

# A scheme estimating the energy of intramolecular hydrogen bonds in diols

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**Abstract**—The relative energies of conformers of 1,2-ethanediol, 1,3-propanediol, and 1,4-butanediol are split into a sum of five different terms including the intramolecular OH···O interaction. This scheme allows to estimate the energy of the O–H···O intramolecular hydrogen bond of the tGG'g and gGG'g conformers of 1,3-propanediol, the g'GG'Gt and g'GG'Gg conformers of 1,4-butanediol, and the energy of the non-bonded O–H···O interaction in the g'Gt, g'Gg and g'Gg' conformers of 1,2-ethanediol. This scheme provides pure hydrogen bond energies without assuming the geometry and/or electronic features to be constant between the conformation having a IHB and a reference conformation. The fitted energies show a perfect linear correlation with the corresponding  $r(\text{H}\cdots\text{O})^{-1}$  values. QTAIM atomic electron population and energies of the donor hydrogen calculated along the H–O–C–C internal rotation are found to be linearly correlated. These linear correlations display small changes at the BCP formation in 1,3-propanediol.

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## 1. Introduction

The sequence of stability of the different conformers of 1,2-diols and 1,3-diols have been traditionally explained by the presence of O–H···O intramolecular hydrogen bonds<sup>1–8</sup> (IHBs), however, other important features can play an important role in the stability of these compounds.

The energy of most intermolecular hydrogen bonds can be calculated to a good approximation as the difference between the energies of dimer and monomers (as long as no other important interactions or geometry distortions accompany the dimer formation and the basis set superposition error, BSSE, correction is included in the calculation<sup>9</sup>). However, when a similar formula is applied to IHB (in this case using the energies of conformers with and without hydrogen bonding), it yields a very crude estimation, principally owing to the fact that other internal interactions display significant changes and appear or disappear from one conformer to another (as those mentioned below for 1,2-diols and 1,3-diols). Thus, most of the IHB energies provided previously were obtained by assuming that IHB was the sole structural feature that modified the energy with regard to an arbitrary chosen reference conformation in which the

IHB is broken. Therefore, several different IHB energies could only be given for a certain conformer of a given molecule.

In a previous work, Lipkowski et al. estimated the energy of O–H···N IHBs in chloro-derivates of 2-(*N*-dimethylamino-methyl)-phenols<sup>10</sup> by using the energies of several conformers, which display different steric effects. They were able to separate these steric effects from the energy of the IHB. The so obtained values were correlated with the donor/acceptor distances,  $r(\text{N}\cdots\text{H})$ . This work aims to achieve this goal in diols by splitting relative conformational energies into several energy terms. These terms were selected on the basis of the variations displayed by atomic energies computed within the framework of the quantum theory of atoms in molecules (QTAIM)<sup>11,12</sup> for diverse conformers and molecules.

The conformational features of 1,2-ethanediol and 1,3-propanediol were largely studied by Bultinck et al.<sup>3</sup> who described all the conformers of both compounds. However, as this work dates from 1995, only HF levels were employed for geometry optimizations, using 6-31++G\*\* and 4-31+G\* basis sets for 1,2-ethanediol and 1,3-propanediol, respectively. The energies of the different conformers were also calculated at the MP2 level and two possible IHBs were characterized (only using geometrical criteria) for the g'Gt and g'Gg conformers of 1,2-ethanediol and tGG'g and g'GG'g conformers of 1,3-propanediol.

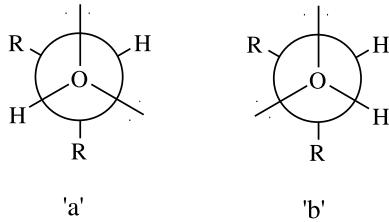
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Other works have also treated the issue of the IHB in diols using only geometrical criteria. Thus, Reiling et al.<sup>4</sup> proposed the presence of a double IHB in the g'Gg' conformer of 1,2-ethanediol.

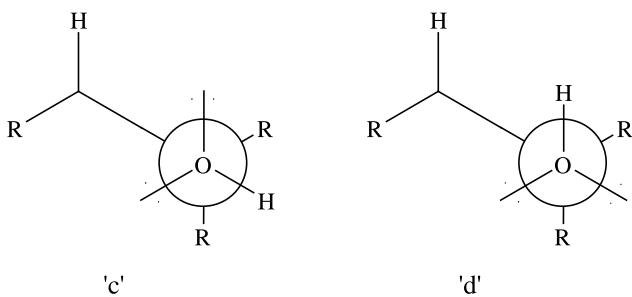
The QTAIM supplies a rigorous way to characterize IHBs. The presence of a hydrogen bond requires a bond critical point (BCP) placed between donor and acceptor atoms and a bond path linking them<sup>13,14</sup>. This topological criterion was applied in diols by Klein<sup>15,16</sup>, and more recently by Mandado et al.<sup>17</sup> No topological hydrogen bond was found in these studies for the conformers of 1,2-ethanediol. On the contrary, some conformers of 1,3-propanediol display BCP's associated to IHB.<sup>15</sup>

It has recently been found, using the framework of the QTAIM, that the stability of the gauche conformers in anomeric molecules, such as methanediol, can be explained by the migration of some electron population from the methylene hydrogens to the central carbon and oxygens.<sup>18</sup> This migration takes place when the hydrogens are gauche with respect to the lone pairs (LPs) of the oxygens (conformation 'a' in Scheme 1). The reduction of electron population increases the energies of the hydrogens but is accompanied by a larger decrease of the energies of the central carbons and oxygens, yielding conformer stabilization. The two hydroxyl groups in diols can adopt different conformations with respect to their  $\alpha$ -methylene, where such stabilization may be present or not, playing an important role for the relative conformational energy.



Scheme 1.

Also, for the same arrangement of the molecular backbone formed by C and O atoms, the disposition of the hydroxyl group gives rise to very different steric interactions with its  $\beta$ -methylene (conformations 'c' and 'd' in Scheme 2) as indicated by the corresponding OH...HC distances. Obviously, they can alter significantly the conformational energy, with hydrogens being stabilized in the 'c' conformation.



Scheme 2.

