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Ab Initio Calculations of Cooperativity Effects on Clusters of Methanol, Ethanol, 1-Propanol, and Methanethiol

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The results of ab initio calculations for cyclic clusters of methanol, ethanol, 1-propanol, and methanethiol are presented. Dimer, trimer, and tetramer clusters of all four compounds are studied, as are pentamer and hexamer clusters of methanol. From optimized clusters at HF/6-31G**, total energies and binding energies were calculated with both the HF and MP2 theories using the aug-cc-pVDZ basis set. Accurate binding energies were also calculated for the dimer and trimer of methanol using symmetry-adapted perturbation theory with the same basis set. Intermolecular and intramolecular distances, charge distribution of binding sites, binding energies, and equilibrium constants were computed to determine the hydrogen bond cooperativity effect for each species. The cooperativity effect, exclusive to hydrogen bonding systems, results from specific forces among the molecules, in particular charge-transfer processes and the greater importance of interactions between molecules not directly hydrogen bonded because of the longer range of the interactions. The ratios of equilibrium constants for forming multimer hydrogen bonds to that for dimer hydrogen bond formation increase rapidly with the cluster size, in contrast to the constant value commonly used in thermodynamic models for hydrogen bonding liquids.

Introduction

Hydrogen bonds (H-bond) play a vital role in chemical, physical, and biological processes. While many experimental and theoretical studies have been directed toward understanding hydrogen bonding, it remains an area of active research. Hydrogen bonds can be viewed both as a chemical and as a physical interaction as the bond strength is between that of a weak chemical bond and a strong intermolecular interaction, and it is a challenge to properly model the thermodynamic properties of hydrogen bonding fluids. There are many models used to describe hydrogen bonding fluids, such as chemical equilibria[1], lattice,[2−7] statistical association,[8−11] and perturbed-hard-chain[12−14] theories (see Economou and Donohue[15] for a review and comparison of these theories). All of these models are based on some measure of the strength and number of hydrogen bonds formed. An important concept in the theory of hydrogen bonding fluids is hydrogen bond cooperativity, which is the enhancement to the formation of additional hydrogen bonds as a result of an already formed hydrogen bond. However, most thermodynamic models neglect this cooperativity effect and assume the same value for the equilibrium constants for the formation of a dimer from two monomers, a trimer from a dimer and a monomer, etc.

Recently, Gupta and Brinkley[16] measured spectroscopically the hydrogen bond cooperativity of dilute 1-pentanol and 1-hexanol separately in *n*-hexane, and have modeled the cooperativity effect based on the lattice theory.[2,3] Their findings suggest that the equilibrium constant for the $X + X_n \rightarrow X_{n+1}$ ($n \geq 2$) hydrogen bond formation is approximately 10 times larger than for the $2X \rightarrow X_2$ hydrogen bond due to cooperativity effects. They expressed this using the ratio of the equilibrium constants for multimer hydrogen bond formation to that for dimer hydrogen bonds. Although Gupta and Brinkley recognized the effect of hydrogen bond cooperativity, they concluded that the effect was independent of the number of hydrogen bonds formed beyond the first.

Hydrogen bond cooperativity can be examined computationally by ab initio methods, and it has been a subject of extensive research[17−22] (also see the references therein). Most studies have focused on water and methanol systems because they are small molecules and extensive experimental data are available. These studies predicted the structure, binding energies, and vibrational frequencies of clusters (dimers to hexamers) using ab initio methods[17−22] (HF and MP2) and density functional theory.[21−23] However, there has been no comprehensive study of the energetics of hydrogen bond cooperativity, and its dependence on molecular and cluster size. Most of the emphasis in recent studies has been on structure and the vibrational spectra.

Here we investigate hydrogen bond cooperativity for clusters of methanol, ethanol and 1-propanol and, for comparison, non-hydrogen bonding methanethiol using ab initio methods to provide greater insight into the energetics of the cooperativity effect and to examine theoretically the conclusion of Gupta and Brinkley on the strength of hydrogen bonds. To our knowledge, no studies have been performed on the cooperativity effect with alcohols larger than methanol, such as ethanol and 1-propanol considered here. This work also compares the cooperativity effect of alcohols to a thiol analogue of methanol that does not form hydrogen bonds. Such comparison is useful in distinguishing between hydrogen bond cooperativity and weaker molecular proximity effects.

Computational Method

Methanol, ethanol, and 1-propanol were chosen as models for 1-alkanol compounds. The measurements of Gupta and

