with the carbonyl oxygen atom is characterized by $\rho_b = 0.032 \pm 0.010$ a.u. The same range of ρ_b values is observed in the carbonyl-amide N–H...O interactions. The upper ρ_b boundary for C–H...O interactions is $\rho_b = 0.020$ a.u. Threshold value for the weakest interactions in the sample corresponds to C–H...O contact where $\rho_b = 0.004$ a.u. and $d_{H...O} = 2.91$ Å.

Strong intramolecular O...H bonds exist in the monoanions of dicarboxylic acids, where the hydrogen atom binds a pair of oxygen atoms. Examples of such compounds from our sample are given in Fig. 3. The calculations show that the values of ED

$\rho_b = 0.180 \pm 0.030$ a.u. are observed for each such pair of O–H/H...O bonds. In particular, the absolute difference in the ρ_b values for such bonds in 4,5-dichloro-phthalate anion is 0.001 a.u., and in the hydrogen maleate anion it is 0.028 a.u. The latter H-bond is very strong; it is characterized by the negative Laplacian values at the bond CP: $-0.560 < \nabla^2\rho_b < -0.310$ a.u. These H-bonds correspond to the short interatomic distances $d_{O-H} \leq 1.23$ Å and exhibit the mean value $\rho_b = 0.320 \pm 0.030$ a.u. Most of these bonds are commonly described as typical covalent O–H bonds [22,25].

We note that covalent bonds in water molecules and hydroxyl-groups are characterized by the value of $\rho_b = 0.330 \pm 0.010$ a.u., O–H bonds of carboxyl groups in carboxylic acids exhibit lower values of $\rho_b = 0.310 \pm 0.040$ a.u.; even lower values of $\rho_b = 0.290 \pm 0.010$ a.u. are observed in CP of O–H bonds in strongly hydrated carboxyl groups. Thus our calculations reveal a regular decrease in the electron density at the critical points of covalent O–H bonds, the atoms of which are involved in intermolecular interactions.

3.2. Evaluation of the bond order indices for H-bonds using the quantum-topological characteristics

The calculated Cioslowski–Mixon bond order indices, n_{CM} , (1) are within the range of 0.38–0.51 for covalent O–H bonds of carboxyl groups. In cyclic dimers of carboxylic acids, the average n_{CM} value for O–H bonds exceeds that in the cases when the carboxyl group is hydrated. The O–H bond order indices in water molecules vary from 0.45 till 0.58, they are larger than the corresponding values in carboxylic groups. The hydrogen bond formation leads to the elongating of O–H bond and, respectively, to the decreasing of n_{CM} values. Therefore, the n_{CM} values of the covalent O–H bonds exhibit the characteristic ranges for different functional groups (Fig. 4a) and reflect the degree of a proton participation in hydrogen bonding: stronger a proton is involved to an intermolecular interaction, longer the covalent bond and lower the bond order index.

The majority of H...O bonds in the studied sample correspond to the interatomic distances of $1.38 \leq d_{H...O} \leq 2.91$ Å and $n_{CM} < 0.20$ (Fig. 4b). Typically, the greatest distances $2.11 < d_{H...O} < 2.91$ Å are observed for the C–H...O bonds with the bond order indices $0.014 < n_{CM} < 0.073$. It is interesting to note that the longest C–H...O bonds by no mean correspond to the lowest n_{CM} index. For example, the lowest values of the bond order indices in the sample $n_{CM(O-H...O)} = 0.008$ (2.45 Å) and 0.012 (2.48 Å) are met in the fragments, where a proton forms bifurcated H-bond with O atoms of the carbonyl group of the same molecule and O atoms of the functional groups of adjacent molecules.