In the present study, we have performed an estimation of the energy of bonding and non-bonding OH...O interactions in 1,4-butanediol, 1,3-propanediol, and 1,2-ethanediol using the energies of different conformers and considering the main conformational features, which govern the order of stability in these compounds. All stable conformers of 1,2-ethanediol were considered, nevertheless only the stable nGG'n (with n=t,g,g') conformers of 1,3-propanediol and the nGG'Gn conformers of 1,4-butanediol were considered as they are the only ones in which allow the possibility of an IHB. We have also investigated the relations between these energies and the donor/acceptor distances,  $r(O\cdots H)$ , and have compared them with those in the intermolecular bonding in the methanol dimer.

### 1.1. Methodology and geometrical features

The geometries and electron densities of all stable conformers of 1,2-ethanediol were determined at the B3LYP/6-311++G(2d,2p) level. Ten different conformers (shown in Fig. 1) were obtained and are named using the nomenclature presented by Radom et al.<sup>2</sup> The values of  $r(OH\cdots O)$  distances are shown in Figure 1 for all the conformers, which are susceptible to have an OH...O IHB. The hydrogen or carbon atoms stabilized by 'gauche' interactions with oxygen lone pairs (as mentioned in the introduction) and those stabilized by the hydroxyl arrangement with regard to  $\beta$ -methylene, are also indicated in Figure 1 by displaying the atoms in question in parenthesis or brackets, respectively.

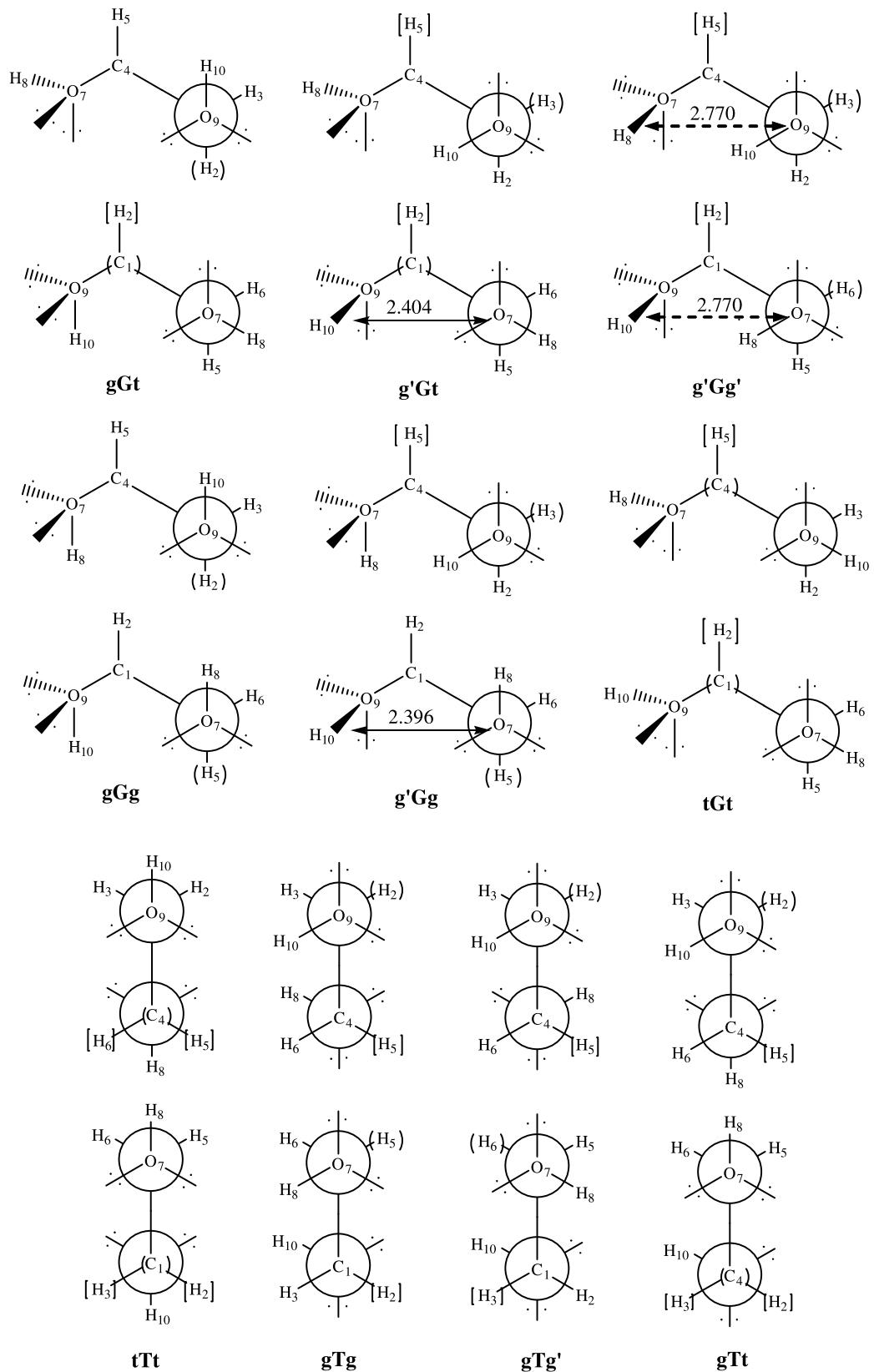
Although the OH...O distance is not exactly the same in g'Gt and g'Gg conformers, the difference is so small that we consider the OH...O interaction to be the same in both molecules (referred to as  $\Delta E_{OH\cdots O}$  in this work). This interaction is certainly different in the g'Gg' conformer, where the two OH...O distances are quite different with respect to those of g'Gt and g'Gg. Therefore, a different energy will be given to this interaction in this conformer.

On the other hand, 'gauche' interactions are supposed to be very similar in different conformers. Consequently, a common value denoted by, respectively,  $\Delta E_{g(H)}$  and  $\Delta E_{g(C)}$ , for hydrogens and another for carbons are given to these interactions. In order to simplify the calculations, the energy difference between c and d conformations (Scheme 2), due to the different interactions among  $\beta$ -methylenes and the hydroxyl group, is represented by a common value for all the conformers,  $\Delta E_{OH\cdots HC}$ . This is equivalent to use average values for both terms. The results obtained for  $\Delta E_{OH\cdots O}$ , which will be commented on in the next chapter, indicate this is not too crude an approximation.

