Hydrogen bond cooperativity in polyols: A DFT and AIM study

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Hydrogen bond cooperativity in polyols: A DFT and AIM study

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ABSTRACT

Density functional theory calculations, and atoms in molecules analyses are performed to investigate both the strength and the cooperative enhancement of intramolecular O—H···O—H hydrogen bonding interactions occurring in polyols. The relative strength of the O—H···O—H interaction is evaluated in two basic model systems: 1,3-propanediol, and 1,8-napthalenediol. The backbone of the former model is aliphatic, whereas that of the latter is aromatic. The cooperative enhancement of the O—H···O—H interaction is evaluated by extending symmetrically the polyol chain of each model system on both sides of the interaction in the basic unit. Specifically, we considered polyols with an odd number of H bonds running from one to eleven depending on the size of the polyol. The polyols are chosen so that there is a carbon atom located in between adjacent hydroxyl groups. Pertinent geometrical, and topological parameters are used as primary indicators of H bond strength, and consequently for cooperativity assessment. Also, the Lippincott and Schroeder hydrogen bond model, LS-HB, is used to estimate intramolecular hydrogen bonding energies.

1. Introduction

An important concept in the theory of hydrogen bonding is cooperativity, wherein each one of the individual H bonds making up a chain of inter-linked H bonds is more strongly bound than it would be in the absence of the others [1–5]. Cooperativity is frequently applied in theoretical work and for the interpretation of experimental data. For example, cooperativity has been extensively studied in chains of intermolecular H bonds including amides, hydrogen halides, hydrogen cyanide, water, and simple alcohols [6–22]. In particular, the extent of cooperativity in intermolecular O—H···O—H chains has been the subject of intense research. For instance, Karpfen and Schuster reported ab initio studies on the structure of infinite chains of methanol and water molecules [15]. Ojamäe and Hermanson reported an ab initio study of cooperativity in water chains containing up to seven H_2O molecules [16]. Also, Suhai carried out ab initio calculations to investigate cooperativity in water oligomers, and in an infinite extended water chain [17]. Although water molecules tend to cluster in three-dimensional arrangements, it is worth noting that the linear chain structure of H bonded water molecules is often used as a convenient model to investigate the extent of cooperativity in an H bonded lattice; it has also been employed as a valuable model to study proton transfer in biological proton pumps [23–26]. Studies of cooperativity in intramolecular H bonded systems, on the other hand, have been much scarce. Of particular relevance is the

work by Deshmukh et al. who have estimated cooperative effects in intramolecular O—H···O—H hydrogen bonds in carbohydrates via the molecular tailoring approach [27]. The influence of intramolecular O—H···O—H H bond cooperativity on the conformational stability of supramolecular receptors such as calixarenes, thiacalixarenes, and resorcinarenes has been reported [28]. Moreover, the impact on water structure in solution of cooperativity of a network of O—H···O—H hydrogen bonds such as those present in carbohydrates and polyols have been recently reported [29,30]. Such intramolecular O—H···O—H hydrogen-bond chains serve as important models for charge conduction in biological membranes. For example, the extent of proton polarizability enlargement due to a collective proton motion in a chain of intramolecular O—H···O—H interactions in a network of five phenolic groups has been reported [31]. In this study, the authors proposed that the chain of four intramolecular O—H···O—H hydrogen bonds is suitable for charge conduction and may be a model of a proton wire in a biological membrane. Quite recently, Carpentier et al. carried out dielectric studies of the mobility of pentitols, and showed that the formation of an extended intramolecular H bond network is responsible for a stronger character of the temperature variation of the primary relaxation times [32]. Tian et al. investigated the enhancement of acidity caused by intramolecular H bond cooperativity in a series of polyols [33]. The importance of intramolecular OH···OH hydrogen bonds in the effective molecular recognition of carbohydrates has been highlighted by López de la Paz et al.; these authors showed that the intramolecularly H bonded OH groups of carbohydrates can be considered as multidentate units capable of H bonding cooperativity [34].

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In this paper, we expand our current knowledge of H bond cooperativity by investigating the impact that polyol chains has on the strength of regular intramolecular O—H···O—H hydrogen bonds. To accomplish this goal, we use two basic polyol systems having either aliphatic or aromatic backbones. The extent of cooperativity is determined by systematically increasing the size of the corresponding polyol chains.

