International Journal of Chemical and Biomolecular Science
Vol. 1, No. 3, 2015, pp. 197-210
http://www.aiscience.org/journal/ijcbs

Ab Inito Calculations of Methanol Clusters and Its Electrical Parameters

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Abstract

Extensive ab inito calculations have been performed in HF, DFT and MP2 levels for several possible structures of methanol clusters $(CH_3OH)_n$, n = 1-6. The calculations of the structures, primary and secondary hydrogen bond properties, stabilization energy, vibrational frequencies and intensities of eighteen minima of methanol clusters have been presented perfectly. In this work, a systematic study for 18 possible structures of methanol clusters, from isolated molecule to six molecules in the gas phase. This work reports all of the stable geometry parameters, O-H stretching frequencies in clusters and denotes to distinguished molecules with intensities at any molecules, oxygen and hydrogen charge in clusters and primary and secondary hydrogen bond strength performed with the methods. Cyclic, chain and branched-cyclic are structural types that methanol clusters have been shown in these frameworks.

Keywords

Ethanol-Water Clusters, Secondary Hydrogen Bond, Electron Density, Hydrogen Bonds

Received: August 3, 2015 / Accepted: August 29, 2015 / Published online: September 7, 2015

1. Introduction

Ethanol clusters, groups of methanol held together by hydrogen bonds, have been the subject of a number of intense experimental and theoretical investigations because of their importance in understanding solution chemistry (Islam, Pethrick and Pugh, 1998), in the industry of renewable fuels (Choi, et. al., 2004), and a large number of chemical and biochemical processes (Azizi, et. al., 2007). From a theoretical point of view, many different models of methanol clusters have been studied for understanding the characteristics of hydrogen bonds. A number of ab initio calculations have also been carried out to investigate the strength of the hydrogen bonds and their cooperativity but all of them have not been arrived in details of these bonds and its clusters. Hartree-Fock, Density Functional, Moller-Plesset Perturbation theories and Monte Carlo, simulations have been previously carried out on methanol clusters (Sum and Sandler, 2000, Boyd, S.L. and Boyd, R.J., 2007, Haughney, Ferrario, and McDonald, 1987, Handgraaf, Van Erp and Meijer, 2003, Morrone and Tuckerman, 2002).

In this work, a systematic study for 18 possible structures of methanol clusters, from isolated molecule to six molecules in the gas phase. This work reports all of the stable geometry parameters, O-H stretching frequencies in clusters and denotes to distinguished molecules with intensities at any

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molecules, oxygen and hydrogen charge in clusters and primary and secondary hydrogen bond strength performed with the methods which few investigations (Mejia, Espinal and Mondragon, 2009) are showing this effect.

2. Computational Details

In this work all of the structures optimized by the polarized basis set, 6-31G (d) in DFT, MP2 and HF methods. The selection of the computational approaches was based on three criteria. First, DFT is showed in many investigations to be useful for describing hydrogen bonded systems (Boyd, S.L. and Boyd, R.J., 2007). Secondly, MP2 is used according to the recommendation by A. Garcia-Muruais and et al., (Garcia-Muruais, 2000). Thirdly, HF method was selected in order to compare with earlier methods. The Basis set (6-31G(d)) was selected according to the recommendation by A. Garcia-Muruais and et.al., (Garcia-Muruais, 2000), too. All of calculations are carried out with the Gaussian 03 software package (Frisch, 1998). B3LYP is selected as DFT method. To facilitate the representation of different combinations of same size structures, the IUPAC naming rule will be used in spite of different that methanol molecules will be substituted carbon atoms and digits are engraved on oxygen atoms. In this study, we will be investigated methanol clusters from one to six molecules with following details: 1 - Expansive conformers particularly for hexamer cluster, 2 - Identification of primary and secondary hydrogen bond and its effects in stability of clusters, 3 - Oxygen and hydrogen atoms charges 4- the distinguish vibrational frequencies between each molecules in clusters and its intensities, the fact that these details were not found in previous calculations. The average energy of a single methanol molecule in a methanol cluster can be calculated as

$$E\text{^}n,\text{^}average = E\text{^}n/n \qquad (1)$$

The Stabilization energy (SE in Kcal/mol) for each cluster is obtained as showe below.

$$SE = E\text{^}cluster - n{*}E\text{^}monomer \qquad (2)$$

$E_{cluster}$: Total energy of cluster, $E_{monomer}$: Energy of a single methanol molecule, n: number of monomers.

The stabilization energy per hydrogen bond (SE/nH) and delta's SE (delta SE) for each cluster is obtained, in order to indicate change in strength of hydrogen bond with increasing cluster size.

The counterpoise procedure was used to correct the stabilization energy for the basis set superposition error (BSSE) (Boys and Berardi, 1970). The AIM2000 package (Bader, Biegler-Konig and Schonbohm, 2002) was applied to obtain the nature of hydrogen bonding interactions, the characteristics of the hydrogen bond critical points (BCP) appearing in the studied clusters. The total electron density $\rho_{(r)}$ is calculated from the wave function of the equilibrium geometry of the various clusters at B3LYP/6-31G(d) level.

