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Molecular Interaction of (Ethanol)$_2$−Water Heterotrimers

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The potential energy surface of the (ethanol)$_2$−water heterotrimers for the trans and gauche conformers of ethanol was studied using density functional theory. The same approximation was used for characterizing representative clusters of (ethanol)$_3$, (methanol)$_3$, and (methanol)$_2$−water. Trimerization energies and enthalpies as well as the analysis of geometric parameters suggest that the structures with a cyclic pattern in the three hydrogen bonds of the type O−H---O (primary hydrogen bonds), where all molecules are proton donor−acceptor at the same time, are more stable than those with just two primary hydrogen bonds. Additionally, we propose the formation of "secondary hydrogen bonds" between hydrogen atoms of the methyl group of ethanol and the oxygen atom of water or other ethanol molecule (C−H---O), which were found to be weaker than the primary hydrogen bonds.

1. Introduction

Molecular systems bound through hydrogen bonds are very important in many fields of physics, chemistry, and biochemistry.[1−3] For example, they are the basis to explain, at a molecular level, the formation of molecular clusters such as those formed by the ethanol−water azeotrope (96% of ethanol and 4% of water). Recently, this azeotrope has received a lot of attention due to the use of anhydrous ethanol as additive in gasoline, which requires a high degree of separation of the ethanol−water mixture.[4−7] Nevertheless, the available information at the molecular level obtained by experimental and computational techniques for the ethanol−water system is still very limited, because there are only a few studies published in this subject. Masella and Flament[8] evaluated the interaction in heterodimers between a water molecule and a molecule of ethanol, methanol, or dimethyl ether by means of ab initio calculations at the MP2 level and various basis sets (6-31+G(d,p), 6-311+G(d,p), and 6-311+G(2df,2p)). Several properties of the hydrogen bonds were investigated, such as inter-oxygen distances and O−H bond lengths. These results showed that, if water acts as a proton donor species, there is a larger stability of the heterodimers than when water is the proton acceptor molecule. Later, van Erp and Meijer[9] used DFT-based Car−Parrinello molecular dynamics to study the aqueous solvation of ethanol and ethylene. It was found that ethanol can be easily accommodated in the hydrogen-bonded network of water molecules without altering its structure. Recently, Oliveira and Vasconcellos[10] employed the charges from electrostatic potentials using a grid based method (CHELPG) and the atoms in molecules (AIM) theory to evaluate the proton donor−acceptor behavior of the water molecule within the ethanol−water heterodimer considering just the ethanol gauche conformer. The results suggest that in addition to the formation of a hydrogen bond between the oxygen atom of the water molecule and the hydrogen atom of the hydroxyl group, there is the formation of a hydrogen bond between the oxygen atom of the water molecule and one of the hydrogen atoms of the methyl group of the ethanol molecule. Additionally, Katrib et al.[11] used the droplet train technique coupled to mass spectrometric detection to describe the gas uptake process of ethanol molecules by aqueous surfaces and reported the experimental dimerization enthalpies for ethanol−water heterodimers, which is in the range of −5.6 ± 1.5 kcal/mol. They also carried out DFT molecular modeling to calculate dimerization enthalpies for the water-trans heterodimer, −4.5 kcal/mol, and the *trans*-water heterodimer, −5.4 kcal/mol (see Figure 1).

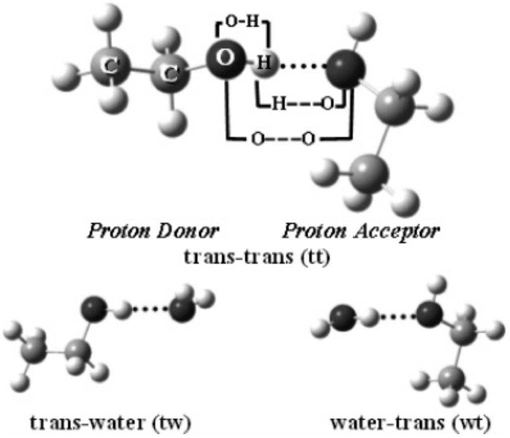

Figure 1. Optimized geometries of the *trans*-ethanol−*trans*-ethanol (tt) dimer and *trans*-ethanol−water (tw) and water−*trans*-ethanol (wt) heterodimers. Hydrogen bonds are represented by black dotted lines (H---O). O−H bond and O---O intermolecular distances are also indicated in the figure.