On the other hand, the relatively short (less than 1.30 Å) hydrogen bonds, which take place in the dicarboxylic acids or their monoanions, where a proton is split between the oxygen atoms of adjacent carboxyl groups, show $0.29 < n_{CM} < 0.31$. Thus, studied array of n_{CM} values has two small gaps in the areas $0.20 < n_{CM} < 0.28$ and $0.32 < n_{CM} < 0.35$, resulting in the three intervals of bond order

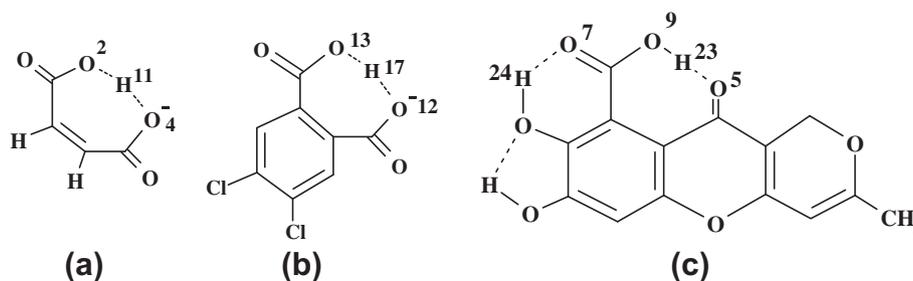


Fig. 3. The H-bonds in the hydrogen maleate ion (a), hydrogen 4,5-dichloro-phthalate ion (b) and 7,8-dihydroxy-3-methyl-10-oxo-1H,10H-pyrano[4,3-b]chromene-9-carboxylic acid (c).