3. Results and Discussion

3.1. Cluster Geometry

Figure S1(was showed in supplementary data) expressions the schematic representation of the stable geometry for $(CH_3OH)_n$, n =1-4, along with the number of hydrogen bonds (nH) and total dipole moment values in Debye as obtained from DFT calculations. The values in parentheses and brackets correspond to the μ values obtained from MP2 and HF calculation respectively. The dipole moment value in experimental liquid phase molecule is 1.7 D (Garcia-Muruais, 2000). The methanol dimmer, the smallest methanol cluster which constitutes the fundamental step in the study of methanol clusters, has been studied in great detail experimentally (Lovas, 1995) as well as theoretically (Odutola and Dyke, 1980). According to the figure S1 and table S1 (was showed in supplementary data), it has been established that the most stable structure of a methanol dimmer is of the *Cs* symmetry and that it has a single hydrogen bond with strength of - 7.5, - 4.9 and - 5.5 kcal /mol at the DFT, MP2 and HF methods respectively.

The equilibrium geometry for the cyclic trimmer is flat, resulting in poor overlap of the sp^3 orbital compared to the probable noncyclic structures. In such the structure, each monomer behaves as a donor as well as an acceptor.

To facilitate the representation of different combinations of same size structures, the IUPAC naming rule will be used in spite of different that methanol molecules will be substituted carbon atoms and digits are engraved on oxygen atoms. Tetramer clusters in figure S1 according to IUPAC naming rule, consist of:

1) 4-Chain: butane methanol

2) 1-M-CPr: 1- methanol cyclopropane methanol

3) 4-Cyclic: Cyclo butane methanol

All of the methods have established an almost harmonic cyclic structure with *C1* symmetry to correspond to the global minimum for the tetramer. In these geometries, 4cyclic with the methyl agents periodically above and below the plane of the O-O-O-O ring is the most stable of all conformers. As a result, excessive rise was showed in the stabilization energy and excessive drop was indicated in the dipole moment, if we don't take into account ZPE correction. If we include the ZPE corrections, the 1MCPr structure is found to be more stable than the 4 Cyclic by 6.6 kcal/mol at the DFT/6-31G(d) level (see table S1). The triangular ring in conformer of 1MCPr is like in structure to triangular ring in trimmer conformer excepting length of faces which in 1MCPr face of (1-3) decreased and faces of (1-2) and (2-3) in order to steric hindrance increased, that numbers within parentheses means the methanol numbers in interested clusters.

The pentamre isomers studied were the:

1) 5Chain: pentane methanol

2) 1-M$_2$-CPr: 1-(methanol)$_2$ cyclopropane methanol

3) 1-M-CBu: 1-methanol cyclobutane

4) 5Cyclic: cyclopentane methanol

According of the figure 1 and table S2, the above arrangement is in stabilization energies parameters including the ZPE and BSSE corrections for pentamer isomers. In the other word, pentagonal ring of methanol molecule, similar else clusters, is the most stable structure for the pentamer and can be resulted that hydrogen bonding length is the lowest. A detail of the hydrogen bonding length is given in table 1 and discussed later in the text.