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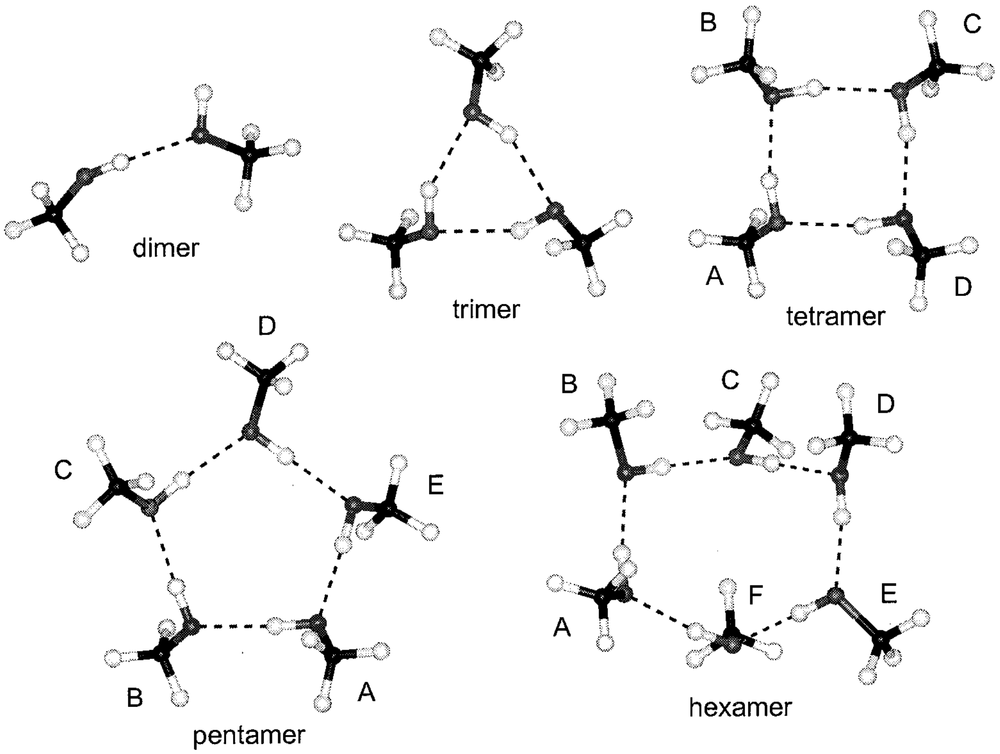

Figure 1. Geometry for methanol clusters optimized at HF/6-31G**.

Brinkley[16] were on 1-pentanol and 1-hexanol; however, clusters of these molecules are too large to be investigated at the ab initio level at the present time. The shorter chain 1-alkanols chosen mimic the behavior of longer chain molecules since the prevailing type of interaction is hydrogen bonding, although we also recognize that steric effects may play an important role in the configurations of the clusters. Calculations were also done for methanethiol, which does not form hydrogen bonds, to demonstrate the difference from hydrogen bonding systems.

Clusters of different sizes were constructed for methanol, ethanol, 1-propanol and methanethiol. For each compound, dimer, trimer and tetramer clusters were considered, as well as pentamer and hexamer clusters for methanol. The number of molecules, or atoms, that can be considered is limited by the computational demands of the ab initio calculations.

The clusters were optimized by minimizing their total energy at the Hartree−Fock (HF) level with the 6-31G** basis set. Using this optimized cluster geometry, total energies and binding energies associated with the formation of hydrogen bonds were calculated with the HF and second-order Møller−Plesset (MP2) theories (except for the pentamer and hexamer of methanol, and all clusters of 1-propanol) using the aug-cc-pVDZ basis set. Recently, the importance of using a large basis set (e.g., cc-pV5Z) and electron correlation to appropriately describe the interaction of hydrogen bonding systems[24] has been suggested; however, the use of such a large basis set is not computationally practical for the study of the large molecules and clusters considered here. We have done calculations for all dimers with the aug-cc-pVTZ basis set to show that our results are not greatly affected by basis set size. Note that our calculations are for isolated clusters in a vacuum.

For each cluster of size *n*, binding energies were calculated for all dimer and multimer interactions using the supermolecular approach.[25,26] For example, for the tetramer cluster of methanol in Figure 1 calculations were made for the four dimers (**AB**, **BC**, **CD**, and **AD**), eight trimers formed from the dimers (**A** to **BC** and **DC**, **B** to **CD** and **AD**, **C** to **DA** and **BA**, and **D** to **AB** and **CB**), and four tetramers formed from the trimers (**A** to **BCD**, **B** to **ACD**, **C** to **ABD**, and **D** to **ABC**). All the binding energies were corrected for basis set superposition error[27] (BSSE) using the full counterpoise procedure[28] using the Gaussian 98 computational chemistry program,[29] though zero-point corrections were not included. In addition, binding energies for the dimer and trimer of methanol were calculated using the symmetry-adapted perturbation theory[30−32] (SAPT) method, which yields accurate interaction energies without the need to correct for BSSE. An advantage of this method is that the electrostatic, induction, dispersion, and exchange energies are separately calculable. However, SAPT is very demanding of computational resources (CPU time and temporary disk storage), and is also currently limited to 255 basis functions. The aug-cc-pVDZ basis set was also used in the SAPT calculations. The results of all our calculations are available as Supporting Information.

Total binding energies (*BE*) are calculated as

$$BE = E_{\text{cluster}} - \sum_{i}^{n} E_i \tag{1}$$

where E_{cluster} is the total energy of the cluster, E_i is the energy of individual molecules in the cluster geometry (corrected for BSSE), and n is the size of the cluster (integer greater than 2). We define an excess energy (*EE*) as

$$EE = BE - \sum_{i}^{n} \Delta E_i \tag{2}$$

where ΔE_i is the interaction energy of the hydrogen-bonded pairs in the cluster (calculated with the basis set of the entire cluster).

We were also interested in calculating the ratio of the equilibrium constant of forming multimer hydrogen bonds relative to that for the formation of a dimer. Equilibrium

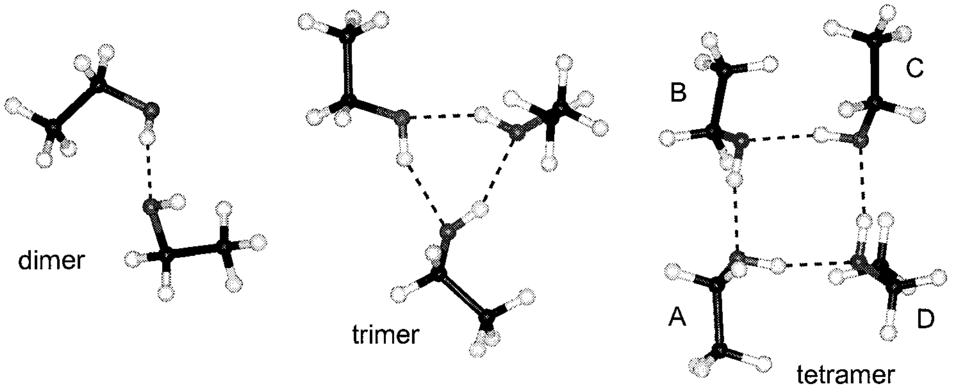

Figure 2. Geometry for ethanol clusters optimized at HF/6-31G**.