The lack of studies for clusters of bigger size, between several ethanol molecules and one water molecule, might be due to the existence of three major conformers of ethanol, which have been characterized by experimental methods,[12−16] they are identified as the trans ethanol monomer (t) and two gauche ethanol enantiomers (g1 and g2). These conformers are differentiated by their dihedral angles formed among the C, C, and O atoms and the H that is connected to the oxygen atom, approximately +180°, +60°, and −60° for t, g1 and g2, respectively. These three conformers are very close in energy, with a difference of 41.2 ± 5 cm^{-1} (0.119 ± 0.014 kcal/mol) as reported by Kakar

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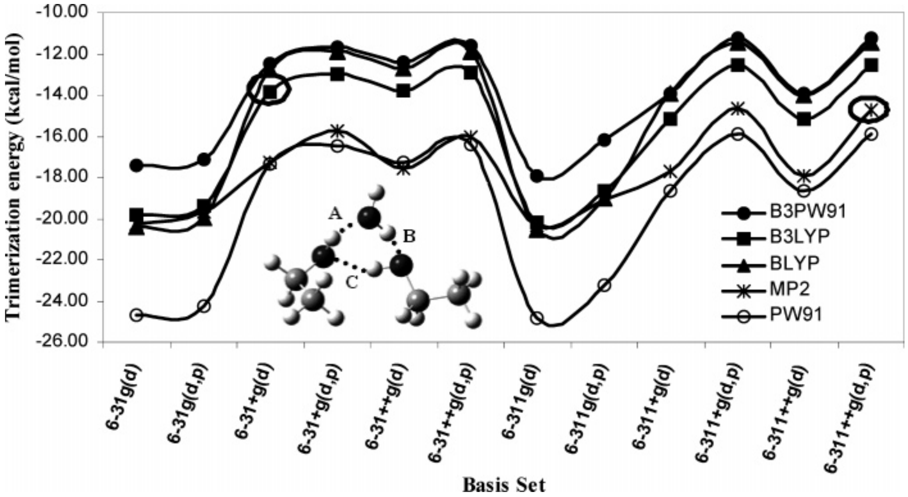

Figure 2. Trimerization energy in kcal/mol for the cg2wt heterotrimer at different levels of theory with various basis sets (data after ZPE correction). The reference energy and the energy for the selected theory level and basis set are the circled values.

and Quade.[17] A similar value was reported in a study of the microwave spectrum of ethanol in the region from 51 to 505 GHz, where this difference of energy is 39.2 cm^{-1} (0.113 kcal/mol),[18] in all cases the trans conformer of ethanol being more stable than the gauche one. However, Shaw et al.[19] reported that the gauche ethanol is favored in the gas phase by a ratio of 6:4 and it was concluded that ethanol exists as a mixture of 42:58 of the forms trans:gauche due to the existence of its two equivalent enantiomers: gauche 1 and gauche 2.

Considering the experimental evidence, it becomes necessary to take into account these three conformers of ethanol for a proper description of the ethanol−water interaction in a similar way as has been considered for the ethanol−ethanol system. For example, González et al.[20] carried out a study of ethanol dimers and cyclic trimers where it was reported that the most stable dimer is the one that corresponds to two trans molecules (see Figure 1). This result was refuted by Dyczmons,[21] who proposed that the global minimum is of the type gauche−gauche. Another reason that makes difficult the study of systems bonded by hydrogen bonds is the high computational cost demanded by the use of high-level ab initio formalisms. For this reason, several authors have chosen to use density functional theory (DFT) because of the good results obtained at a considerably lower computational cost.[22−25] It is important to mention that even though DFT fails in the description of dispersion forces, hydrogen bonds are mainly of electrostatic character, which is included in DFT.[26]

As a first step toward understanding the behavior of the ethanol−water system, taking into account what has been already published about heterodimers, the purpose of the present research was to study gas phase (ethanol)$_2$−water heterotrimers (two ethanol molecules and one water molecule) considering the trans and gauche conformers of ethanol and to analyze the trimerization energies and enthalpies as well as the distance and the bond order of the hydrogen bonds. Additionally, knowing that water does not form an azeotrope with methanol, we optimized structures of methanol−water heterotrimers, and ethanol−ethanol and methanol−methanol trimers, for comparison with the data obtained from the (ethanol)$_2$−water heterotrimers.

2. Computational Details

Full optimization of (ethanol)$_2$−water heterotrimers was carried out at the DFT level of theory using the B3LYP hybrid functional and the 6-31+G(d) basis set. Harmonic vibrational frequencies and zero point energy (ZPE) correction to the trimerization energy were calculated at the same level of theory, because it is known that the ZPE value is significant in hydrogen-bonded systems.[27] In addition, the trimerization energy includes the correction for the basis set superposition error (BSSE) through the counterpoise method.[28] Therefore, the trimerization energy was calculated as $\Delta E_{\mathrm{trim}}(0\ \mathrm{K}) = E_{\mathrm{cluster}} - \Sigma E_{\mathrm{monomers}}$; trimerization enthalpy was calculated in a similar way: $\Delta H_{\mathrm{trim}}(298\ \mathrm{K}) = H_{\mathrm{cluster}}(298\ \mathrm{K}) - \Sigma H_{\mathrm{monomers}}(298\ \mathrm{K})$.