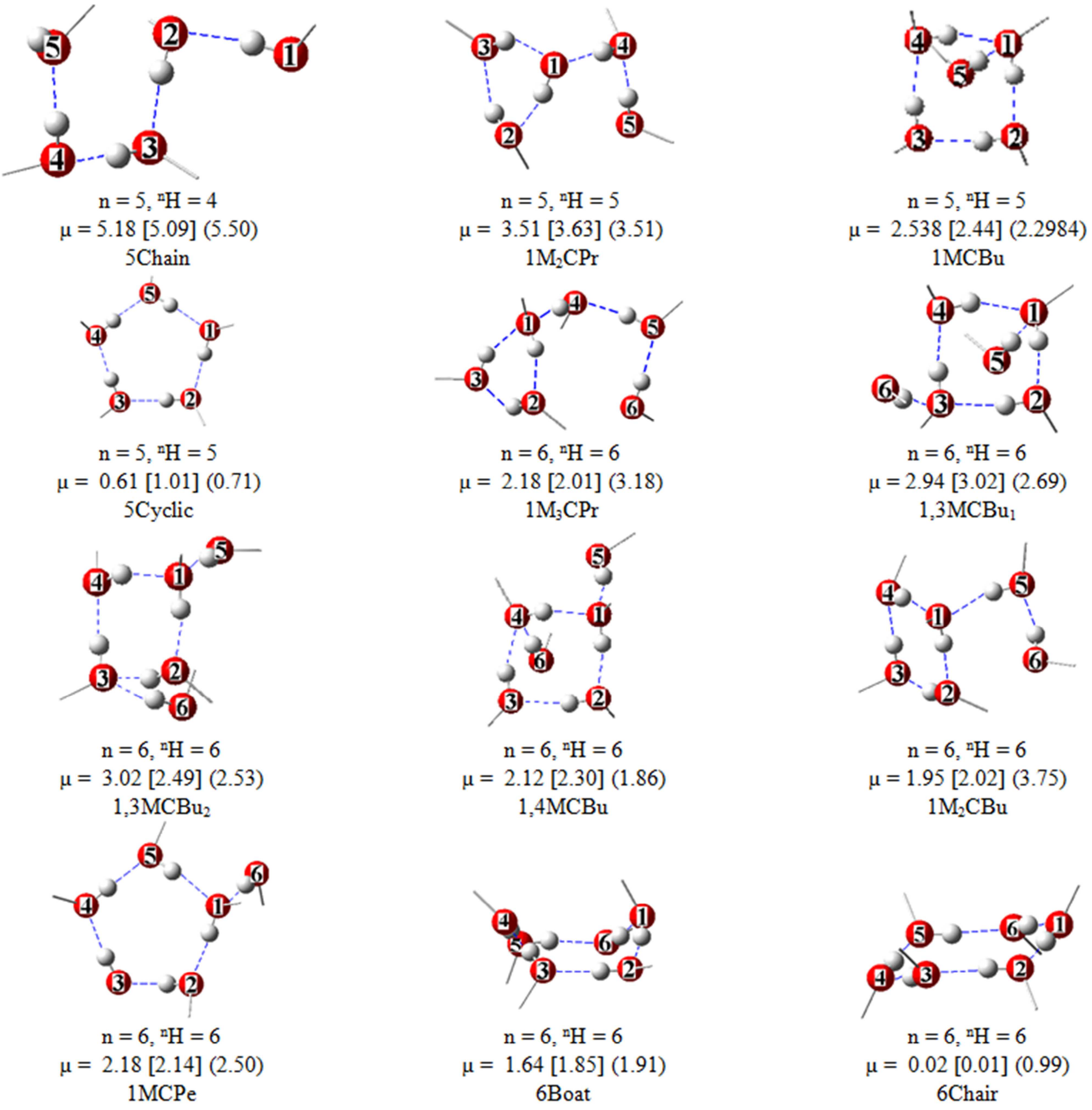


Figure 1. Schematic representation of the most stable geometry for $(CH_3OH)_n$, n =1-4, along with the total stabilization energy (SE) values in kcal/mol, the number of hydrogen bonds (nH) and total dipole moment values in Debye as obtained from HF calculations using the 6-31G(d) basis set. The values in parentheses correspond to SE and μ values obtained from DFT calculations using B3LYP parameterization.

Table 1. Primary hydrogen bonding length, electron density ($\rho_{(r)}$) and Laplacian of electron density at BCP ($\nabla^2_{\rho BCP}$) in methanol clusters from 5 to 6 molequels at the DFT/6-31G(d) method. $\nabla^2_{\rho BCP}$ is in negative values. All of data were calculatet in DFT level.

Structure	$(H…O)_{1,2}$	$(H…O)_{2,3}$	$(H…O)_{3,4}$	$(H…O)_{4,5}$	$(H…O)_{5,6}$	$(H…O)_{6,1}$
5Chain	1.830/0.037/0.026	1.685/0.05/0.037	1.745/0.044/0.032	1.784/0.039/0.029		
1M$_2$CPr	1.707/0.048/0.035	1.898/0.031/0.023	1.921[a]/0.03/0.022	1.793[b]/0.04/0.029	1.822[c]/0.036/0.027	
1MCBu	1.647/0.055/0.039	1.728/0.046/0.033	1.775/0.041/0.030	1.784[b]/0.039/0.029	1.884[d]/0.032/0.023	
5Cyclic	1.695/0.049/0.036	1.697/0.049/0.035	1.713/0.046/0.034	1.696/0.049/0.035	1.696[d]/0.049/0.036	
1M$_3$CPr	1.712/0.047/0.034	1.906/0.031/0.023	1.907[a]/0.030/0.022	1.806[b]/0.037/0.028	1.735[e]/0.046/0.033	1.796[c]/0.039/0.028
1,3MCBu$_1$	1.674/0.052/0.037	1.780/0.041/0.029	1.677/0.051/0.037	1.799[b]/0.038/0.028	1.887[d]/0.032/0.023	1.875[f]/0.033/0.024
1,3MCBu$_2$	1.652/0.054/0.039	1.789/0.040/0.029	1.679/0.051/0.037	1.801[b]/0.039/0.028	1.859[d]/0.033/0.025	1.898[f]/0.031/0.022
1,4MCBu	1.634/0.057/0.040	1.758/0.043/0.030	1.829/0.035/0.027	1.744[b]/0.044/0.032	1.874[d]/0.032/0.024	1.882[g]/0.033/0.023
1M$_2$CBu	1.623/0.058/0.041	1.734/0.045/0.033	1.748/0.044/0.031	1.780[b]/0.040/0.029	1.788[d]/0.040/0.029	1.822[c]/0.037/0.027
1MCPe	1.660/0.053/0.038	1.682/0.050/0.037	1.703/0.048/0.035	1.698/0.049/0.035	1.781[d]/0.040/0.029	1.885/0.032/0.023
6Boat	1.718/0.046/0.034	1.714/0.047/0.034	1.715/0.045/0.034	1.686/0.050/0.036	1.687/0.049/0.036	1.691/0.049/0.036
6Chair	1.692/0.049/0.036	1.692/0.049/0.036	1.691/0.049/0.036	1.692/0.049/0.036	1.691/0.049/0.036	1.691/0.049/0.036

[a] For Hydrogen Bonding between $(H…O)_{3,1}$.
[b] For Hydrogen Bonding between $(H…O)_{4,1}$.
[c] For Hydrogen Bonding between $(H…O)_{6,5}$.
[d] For Hydrogen Bonding between $(H…O)_{5,1}$.
[e] For Hydrogen Bonding between $(H…O)_{5,4}$.
[f] For Hydrogen Bonding between $(H…O)_{6,3}$.
[g] For Hydrogen Bonding between $(H…O)_{6,4}$.

The pentagonal ring in 5Cyclic is no planar, with a structure that resembles an envelope. According to the above arrangement, in n = 5, with increasing ring's size stability of structure increased. Comparing of the average energy of a single methanol molecule in these clusters in third methods showed that average stabilization energy of a single methanol molecule in DFT calculations is -2.81 kcal/mol larger than HF calculations and -3.41 kcal/mol larger than MP2 calculations. The strongest hydrogen bond (1.647 Å) related to interaction between hydroxyl agents of the first molecule with oxygen atom of the second molecule in 1-M-CBu cluster (see table 1 and figure 1). Comparing of stabilization energy between 5Chain with 4Chain, 1-M$_2$-CPr with 1-M-CPr and 5Cyclic with 4Cyclic will be show that increasing one chain methanol to structure will be cause to increasing stability in this set: cyclo butane structures > cyclo propane structures > chain structures.