Thus, the equation employed in this study to rationalize the interactions in the different conformers is:

$$\Delta E_{conf}^{C_1-C_2} \approx \Delta E_{OH\cdots O} + (n^{C_1} - n^{C_2})_{OH\cdots HC} \Delta E_{OH\cdots HC} \\ + (n^{C_1} - n^{C_2})_{g(H)} \Delta E_{g(H)} \\ + (n^{C_1} - n^{C_2})_{g(C)} \Delta E_{g(C)} + \Delta E' \quad (1)$$

When the two conformations compared have the same backbone conformations, both G or both T,  $\Delta E'$  is equal to

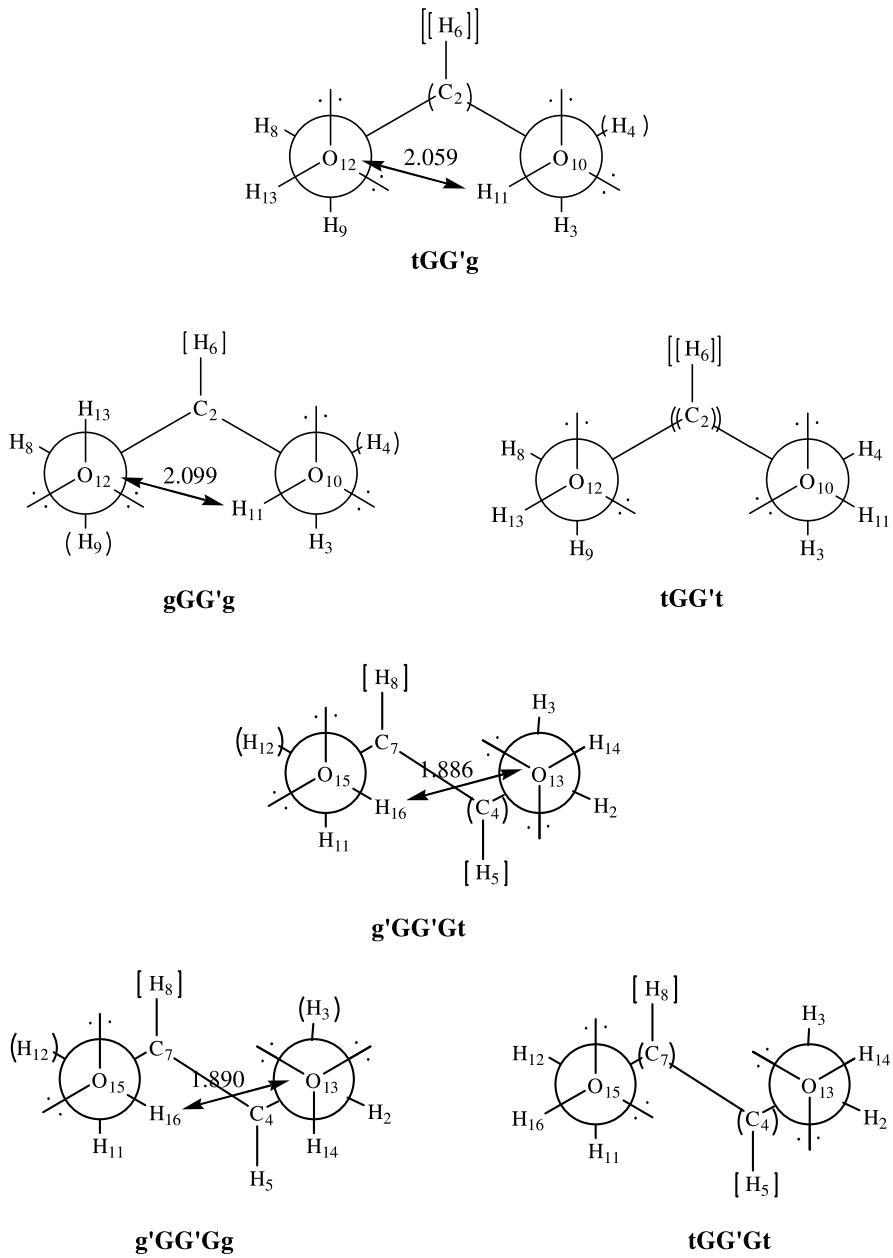


**Figure 1.** Plot of all stable conformers of 1,2-ethanediol. The nomenclature, atomic numbering and OH···O distances are shown. The 'gauche' stabilizations of hydrogens and carbons are marked by displaying the corresponding atoms in parenthesis, while stabilizations due to the relative arrangements of  $\beta$ -methylene and hydroxyl groups are indicated by displaying the corresponding atoms in brackets.

zero, as is  $\Delta E_{\text{OH}\cdots\text{O}}$  for those conformations where no IHB is present.  $(n^{C_1} - n^{C_2})_{\text{OH}\cdots\text{HC}}$  represent the difference in the number of  $\text{OH}\cdots\text{HC}$  interactions in conformations 1 ( $n^{C_1}$ ) and in conformation 2 ( $n^{C_2}$ ). Terms involving  $g(\text{H})$  and  $g(\text{C})$  have a similar meaning.

Calculations of atomic populations,  $N(\Omega)$ , and atomic energies,  $E(\Omega)$ , of all the conformers studied for 1,2-ethanediol and 1,3-propanediol have been performed in order to interpret the results provided by the energy partitioning proposed by Eq. 1. These atomic properties were obtained within the framework of the QTAIM<sup>11,12</sup>. We have paid special attention on the atomic properties of hydrogens as these atoms are involved in all the interactions included in Eq. 1, and the effect of the conformational changes will reflect on them.

The B3LYP/6-311++G(2d,2p) level was also employed to calculate the geometries and electron densities of the conformers of 1,3-propanediol and 1,4-butanediol that are susceptible to present IHB. Thus, only the nGG'n and nGG'Gn arrangements were considered for 1,3-propanediol and 1,4-butanediol, respectively, yielding three stable conformers for each molecule, which are shown in Figure 2 together with their  $r(\text{OH}\cdots\text{O})$  distances. The ‘gauche’ stabilization of hydrogens or carbons due to the oxygen lone pairs and those due to the hydroxyl arrangement with regard to  $\beta$ -methylene, are also indicated in Figure 2 similarly as in Figure 1 for 1,2-ethanediol. The gGG'g conformation of 1,3-propanediol was not characterized as a stable conformer, contradicting the results obtained by Bultinck et al.<sup>3</sup> at HF level of theory. The estimation of  $\Delta E_{\text{OH}\cdots\text{O}}$  in 1,3-propanediol and 1,4-butanediol was performed constraining



**Figure 2.** Plot of the conformers of 1,3-propanediol and 1,4-butanediol here studied. The nomenclature, atomic numbering and  $\text{OH}\cdots\text{O}$  distances are shown. The ‘gauche’ stabilizations of hydrogens and carbons are marked by displaying the corresponding atoms in parenthesis while stabilizations due to the relative arrangements of  $\beta$ -methylene and hydroxyl groups are indicated by displaying the corresponding atoms in brackets.