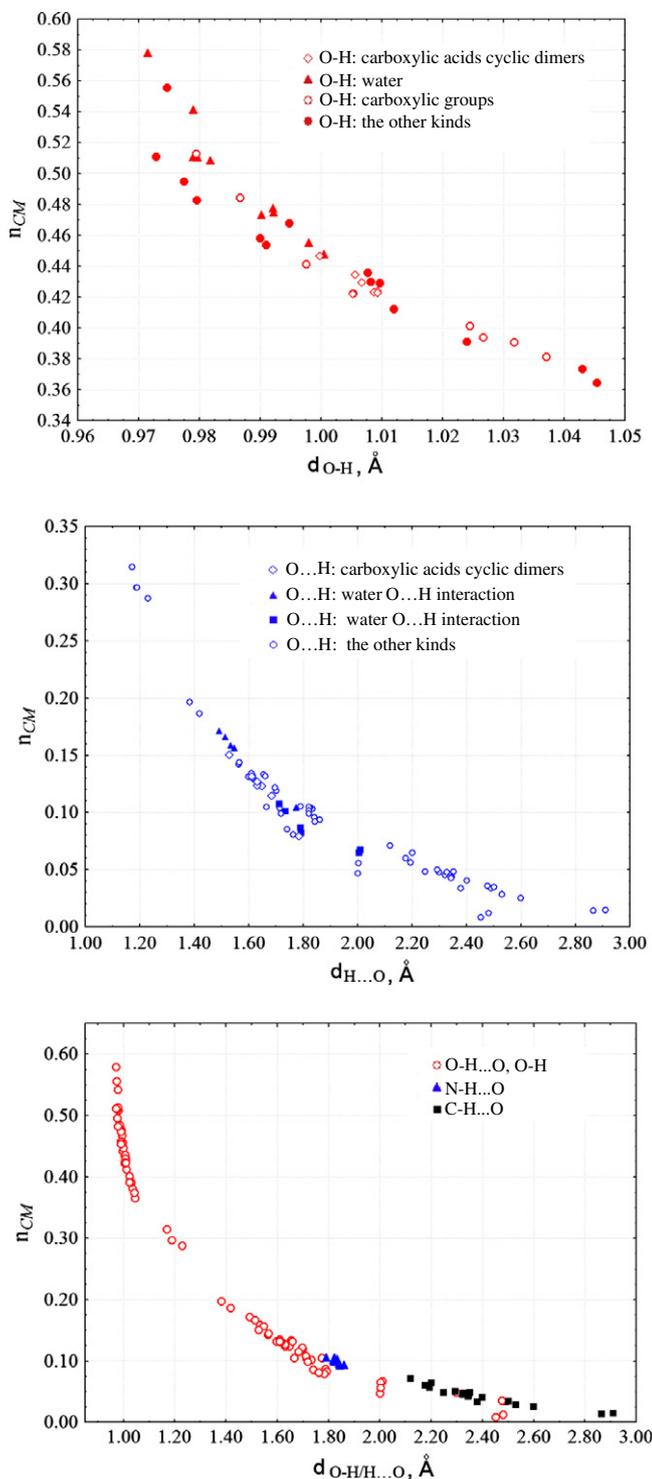


Fig. 4. The bond-order indices n_{CM} versus the O–H/H...O interatomic distances, $d_{O-H/H...O}$: (a) the O–H bonds for various functional groups in organic molecules: triangles show the covalent bonds in water, empty markers show bonds in carboxylic groups; (b) the X–H...O bonds with water O or H atoms participations as well as those in carboxylic acid cyclic dimers; (c) The whole set of the O–H...O (red), N–H...O (blue) and C–H...O (black) bonds studied in this work. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

indices. The n_{CM} values corresponding to the relevant interatomic distances are presented in Fig. 4c. The first interval characterizes the weak and moderate H-bonds, while the second one includes the strong H-bonds, and the third one describes the covalent bonds including those that are elongated as a result of intermolecular

interactions. The areas of these intervals are point-depleted due to a relatively low probability of the stable configurations for the structures with bonds of intermediate character. Our methodology for sampling bonds which vary slightly because of the geometry optimization provides only a little expansion for existing gaps. The gaps are caused by fundamental inherent deficiency of bonds of intermediate character.

Searching for the “quantum-topological” bond order indices, n_{topo} , first of all, we tested Eq. (2), where only the features of the electron density at bond critical points are considered as the factors (the atomic units are used throughout this work):

$$n_{topo,1} = a_0 + a_1 \rho_b + a_2 (\lambda_1 + \lambda_2) + a_3 \lambda_3. \quad (2)$$

The following physical interpretation can be given to this expression with regard to the hydrogen bonds: ρ_b and λ_3 values characterize the strength and length of H-bonds, whereas the ED curvature parameters, λ_1 and λ_2 , perpendicular to the bond line, estimate the degree of contraction of the electron density to the bond path [26].

The a_i parameters from Eq. (2) were found for both all O–H/H...O bond from the sample, as well as for the covalent and H-bonds separately. We found that the covalent bond order indices, $n_{topo,1}(O-H)$, calculated by Eq. (2), reproduce the n_{CM} values well: the deviation distribution obeys the normal law, and the deviation values do not exceed $\Delta = -0.017$, where $\Delta = n_{CM} - n_{topo,1}(O-H)$. However, the term a_0 in (2) appears to be small (<0.01) for H-bonds. Therefore we have put $a_0 = 0$ and calculated the parameters of new equation:

$$n_{topo,2} = a_1 \rho(r_b) + a_2 (\lambda_1 + \lambda_2) + a_3 \lambda_3. \quad (3)$$

The results are shown in Fig. 5. In this case, relatively small difference between “quantum-topological” H-bonds order and n_{CM} (Table 1) have also been observed, the largest of which was $\Delta = -0.029$, where $\Delta = n_{CM} - n_{topo,2}(O...H)$. The error percentage is also small confirming a suitability of the model (3) for the description of H-bond order indices.

According to the Table 1, different types of H-bonds, such as O–H...O, N–H...O and C–H...O, have the n_{topo} values comparable to those for the O–H...O bonds only. On the one hand, this may be considered as a sign of universality of Eq. (3). On the other hand, it may result from a limited set of the N–H...O and C–H...O bonds presented in the sample. More reliable conclusions would require the analysis of larger amount of stronger N–H...O hydrogen bonds.