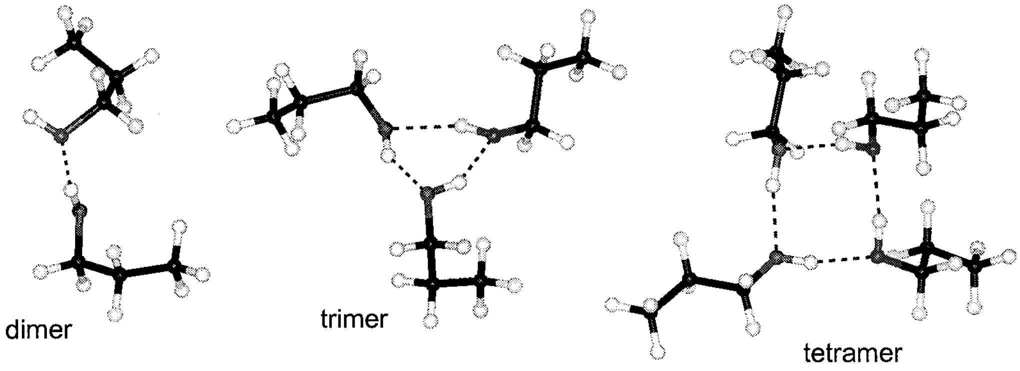

Figure 3. Geometry for 1-propanol clusters optimized at HF/6-31G**.

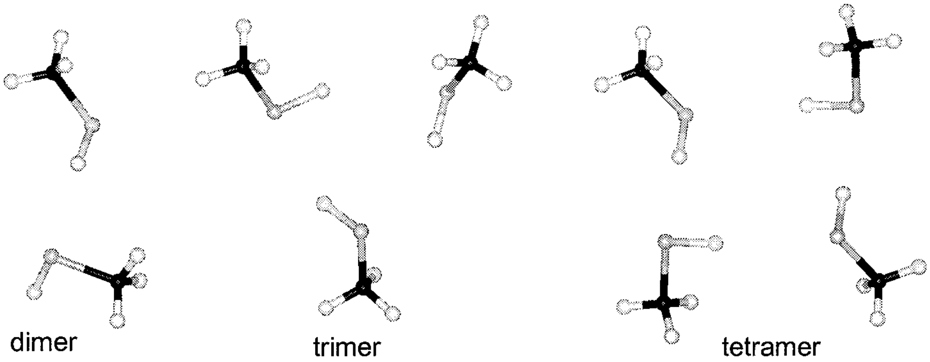

Figure 4. Geometry for methanethiol clusters optimized at HF/6-31G**.

constants were calculated from the Boltzmann factor of the Gibbs free energy change; that is,

$$\frac{K_{n\rightarrow n+1}}{K_{1\rightarrow 2}} = \exp\left(-\frac{\Delta G_{n\rightarrow n+1} - \Delta G_{1\rightarrow 2}}{RT}\right) \quad (3)$$

where $K_{n\rightarrow n+1}$ and $K_{1\rightarrow 2}$ are the equilibrium constants of forming a multimer and dimer hydrogen bonds, respectively, $\Delta G_{n\rightarrow n+1}$ and $\Delta G_{1\rightarrow 2}$ are the Gibbs free energy changes, and n is an integer greater than 2.

From ab initio calculations, one can only obtain changes in energy. The Gibbs free energies can be expressed as

$$\Delta G_{1\rightarrow 2} = \Delta E_{1\rightarrow 2} + P\Delta V_{1\rightarrow 2} - T\Delta S_{1\rightarrow 2}$$

$$\Delta G_{n\rightarrow n+1} = \Delta E_{n\rightarrow n+1} + P\Delta V_{n\rightarrow n+1} - T\Delta S_{n\rightarrow n+1} \quad (4)$$

Since our interest here is in hydrogen bonding in the liquid phase at low pressure, the change in volume terms can be neglected. We assume, and this is a significant assumption, that the change in entropy due to the addition of one molecule to a hydrogen bond chain is independent of the chain length. Thus,

$$\frac{K_{n\rightarrow n+1}}{K_{1\rightarrow 2}} \cong \exp\left(-\frac{\Delta E_{n\rightarrow n+1} - \Delta E_{1\rightarrow 2}}{RT}\right) \quad (5)$$

Therefore, computing the difference in energy changes on forming an additional hydrogen bond in a cluster of n molecules from that of forming a dimer from monomers provides an estimate of the ratio of equilibrium constants. The deviation of this ratio from unity is a measure of hydrogen bond cooperativity.