**Table 1.** Molecular total energies ( $E$ ) and energy differences ( $\Delta E$ ) relative to the stablest conformation, energy differences calculated using QTAIM theory ( $\Delta E^{\text{AIM}}$ ) and their differences to  $\Delta E$  in parenthesis, energy differences calculated using Eq. 1 ( $\Delta E^{\text{conf}}$ ) and their differences to  $\Delta E$  in parenthesis, for all conformers of 1,2-ethanediol and the nGG'n and nGG'Gn conformers of 1,3-propanediol and 1,4-butanediol, respectively

	$E$ (au)	$\Delta E$ (kcal mol $^{-1}$ )	$\Delta E^{\text{AIM}}$ (kcal mol $^{-1}$ )	$\Delta E^{\text{conf}}$ (kcal mol $^{-1}$ )
g'Gt	−230.3465	0.00 <sup>a</sup>	0.00 (0.00)	0.00 (0.00)
g'Gg	−230.3460	0.32 <sup>a</sup>	0.14 (−0.18)	0.10 (−0.22) <sup>b</sup>
g'Gg'	−230.3452	0.83 <sup>a</sup>	0.41 (−0.42)	0.80 (−0.03)
gGg	−230.3421	2.77 <sup>a</sup>	2.45 (−0.32)	2.78 (0.01)
tGt	−230.3419	2.94 <sup>a</sup>	2.74 (−0.20)	2.94 (0.00)
gGt	−230.3412	3.35 <sup>a</sup>	3.20 (−0.15)	3.04 (−0.31) <sup>b</sup>
gTg'	−230.3427	2.43 <sup>a</sup>	2.36 (−0.07)	2.47 (0.04)
tTt	−230.3426	2.47 <sup>a</sup>	2.56 (−0.09)	2.47 (0.00)
gTt	−230.3425	2.52 <sup>a</sup>	2.33 (−0.19)	2.57 (0.05) <sup>b</sup>
gTg	−230.3423	2.64 <sup>a</sup>	2.55 (−0.09)	2.67 (0.03)
tGG'g	−269.6738	0.00 <sup>c</sup>	0.00 (0.00)	0.00 (0.00)
gGG'g	−269.6737	0.05 <sup>c</sup>	−0.30 (−0.35)	0.00 (−0.05)
tGG't	−269.6652	5.37 <sup>c</sup>	5.12 (0.29)	5.37 (0.00)
g'GG'Gt	−309.0009	0.00 <sup>d</sup>		0.00 (0.00)
g'GG'Gg	−309.0005	0.25 <sup>d</sup>		0.00 (−0.25)
tGG'Gt	−308.9901	6.78 <sup>d</sup>		6.78 (0.00)

<sup>a</sup> Values calculated with respect to the g'Gt conformer.

<sup>b</sup> Conformers, which were not used to calculate  $\Delta E^{\text{conf}}$  parameters.

<sup>c</sup> Values calculated with respect to the tGG'g conformer.

<sup>d</sup> Values calculated with respect to the g'GG'Gt conformer.

$\Delta E_{\text{OH}\cdots\text{HC}}$ ,  $\Delta E_{\text{g}(\text{H})}$ , and  $\Delta E_{\text{g}(\text{C})}$  to their values obtained for 1,2-ethanediol. This assumption is based on the fact that the values of  $r(\text{OH}\cdots\text{HC})$  distances and the QTAIM atomic properties, are all quite similar.

Finally, some conformational interchange processes of 1,2-ethanediol and 1,3-propanediol were studied, in particular we have studied the changes displayed by the atomic properties of hydrogens involved in IHB.

The geometrical optimization and the calculation of the electron density were performed with Gaussian03 program.<sup>19</sup> The atomic properties were determined using the AIMPAc suite of programs<sup>20</sup> and the drawings of the electron density were plotted using the MORPHY program.<sup>21</sup> All calculated atomic properties were obtained with integrated values of the laplacian of the charge density,  $L(\Omega)$ , which did not differ from zero (the ideal value<sup>12</sup>) by more than  $10^{-3}$  au.

## 2. Results and discussion

### 2.1. Calculation of intramolecular interactions

Table 1 collects the relative energies calculated from the total electronic energies,  $\Delta E$ , those calculated by summing the QTAIM atomic energies,  $\Delta E^{\text{AIM}}$ , and those calculated by using Eq. 1,  $\Delta E^{\text{conf}}$ . The source of error giving rise to differences between  $\Delta E$  and  $\Delta E^{\text{AIM}}$  is the numerical integration performed to obtain the latter. As the integration was done with a large number of grid points and using second and third intersections to delimitate the interatomic surfaces, these differences never exceed 0.5 kcal mol $^{-1}$ . Differences between  $\Delta E$  and  $\Delta E^{\text{conf}}$  are inherent to the partitioning shown in Eq. 1 and due to considering constant  $\Delta E_{\text{OH}\cdots\text{HC}}$ ,  $\Delta E_{\text{g}(\text{H})}$  and  $\Delta E_{\text{g}(\text{C})}$  values for all the conformers. The differences between  $\Delta E$  and  $\Delta E^{\text{conf}}$  are only noticeable for g'Gg and gGt conformers of 1,2-ethanediol

and for g'GG'Gg conformer of 1,4-butanediol. The g'Gg and gGt are two of the three conformers (within a total of ten) not used in the calculation of  $\Delta E_{\text{OH}\cdots\text{O}}$ ,  $\Delta E_{\text{OH}\cdots\text{HC}}$ ,  $\Delta E_{\text{g}(\text{H})}$ ,  $\Delta E_{\text{g}(\text{C})}$ , and  $\Delta E'$  with Eq. 1. The small deviations of  $\Delta E^{\text{conf}}$  with respect to  $\Delta E$  for these two conformers (−0.22 and −0.31 kcal mol $^{-1}$  in g'Gg and gGt, respectively) indicate that the use of Eq. 1 was not too rough an approximation. Moreover, the highest deviation of  $\Delta E^{\text{conf}}$  (−0.31 kcal mol $^{-1}$ ) is smaller than that of  $\Delta E^{\text{AIM}}$  (−0.42 kcal mol $^{-1}$ ), so that one can establish that the deviations on the conformational energy due to the model proposed are smaller than those due to the accuracy of the numerical integration within the QTAIM atoms.