2. Computational details

Geometry optimizations and frequency calculations were carried out using the GAUSSIAN 09 program [35]. These calculations were performed with the 6-311G(d,p) basis set [36,37], and the B3LYP implementation of density functional theory [38–41]. The calculated harmonic vibrational frequencies confirmed that each optimized geometry corresponded to a minimum on the potential energy surface. The theory of atoms in molecules (AIM) of Bader [42] was employed to analyze topological features of electron density on wave functions obtained at the B3LYP/6-311++G(d,p) level using the AIM2000 software package [43]. Here, cooperative effects are studied using several indicators of H bond strength such as the hydrogen bond O—H···O—H distance, $d_{O···H}$, and the corresponding frequency shifts undergone by the harmonic O–H stretching modes. Topological parameters such as the electron density at the H bond critical point, ρ_c, are also often used as descriptors of H bond strength, and hence as suitable tools to study cooperativity [44,45].

3. Results and discussion

3.1. Geometries

The relative strength of a regular intramolecular O—H···O—H interaction is investigated in two different systems: 1,3-propanediol [46–48], and 1,8-napthalenediol [49–51]. The former system, which we will refer to as AL_2OH, is the basic or reference aliphatic polyol, while the latter system, which we will refer to as AR_2OH, is the reference aromatic polyol. As shown in Fig. 1, each H bond in a given system is part of a six-membered ring. Some relevant geometrical, and topological parameters are summarized in Table 1. Inspection of Table 1 reveals that the H bond in AL_2OH is somewhat weaker than that in AR_2OH. The weaker interaction in AL_2OH is reflected, for example, in a longer (by about 0.20 Å) H bond distance, and narrower (by about 4°) H bond angle.

3.2. Atoms in Molecules Analysis

The strength of the intramolecular O—H···O—H hydrogen bond in each of the model systems was further evaluated using the theory of atoms in molecules (AIM). In particular, the electron densities, ρ_c, and their Laplacians, $\nabla^2\rho_c$, evaluated at the H bond critical

Table 1
Geometrical and topological parameters used as descriptors of H bond strength in the model polyols.[a]

System	$d_{H—O}$	$d_{H···O}$	$d_{O···O}$	$A_{O—H···O}$	$t_{O—H···O—C}$
AL_2OH	0.966	1.993	2.800	139.6	−16.2
AR_2OH	0.968	1.786	2.628	143.4	0.0

System	ρ_c	$\nabla^2\rho_c$	G_c	V_c	H_c	$-G_c/V_c$
AL_2OH	0.0234	0.0888	0.0203	-0.0184	0.0019	1.10
AR_2OH	0.0354	0.1378	0.0339	-0.0334	0.0005	1.02

B3LYP/6-311++G(d,p) topological parameters in atomic units.
[a] B3LYP/6-311G(d,p) optimized geometries. Distances in Å, and angles in degrees.

points are frequently used as indicators of H bond strength. For instance, an increase in both ρ_c and $\nabla^2\rho_c$ correlates well with a decrease in the $d_{H···O}$, which in turn parallels an increase in the strength of the H bond. In addition to the electron densities and Laplacians, the electron energy density (H_c) at the H bond critical point, as well as its components, the kinetic (G_c) and potential (V_c) electron energy densities are often used to gain additional insight on the strength and nature of a given H bond [52–55]. Moreover, an empirical relationship has been proposed between the H bond energy and the local potential electron energy density as $E_{HB} = 0.5V_c$ [52]. It should be noted, however, that the energy derived approximates the electrostatic component of the total energy, rather than the total interaction energy itself. The nature, non-covalent or partly covalent, of a hydrogen bond may also be assessed. Previous studies have established that a partly covalent H bond can be said to exist if $\nabla^2\rho_c$ is positive and H_c is negative [56,57]. An alternative tool for assessing the nature of a H bond is the ratio $-G_c/V_c$ [58]. Accordingly, if $-G_c/V_c > 1$, then the H bond is non-covalent. On the other hand, if $0.5 < -G_c/V_c < 1$, then the interaction is partly covalent. Examination of Table 1 corroborates the statement, based on geometrical grounds, that the H bond in AL_2OH is somewhat weaker than that in AR_2OH. For example, the ρ_c and $\nabla^2\rho_c$ values in AR_2OH are about 1.5 times larger than those in AL_2OH; in addition, the estimated critical-point kinetic and potential energy values in AR_2OH are about 1.7 times larger than those of the aliphatic alcohol. The H bonds in both model systems are found, however, to be non-covalent nature ($-G_c/V_c > 1.0$).