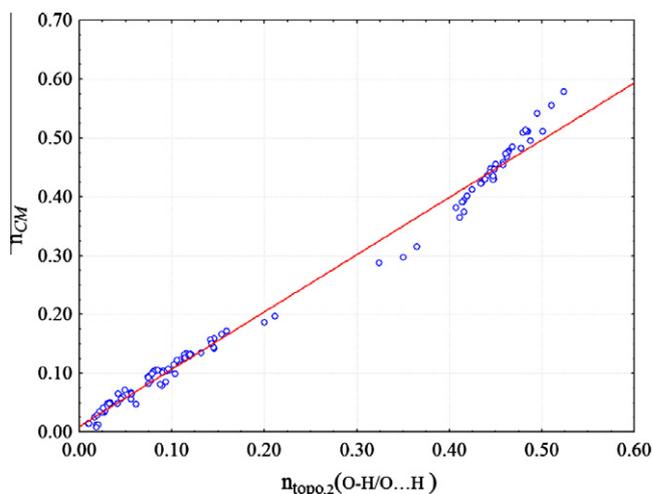


Fig. 5. The bond-order indices $n_{topo,2}$, Eq. (3), versus n_{CM} values for the whole sample of O–H/O...H bonds.

Table 1

Summary of the bond-order model parameters. All values are given in the atomic units.

Bond (bonds number)	a_1	a_2	a_3	a_0
<i>Model (3)</i> $n_{topo,2} = a_1\rho(r_b) + a_2(\lambda_1 + \lambda_2) + a_3\lambda_3 + a_0$				
O–H (40)	5.27	0.11	–0.59	0.0
O–H/H··O (109)	3.32	0.14	–0.10	0.0
O–H··O (42)	3.45	0.23	–0.05	0.0
O–H··O/N–H··O/C–H··O (69)	5.29	0.36	–0.25	0.0
<i>Model (4)</i> $n_{topo,g} = a_1\rho_b + a_2(\lambda_1 + \lambda_2) + a_3g_b$				
O–H/H··O (109)	8.24	0.55	–5.18	0.0
<i>Model (5)</i> $n_{topo,v} = a_1\rho_b + a_2v_b + a_0$				
H··O (69)	2.62	0.64	0.0	0.015

The number of these bonds, available for analysis, is however very limited (see [59]).

An attempt to describe both H··O and O–H bonds by the same Eq. (3) showed that this model demonstrates a significant deviation of calculated values $n_{topo,2}$ for strong hydrogen bonds in monoanions of dicarboxylic acids. There is a significant deviation of the points at the middle of the range below the straight line corresponding to Eq. (3) – see Fig. 5. The overestimation of the bond order indices for strong hydrogen bonds makes them quantitatively indistinguishable from ones for covalent bonds. This complicates the prediction of bond order values. Moreover, it is clear that the linear model (2) provides the correct bond order indices separately for covalent or H-bonds. The comparison of the parameters for different bond types with data presented in Fig. 5 leads us to the conclusion that the model (3) is not applicable for simultaneous consideration of covalent and H-bonds.

3.3. Models for the quantum topological bond order indices of H-bonds based on the kinetic and potential energy densities

To minimize the deficiency noted for monoanions of dicarboxylic acid and preserve the relevance of all factors describing the bond order indices for the different ranges of values, we have modified the model and considered different combinations of pairs and triples of such factors as electron density, ρ_b , Laplacian of electron density, $\nabla^2\rho_b$, electron density curvatures, λ_1 , λ_2 and λ_3 , as well as kinetic, g_b , potential, v_b , electronic energy density at a bond critical point. The entire range of O–H/H··O interatomic distances has been taken into consideration. As a result, the new equation:

$$n_{topo,g} = a_1\rho_b + a_2(\lambda_1 + \lambda_2) + a_3g_b \quad (4)$$

has been found: it provides the QTAIMC bond order indices that correlate well with the Cioslowski–Mixon n_{CM} values. The kinetic energy density of electrons in Eq. (4) is $g_b(\mathbf{r}) = \frac{1}{2}\sum_i\nabla\phi_i(\mathbf{r})\cdot\nabla\phi_i(\mathbf{r})$. The parameters of model (4) have been obtained for the range of interatomic distances of $0.97 < d_{O-H/H\cdots O} < 2.91$ Å without significant deviations for the strong H-bonds, which had previously been observed in monoanions of dicarboxylic acids. The correlation coefficients and the deviation range (Table 2), represented by its extreme values, Δ_{max} , show that the model (4) is highly competitive with (3). The model enables us to evaluate the bond order indices for intermediate covalent and hydrogen O–H/H··O bonds. Fig. 6 shows the correlation between $n_{topo,g}$ (4) and n_{CM} values for the entire considered range of O–H/H··O bonds.

Extrapolation of the relationship (4) to the adjacent ranges of bond order indices does not make the quality of the model worse. Therefore, we can conclude that an accurate uniform description of QTAIMC bond order indices for covalent and hydrogen O–H/H··O bond type is feasible. We can speculate that the corresponding model can be considered as a universal one in a wide range of interatomic distances.

Table 2

Summary of the statistics of the bond-order models.

Bond (the bond number)	R	Deviation range, max Δ /min Δ	$\Delta^2 = \Sigma$ (pred – obs) ²
<i>Model (3)</i>			
O–H (40)	0.994	0.010/–0.017	0.001
O–H/H··O (109)	0.994	0.055/–0.054	0.041
O–H··O (42)	0.993	0.010/–0.021	0.003
O–H··O/N–H··O/C–H··O (69)	0.991	0.013/–0.029	0.006
<i>Model (4)</i>			
O–H/H··O (109)	0.998	0.033/–0.024	0.009
<i>Model (5)</i>			
H··O (69)	0.991	0.015/–0.023	0.006

We have also tested the model relating the bond order indices for H-bonds with potential energy density, v_b , which becomes more negative with increasing the bond strength. At the equilibrium geometry

$$v_b(\mathbf{r}) = -\sum_a\rho(\mathbf{r})\frac{Z_a}{\mathbf{r}-\mathbf{R}_a} + \int\frac{\Gamma(\mathbf{r},\mathbf{r}')}{\mathbf{r}-\mathbf{r}'}d\mathbf{r}' + V_n(\mathbf{r})$$

where $\Gamma(\mathbf{r},\mathbf{r}_1)$ is two-electron density matrix, calculated with MO ϕ_i , where Z_a is a nuclear a charge; V_n stands for the nuclear–nuclear repulsion energy density. We have found that the relationship

$$n_{topo,v} = a_0 + a_1\rho_b + a_2v_b \quad (5)$$

is suitable for determination of H··O bond orders: the correlation coefficient between n_{CM} values and $n_{topo,v}$ (H··O) is 0.991 (Fig. 7). The number of factors in Eq. (5) is reduced with Eq. (4). Good accuracy of fitting was reached: the deviation $\Delta_3 = n_{CM} - n_{topo,v}$ (H··O) does not exceed –0.023. This indicates that the model (5) is preferable in comparison with the models (2), (3) and (4).

According to (5), the bond order index of the hydrogen bonds increases when ρ_b increases and v_b decreases. Note that with v_b decreasing, $n_{topo,v}$ of weak H-bond ($d_{O\cdots H} > 1.72$ Å) increases more rapidly than $n_{topo,v}$ of relatively strong H-bonds. Very weak hydrogen bonds are characterized by small negative values v_b , which are very close to zero.

Thus, potential energy density at the critical point of H-bond, v_b , serves as an important factor in estimating H··O bond order indices. Because v_b is sometimes used to estimate H··O bond energy [60], we will discuss this point below.