Finally, the bond orders of the hydrogen bonds of the different clusters were obtained with the natural bond orbital (NBO) analysis to have an indication of the strength of the hydrogen bonds, in addition to the analysis of the distance of such interactions. The angle formed by the O−H---O atoms for each hydrogen bond of this type also was analyzed. Similar methodology was employed for the (ethanol)$_3$, (methanol)$_3$, and (methanol)$_2$−water clusters. All calculations were carried out with the Gaussian 03 program.[29]

3. Results and Discussion

Theory Level and Basis Set Selection. Initially, the search for an appropriate computational method was carried out (theory level/basis set) that allowed us to obtain reliable information of the hydrogen bonds at a reasonable calculation time. Due to the lack of experimental information for ethanol−water clusters that contain more than two molecules to validate the computational results obtained for heterotrimers, we compared the DFT results with the ab initio method MP2 at the highest basis set evaluated. Four functionals, B3PW91, PW91, BLYP, and B3LYP, as well as the MP2 method were used. These approximations have been used widely in the scientific literature with good results in predicting this type of interaction.[26,30−34] All the functional/Hamiltonian levels were combined with the following basis sets: 6-31G(d), 6-31G(d,p), 6-31+G(d), 6-31+G(d,p), 6-31++G(d), 6-31++G(d,p), 6-311G(d), 6-311G(d,p), 6-311+G(d), 6-311+G(d,p), 6-311++G(d), and 6-311++G(d,p). The goal was to observe the effect of systematically increasing the quality of the basis set on the trimerization energy of the heterotrimer cg2wt (see inset in Figure 2), which was taken as a representative cluster of the ethanol−water interaction. The letter c makes reference to the cyclic pattern that is shown for the three hydrogen bonds O−H---O, which we

TABLE 1: Selected Geometric Parameters for Gauche 2 (g2) and Trans (t) Ethanol Monomers, as Well as the Water (w) Monomer and cg2wt Heterotrimer, Obtained with the Chosen Theory Level and Basis Set and That of the Reference

					heterotrimer cg2wt					
	monomers						bond length (Å)			
method		g2	w	t		Φ (deg)[a]	O−H		O---O	H---O
B3LYP/6-31+G(d)	Φ (deg)[a]	−61.66	105.39	179.99	g2	−64.31	0.982	A	2.791	1.902
	O−H (Å)	0.970	0.969	0.969	w	106.37	0.987[b]	B	2.758	1.844
					t	178.03	0.983	C	2.786	1.900
MP2/6-311++G(d,p)	Φ (deg)[a]	−57.04	103.37	179.95	g2	−60.30	0.971	A	2.817	1.934
	O−H (Å)	0.961	0.960	0.961	w	104.99	0.974[b]	B	2.764	1.867
					t	171.78	0.972	C	2.799	1.923

[a] Φ = H−O−H angle for water and dihedral angle C−C−O−H for ethanol conformer. [b] Proton donor bond length.

identify as primary hydrogen bonds, in this structure the three molecules are proton donor and proton acceptor at the same time.

For all the cases, the cg2wt trimer corresponds to a minimum on the potential energy surface, because no imaginary frequencies were found for the optimized geometry. The trimerization energy determined with MP2/6-311++G(d,p) was −14.8 kcal/mol. This is considered our most reliable value because of the better treatment of electron correlation. All the curves show a similar tendency. For the same theory level, adding a second diffuse function on the basis set does not significantly affect the trimerization energy, but adding the p polarization function makes the trimerization energy a little less negative in comparison to the values obtained with just the d polarization function. In addition, all the functionals, except PW91, produced trimerization energies that are less exothermic than the results obtained with MP2 for each basis set.

On the basis of the comparison of the trimerization energies, the B3LYP functional with the 6-31+G(d) basis set produced the best compromise between accuracy and computational cost. The trimerization energy difference with that of the reference is about 6.2% less exothermic. The values of the geometrical parameters such as the dihedral angle C−C−O−H for ethanol conformers and bond lengths are slightly overestimated for isolated monomers because geometry optimizations were carried out without imposing symmetry constraints. A similar behavior was found for these molecules when they become part of the cluster, see values in Table 1. However, the values for the O---H and O---O intermolecular distances in the cg2wt heterotrimer are slightly underestimated with respect to those obtained with MP2/6-311++G(d,p).