The structure of $(CH_3OH)_6$ represents eight conformers with following SE arrangement:

1) 1-M$_3$-CPr: 1-(methanol)$_3$ cyclo propane methanol

2) 1, 3-M-CBu$_1$: 1, 3-di methanol cyclo butane methanol (trans isomer)

3) 1, 3-M-CBu$_2$: 1, 3-di methanol cyclo butane methanol (cis isomer)

4) 1, 4-M-CBu: 1, 4-di methanol cyclo butane methanol

5) 1-M2-CBu: 1-(methanol)$_2$ cyclo butane methanol

6) 1-M-CPe: 1-methanol cyclo pentane methanol

7) 6Boat: cyclo hexane methanol (boat isomer)

8) 6Chair: cyclo hexane methanol (chair isomer)

Table S1 and table 2 were dictated that there are two large ring clusters in hexamer isomers that at HF and MP2 methods, 6Chair is the most stable cluster and at DFT method, 6chair in company with 6Boat are the most stable clusters. The mean value of H-O-H bond angles in Chair and Boat conformers at DFT method is 114.8° and 109.5° and comparing its between both ring clusters show that the Chair conformation is the most favored structure because there isn't angle strain since all bond angles remain in the beast position. Another difference is pattern of orientation of the methyl groups. In the Chair conformer the methyl groups are being above and below alternately with the ring plane. Though, in the Boat conformer they are being above below-in planar.

According of the table 2 and table S1, SE comparing of cis and trans isomers that is known as geometric isomerism, show that against the general cis and trans isomers 1,3-M-CBu$_2$ (cis) is higher than 1,3-M-CBu$_1$ (trans) albeit there is steric hindrance in cis isomer. The cause of this effect is the formation of three robust secondary hydrogen bond between $O_5…..H_{C4}$, $O_5…..H_{C6}$ and $O_6…..H_{C2}$ with bond length of 2.415, 2.572, 2.385 Å respectively (O_x and H_{Cx} are oxygen and methyl's hydrogen of X molecule) (see next section, Table 3). We effort for optimized 6chain have been jointed with failure and this structure has been exchanged to 1-M$_3$-CPr. With an increase in the size of methanol clusters, the number of structural parameters also increased. Therefore, we have plotted the mean values <r>C-O (Figure 2a), <r>O-H (Figure 2b), <r>O…H (Figure 2c), $\angle COH$ (Figure 2d) and $\angle OHO$ (Figure 2e) for different values of n, in Figure 2. According to the Figure 2a, the C-O bond length at HF method in all of clusters have a constant amount and involve

1.40 (Å) values. Although, DFT and MP2 values consistently larger than the HF values however have not a constant imitation. The values of <r>O-H and <r>O…H are exactly on basis of hydrogen bonding existence conversely. Both parameters follows on a regular base, it means in all of clusters with equal molecules increasing of <r>O-H and decreasing of <r>O…H will be show in parts b and c of Figure 2 along with cluster stability. It is a next result that with arise of molecule number; the above consequence will be interrupt. However, it must be added that DFT and MP2 calculations tend to predict slightly stronger and shorter hydrogen bonds than those of HF. Figure 2d deals with the relation between the ∠*COH* value and the cluster size for n=1-6 and its isomers. It is nearly a constant amount for three methods, emphasizing the fact that the "structures" of the methanol molecules in clusters predicted by the each calculations are nearly the same and also in Figure 2e, the almost identical lines for anyone calculations, are emphasizing the fact that the "shapes" of the clusters predicted are nearly the same. With an increase in the size of the methanol clusters, there is an increase in stabilization energy (SE) values, as shown in Figure 3.