Results and Discussion

Figures 1−4 show the geometry of the optimized clusters in a vacuum (no solvation effects are considered). The alcohol clusters are mainly cyclic structures due to hydrogen bonding. Even though methanethiol does not form hydrogen bonds, it also forms cyclic structures due to the polarity of the SH group

TABLE 1: Intermolecular Distance of Bonding Sites for Alcohols and Thiol Clusters (Geometry of Clusters Optimized at HF/6-31G)**

cluster size *n*	distance (Å)						average
methanol			O···O				
2	2.9529						2.9529
3	2.8836	2.8696	2.8722				2.8751
4	2.8303	2.8311	2.8301	2.8303			2.8305
5	2.8174	2.8126	2.8127	2.8160	2.8303		2.8178
6	2.8434	2.8218	2.8127	2.8060	2.8038	2.8324	2.8200
ethanol			O···O				
2	2.9513						2.9513
3	2.8938	2.8805	2.8850				2.8864
4	2.8475	2.8389	2.8383	2.8473			2.8430
1-propanol			O···O				
2	2.9554						2.9554
3	2.8796	2.8802	2.8637				2.8745
4	2.8378	2.8377	2.8493	2.8375			2.8406
methanethiol			S···S				
2	4.4700						4.4700
3	4.4356	4.4385	4.5066				4.4602
4	4.3932	4.4534	4.3909	4.4515			4.4223

TABLE 2: Intramolecular Distance of Bonding Sites for Alcohols and Thiol Clusters (Geometry of Clusters Optimized at HF/6-31G)**

cluster size *n*	distance (Å)						average
methanol			O−H				
2	0.9467	0.9429					0.9448
3	0.9500	0.9499	0.9498				0.9499
4	0.9531	0.9531	0.9532	0.9532			0.9532
5	0.9539	0.9539	0.9540	0.9538	0.9535		0.9538
6	0.9550	0.9529	0.9527	0.9531	0.9539	0.9541	0.9536
ethanol			O−H				
2	0.9474	0.9437					0.9456
3	0.9501	0.9499	0.9505				0.9502
4	0.9533	0.9532	0.9534	0.9532			0.9533
1-propanol			O−H				
2	0.9476	0.9428					0.9452
3	0.9485	0.9501	0.9506				0.9497
4	0.9531	0.9531	0.9530	0.9533			0.9531
methanethiol			S−H				
2	1.3274	1.3271					1.3273
3	1.3272	1.3274	1.3274				1.3273
4	1.3273	1.3275	1.3273	1.3275			1.3274

and alignment of their dipoles; these cyclic structures are known to be the most stable. One cyclic structure was studied for each cluster, though other cyclic variations are possible, especially for the pentamer and hexamer of methanol. No attempt was made to determine whether the structures corresponded to a minima or stationary point on the potential energy surface.

Tables 1 and 2 list the intermolecular (O···O and S···S) and intramolecular (O−H and S−H) distances of the bonding sites, respectively. It is seen that for all cases, the intermolecular O···O distance in the *n*-mer is less than that in the dimer, and generally decreases as the number of molecules in the cluster increases. Others have previously observed this trend in clusters of methanol.[17,19,21−23]

Table 2 shows the intramolecular (O−H and S−H) distances in the clusters. For the alcohols, there is a small increase in the O−H bond distance as the cluster size increases. However, no change is observed in the S−H bond distance in methanethiol. This difference is another indication of the cooperativity effect in hydrogen bonding systems. Hydrogen bonding brings the oxygen from different molecules closer and, by doing so, the hydrogen of one O−H group is closer to the oxygen of the other hydrogen bonding O−H group so that there is a more even distribution of charge between the molecules. This is not observed for methanethiol because the S−H groups are weakly bound and sulfur has a slight positive charge (see Table 3 for a summary of the average charge of the binding groups). The oxygen atom in the O−H group has a large negative charge, increasing with the cluster size, and the hydrogen atom has a positive charge, which also increases with cluster size.

To determine the appropriateness of the chosen basis set (aug-cc-pVDZ) for the calculations, we have also determined the binding energies of all dimers with the aug-cc-pVTZ basis set. Table 4 summarizes the results of the binding energies along with the magnitude of the BSSE. We performed calculations at this level of theory only for the dimers because of limited computational resources. Tsuzuki et al.[24] performed a series of calculations with hydrogen bonding complexes with different basis sets (cc-pVXZ, X = D, T, Q, and 5). For the methanol dimer, their calculated binding energies are −2.79 (HF) and −3.77 kcal/mol (MP2), and −2.62 (HF), and −4.72 kcal/mol (MP2) with the cc-pVDZ and cc-pVTZ basis sets, respectively; the BSSE for these corresponding energies are −2.73, −4.62, −1.07, and −2.17 kcal/mol. We should note that, in their calculations, the methanol dimer structure was optimized at MP2/6-311G**, and no diffuse functions are included in the basis set for the energy calculations. The binding energies

TABLE 3: Average Charge on Binding Groups of Alcohols and Thiol Clusters (Mulliken Charges)

	average charge (*D*)	
cluster size *n*	O	H[a]
methanol		
2	−0.6096	0.1518
3	−0.6450	0.2053
4	−0.6822	0.2293
5	−0.6807	0.2612
6	−0.7015	0.2773
ethanol		
2	−0.6818	0.1468
3	−0.7100	0.1933
4	−0.7668	0.2370
1-propanol		
2	−0.6869	0.1698
3	−0.7439	0.2420
4	−0.7676	0.1421

	average charge (*D*)	
cluster size *n*	S	H[a]
methanethiol		
2	0.1207	0.0922
3	0.1129	0.1065
4	0.1246	0.0881

[a] Charge on H covalent bound to O or S.