Heterotrimers Geometries. Due to the different interactions that can exist between the water molecule and the two ethanol molecules, there are several spatial possible arrangements. In this work, 36 structures were considered, which correspond to minima of the potential energy surface. To facilitate our analysis, we propose a classification in six groups according to the proton acceptor or proton donor nature of the water molecule as well as the cyclic pattern observed for the heterotrimers that form "primary hydrogen bonds: O−H---O" and "secondary hydrogen bonds: C−H---O". Figures 3−8 show the structures that belong to each group, where the hydrogen bonds are named with the letters A, B, C, and/or D. Secondary hydrogen bonds were postulated when the bond order is greater than 0.10×10^{-2} and are represented by gray dashed lines.

Group 1 includes clusters where the water molecule behaves as a double proton acceptor forming two primary hydrogen bonds. The clusters of this group are identified as g1g1w, g1g2w, g2g2w, tg1w, tg2w, and ttw; the structures are shown in Figure 3.

Group 2 includes clusters where the water molecule acts as a double proton donor species forming two primary hydrogen bonds and in some cases acts as a single or double proton acceptor forming secondary hydrogen bonds, as in the case of the structures wtg2 and wtg1, see Figure 4. The clusters of this group are identified as wg1g1, wg1g2, wg2g2, wtg1, wtg2, and wtt.

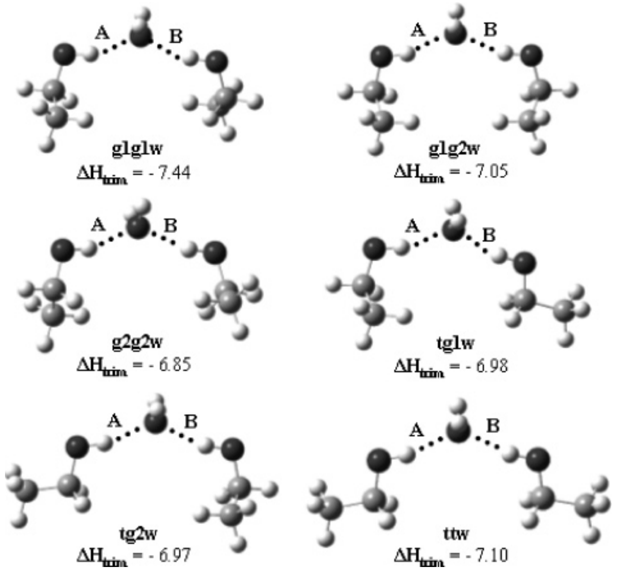

Figure 3. Optimized geometries of heterotrimers that belong to group 1. Primary hydrogen bonds are named A and B, and they are represented by dotted lines. Trimerization enthalpies (ΔH_{trim}) are in kcal/mol.

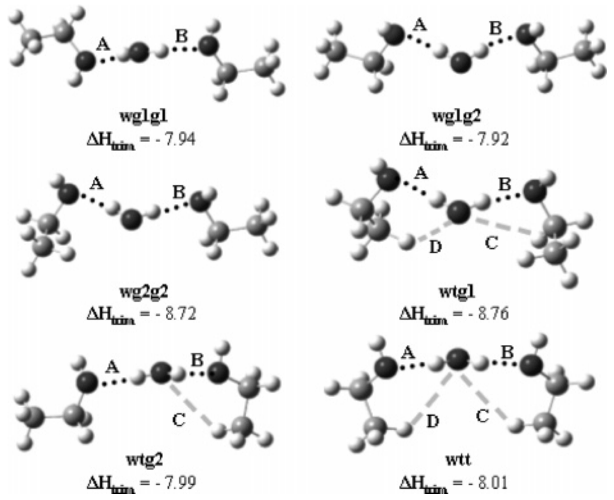

Figure 4. Optimized geometries of heterotrimers that belong to group 2. Primary hydrogen bonds are named A and B and are represented by dotted lines. Secondary hydrogen bonds are named C and D, and they are represented by gray dashed lines. Trimerization enthalpies (ΔH_{trim}) are in kcal/mol.

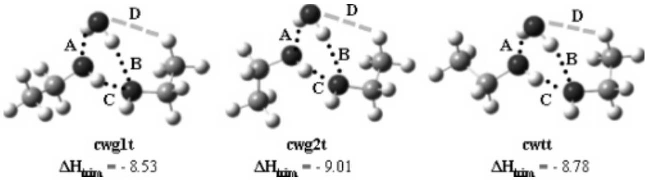

Figure 5. Optimized geometries of heterotrimers that belong to group 3. Primary hydrogen bonds are named A, B, and C and are represented by dotted lines**.** The secondary hydrogen bond is named D, and it is represented by a gray dashed line. Trimerization enthalpies (ΔH_{trim}) are in kcal/mol.