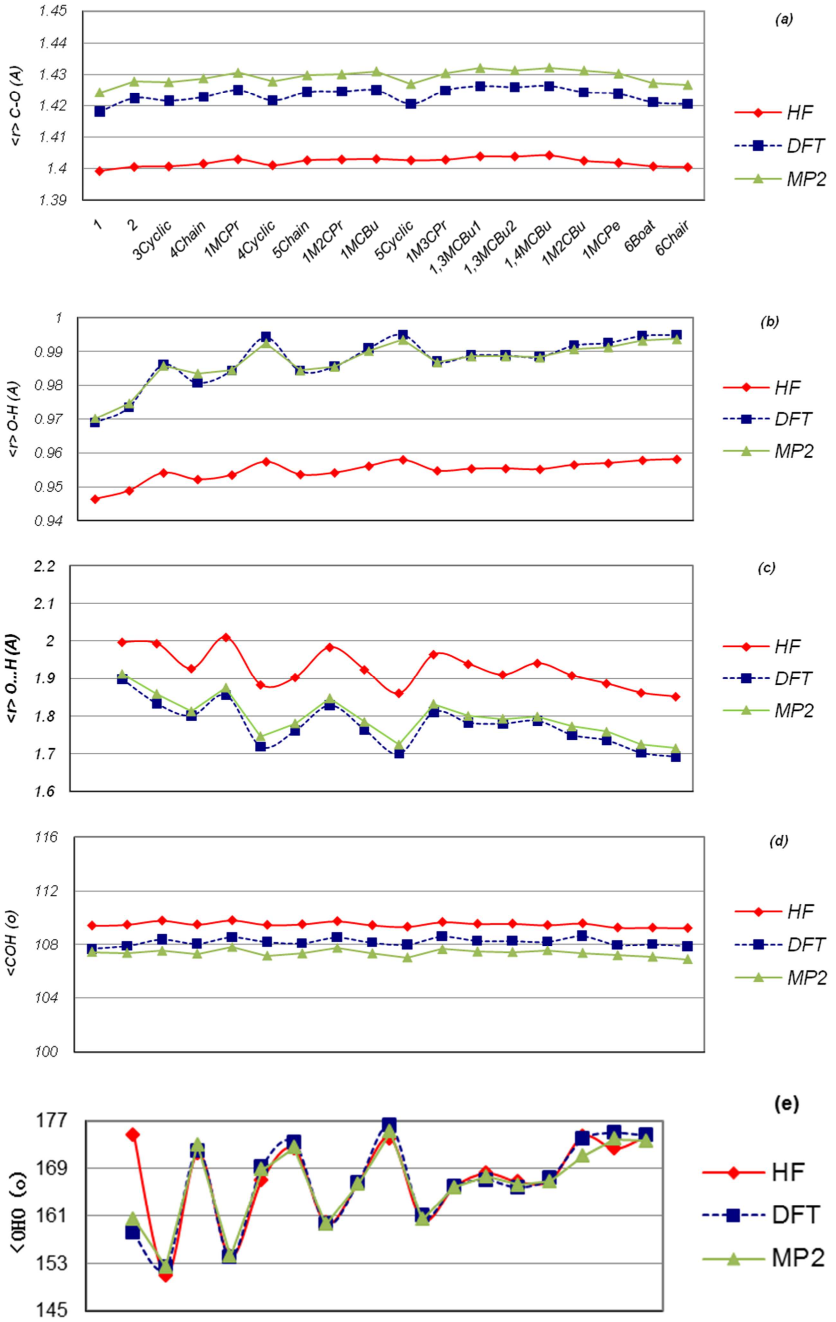


Figure 2. Schematic representation of some of the different possible low-energy structures of $(CH_3OH)_n$, n=5-6, which is omitted methyl agent for the sake of clarity, along with the total stabilization energy (SE) values in kcal/mol, the number of primary hydrogen bonds (nH) and total dipole moment values in Debye as obtained from HF calculations using the 6-31G(d) basis set.

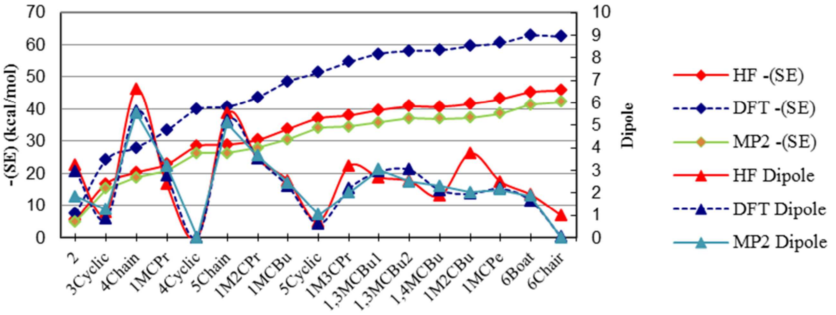
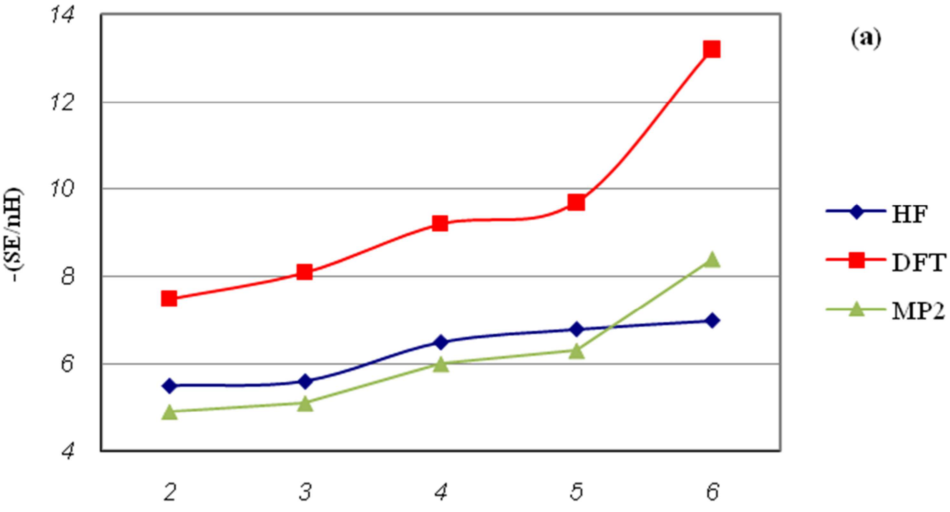
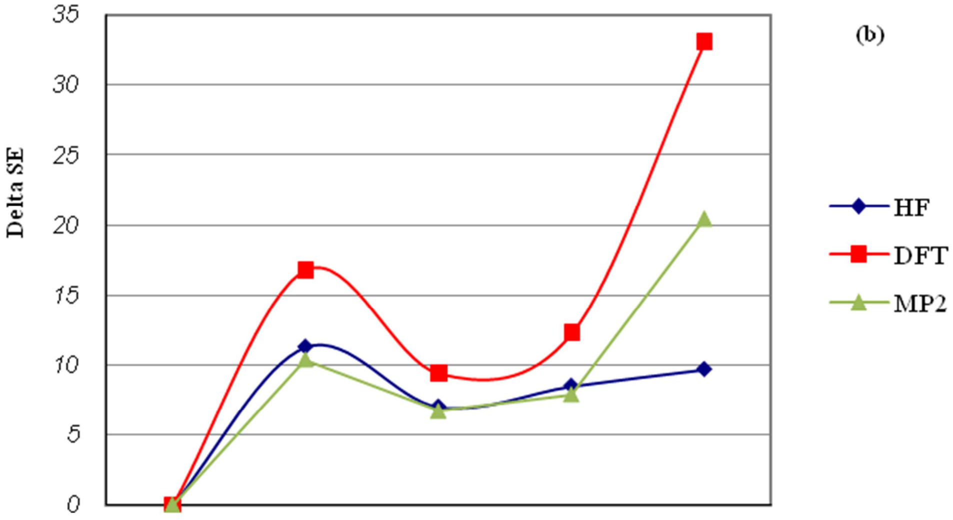