Two different  $\Delta E_{\text{OH}\cdots\text{O}}$  values were calculated for 1,2-ethanediol, one for g'Gt and g'Gg conformers (2.19 kcal mol $^{-1}$ ) and another one for g'Gg' (0.12 kcal mol $^{-1}$ ). The latter conformer shows a double interaction (Fig. 1), which, according to its very small energy, can be considered almost negligible. Only one  $\Delta E_{\text{OH}\cdots\text{O}}$  value was calculated for 1,3-propanediol (4.40 kcal mol $^{-1}$  for tGG'g and gGG'g) and 1,4-butanediol (5.79 kcal mol $^{-1}$  for g'GG'Gt and g'GG'Gg) as  $r(\text{OH}\cdots\text{O})$  distances are very similar for the two conformers of each molecule and the conformational energy only differs in 0.05 and 0.25 kcal mol $^{-1}$ , respectively. The calculated values for the different parameters used to model the IHB's using Eq. 1 are given in Table 2.

**Table 2.** Calculated values for the parameters of Eq. 1

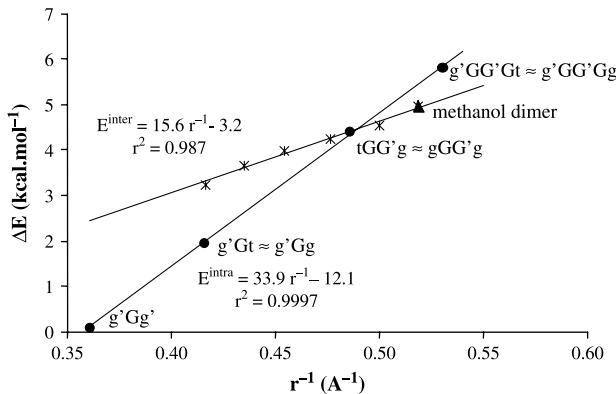
$\Delta E_{\text{OH}\cdots\text{O}}$	$\Delta E_{\text{OH}\cdots\text{CH}}$	$\Delta E_{\text{g}(\text{H})}$	$\Delta E_{\text{g}(\text{C})}$	$\Delta E'$
2.19 (g'Gt) <sup>a</sup>				
0.12 (g'Gg')		0.97		
4.40 (tGG'g) <sup>b</sup>			1.52	0.55
5.79 (g'GG'Gt) <sup>c</sup>				1.47

All values in kcal mol $^{-1}$ .

<sup>a</sup> The same value for g'Gg.

<sup>b</sup> The same value for gGG'g.

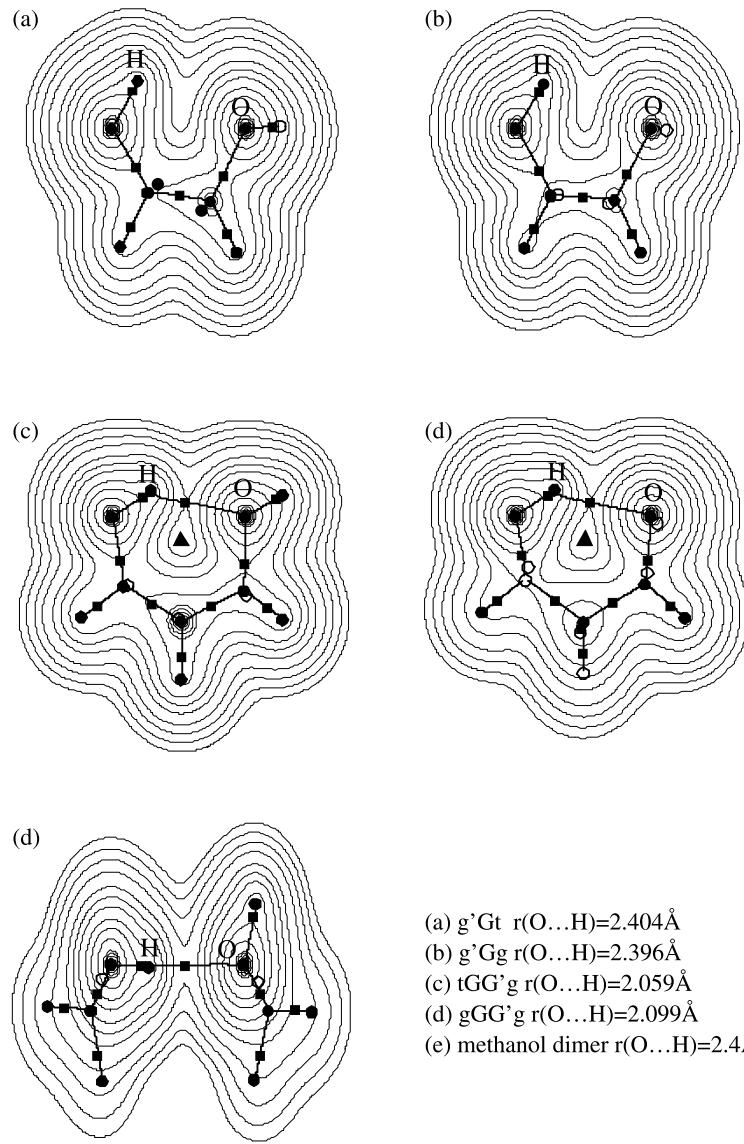
<sup>c</sup> The same value for g'GG'Gg.



**Figure 3.** Plots of  $\Delta E_{\text{OH}\cdots\text{O}}$  versus  $r(\text{O}\cdots\text{H})^{-1}$  linear correlations for diols studied and for the methanol dimer. Boldface circles represent the conformers of 1,2-ethanediol, 1,3-propanediol and 1,4-butanediol. The boldface triangle represents the optimized geometry of methanol dimer and crosses represent the methanol dimer at different  $r(\text{O}\cdots\text{H})$  distances.