3.3. Cooperativity in Intramolecular O—H···O—H Hydrogen Bonds

Having established the nature and strength of the O—H···O—H interactions in the two selected model systems, AL_2OH, and AR_2OH, we next examine the extent to which these interactions are cooperatively enhanced by the presence of additional intramolecular H bonds. To this end, we modified each model system by extending their backbones with the addition of polyol chains. Optimized geometries of the smallest and largest resulting polyol chains are shown in Figs. 2 and 3, for the aliphatic and aromatic polyols respectively. Cooperative enhancement, relative to a pertinent reference system, is expected to result in a sizeable elongation of the covalent O—H bond length, along with a contraction of the corresponding H bond distance. Thus, the extent of cooperativity, upon polyol expansion, can be gauged by calculating the percentage changes in the covalent O—H bond length, $d_{O—H}$, and the H···O hydrogen bond distance, $d_{H···O}$, and the results are summarized in Table 2 for both the aliphatic and aromatic polyols. For convenience, we selected three distinct H bonds, for polyols with $n \geqslant 3$ H bonds, to assess the extent of cooperative enhancement relative to the H bond in the corresponding parent diols. In reference to Figs. 2 and 3, the leftmost O—H group is a H bond donor, while the rightmost O—H group is a H bond acceptor. The central O—H groups act simultaneously as donors and acceptors. As may
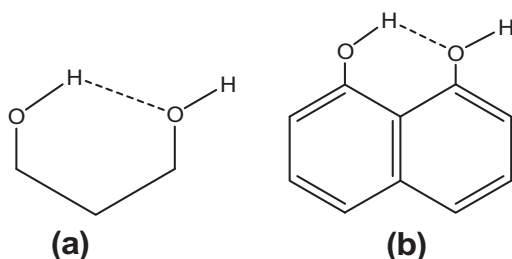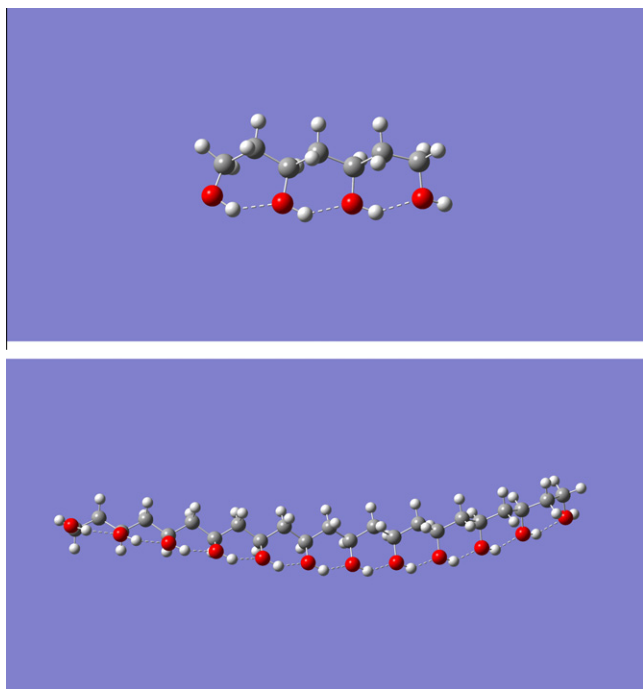

Fig. 1. Model systems used to investigate O—H···O—H hydrogen bonding interactions: (a) 1,3-propanediol (referred to as AL_2OH) (b) 1,8-napthalenediol (referred to as AR_2OH).