TABLE 4: Basis Set and BSSE Effect on Binding Energies of Dimers of Alcohols and Thiol (All Energies in kcal/mol)

		HF		MP2	
cluster	basis set	binding energy	BSSE	binding energy	BSSE
methanol	aug-cc-pVDZ	−3.716	−0.280	−5.023	−0.994
dimer	aug-cc-pVTZ	−3.688	−0.099	−5.290	−0.571
ethanol	aug-cc-pVDZ	−3.545	−0.405	−5.761	−1.515
dimer	aug-cc-pVTZ	−3.507	−0.110	−6.106	−0.762
1-propanol	aug-cc-pVDZ	−3.624	−0.442		
dimer	aug-cc-pVTZ	−3.599	−0.114		
methanethiol	aug-cc-pVDZ	−0.705	−0.184	−1.834	−0.627
dimer	aug-cc-pVTZ	−0.637	−0.042	−1.896	−0.274

TABLE 5: Binding Energies of Dimer and Trimer of Methanol (Basis Set aug-cc-pVDZ)

methanol cluster	binding energy (kcal/mol)			correlation
	HF	MP2	SAPT	
2	−3.716	−5.023	−4.533	−0.817
3	−7.544	−10.263	−9.248	−1.704
	−7.544	−10.285	−9.263	−1.719
	−7.889	−10.649	−9.575	−1.687

calculated in this work differ from the ones by Tsuzuki et al. mainly because we use diffuse functions in our basis set, and these are usually very important to properly describe interaction energies, as well as to minimize the BSSE effects (our results show diffuse functions lower the BSSE by as much as one order of magnitude). The results in Table 4 show the energies calculated with the aug-cc-pVDZ basis set are not significantly different from those with the aug-cc-pVTZ basis set, thus suggesting the energies are close to the basis set limit. Though the BSSE is greatly reduced with the aug-cc-pVTZ basis set, it is impractical to perform all calculations with such a large basis set.

Table 5 summarizes the results obtained from SAPT and provides a comparison with the energies calculated using HF and MP2. The binding energies for the trimer are the energies of each molecule interacting with the cluster (i.e., from Figure 1, **A** interacts with **BC**, **B** with **AC**, and **C** with **AB**). These more accurate SAPT energies serve as a reference of the extent to which HF underestimates and MP2 overestimates the binding energies. On average the HF and MP2 energies deviate 18% and 11%, respectively, from the SAPT energies for the alcohols (hydrogen bonding systems). However, this difference in binding energies of the different methods does not change our conclusions.

TABLE 6: Total Binding Energy (kcal/mol) and Average Bond Energy (kcal/mol) for Alcohols and Thiol

	total binding energy		energy per H-bond[a]	
cluster size *n*	HF	MP2	HF	MP2
methanol				
2	−3.716	−5.023	−3.716(0.0%)	−5.023(0.0%)
3	−10.717	−14.809	−3.572(−3.9%)	−4.936(−1.7%)
4	−19.338	−26.031	−4.834(30.1%)	−6.508(29.6%)
5	−27.769		−5.554(49.5%)	
6	−30.889		−5.148(38.6%)	
ethanol				
2	−3.545	−5.761	−3.545(0.0%)	−5.761(0.0%)
3	−10.426	−15.434	−3.475(−2.0%)	−5.145(−10.7%)
4	−18.840	−27.289	−4.710(32.9%)	−6.822(18.4%)
1-propanol				
2	−3.624		−3.624(0.0%)	
3	−10.567		−3.522(−2.8%)	
4	−18.641		−4.660(28.6%)	
methanethiol				
2	−0.705	−1.834	−0.705(0.0%)	−1.834(0.0%)
3	−1.854	−4.962	−0.618(−12.4%)	−1.654(−9.8%)
4	−2.900	−7.825	−0.725(2.8%)	−1.956(6.7%)

[a] Values in parentheses represent percentage deviation from dimer energy.

The total binding energy, given by eq 1, and the average bond energy (*BE* divided by number of H-bonds or S-bonds) are shown in Table 6. The deviation of the average bond energy from the dimer binding energy is another indication of the extent of hydrogen bond cooperativity. Sauer et al.[19] also computed the average bond energy at the HF level for clusters of methanol and obtained −5.067, −4.804, −6.286, −6.716, and 6.979 kcal/mol for the dimer to the hexamer, respectively. Hagemeister et al.[23] also calculated binding energies for clusters of methanol at the B3LYP/6-31+G* level. Their average bond energy from the binding energies are −4.820, −4.033, −6.798, and −7.200 kcal/mol for the dimer to pentamer, respectively. The energies by Sauer et al.[19] and Hagemeister et al.[23] are much lower from those in Table 6, but we should note both did not correct for BSSE and used a different basis set. In addition, the energies by Hagemeister et al.[23] are corrected for zero-point energy (ZPE). However, their values and the ones in Table 6 follow the same trend.

For all the alcohols and the thiol, it is seen the average bond energy of the trimer is always lower than that of the dimer. This bond energy lowering is due to the unfavorable binding configuration of the cyclic trimers, as there is considerable bond angle distortion from the normal H-bond and S-bond. This is also observed in the results of Sauer et al.,[19] Hagemeister et al.,[23] and Mó et al.[17] The numbers in parentheses in the Table 6 are the percentage deviation from the dimer energy, and it is clear that there is a significant increase in the magnitude of the bond energy for large clusters ($n \geq 4$). The increase in bond energy for methanethiol is small compared to the alcohols, again, indicating there is no cooperativity effect, and is simply a result of the proximity of other molecules due to clustering.

The excess energy, given by eq 2 and shown in Table 7, is a good measure of the hydrogen bond cooperativity effect. These energies are a measure of the indirect interaction among the molecules in the cluster, that is, as a result of molecules that are not hydrogen bonded to each other. As seen, for meth-

TABLE 7: Excess Energy of Alcohols and Thiols Clusters

	excess energy[a] (kcal/mol)	
cluster size *n*	HF	MP2
methanol		
3	−1.542	−1.579
4	−6.426	−7.011
5	−12.132	
6	−12.636	
ethanol		
3	−1.475	−1.491
4	−6.124	−6.955
1-propanol		
3	−1.407	
4	−5.871	
methanethiol		
3	−0.179	−0.182
4	−0.844	−1.062

[a] Excess energy from eq 2.