4. Discussion

Comparing the models (3), (4) and (5), we can stress the deficiencies and advantages for each of them. Eq. (3) with separately fitted parameters for covalent and H-bonds yields reasonable n_{CM} description, $R = 0.994$ and 0.991 , respectively (Table 2). Model (4) does not have such shortcoming as it does not require correction of the parameters used for calculating of covalent and H-bond order indices, $R = 0.998$. Model (5) includes only two factors however it is applicable to the H-bonds only, $R = 0.991$.

It is worth to stress that Eq. (3) includes experimental observable quantities, namely, the curvatures of the electron density and the electron density itself, all evaluated at the BCP. This is quite significant because in this case the bond-order indices can be determined immediately from the experimental (X-ray) density. The other equations are also important and interesting of course, but they correlate quantities only accessible through quantum mechanical calculations or ask for additional approximations.

Comparing the H-bond dissociation energy and $v_b(d_{O\cdots H})$ dependence, Espinosa et al. [60] have revealed the correlation between hydrogen bond energy, E_{H-bond} , and electronic potential energy at

the bond CP, v_b : $E_{\text{H-bond}} = -\frac{1}{2} v_b$ (in the atomic units). This relationship has been used to estimate the H-bond energies in the gas-phase systems and molecular crystals [61–64]. The present study deals with mostly moderate or weak H-bonds (see Table S1) and their average H-bond energy according to Espinosa is ~ 12 kcal/mol. However the estimation of $E_{\text{H-bond}}$ for strong H-bonded systems with a charged $\text{O} \cdots \text{H} \cdots \text{O}$ fragment (maleate anion, H_5O_2^+ , etc.) would result in too large values achieving 90 kcal/mol. Thus, the Espinosa equation [60] is not suitable to estimate the energy of strong H-bonds in the gas-phase systems. In our opinion, this equation is applicable for the gas-phase systems with moderate and weak H-bonds ($d_{\text{O} \cdots \text{H}} > 1.6 \text{ \AA}$). This conclusion is supported by comparison with the energies evaluated by the alternative methods, e.g. see [39].

We have found that consideration of the wider range of interatomic distances (Fig. 8) reveals the non-linear behavior of v_b as function of $d_{\text{O} \cdots \text{H}}$. Neglecting this nonlinearity for short H-bonds, as well as linear [61] extrapolation to the bonds of other types, with unknown ranges of linear behavior, will lead to the incorrect energy characteristics. This conclusion, in particular, confirms the results of [65].

Note, that the explicit account for electron correlation in X–H/H \cdots X bonds using MP2 method leads to the changes in ED and Laplacian of the ED at the bond critical point by 0.004 and 0.04

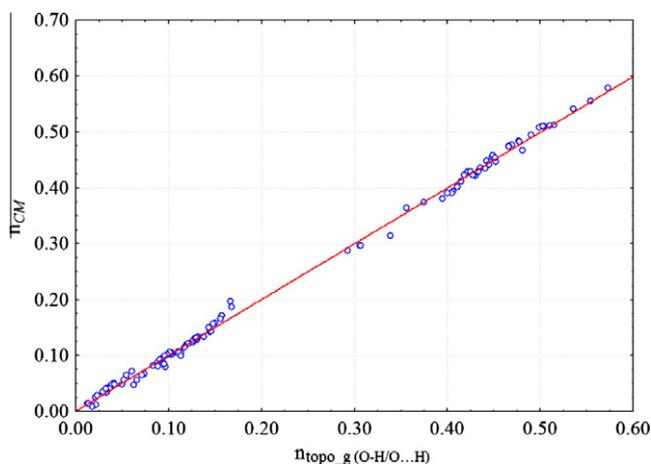


Fig. 6. The bond-order indices n_{topo_g} , Eq. (4), versus n_{CM} values for the whole sample of O–H/O \cdots H bonds.