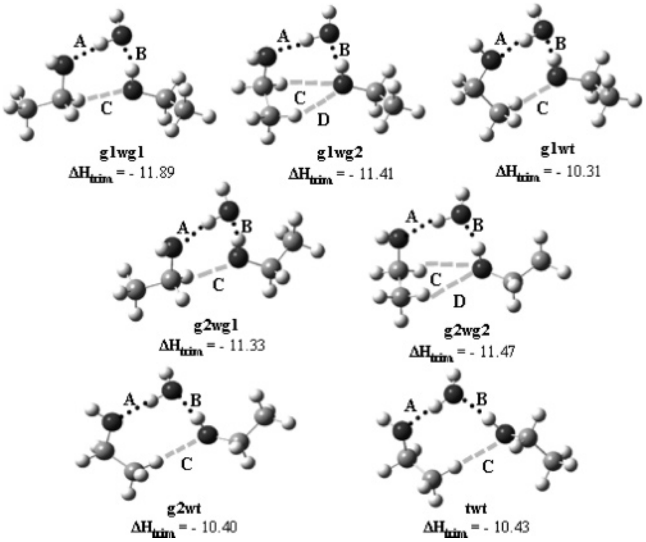

Figure 6. Optimized geometries of heterotrimers that belong to group 4. Primary hydrogen bonds are named A and B and are represented by dotted lines. Secondary hydrogen bonds are named C and D, and they are represented by gray dashed lines. Trimerization enthalpies (ΔH_{trim}) are in kcal/mol.

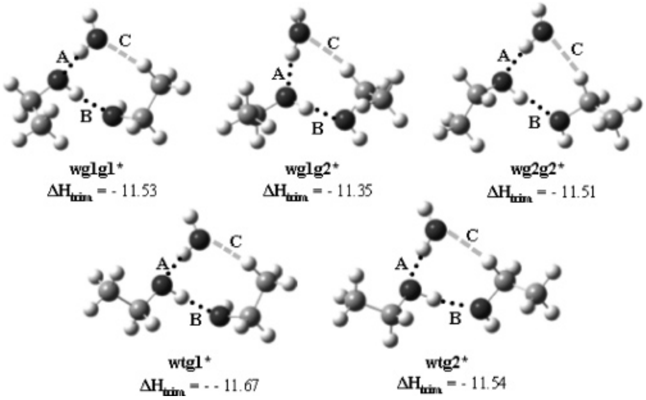

Figure 7. Optimized geometries of heterotrimers that belong to group 5. Primary hydrogen bonds are named A and B and are represented by dotted lines. The secondary hydrogen bond is named C, and it is represented by a gray dashed line. Trimerization enthalpies (ΔH_{trim}) are in kcal/mol.

Group 3 has systems where the water molecule is a double proton donor within a cyclic pattern formed by three primary hydrogen bonds. In addition, there is formation of an ethanol−water secondary hydrogen bond; see structures cwg1t, cwg2t, and cwtt in Figure 5.

Group 4 has clusters where the water molecule acts as a proton donor and proton acceptor at the same time, forming two primary hydrogen bonds. There is the formation of one or two secondary hydrogen bonds between the ethanol molecules, as can be seen in structures g2wt and g1wg2 (see Figure 6). Clusters of this group are identified as g1wg1, g1wg2, g1wt, g2wg1, g2wg2, g2wt, and twt.

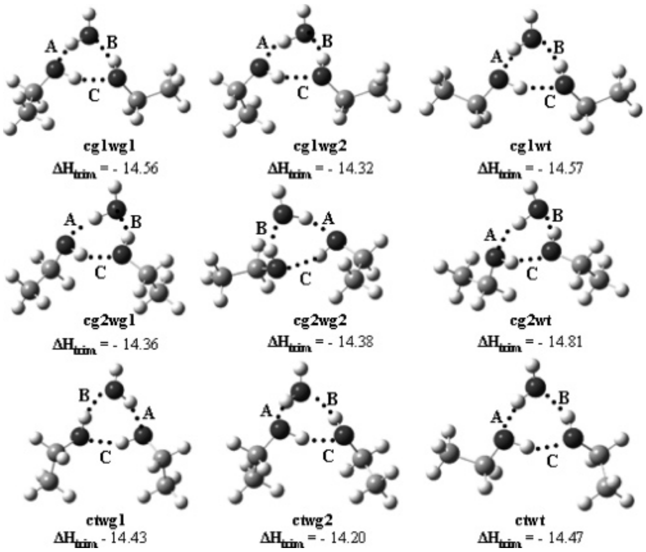

Figure 8. Optimized geometries of heterotrimers that belong to group 6. Primary hydrogen bonds are named A, B, and C, and they are represented by dotted lines. Trimerization enthalpies (ΔH_{trim}) are in kcal/mol.

Group 5 contains clusters for which the water molecule is a proton donor in a primary hydrogen bond and a proton acceptor in one secondary hydrogen bond. Structures of this group are identified as wg1g1*, wg1g2*, wg2g2*, wtg1*, and wtg2*; all these clusters are shown in Figure 7. The asterisk (*) is used to differentiate the structures of this group from the structures that belong to group 1.