TABLE 8: Non-Hydrogen Bonded and Nonbonded Pair Interaction Energies

	interaction energy (kcal/mol)	
cluster size *n*	HF	MP2
methanol		
4	−1.245/−1.240	−1.454/−1.449
5	−0.907/−0.915	
	−0.819/−0.838	
	−0.864	
6	−0.574/−0.653	
	−0.175/−0.871	
	−0.788/−0.679	
	−0.652/−0.832	
	−0.303	
ethanol		
4	−1.159/−1.233	−1.595/−1.496
1-propanol		
4	−1.167/−1.153	
methanethiol		
4	−0.206/−0.235	−0.294/−0.338

anethiol, the excess energy is very small, suggesting there is little contribution from the nonadjacent pair interactions. However, the alcohols have large excess energies, which indicates that as a result of the longer range of the predominantly electrostatic interactions, molecules not directly involved in the formation of a new hydrogen bond contribute to the cooperativity effect. Table 8 quantifies this contribution for the alcohols and methanethiol. These interaction energies clearly show that, as a result of interactions of non-hydrogen bonded pairs, hydrogen bond cooperativity is different from a simple clustering effect. In particular, methanethiol does not form hydrogen bonds, and the interactions between molecules are short-ranged and largely limited to adjacent molecules. Consequently, its non-hydrogen bonded interaction energy is small compared to that of the alcohols.

As mentioned in the Introduction, a goal of this work was to determine the ratio of equilibrium constants for the formation of multimer hydrogen bonds in clusters compared to dimer hydrogen bonds. Table 9 summarizes the results of the calculated binding energies, and Table 10 gives the ratio of equilibrium constants calculated using eq 3. For each cluster ($n \geq 3$), the binding energy of forming a dimer, trimer, and so on, were calculated in the fixed geometry of each optimized cluster. Table 9 only shows the average values of the calculated binding energies (a complete list of all the energies can be found in the Supporting Information). The binding of a molecule resulting in the formation of a cyclic structure forms two hydrogen bonds; however, we are interested in the binding energy of forming only one hydrogen bond. We corrected for the energy corresponding to the closure of the cyclic structure by subtracting the additional binding energy associated with the formation of the extra hydrogen bond (e.g., for the tetramer cluster of methanol in Figure 1, the binding energy of **A** to **B** in the trimer BCD was corrected for the interaction of **A** with **D**). Therefore, for each binding molecule closing a cyclic structure, there are two binding energies, each corresponding to a binding site. The corrected energies are listed in Tables 5S−8S of the Supporting Information. For the pentamer and hexamer of methanol and all the 1-propanol clusters only HF energies were calculated, as it was not possible to calculate MP2 energies with the available computational resources; however, we would expect the results of such calculations to follow the same trends as the HF energies.

There are trends seen in Table 9 worth mentioning. The binding energy of the alcohol dimers slightly weakens as the cluster size and alkyl chain length increases. This may be explained by the steric hindrance caused by the CH_2 and CH_3 groups as the molecules cluster to form cyclic structures. Also, the correlation energy is an important contribution to the binding energy of methanethiol, and in this case the HF energies greatly underpredict the binding energies, since the interaction between methanethiol molecules is not predominantly electrostatic, but due to weaker interactions such as van der Waals and dispersion forces.

Table 10 summarizes the ratio of the equilibrium constants of forming a multimer hydrogen bond to that of a dimer hydrogen bond. There it is clearly seen that hydrogen bond cooperativity is present for the alcohols as the ratios greatly differ from unity. The larger the cluster, the more pronounced is the hydrogen bond cooperativity effect. One would expect that as very large clusters are formed, the effect of hydrogen bond cooperativity would asymptotically approach a constant value. On the basis of the HF results for methanol, the hydrogen bond cooperativity effect seems to initially increase exponentially with the size of the cluster until it approaches an asymptotic value, as illustrated in Figure 5. Note that in Figure 5 average values of the ratio of the equilibrium constants in Table 9 are plotted, which are based on the average of the binding energies. The average values reflect the binding energies of molecules in the geometry of the cluster. A study of larger clusters and including electron correlation, both for methanol and the other alcohols, should be made to determine whether there is indeed an asymptotic value for hydrogen bond cooperativity, but this is not computationally feasible at this time.

The ratio of equilibrium constants for methanethiol deviate slightly from unity, which does not indicate there is a cooperativity effect between methanethiol molecules, but simply that clustering is favorable for molecules. Our results for the ratio of the equilibrium constants for the formation of the $X + X_2 \rightarrow X_3$ hydrogen bond to the $2X \rightarrow X_2$ hydrogen bond is in reasonable agreement with Gupta and Brinkley,[16] who suggested a constant value of 10. We also observe that there is no cooperativity effect of that magnitude for methanethiol, as expected since it does not form hydrogen bonds.