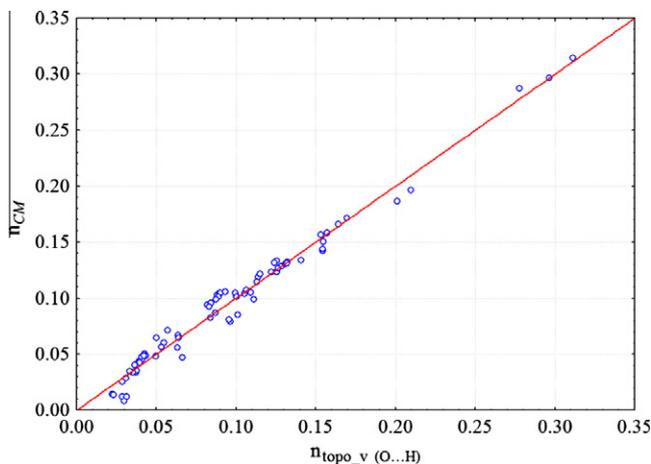


Fig. 7. The bond-order indices n_{topo_v} , Eq. (5), versus n_{CM} values for the whole sample of O–H/O \cdots H bonds.

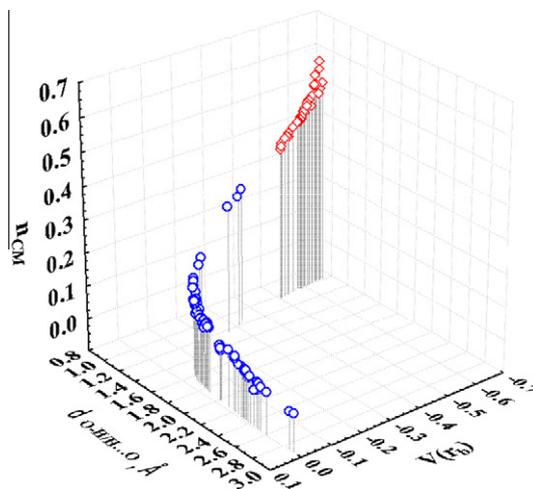


Fig. 8. Interdependence of the densities of the potential energy values v_b (a.u.), bond orders (n_{CM}) and O–H/O \cdots H interatomic distances ($d_{\text{O-H/O} \cdots \text{H}}$, Å).

a.u., correspondingly [66]. Therefore our results do not need to be corrected for electron correlation using empirical method of the DFT-D type [67,68].

To put our results to the perspective, we note that the bond order index is connected to the delocalization index [69–72] measuring the number of pairs shared between any two atoms in a molecule [73]. It can also be related to the bond energies as suggested in [74,75]. Therefore, the further exploration of these dependencies might be useful for the properties prediction. It is also important that the model parameters derived in this study can be directly applied to estimate the H-bond order indices in crystals using experimental electron density, because structural modifications do not change the exponential relation between ρ_b and $d_{\text{H} \cdots \text{O}}$. The work in this direction is now in progress in our group.

5. Summary

We have demonstrated that the parametric model relating the bond order indices with the properties of electron density at the bond critical point, such as ρ_b , λ_1 , λ_2 and λ_3 can be applied for the description of hydrogen bonds. The parameters of the model which give a satisfactory description of the bond order indices for both H-bonds and the O–H covalent bonds have been found as well.

The new models describing good quality H-bond order indices in molecular clusters and crystals in terms of quantum topological characteristics $\rho_b(\lambda_1 + \lambda_2)$ and g_b (Eq. (4)) or ρ_b and v_b (Eq. (5)) have been suggested. Applicability of these models for the description of weak H-bonds in N–H \cdots O and C–H \cdots O fragments has also been demonstrated. The uniform description of the X–H and H \cdots O bonds forming the X–H \cdots O fragment, with X = O, N, C, has been achieved.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.comptc.2011.06.025.

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