A very good linear correlation was found relating  $\Delta E_{\text{OH}\cdots\text{O}}$  values to  $r(\text{OH}\cdots\text{O})^{-1}$ . Figure 3 shows this linear correlation for the conformers of Table 1 as well as that calculated for the methanol dimer. It is noticed that the data obtained for formally ‘bonding’ IHB conformers in 1,3-propanediol and 1,4-butanediol lie on the same line as those computed for formally ‘non bonding’ IHB conformers in 1,2-ethanediol. This shows that the formal QTAIM distinction between IHBs featuring a BCP and those that do not, does not imply any significant energy variation as was previously shown.<sup>22,24</sup>

As mentioned in the introduction, the  $\Delta E_{\text{OH}\cdots\text{O}}$  values for the intermolecular HB in methanol dimer were calculated as differences between dimer and monomer energies, correcting the BSSE error by using the counterpoise method.<sup>9</sup> The calculations were done on geometries where the  $r(\text{OH}\cdots\text{O})$  distance was fixed while the rest of the geometrical parameters were optimized. The geometry of minimum



**Figure 4.** Plots of the electron density in the  $\text{O}-\text{H}\cdots\text{O}$  plane for different conformers of 1,2-ethanediol and 1,3-propanediol and for the methanol dimer at  $r(\text{O}\cdots\text{H})=2.4\text{\AA}$ . Bond critical points and ring critical points are represented by ■ and ▲, respectively.

energy of the dimer was taken from a previous work<sup>22</sup> at B3LYP/6-311++G(d,p) level and re-optimized at the B3LYP/6-311++G(2d,2p) level.

The decrease of the HB energy as the O···H distance increases is steeper for the intramolecular case (Fig. 3) than for the intermolecular case. This is in line with ring-strain effects involved in the cyclic IHB structures of diols, which favor stronger (more stabilizing) IHBs for larger (more flexible) rings. The different behavior found for the topology of the electron density (Fig. 4): the dimer of methanol displays a BCP associated with the HB when the O···H distance is (or even exceeds) 2.4 Å, while no BCP is obtained for 1,2-ethanediol at the O···H distances presented by g'Gt and g'Gg conformers (2.404 and 2.396 Å, respectively) can be considered a consequence of these ring-strain effects. Thus, according to the electron density drawn Figure 4, the OH···O interaction in 1,2-ethanediol represents a non-bonding situation whereas it is a topological IHB in 1,3-propanediol, with the corresponding BCP on a pathway linking donor and acceptor atoms and a ring critical point (RCP) associated to a six member ring.

## 2.2. Variations on the atomic properties upon the conformational changes

Figure 5 shows the process of interconformational change studied for 1,2-ethanediol and 1,3-propanediol. Those corresponding to 1,2-ethanediol are named 1,2<sup>n</sup> and those corresponding to 1,3-propanediol 1,3<sup>n</sup> (n=1 or 2). Two processes were studied for 1,2-ethanediol, in both processes a conformer with non-bonding OH···O interaction turns into a conformer without any OH···O interaction. Other two processes were studied for 1,3-propanediol, nevertheless one of them, 1,3,<sup>2</sup> involves two conformers with OH···O IHB (see Fig. 5).

Table 3 collects the variations of atomic electron population and energy upon the processes plotted in Figure 5. The values of  $\Delta N(H)$  and  $\Delta E(H)$  can be rationalized approximately in terms of Eq. 1.

Processes 1,2<sup>1</sup> and 1,2<sup>2</sup>: the main variations of  $\Delta N(H)$  and  $\Delta E(H)$  correspond to H<sub>2</sub>, H<sub>3</sub>, H<sub>5</sub>, and H<sub>10</sub>. H<sub>2</sub> and H<sub>3</sub> present ‘gauche’ stabilization at gGt and g'Gt, respectively, so that when the gGt turns into g'Gt these atoms display similar

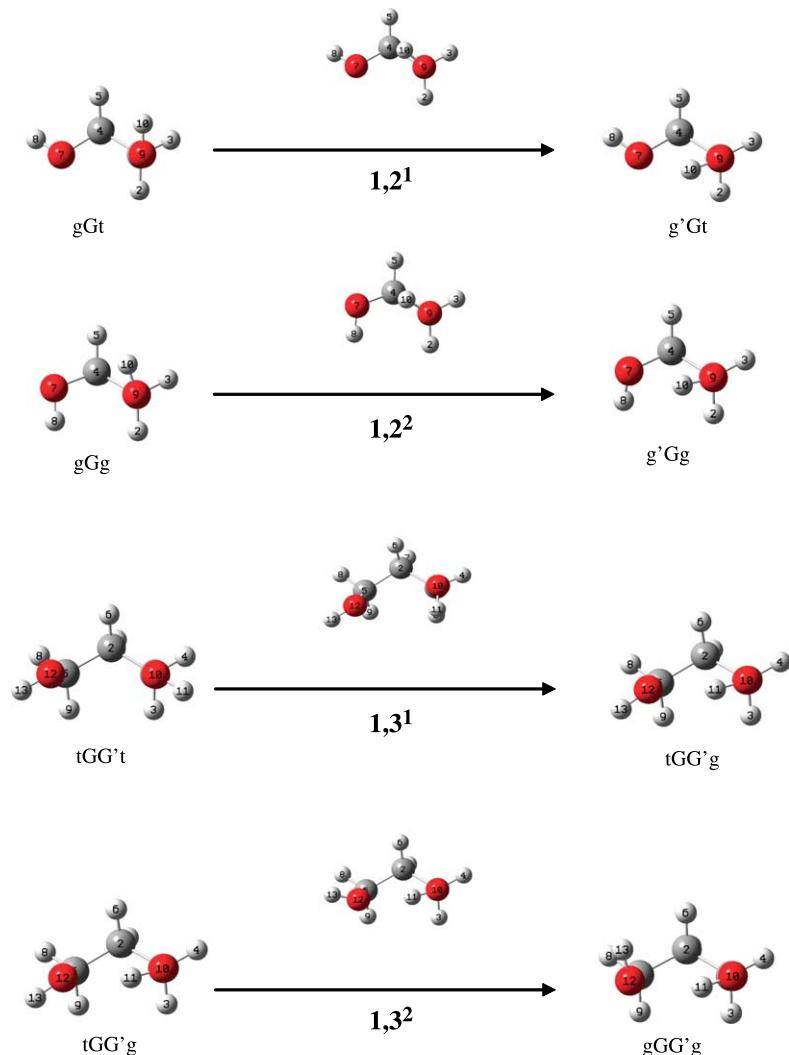


Figure 5. Process of interconformational change of 1,2-ethanediol and 1,3-propanediol studied in this work.