Fig. 2. B3LYP/6-311G(d,p) optimized geometries of the smallest and largest aliphatic polyols studied in this work.
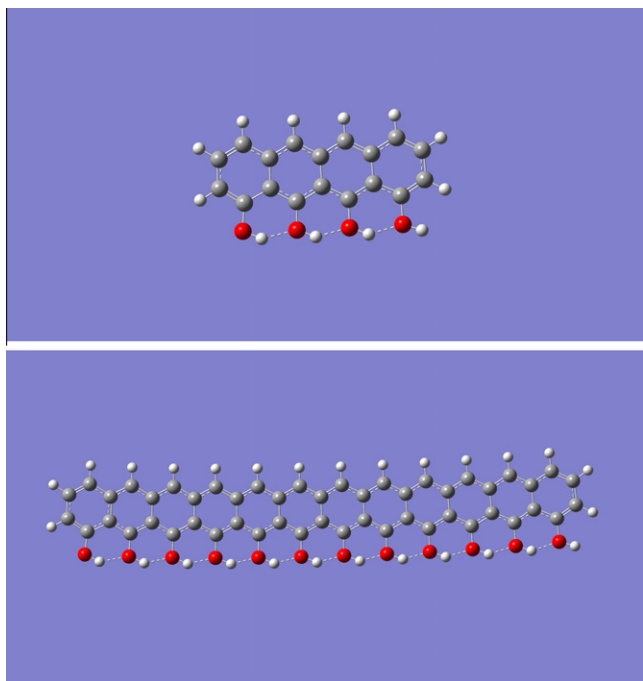

Fig. 3. B3LYP/6-311G(d,p) optimized geometries of the smallest and largest aromatic polyols studied in this work.

be noted in Table 2, the covalent O—H bond length changes very little upon polyol expansion, with the central O—H group exhibiting the most change (0.63% aliphatic polyol; 1.4% aromatic polyol). Much more sensitive to polyol expansion is the H bond distance, $d_{\text{H}\cdots\text{O}}$. It is apparent that increasing the size of the polyol brings about an important reduction in the H bond distances, with the effect being most significant in the central H bond. Indeed, the extent of cooperativity for the three H bonds considered follows the order central > rightmost > leftmost. Specifically, the percentage changes of the H bond distance, %$\Delta d_{\text{H}\cdots\text{O}}$, for the central H bond as a function of $1/n$ are plotted in Fig. 4 for both model polyols. Clearly, $d_{\text{H}\cdots\text{O}}$ changes linearly with $1/n$ for either polyol system, and the percentage changes for the aliphatic and aromatic polyols are within 1% of each other. Based on the noted linear correlations, the percentage reduction in the H bond distances are estimated to be 9.0% (aliphatic), and 9.5% (aromatic) in the limit of an infinite chain.

Vibrational frequencies are often used to estimate the extent of cooperativity in H bonding interactions [1–5]. Changes in geometrical parameters usually cause shifts to related vibrational frequency modes. In particular, the lengthening of the covalent O—H bond with increasing strength of the H bond results in a shift to lower frequencies of the corresponding O—H stretching mode. Although the stretching frequencies are not necessarily identified with a particular O—H bond, we were able, by animation of the normal modes, to focus on the stretching modes involving mostly one of the O—H covalent bonds located at the leftmost (donor), central, or rightmost (acceptor) group. The results for both aromatic and aliphatic polyols are summarized in Table 3. A shift to lower frequencies (red shift) is calculated for all H bonds; however, the relative changes are different and, as expected, parallel the changes in the O—H bond length, and H⋯O distances: central > rightmost > leftmost. Moreover, the changes in the aromatic polyols, specially for the central H bond, are more than twice larger than those in the aliphatic counterparts in agreement with the somewhat stronger H bonds of the aromatic polyols.

The extent of cooperativity revealed in the geometrical parameters, and the O—H stretching frequencies is mirrored in topological parameters such as the electron density at the H bond critical point, ρ_c. A summary of the percentage changes of some relevant topological parameters is given in Tables 4 and 5 for the aliphatic and aromatic polyols respectively. The changes in the topological parameters are calculated at the B3LYP/6-311++G(d,p) relative to the corresponding parent diols AL_2OH (aliphatic) and AR_2OH (aromatic). One may note, by inspection of Tables 4 and 5, that in addition to larger values of ρ_c, cooperativity is evident in an increase in the magnitudes of both G_c, and V_c. The increased magnitude of the potential energy density, V_c, reflects a greater capacity to accumulate electrons at the H bond critical point, which then implies an increase in electron–electron repulsion. The larger electronic repulsion results unsurprisingly in an increase in the local kinetic electron energy density. Additionally, cooperativity gives rise to a decrease in $-G_c/V_c$ values. Inspection of Table 4 reveals that all of the H bonds considered for the aliphatic polyols appear to exhibit a significant cooperative enhancement upon expansion from $n = 1$ to $n = 3$ H bonds. The extent of cooperativity is largest for the central H bond followed by the rightmost, and then the leftmost H bond. Increasing the size of the polyol from $n = 3$ to $n = 5$ results in small but still important additional changes in the topological parameters for the terminal H bonds. However, no significant changes in the topological parameters are observed for the terminal H bonds for aliphatic polyols with $n > 5$. In contrast, the central H bond appears to be continuously enhanced even for $n > 5$, although it seems to be getting close to saturation at $n = 11$. Similarly, all of the H bonds considered for the aromatic polyols appear to exhibit a significant cooperative enhancement upon expansion from $n = 1$ to $n = 3$ H bonds, as indicated by inspection of Table 5. The extent of cooperativity parallels that of the aliphatic polyols, with the central H bond showing the largest cooperativity followed by the rightmost, and then the leftmost H bond. Cooperativity for the terminal H bonds seems to have already reached saturation since increasing the size of the polyol to $n > 3$ brings about negligible changes (1% or less) in the topological parameters. Conversely, the central H bond appears