Figure 3. Mean values of various geometrical parameters for the all of the conformers of $(CH_3OH)_n$, n=1-6, as obtained from HF calculation (solid line) and DFT calculations (dash line).

Table 2. Effect of BSSE and ZPE corrections on SE (kcal/mol) at the DFT/6-31G(d) level for $(CH_3OH)_n$, n=6.

		-SE		
Structure	**BSSE**	**Uncorrected for BSSE and ZPE**	**BSSE corrected**	**ZPE corrected**
1M3CPr	-16.6	54.6	38.0	45.7
1,3MCBu1	-17.8	57.2	39.4	48.2
1,3MCBu2	-16.6	58.1	41.5	55.3
1,4MCBu	-17.6	58.3	40.7	55.8
1M2CBu	-16.5	59.6	43.0	50.7
1MCPe	-15.6	60.5	45.0	51.8
6Boat	-14.7	62.8	48.1	54.3
6Chair	-12.8	62.5	49.6	54.4





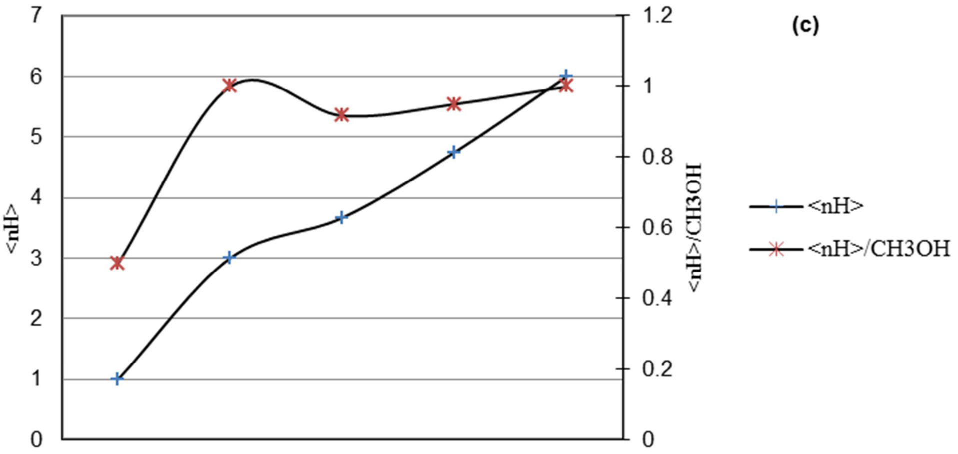


Figure 4. Variation of the SE value and dipole value for the most stable geometry $(CH_3OH)_n$, n=2-6 as obtained from HF and DFT calculations

There is a little increase in the mean strength of the primary hydrogen bonds as n goes from 3 to 4 in HF calculations and there is noticeable increasing as n goes from 5 to 6 in other methods. In HF method, for n = 5 and 6, there is a very slight increase in the mean primary hydrogen bond strength. It becomes clear from the incremental values of absolute SE (i.e., the increase in absolute SE values with the increase in n by 1) plotted as a function of n in Figure 4b that there is an alternation in stability as n increases. The old n-mers have a slightly greater stability than the even n-mers. Methanol clusters with n = 3, 5 become particularly more stable. The average number of primary hydrogen bonds ($<nH>/CH_3OH$) per methanol molecule increases up to n = 3 but then levels of around one as n approaches 6.

3.2. Atom in Molecules Analysis

In order to characterize the hydrogen bonding interaction between two methanol molecules, the electron density ($\rho_{(r)}$) at bond critical points was taken into account. According to AIM theory, any chemical bond including closed-shell interactions (e.g. hydrogen bonding) is characterized by the bond critical points (BCP). The BCP (3, -1) are characterized by a rank (ω) of 3 and a signature (σ) of -1. This means that the electron density at this point is a maximum in the plane defined by the corresponding eigen vectors but is a minimum along the third axis which is perpendicular to this plane. Although, in some of the studied clusters, ring critical points (RCP) and cubic critical points (CCP) were obtained.

In order to the same results in geometry parameters for DFT and MP2 levels, other theoretical calculations including AIM analysis and vibrational frequencies were performed only in DFT level. Tables 1, 3 and S3 shows the variation of the electron density ($\rho_{(r)}$), Laplacian of electron density at BCP ($\nabla^2_{\rho BCP}$), primary and secondary hydrogen bonding length of interested structures. Figure 5 gives a picture of how cluster size and different spatial arrangements impact electron density of a methanol cluster. The maximum $\rho_{(r)}$ values are observed in the cyclic structures even though from n=4 onwards they are uniformly around 0.048 a. u. .