Group 6 has clusters that only form primary hydrogen bonds in a cyclic pattern, all the molecules being proton donors and proton acceptors, at the same time. Structures belonging to this group are cg1wg1, cg1wg2, cg1wt, cg2wg1, cg2wg2, cg2wt, ctwg1, cwtg2, and ctwt. The complete set of structures of this group is in Figure 8.

Structures that belong to groups 1 and 2, where the water molecule is a double proton acceptor and a double proton donor, respectively, are formed by two almost equivalent primary hydrogen bonds in each structure. Nevertheless, the distances of these hydrogen bonds for the heterotrimers of group 1 are larger than the corresponding ones for the heterotrimers of group 2. This may be due to the fact that the hydrogen bonds of the clusters where the ethanol molecule is proton acceptor are stronger. This behavior could probably be explained by the inductive effect of the alkyl group of ethanol that makes the electronic density of the oxygen atom more available, as was already addressed by Masella et al.[8] in their computational study of ethanol−water, methanol−water, and dimethyl ether−water heterodimers. Masella et al. concluded that the dimethyl ether−water heterodimer presents the strongest hydrogen bond due to the higher number of alkyl groups bonded to the oxygen atom in the proton acceptor molecule (dimethyl ether). This result was obtained by analysis of electronic density at the hydrogen bond critical point (at the HF/6-311+G(2d,2p) level) for the interaction of dimethyl ether, methanol, and ethanol with the water molecule. These densities are 2.56, 2.50, and 2.48 given in 10^{-2} e/au, respectively. In addition, for the dimethyl ether−water heterodimer, the O---O distance is shorter than for the other heterodimers and the O−H bond is larger than for the other heterodimers where the water molecule is proton donor.

TABLE 2: Hydrogen Bond Lengths, Bond Orders, and O−H---O Angles of Some Heterotrimer Representatives of Each One of Six Groups

	hydrogen bond lengths (Å)				bond orders x 10^2				O−H---O angle (deg)		
heterotrimer	A	B	C	D	A	B	C	D	A	B	C
tg2w (group 1)	1.976	1.979			3.17	3.05			165.83	162.90	
wtg2 (group 2)	1.936	1.935	3.105		3.63	3.53	0.23		166.94	165.54	
wtg1 (group 2)	1.933	1.933	2.878	3.210	3.63	3.59	0.24	0.20	167.81	165.55	
cwg2t (group 3)	2.053	2.243	1.967	3.223	2.85	1.29	3.41	0.20	148.13	146.47	158.43
g2wt (group 4)	1.807	1.857	2.582		4.86	5.23	1.16		177.31	171.31	
g1wg2 (group 4)	1.805	1.861	2.607	3.312	5.36	5.21	0.58	0.19	169.40	166.40	
wg1g2* (group 5)	1.838	1.825	2.448		4.87	5.77	0.91		167.37	167.65	
cg1wt (group 6)	1.894	1.897	1.891		5.62	4.73	4.97		151.76	149.59	149.46

In the present investigation, based on the analysis of bond orders, we found the existence of secondary hydrogen bonds in some heterotrimers of group 2, except for wg1g1, wg1g2, and wg2g2 structures (see Figure 4). The results show that wtt and wtg1 clusters have two secondary hydrogen bonds. However, primary hydrogen bonds are 15 times stronger than these interactions for clusters of this group having distances as large as 3.60 Å (see Table 2). These results are in good agreement with those reported in the scientific literature for other type of systems with hydrogen bonds that do not involve two oxygen atoms, such as C−H---π and C−H---O, which are for each particular system weaker than the primary hydrogen bonds.[23,35−37] In these studies, the interactions were characterized with tools such as electron density at the bond critical points using the AIM theory. For example, Parthasarathi et al.[36] reported hydrogen bonds with distances as long as 4.30 Å for hydrogen bonds of the type C−H---π with HF/6-31+G(d) and 3.60 Å with MP2/6-31+G(d) in cyclic phenol trimers.

The structures of group 3 formed a secondary hydrogen bond (see Figure 5) with a distance of no more than 3.20 Å. For this group, primary hydrogen bonds form a cyclic pattern and are more than 17 times stronger than this interaction. Clusters of group 4 form secondary hydrogen bonds with a distance between 2.50 and 2.60 Å and a bond order that suggests a strength almost one-fifth that of the corresponding strength of primary hydrogen bonds in five of the seven clusters of this group. The primary hydrogen bonds of these structures are among the shortest and strongest when compared to the other heterotrimers, they have distances as short as 1.80 Å and bond orders similar to the corresponding hydrogen bonds of the heterotrimers of group 6. As an example, if the primary hydrogen bond with the highest bond order of the cg1wt heterotrimer (group 6), that is, hydrogen bond A, is compared with the corresponding bond order of hydrogen bond B of the g2wt heterotrimer (group 4), the difference is just 0.39×10^{-2}. This behavior may be due to the influence of the secondary hydrogen bonds that, in spite of being very weak interactions, may force the structures of group 4 to take a configuration in which the other hydrogen bonds are favored. The g1wg2 and g2wg2 structures were the exceptions within this group because these form two secondary hydrogen bonds, which share the same oxygen atom of the gauche 2 ethanol, obtaining a smaller bond order for these interactions in comparison with the ones that correspond to the bonds of this type in the other structures of group 4, perhaps due to the fact of sharing a single electronic density by two protons (see Figure 6 and Table 2).