Table 2
Percentage changes in O—H, and H···O distances of selected H-bonds in polyols with n H-bonds.[a]

	Aliphatic polyols					
	d_{O-H}			$d_{H\cdots O}$		
n	Leftmost (%)	Central (%)	Rightmost (%)	Leftmost (%)	Central (%)	Rightmost (%)
3	0.14	0.33	0.25	−2.32	−5.57	−4.08
5	0.18	0.49	0.31	−2.66	−6.85	−4.71
7	0.19	0.58	0.32	−2.76	−7.52	−4.70
9	0.20	0.61	0.32	−2.92	−7.90	−4.79
11	0.19	0.63	0.33	−2.83	−7.98	−4.96
Aromatic polyols						
3	0.18	0.7	0.62	−2.59	−6.34	−4.61
5	0.17	1.0	0.70	−2.63	−7.65	−4.75
7	0.17	1.2	0.73	−2.60	−8.12	−4.81
9	0.16	1.3	0.74	−2.55	−8.48	−4.84
11	0.18	1.4	0.68	−2.43	−8.60	−4.72

[a] Changes relative to AL_2OH (aliphatic), and AR_2OH(aromatic) respectively. See Table 1.
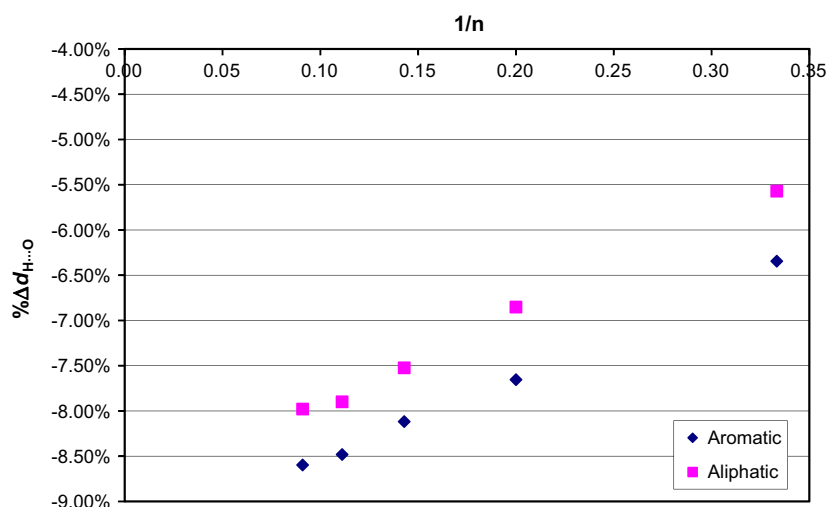
Fig. 4. Linear correlations between the percentage changes of the H bond distances, $d_{H\cdots O}$, and the reciprocal of the number of H bonds, $1/n$, in the aliphatic and aromatic polyols.