As discussed earlier, hydrogen bond cooperativity can also be partly attributed to the interactions of cluster molecules other than the ones directly forming the hydrogen bond. These molecules help to lower the binding energy by indirect interactions, that is, even though the molecules are not directly interacting with the binding molecule, because of the strength and range of hydrogen bonding interactions, their interaction with the binding molecule is significant (see Table 7). This effect

TABLE 9: Binding Energies (kcal/mol) of Alcohols and Thiol Clusters

	HF energies					MP2 energies		
cluster size *n*	$\Delta E_{1\rightarrow 2}$	$\Delta E_{2\rightarrow 3}$	$\Delta E_{3\rightarrow 4}$	$\Delta E_{4\rightarrow 5}$	$\Delta E_{5\rightarrow 6}$	$\Delta E_{1\rightarrow 2}$	$\Delta E_{2\rightarrow 3}$	$\Delta E_{3\rightarrow 4}$
methanol								
2	−3.716					−5.023		
3	−3.063	−4.601				−4.393	−5.989	
4	−3.231	−5.408	−7.480			−4.737	−7.156	−9.353
5	−3.127	−4.872	−6.257	−10.392				
6	−3.196	−4.622	−5.317	−6.709	−8.535			
average	−3.267	−4.876	−6.352	−8.550	−8.535	−4.718	−6.572	−9.353
ethanol								
2	−3.545					−5.761		
3	−2.983	−4.459				−4.624	−6.139	
4	−3.131	−5.350	−7.220			−5.058	−7.359	−9.584
average	−3.219	−4.904	−7.220			−5.148	−6.749	−9.584
1-propanol								
2	−3.624							
3	−3.053	−4.460						
4	−3.181	−5.189	−7.064					
average	−3.286	−4.825	−7.064					
methanethiol								
2	−0.705					−1.834		
3	−0.560	−0.737				−1.590	−1.775	
4	−0.517	−0.833	−1.043			−1.688	−2.105	−2.337
average	−0.594	−0.785	−1.043			−1.704	−1.940	−2.337

TABLE 10: Equilibrium Constants Ratio for Alcohols and Thiol Clusters at $T = 300$ K

	HF energies				MP2 energies	
cluster size *n*	$K_{2\rightarrow 3}/K_{1\rightarrow 2}$	$K_{3\rightarrow 4}/K_{1\rightarrow 2}$	$K_{4\rightarrow 5}/K_{1\rightarrow 2}$	$K_{5\rightarrow 6}/K_{1\rightarrow 2}$	$K_{2\rightarrow 3}/K_{1\rightarrow 2}$	$K_{3\rightarrow 4}/K_{1\rightarrow 2}$
methanol						
3	4.41				5.05	
4	17.1	553			35.8	1427
5	6.96	71.0	73098			
6	4.57	14.7	152	3246		
average[a]	14.9	177	7071	6896	22.5	2382
ethanol						
3	4.63				1.88	
4	20.7	476			14.7	610
average[a]	16.9	822			5.24	1706
1-propanol						
3	4.07					
4	13.8	321				
average[a]	13.2	566				
methanethiol						
3	1.06				0.91	
4	1.24	1.76			1.58	2.32
average[a]	1.38	2.12			1.49	2.89

[a] Based on average interaction energy value, and is not the average of the equilibrium constants.

is also seen from the energies in Table 9. Compare, for example, the binding energy $\Delta E_{3\rightarrow 4}$ for the pentamer and hexamer of methanol. The binding energy for the pentamer is lower because molecules not involved in forming the new bond are closer to the binding molecules. For example, in Figure 1, molecule **A** binding to **BCD** is not directly interacting with molecules **C** and **D**, but **C** and **D** are closer to **A** in the pentamer than in the hexamer.

As stated earlier, to calculate the equilibrium constant ratios, we assumed the change in entropy due to the addition of one molecule to a hydrogen bond chain is independent of the chain length. The increase observed from $K_{2\rightarrow 3}/K_{1\rightarrow 2}$ to $K_{3\rightarrow 4}/K_{1\rightarrow 2}$ for the alcohols differ by one or more orders of magnitude. This increase, which seems unrealistic, is likely due to the neglect in the change of entropy of forming cyclic structures relative to that of the dimer ($\Delta S_{n\rightarrow n+1} - \Delta S_{1\rightarrow 2}$, for $n \geq 2$). This change in entropy is not easily estimated. For small cyclic structures, the change in entropy will be highly dependent on the arrangement of the molecules, but as the cluster size increases, the addition of molecules to a cluster is more likely to follow a linear dependence for the change in entropy.

As it is computationally unfeasible to perform calculations for larger clusters, another approach is to compare the equilibrium constant ratios of the cyclic structures to those of the linear structures, that is, structures that do not form closed hydrogen bonded rings. Figure 6 shows two linear structures of methanol optimized in this study. The linear structures may provide closer approximation to the case in which a linear relationship for the change in entropy with the size of the cluster is followed. Similar energy calculations as previously were performed for the two clusters in Figure 6, and the results presented in Table 11. While the energies of the linear trimer are very similar to those of the cyclic trimer of methanol, we see a large difference in the energies and equilibrium constants ratio for the tetramer. For these linear structures, the increase from $K_{2\rightarrow 3}/K_{1\rightarrow 2}$ to $K_{3\rightarrow 4}/K_{1\rightarrow 2}$ is less than one order of magnitude, which seems to be a more realistic representation of the equilibrium constants ratio, so that the assumption we have made about the change in entropy may be reasonable for this case. Note that the value