**Table 3.** Variations of atomic electron populations and atomic energies for the process of interconformational change for 1,2-ethanediol and 1,3-propanediol drawn in Figure 3

	1,2 <sup>1</sup>		1,2 <sup>2</sup>		1,3 <sup>1</sup>		1,3 <sup>2</sup>	
	$10^2\Delta N$	$\Delta E$ (kcal mol <sup>-1</sup> )	$10^2\Delta N$	$\Delta E$ (kcal mol <sup>-1</sup> )	$10^2\Delta N$	$\Delta E$ (kcal mol <sup>-1</sup> )	$10^2\Delta N$	$\Delta E$ (kcal mol <sup>-1</sup> )
C1	-0.2	-3.23	-0.6	-2.01	C1	-1.0	2.24	0.3
C4	1.9	-10.31	2.0	-11.63	C2	1.4	-5.67	0.7
H2	2.8	-5.40	2.2	-3.07	C5	3.0	-13.28	-0.3
H3	-2.5	4.60	-1.8	3.20	H3	0.2	0.24	-0.4
H5	-2.1	4.08	-2.2	5.09	H4	-2.2	4.39	-0.1
H6	-0.4	1.08	0.0	0.11	H6	1.1	-2.96	2.0
H8	-0.7	2.44	0.2	-1.38	H7	-0.5	2.65	-0.1
H10	-2.4	8.24	-1.4	5.03	H8	-1.3	3.37	0.0
O7	1.6	0.09	0.3	5.30	H9	-0.9	1.62	-2.3
O9	1.7	-5.05	1.0	-3.19	H11	-4.1	14.47	0.5
					H13	-1.4	4.87	-0.9
					O10	3.9	-12.79	3.68
					O12	2.1	-4.01	-1.12

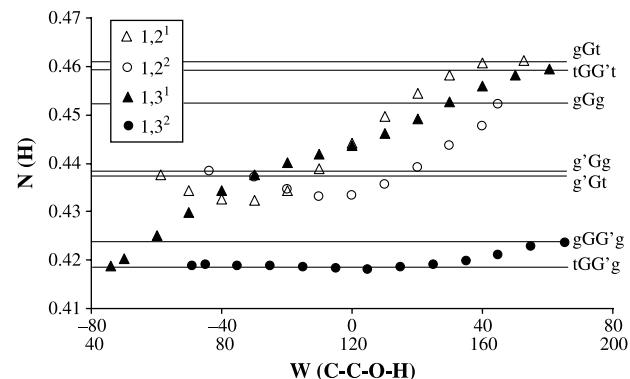
values of  $\Delta N(H)$  and  $\Delta E(H)$  with opposite sing. H<sub>5</sub> presents an OH···HC interaction at g'Gt, so that when the gGt turns into g'Gt this atom is destabilized and its electron population decreases. H<sub>10</sub> presents OH···O non-bonding interaction at g'Gt, so that when the gGt turns into g'Gt this atom is destabilized (with larger destabilization comparing to the H<sub>5</sub>) and its electron population decreases.

Process 1,3<sup>1</sup>: the main variations of  $\Delta N(H)$  and  $\Delta E(H)$  correspond to H<sub>4</sub> and H<sub>11</sub>. H<sub>4</sub> presents a ‘gauche’ stabilization for tGG'g, so that when the tGG't conformer turns into tGG'g this atom is destabilized and its electron population decreases. H<sub>11</sub> presents OH···O IHB at tGG'g, so that when the tGG't turns into tGG'g this atom is destabilized and its electron population decreases (with larger destabilization comparing to H<sub>10</sub> in 1,2<sup>1</sup> and 1,2<sup>2</sup>).

Process 1,3<sup>2</sup>: the main variations of  $\Delta N(H)$  and  $\Delta E(H)$  correspond to H<sub>6</sub>, H<sub>9</sub>. H<sub>6</sub> presents an OH···HC interaction in tGG't, so that when the tGG't turns into tGG'g this atom is stabilized and its electron population increases. H<sub>9</sub> presents ‘gauche’ interaction in tGG'g, so that when tGG't turns into tGG'g this atom is destabilized and its electron population decreases.

Notice that according to the QTAIM atomic properties the ‘stabilizing interactions’ in these systems always are concurrent with a destabilization of the hydrogens and a decrease in the electron population as previously found at hydrogen bonding systems.<sup>23,17,24</sup>

Figure 6 displays the values of N(H) versus w(C–C–O–H), where w(C–C–O–H) is the reaction coordinate for the 1,2<sup>n</sup> and 1,3<sup>n</sup> processes. N(H) corresponds to the electron population of the H involved in the O–H···O non-bonding or bonding interaction in the process considered. Some differences between the behavior on 1,2<sup>n</sup> and 1,3<sup>n</sup> were found. For instance, the total variation of N(H) is larger for 1,3<sup>1</sup> in agreement with stronger interactions. In contrast, the values of N(H) hardly change for 1,3<sup>2</sup> as both the conformers display IHB. On the other hand, the values of N(H) at 1,2<sup>n</sup> display a minimum before reaching the final conformer. This is due to the fact that the shortest O···H distance (2.264 and 2.304 Å at 1,2<sup>1</sup> and 1,2<sup>2</sup>, respectively) does not correspond to any of the stable conformers, but to the lowest N(H) value.