Table 3
Percentage changes in O—H stretching frequencies for the various polyols with n H bonds.[a]

	Aliphatic polyols			Aromatic polyols		
n	Leftmost (%)	Central (%)	Rightmost (%)	Leftmost (%)	Central (%)	Rightmost (%)
3	−0.5	−1.7	−1.1	−1.1	−4.6	−3.0
5	−0.7	−2.7	−1.3	−1.0	−6.9	−3.5
7	−0.8	−3.3	−1.4	−1.0	−8.0	−3.7
9	−0.8	−3.6	−1.4	−1.0	−8.7	−3.7
11	−0.8	−3.7	−1.4			

[a] Changes relative to Al_2OH (aliphatic), and AR_2OH(aromatic) respectively. See Table 1.

to be continuously enhanced even for $n > 5$, although it seems to be getting close to saturation at n = 11, a result that closely resembles that for the central H bond in the aliphatic polyols. Based on the percentage reductions in the $-G_c/V_c$ ratios for the aliphatic polyols shown in Table 4, we note that the H bonds remain non-covalent in nature, with the ratios for the largest polyol following the order: leftmost (1.09) > rightmost (1.06) > central (1.03). Conversely, the H bonds in the aromatic polyols become partly covalent upon expansion to n = 3, and for the largest polyol, n = 11, the $-G_c/V_c$ ratios are in the order: leftmost (0.97) > rightmost (0.95) > central (0.88). Thus, the somewhat stronger character of the H bond in the aromatic polyols is then revealed also in its partly-covalent nature.

3.4. General correlations between intramolecular O—H···O—H distances and topological parameters

Because different indicators are often used to evaluate H bond strength, it is convenient to determine how these different indicators correlate with one another. In particular, the relationships between the H bond distances and some topological parameters for all model systems considered in this study are displayed in Figs. 5 and 6. It is worth noting that the H···O distances cover a relatively wide range from 1.63 to 1.99 Å. In Fig. 5, V_c and G_c are represented versus their corresponding H bond distances. An exponential dependence of V_c and G_c on $d_{O\cdots H}$ was previously noted by

Table 4
Percentage changes in H bond distances and topological parameters for aliphatic polyols having n H bonds.[a]

n	$d_{H\cdots O}$ (%)	ρ_c (%)	$\nabla^2\rho_c$ (%)	G_c (%)	V_c (%)	$-G_c/V_c$ (%)
Leftmost						
3	−2.3	9.0	11.6	12.6	13.9	−1.1
5	−2.7	10.6	13.0	14.4	16.2	−1.5
7	−2.8	11.1	13.4	15.0	16.9	−1.6
9	−2.9	11.8	14.1	15.8	17.9	−1.8
11	−2.8	11.4	13.8	15.4	17.3	−1.7
Central						
3	−5.6	24.1	27.4	31.7	36.9	−3.8
5	−6.9	31.9	33.4	40.2	48.4	−5.5
7	−7.5	35.9	36.6	44.8	54.7	−6.4
9	−7.9	38.4	38.7	47.6	58.5	−6.8
11	−8.0	38.8	38.9	48.1	59.1	−6.9
Rightmost						
3	−4.1	18.1	18.3	22.0	26.4	−3.5
5	−4.7	21.2	21.3	25.8	31.2	−4.1
7	−4.7	21.2	21.2	25.7	31.1	−4.1
9	−4.8	21.6	21.6	26.2	31.7	−4.2
11	−5.0	22.5	22.4	27.2	33.0	−4.4

[a] Changes calculated at the B3LYP/6-311++G(d,p) relative to AL_2OH.

Table 5
Percentage changes in H bond distances and topological parameters for aromatic polyols having n hydrogen bonds.[a]

n	$d_{H\cdots O}$ (%)	ρ_c (%)	$\nabla^2\rho_c$ (%)	G_c (%)	V_c (%)	$-G_c/V_c$ (%)
Leftmost						
3	−2.6	14.1	9.4	14.3	19.3	−4.2
5	−2.6	14.0	9.1	14.0	19.1	−4.3
7	−2.6	13.8	9.1	13.9	18.9	−4.2
9	−2.6	13.6	8.9	13.6	18.6	−4.2
11	−2.4	13.2	8.5	13.1	17.9	−4.1
Central						
3	−6.3	33.1	19.9	33.2	46.9	−9.3
5	−7.7	41.3	22.6	40.4	58.9	−11.6
7	−8.1	44.4	23.5	43.2	63.5	−12.4
9	−8.5	46.8	24.5	45.5	67.1	−13.0
11	−8.6	47.6	24.3	45.9	68.3	−13.3
Rightmost						
3	−4.6	21.2	13.9	21.6	29.6	−6.1
5	−4.7	22.0	13.3	21.7	30.4	−6.6
7	−4.8	22.3	13.4	21.9	30.8	−6.8
9	−4.8	22.5	13.5	22.1	31.0	−6.8
11	−4.7	21.7	13.1	21.4	30.0	−6.6

[a] Changes calculated at the B3LYP/6-311++G(d,p) relative to AR_2OH.