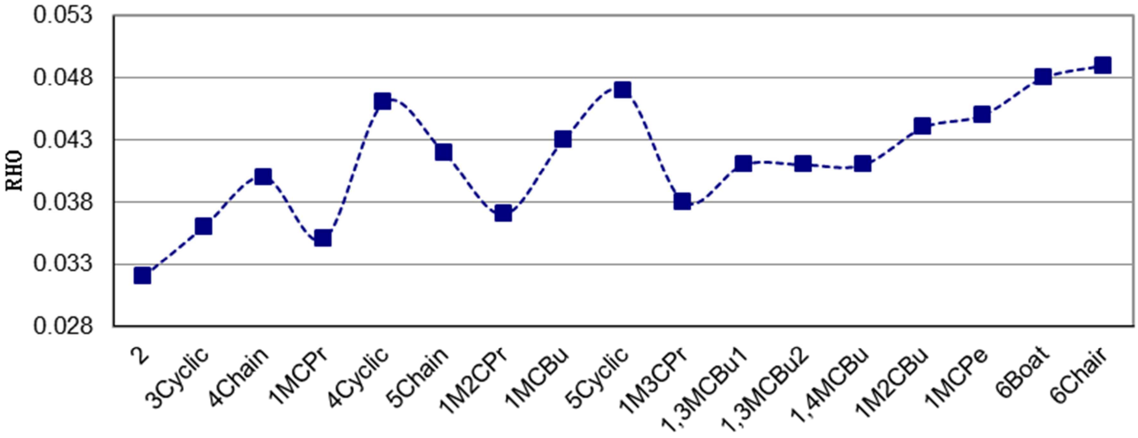


Figure 5. Variation of (a) Stabilization energy per hydrogen bond for $(CH_3OH)n$, n = 2-6, corresponding to the most stable structure of the individual methanol cluster, (b) incremental stabilization energy (delta of SE) for n = 2-6, and (c) the number of primary hydrogen bonds (nH) and the average number of primary hydrogen bonds per methanol molecule (<nH> = nH/n) with an increase in n, as obtained from HF/6-31G(d) calculation. The values of SE are reported in kcal/mol.

Interaction of the methyl's hydrogen of one molecule with oxygen's another molecule is called secondary hydrogen bond. Even though, the C-H…O interactions are weaker than the primary hydrogen bonds, that mentioned in earlier paragraph, they seem to influence the stability of some clusters and its vibrational frequencies that will be explained in next paragraph.

The first secondary hydrogen bonds have been seen in tetramer isomers. According table 3 in 1-M-CPr isomer there are two secondary hydrogen bonds that cause making of differences between triangular ring of this isomer and trimmer ring in 3 Cyclic structure. The first secondary hydrogen bonding with have 2.48 Å bond length is between Oxygen of fourth molecule (O_4) and methyl's Hydrogen of the second molecule (H_{C2}) by electron density of 0.011 a. u., and secondary is between Oxygen of the third molecule O_3 and methyl's Hydrogen of fourth molecule H_{C4} (with bond length 2.70 Å and by electron density of 0.006 a. u.). Electrical parameters comparing of 3Cyclic and ring of 1-M-CPr show that existence of these secondary hydrogen bonding to be caused decreasing $O_1…O_2$ length in spite of that existence steric hindrance of methyl's group. Also, this effect to be caused that primary bonding between O_2 and H_1 is liner than other hydrogen bonds in ring of 1-M-CPr (see Table S4). The above results will be seen at 1-M_2-CPr and at 1-M_3-CPr isomers too. According to the table 3, in square rings the most SHB be found in 1, 3-M-CBu_2 and 1-M-CBu with three SHB and 1, 3-M-CBu1 and 1, 4-M-CBu with four SHB number of its isomers. In addition to AIM results, the mulliken charge for HSB involving oxygen atoms which were presented in table S6, is the other evidence for exist several of secondary hydrogen bond in these isomers.

Table 3. Secondary hydrogen bonding length (SHB), electron density ($\rho_{(r)}$) and Laplacian of electron density at BCP ($\nabla^2_{\rho BCP}$) in methanol clusters at the DFT/6-31G(d) method. $\nabla^2_{\rho BCP}$ is in negative values. Calculation was obtained in DFT method.

Structure	SHB and its length			
	SHB_1	SHB_2	SHB_3	SHB_4
	Length/RHO/ $\nabla^2_{\rho BCP}$	**Length/RHO/ $\nabla^2_{\rho BCP}$**	**Length/RHO/ $\nabla^2_{\rho BCP}$**	**Length/RHO/ $\nabla^2_{\rho BCP}$**
1 MCPr	$O_4…H_{C2}$ 2.4770/0.011/0.008	$O_3…H_{C4}$ 2.703/0.006/0.005		
1 M_2CPr	$O_5…H_{C2}$ 2.340/0.014/0.01	$O_3…H_{C4}$ 2.695/0.006/0.006		
1 M_3CPr	$O_6…H_{C2}$ 2.363/0.013/0.009	$O_6…H_{C4}$ 2.466/0.010/0.008	$O_3…H_{C4}$ 2.768/0.005/0.005	
4 Chain	$O_4…H_{C2}$ 2.431/0.011/0.009			
5 Chain	$O_2…H_{C5}$ 2.354/0.013/0.01	$O_1…H_{C3}$ 2.506/0.01/0.008		
1 MCBu	$O_5…H_{C2}$ 2.691/0.006/0.005	$O_5…H_{C3}$ 2.576/0.009/0.007	$O_4…H_{C5}$ 2.799/0.005/0.005	
1 M_2CBu	$O_6…H_{C1}$ 2.501/0.009/0.008	$O_6…H_{C2}$ 2.473/0.010/0.008		
1,3 $MCBu_1$	$O_5…H_{C3}$ 2.537/0.009/0.008	$O_5…H_{C2}$ 2.628/0.006/0.006	$O_6…H_{C4}$ 2.52/0.010/0.008	$O_4…H_{C5}$ 2.816/0.005/0.004
1,3 $MCBu_2$	$O_5…H_{C4}$ 2.415/0.011/0.009	$O_5…H_{C6}$ 2.572/0.009/0.007	$O_6…H_{C2}$ 2.385/0.013/0.009	
1,4 MCBu	$O_5…H_{C4}$ 2.570/0.008/0.007	$O_5…H_{C6}$ 2.586/0.008/0.007	$O_6…H_{C2}$ 2.407/0.012/0.009	$O_6…H_{C3}$ 2.465/0.010/0.008
1 MCPe	$O_6…H_{C5}$ 2.436/0.012/0.009	$O_4…H_{C6}$ 2.676/0.006/0.005		
6 Boat	$O_4…H_{C1}$ 2.555/0.009/0.007			