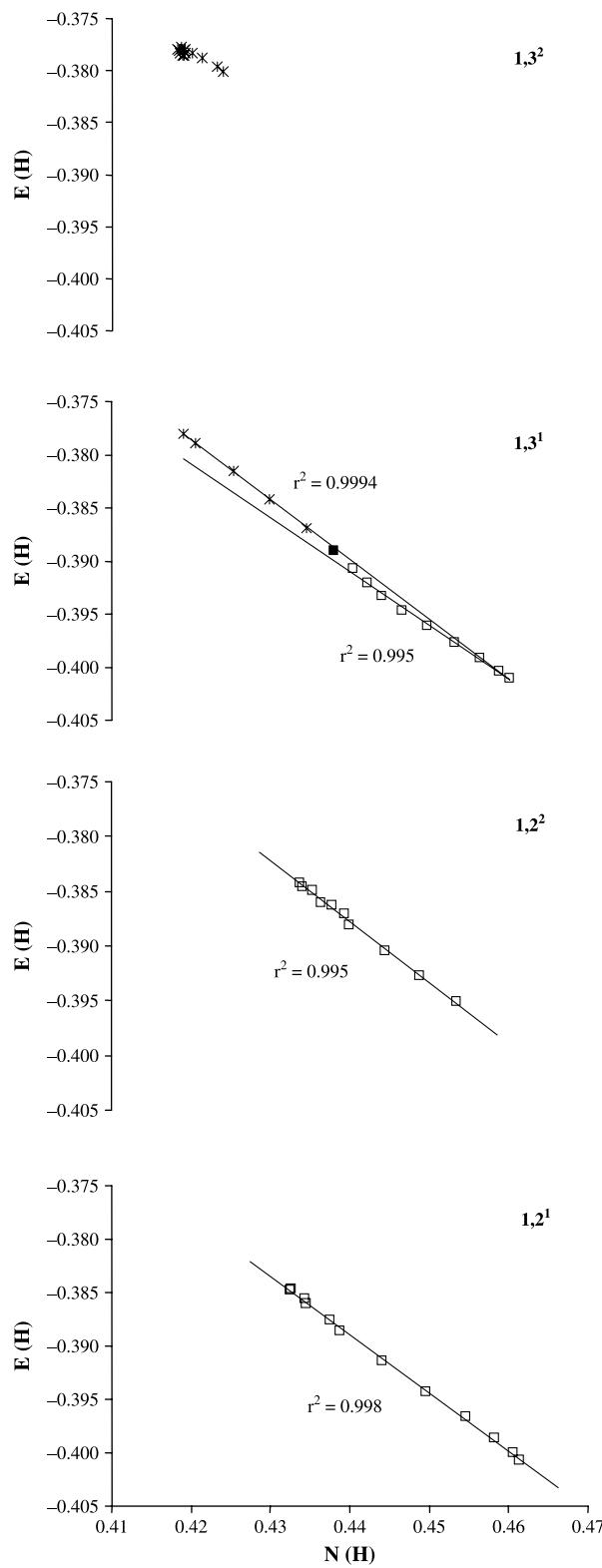


**Figure 6.** Plots of the atomic population (in au) of the hydrogen involved in IHB, N(H), versus the C–C–O–H dihedral angle (in degrees), w(C–C–O–H), for the processes drawn in Figure 5. The first row at the ‘x’ axis represents the values of w(C–C–O–H) for 1,2<sup>n</sup> while the second row represents the values of w(C–C–O–H) for 1,3<sup>n</sup>. Horizontal lines correspond to the different conformers.

In a previous work on  $\beta$ -hydroxyethoxy and  $\beta$ -hydroxyethyl-peroxy radicals<sup>24</sup> linear correlations between  $E(H)$  and  $N(H)$  were found when the O and H atoms approached one another by rotating around dihedral angles or shortening the O···H distance. Moreover, the slope of these linear correlations changed when a BCP linking the O and H was formed. Similar linear correlations have been found for 1,2-ethanediol and 1,3-propanediol in as depicted in Figure 7, where the N(H) values are those collected in Figure 6. Good linear correlations were found for 1,2<sup>1</sup>, 1,2<sup>2</sup> and 1,3<sup>1</sup>, those corresponding to 1,2-ethanediol do not present changes on the slope while a small change on the slope appears for 1,3<sup>1</sup> at the point where the BCP is formed. The very small changes on N(H) and  $E(H)$  at 1,3<sup>2</sup> make the representation of both properties appear as an accumulation of points (see Fig. 7).

### 3. Conclusions

The conformational energy of 1,2-ethanediol, 1,3-propanediol, and 1,4-propanediol can be split to a very good approximation into four different contributions: OH···O interactions,  $\Delta E_{OH\cdots O}$ , ‘gauche’ stabilization of hydrogens and carbons due to the oxygen lone pairs,  $\Delta E_{g(H)}$  and  $\Delta E_{g(C)}$ , and stabilizations due to the relative arrangement of hydroxyl and  $\beta$ -methylene groups,  $\Delta E_{OH\cdots HC}$ .



**Figure 7.** Plots of the atomic energy (in au) of the hydrogen involved in IHB,  $E(H)$ , versus its atomic electron population,  $N(H)$ , (in au) for several points along the processes drawn in Figure 5. Black squares represent the geometry for which the BCP is formed, white squares and crosses represent geometries before and after the BCP formation, respectively.

An additional term has to be included when comparing conformers with different arrangement of the  $O-C-C-O$  unit in 1,2-ethanediol ( $\Delta E'$ ). This partitioning scheme allows to estimate and rationalize the energy due to the

$O-H\cdots O$  interactions,  $\Delta E_{OH\cdots O}$ , from the relative electronic energies of the conformers without neglecting important structural changes between them nor introducing arbitrary chosen reference conformations. Moreover, the topological analysis of the electron density along with the  $\Delta E_{OH\cdots O}$  values shows that the  $OH\cdots O$  interaction must be considered non-bonding at 1,2-ethanediol and bonding in 1,3-propanediol and 1,4-butanediol.

Both the values of  $\Delta E_{OH\cdots O}$  for intramolecular and intermolecular (for instance the dimer of methanol) interactions display a very good linear correlation with the  $r(O\cdots H)^{-1}$  values. These linear correlations indicate a steeper decrease of  $\Delta E_{OH\cdots O}$  when  $r(O\cdots H)$  increases for the intramolecular case than for the intermolecular case, which can be attributed to ring-strain effects. These effects explain also why the donor/acceptor BCP remains present in the methanol dimer for  $r(O\cdots H)$  distances where BCPs are not present in 1,2-ethanediol.

The linear correlations displayed by  $N(H)$  and  $E(H)$  along the rotation over the  $w(C-C-O-H)$  dihedral angles can be employed to characterize  $O\cdots H$  topological hydrogen bonds in these compounds.

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