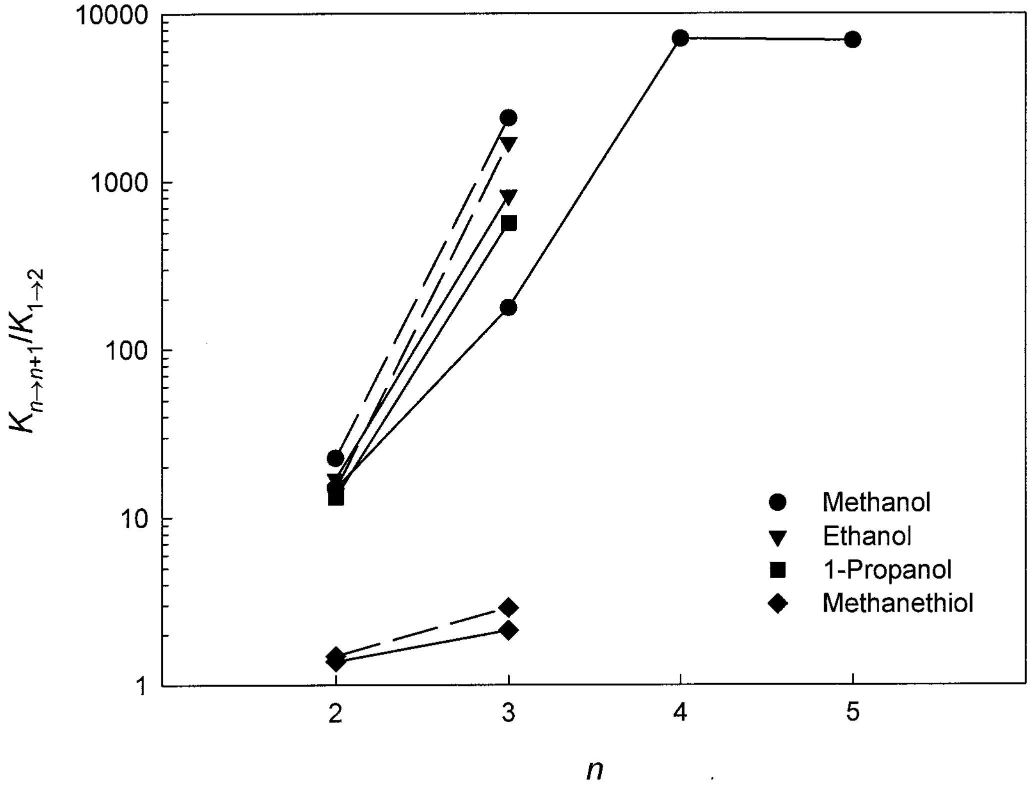

Figure 5. Hydrogen-bond cooperativity dependence on the cluster size (based on average values of Table 8). Solid lines correspond to HF energies and dashed lines to MP2 energies.

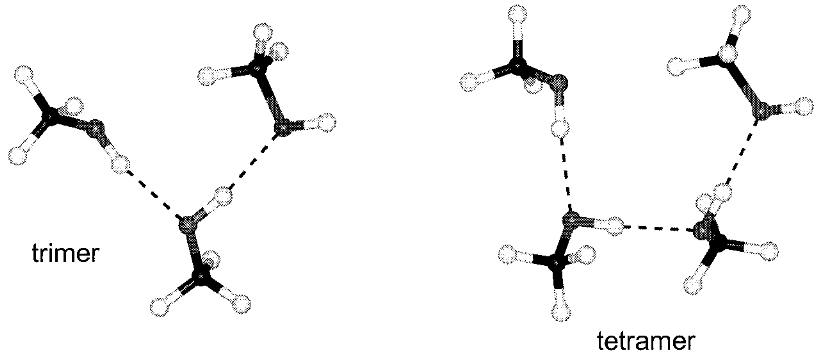

Figure 6. Geometry for linear methanol clusters optimized at HF/6-31G**.

TABLE 11: Binding Energies (kcal/mol) and Equilibrium Constants Ratio at $T = 300$ K for Linear Clusters of Methanol

cluster size n	$\Delta E_{1\to2}$	$\Delta E_{2\to3}$	$\Delta E_{3\to4}$	$K_{2\to3}/K_{1\to2}$	$K_{3\to4}/K_{1\to2}$
HF energies					
2	−3.716				
3	−3.458	−4.419		3.25	
4	−3.429	−5.051	−5.929	9.40	40.9
average[a]	−3.534	−4.735	−5.929	7.50	55.5
MP2 energies					
2	−5.023				
3	−4.869	−5.974		4.93	
4	−4.879	−6.700	−7.547	16.7	69.0
average[a]	−4.924	−6.337	−7.547	10.7	81.6

[a] Equilibrium constants ratio based on average interaction energy value.

for $K_{2\to3}/K_{1\to2}$ for the linear structures of methanol also agrees well with the results of Gupta and Brinkley. Given these results, we recognize the deficiency in our assumption in the change of entropy, however, it is not clear how one would correct for the change in entropy for the cyclic structures.

Conclusions

Ab initio calculations for clusters of methanol, ethanol, 1-propanol, and methanethiol show that hydrogen bond cooperativity effects are present in the formation of multimer hydrogen bonds in alcohols. The cooperativity effect is a combination of interactions between hydrogen bonding molecules involving charge transfer, binding energies, and medium-range interactions resulting from predominantly electrostatic forces. The ratio of the equilibrium constant of forming a multimer to that of forming a dimer hydrogen bond increases exponentially with the number of molecules in small clusters. Methanethiol was used to contrast its properties with those of hydrogen bonding systems, and to indicate where cooperativity effects are important. Our results for the ratio of equilibrium constants for the formation of a second hydrogen bond by the addition of another molecule to a hydrogen bonded dimer (i.e., $K_{2\to3}/K_{1\to2}$) compare favorably with that reported by Gupta and Brinkley. However, our calculations suggest that different equilibrium constants are needed for the formation of third and higher order hydrogen bonds, in contradiction to their assumption.

Supporting Information Available: Complete list of energies calculated for all the clusters. This material is available free of charge via the Internet at http://pubs.acs.org.

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