Espinosa et al. using data from accurate experimental electron density studies involving the X–H···O (X = C, N, O) motif [6]. Indeed, such dependence is confirmed for both topological parameters as shown below:

$$V_c = -9.32\exp(-3.14d_{H\cdots O}) \quad r^2 = 0.998$$

$$G_c = 2.86\exp(-2.48d_{H\cdots O}) \quad r^2 = 0.999$$

Also shown in Fig. 5 is the dependence of H_c on the H bond distance. One sees that the partly covalent character of the interaction (Negative values for H_c) becomes apparent for H bond distances smaller than about 1.80 Å.

In Fig. 6, ρ_c and $\nabla^2\rho_c$ are presented versus their corresponding H bond distances. It is seen that, for the range of H bond distances spanned, the trend for both parameters is to increase their values with decreasing H bond distances. In fact, both topological parameters exhibit an exponential dependence on the H bond distance as follows:

$$\rho_c = 1.88\exp(-2.21d_{H\cdots O}) \quad r^2 = 0.997$$

$$\nabla^2\rho_c = 3.83\exp(-1.88d_{H\cdots O}) \quad r^2 = 0.991$$

A remarkable linear correlation is also found between the H bond distance, and the corresponding O···O distance, $d_{O\cdots O}$:

$$d_{O\cdots O} = 0.826d_{H\cdots O} + 1.152 \quad r^2 = 0.999$$

It should be noted that because the experimental determination of the H atom is usually difficult, $d_{O\cdots O}$ values are often used as alternative indicators of H bond strength [59]. In fact, a semiempirical method by Lippincott and Schroeder, also known as the LS-HB model, is often used for calculating H bond energies starting from their geometries [59,60]. In the particular case of O—H···O systems, the dependence of the H bond energies on the O···O distances, $d_{O\cdots O}$, and corresponding angles, $A_{O—H\cdots O}$, according to the LS-HB model, has been found to obey the relationship below [59]:

$$E_{HB} = (-43.8 + 0.38A_{O-H\cdots O})\exp[-5.1(d_{H\cdots O} - 2.40)]$$

The estimated H bond energies, using the equation above, for the aromatic and aliphatic polyols considered in this work are summarized in Table 6. The results indicate that the H bonds in the aliphatic polyols are rather weak, while those in the aromatic polyols exhibit weak to moderate strength. The results are then consistent with those given by geometrical and topological
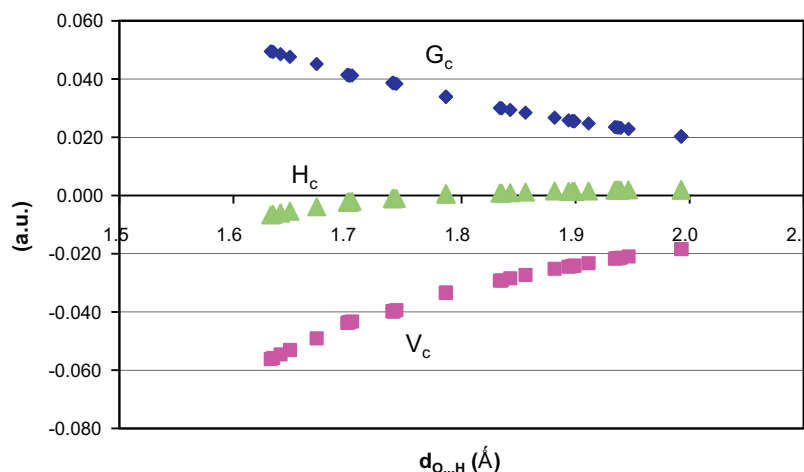