The structures of group 5 also formed a secondary hydrogen bond (see Figure 7), with a distance of up to 2.50 Å. For this group, primary hydrogen bonds are more than 7 times stronger than this interaction. The structures of group 6 present a cyclic pattern of three primary hydrogen bonds where each molecule interacts with the other two by means of two hydrogen bonds being at the same time proton acceptor and proton donor molecules. For this last group, only the homologous cluster with three trans ethanol conformers was obtained, structure (cttt) in Figure 9. This trimer was chosen because it was reported to be the global minimum on the potential energy surface of ethanol trimers by González et al.[20] using DFT calculations. Similarly to the heterotrimers of group 6, this trimer has three primary hydrogen bonds whose distances do not exceed 1.9 Å.

Other geometric parameter that may be used to analyze the strength of the primary hydrogen bonds is the angle formed by the O−H---O, because it is expected that a linear hydrogen bond should be stronger. We found that for groups 1, 2, 4, and 5, which do not have a cyclic pattern, the O−H---O angle is closer to 180° for the strongest hydrogen bonds, as shown in Table 2. However, the structures belonging to groups 3 and 6 show the less linear O−H---O angles found in this study, as observed in Table 2, although group 6 involves the strongest hydrogen bonds. This result can be due to the cyclic pattern of their primary hydrogen bonds, which induce a structural stress, distorting the O−H---O angle.

Thermodynamic Parameters for the Heterotrimers. The results of trimerization energy (ΔE_{trim}) and enthalpy (ΔH_{trim}) organized in ranges for each group are listed in Table 3. Depending on the ΔH_{trim}, the following order of exothermicity for the heterotrimers was found: group 1 < group 2 < group 3 < group 4 ∼ group 5 < group 6.

The less exothermic heterotrimers belong to group 1, where there is formation of two primary hydrogen bonds with trimerization enthalpies in the range −6.85 to −7.44 kcal/mol.

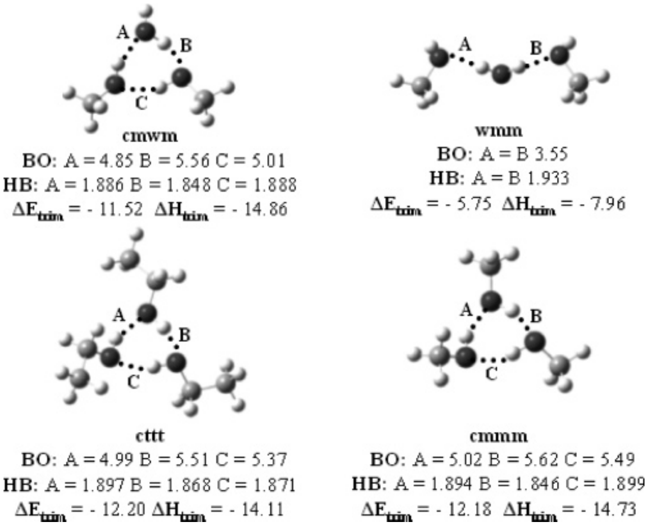

Figure 9. Methanol−water heterotrimers (cmwm, wmm) and cyclic trimers of ethanol and methanol (cttt, cmmm). Bond order (BO) and distances (HB) in Å for primary hydrogen bonds (black dotted lines). Trimerization energies (ΔE_{trim}) and enthalpies (ΔH_{trim}) in kcal/mol. For each hydrogen bond, the bond order is given in 10^{-2}.

TABLE 3: Range of Trimerization Energies (ΔE_{trim}) and Enthalpies (ΔH_{trim}) for Heterotrimers in the Different Groups

group	ΔE_{trim} (0 K)[a] (kcal/mol)	ΔH_{trim} (298 K) (kcal/mol)
group 1	−5.26 to −5.02	−7.44 to −6.85
group 2	−6.29 to −5.97	−8.76 to −7.92
group 3	−6.59 to −6.42	−9.01 to −8.53
group 4	−8.96 to −7.86	−11.89 to −10.31
group 5	−9.30 to −9.08	−11.67 to −11.35
group 6	−11.29 to −11.73	−14.20 to −14.81

[a] Including ZPE correction and counterpoise correction.

It is important to note that the more exothermic trimerization reactions correspond to the formation of the heterotrimers with the shortest and strongest primary hydrogen bonds. This reaction is favored when the water molecule is the proton donor, as is observed in the order of exothermicity for the two first groups (group 1 < group 2), because the hydrogen bonds A and B for group 2 are strengthened by the inductive effect of the alkyl group of the ethanol molecule as a proton acceptor molecule. In addition, it is possible that the secondary hydrogen bonds in group 2 stabilize these clusters in comparison with the heterotrimers that belong to group 1 that do not show such interactions.

Structures that belong to group 6 have the most negative trimerization enthalpies for this kind of cluster with exothermic values below −14 kcal/mol, which may be due to the presence of three short primary hydrogen bonds with high bond orders in these heterotrimers. In other words, the configurations that present cyclic patterns in their primary hydrogen bonds, where all molecules are proton donor−acceptors, are more favorable. In contrast, structures of group 3 that also form three primary hydrogen bonds in a cyclic pattern are less exothermic than structures that belong to groups 4 and 5, which form just two primary hydrogen bonds. This is probably due to the fact that the water molecule is a double proton donor in structures of group 3. This is similar to the reported result about water−water interactions, where it was concluded that the most stable water trimer has a cyclic pattern where the water molecules are proton donor−acceptor.[27]

Comparison between Ethanol−Water Heterotrimers and the Cyclic Ethanol Trimer with Its Homologous Methanol Clusters. The two structures obtained for the heterotrimers of (methanol)$_2$−water along with the cyclic ethanol and methanol trimers are shown in Figure 9, these clusters do not present formation of secondary hydrogen bonds.

It was not possible to optimize (methanol)$_2$−water clusters with geometric patterns similar to the (ethanol)$_2$−water heterotrimers of groups 1, 3, 4, and 5. It was only possible to obtain the structures that correspond to group 2 and group 6 patterns, identified as wmm and cmwm, respectively. The wmm heterotrimer forms two equivalent primary hydrogen bonds, whose distances are larger and bond orders are smaller than those parameters for the hydrogen bonds of the cmwm heterotrimer (see Figure 9). Therefore, methanol behaves similar to ethanol when interacting with the water molecule in clusters of three monomers. However, no secondary hydrogen bonds were found for these two heterotrimer structures. The cmmm and cmwm clusters have three primary hydrogen bonds, which are very similar when we compare the hydrogen bond distances, these differences do not exceed 0.01 Å. Nevertheless, in studies about methanol clusters, secondary hydrogen bonds have been reported for trimers, suggesting that the hydrogen atoms of the methyl group of methanol play an important role in the stabilization of these clusters.[35,38] These methanol trimers that show secondary hydrogen bonds only have two primary hydrogen bonds whereas the trimer that we analyzed (cmmm) has three primary hydrogen bonds in a cyclic pattern, which does not allow the formation of these secondary interactions.

Comparing the thermodynamic parameters of ethanol−water and ethanol clusters with its homologous clusters of methanol−water and methanol, we observe a similar behavior in both the trimerization enthalpy and energy (see Figure 9 and Table 3). This thermodynamic information is correlated with the previously analyzed similarity in the geometric parameters of these aggregates; thus, for example, the methanol−water interaction for the heterotrimer with the cyclic pattern (cmwm) is more favorable than this interaction in the heterotrimer (mwm) with just two primary hydrogen bonds. It is important to emphasize that, for the methanol clusters study, B3LYP/6-31+G(d) is a good approach too, according to the value of trimerization enthalpy for methanol (mmm), because this value differs by just 2.08 kcal/mol considering the experimental rank reported for trimerization enthalpy of −12.53 ± 0.12 kcal/mol.[39]

4. Conclusions

In this research it was found that the B3LYP hybrid functional using the 6-31+G(d) basis set is a suitable approach for the study of weakly bound clusters through hydrogen bonds. The study of clusters with ethanol molecules is difficult because the potential energy surface for those clusters seems to be very flat. We identified a total of 36 stable clusters that were classified in six groups according to the behavior of the water molecule as proton acceptor or proton donor. It was found that structures with a cyclic pattern where all the molecules are proton donor−acceptor in primary hydrogen bonds are the most stable. Thus, the cluster stability seems to increase with the increasing the number of primary hydrogen bonds. Additionally, the presence of the new interactions in ethanol−water clusters (C−H---O) was confirmed. Even though the calculations here reported are for the gas phase, they can be taken as a first approach in the search of a structure(s) that can explain the ethanol−water azeotrope. It is suggested that the presence of secondary hydrogen bonds might play an important role in the formation and stability of ethanol−water azeotrope.

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