Fig. 5. V_c, G_c, and H_c (atomic units) versus their corresponding H bond distances, $d_{O\cdots H}$ (Å), for the O—H···O—H hydrogen bonds considered in this study.
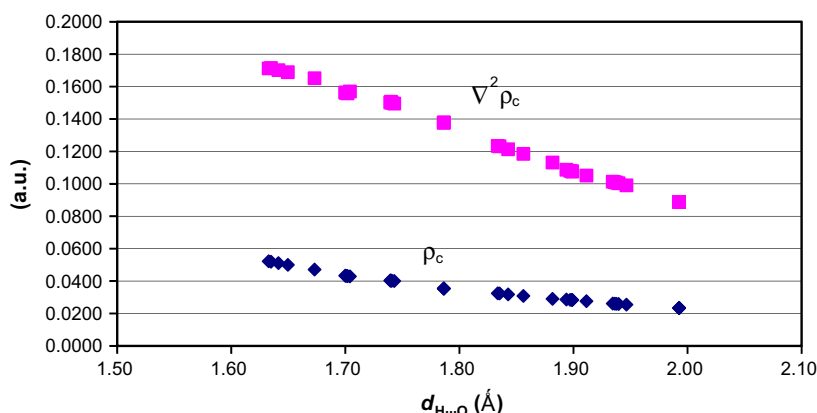
Fig. 6. ρ_c and $\nabla^2\rho c$ (atomic units) versus their corresponding H bond distances, $d_{\text{H}\cdots\text{O}}$ (Å), for the O—H$\cdots$O—H hydrogen bonds considered in this study.

Table 6
Estimated hydrogen bond energies, E_{HB} (kcal/mol), based on $d_{\text{O}\cdots\text{O}}$ (Å), and $A_{\text{O—H}\cdots\text{O}}$(degs.), according to the LS-HB model.

	Aliphatic			Aromatic		
	$d_{\text{O}\cdots\text{O}}$	$A_{\text{O—H}\cdots\text{O}}$	E_{HB}	$d_{\text{O}\cdots\text{O}}$	$A_{\text{O—H}\cdots\text{O}}$	E_{HB}
Leftmost						
1	2.800	139.62	1.21	2.628	143.45	3.35
3	2.753	139.22	1.51	2.587	143.86	4.18
5	2.749	139.58	1.56	2.587	143.92	4.20
7	2.748	139.68	1.57	2.587	143.93	4.19
9	2.746	139.86	1.60	2.588	143.87	4.17
11	2.747	139.67	1.58	2.588	143.61	4.12
Central						
1	2.800	139.62	1.21	2.628	143.45	3.35
3	2.703	140.78	2.07	2.535	145.14	5.70
5	2.684	141.42	2.33	2.516	145.21	6.31
7	2.675	141.80	2.48	2.509	145.22	6.54
9	2.667	141.74	2.57	2.504	145.26	6.72
11	2.667	141.84	2.59	2.503	145.29	6.76
Rightmost						
1	2.800	139.62	1.21	2.628	143.45	3.35
3	2.737	141.54	1.79	2.560	144.46	4.91
5	2.728	141.88	1.90	2.557	144.33	4.95
7	2.728	141.85	1.90	2.557	144.32	4.97
9	2.726	141.83	1.92	2.557	144.38	4.98
11	2.724	141.99	1.95	2.559	144.58	4.95

parameters. Thus, for a particular model system, the strength of the H bond as well as the extent of cooperativity follows the order central > rightmost > leftmost.

Finally, we explore the relationship that exists between the H bond energies estimated using the LS-HB model, and the topological potential energy, V_c. We found an excellent linear relationship between these two quantities expressed in kcal/mol:

$$E_{\text{HB}} = 0.2398V_c - 1.6834 \quad r^2 = 0.998$$

4. Summary

The results of our DFT calculations and AIM analyses show that intramolecular H bonds in polyols, containing the O—H$\cdots$O—H motif, are cooperatively enhanced by a network of hydroxyl groups directionally arranged to act as a H bond donor or acceptor of the hydroxyl groups in the O—H$\cdots$O—H motif. Two model systems, 1,3-propanediol and 1,8-napthalenediol were used to investigate cooperativity. In general, the extent of cooperativity depends on the number of hydroxyl groups in the network, and on the position of the H bond in the network. Thus, of the three selected H bonds in

either of the two model systems considered, the degree of cooperativity is largest for the interior or central H bond, followed by the rightmost, and then the leftmost H bonds. Finally, the degree of cooperativity in the two model systems appear in general to be rather similar. Some general correlations between the intramolecular O—H$\cdots$O—H distances and relevant topological parameters are presented. Also, an excellent linear relationship is reported between the topological potential energies, V_c, and the H bond energies estimated using the semiempirical method of Lippincot and Schroeder.

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