3.3. Vibrational Frequency of Isomers

Frequency calculations have been carried out at the B3LYP/6-31g(d) level. The scaling of the frequencies has been done with a scaling factor of 0.9613 for DFT level as recommended by the Gaussian 03 package. Tables 4 and S7 list the scaled frequencies (cm^{-1}) with all of the intensities for these clusters along with the frequency of a single molecule and intensity of molecule's vibration (IMV in Tables 4 and S). According to these tables secondary hydrogen bonds lead to decreasing of intensities for inclusive oxygen atoms vibration which this effect have been seen in 1,3$MCBu_1$ and 1,3$MCBu_2$ very clearly. For instance, in 1,3$MCBu_1$ isomer in order to exist four SHB containing O_4, O_5 and O_6, will be see the least effect in stretching frequencies of these oxygen atoms in table 4.

Table 4. Stretching frequencies calculated at HF/6-31G(d) optimized geometry for O-H in (CH3OH)$_n$, n = 5,6 and its isomers. Frequencies are unscaled in cm^{-1} and IMV (intensity of molecule's vibration) denotes to O-H intensities at any molecule.

Structure	Frequency	Intensity	IMV	Structure	Frequency	Intensity	IMV
5Chain	3614	27.3	5	1,3MCBu$_2$	3486	502.1	5>>1=4=6
	3384	661.8	1>>2		3457	541.8	6>>2=3=5
	3356	732.7	3=4		3344	707.9	2>>1=3=6>4
	3279	843.5	3>>2=4		3332	624.5	4>>1=3=5
	3132	1061.7	2>>3>1=4		3113	2107.1	1>>3>2
					3018*	334.8	3>>1=4>2=5
1M$_2$CPr	3444	568.0	3>>1=2=4>5	1,4MCBu	3476	471.7	5>>1=3=4=6
	3400	268.3	2=4=5>1=3		3466	574.6	6>>3>4=5
	3392	625.1	2>3=5>>1=4		3405	465.6	3>>6>2=4
	3339	806.5	5>>4>1=2=3		3261	1354.2	4>>2>1=3=5=6
	3097	757.4	1>>2=3=4=5		3235	517.0	2>>1=3=4>5
					2966*	962.3	1>>2=3=4=5
1MCBu	3466	459.4	5>>1=4	1M$_2$CBu	3376	726.3	6>>5>4
	3338	663.8	3=4>>1=2=3		3327	234.5	4>5>1=3=6
	3281	852.0	3=4>2>1=5		3288	649.5	5>3=4>2=6>1
	3160	940.1	2>>1=3>4		3257	1840.4	2=3>4=5>1
	2969*	416.5	1>>2>3=4=5		3184	733.1	2=3>1=4=5
					2939*	297.3	1>>2=3=4
5Cyclo	3235	175.1	2=3>1=4	1MCPe	3456	482.0	6>>1=5
	3227	247.7	1=4=5>2=3		3327	508.0	5>>1=4=6
	3168	2511.3	1=2=3=4=5		3220	452.9	3>>2=4>1
	3160	2664.8	1=2=4=5>3		3154	1750.5	2=4>1=5
	3062	22.3	1=2=3=4=5		3113	1814.1	4>>1=2=3>5
					3000*	390.1	1>>2=3=4>5
1M$_3$CPr	3438	592.7	3>>1=2=4	6Boat	3269	463.2	2=3>>1=4>5=6
	3396	390.6	2>>1=3=4		3240	1130.7	1>>2=3=6>4
	3374	521.3	4>>3=5>2		3202	64.2	5>>2=4=6
	3330	725.1	6>>5>4		3162	1763.6	2>>1=3=5>4=6
	3202	1032.5	5>>6>1=4		3135	2669.9	4=6>1=3>2=5
	3117	711.1	1>>2=3=4=5		3055	286.3	4=5=6>1=2=3
1,3MCBu$_1$	3468	493.7	5>>4>1	6Chair	3240	564.8	1=2=3=4=5=6
	3442	467.7	6>>2=3		3216	N/A	2=3=5=6>1=4
	3367	589.7	4>>1=3=5		3216	N/A	1=2=4=5>3=6
	3266	787.7	2>>1=3=6		3146	3298.6	2=3=5=6>1=4
	3094	1697.4	3>1>2=4=6		3145	3312.5	1=4>3=4=5=6
	3031*	58.0	1>3>2>4		3060	N/A	1=2=3=4=5=6

*: combined vibrational frequency between O-H and C-H.

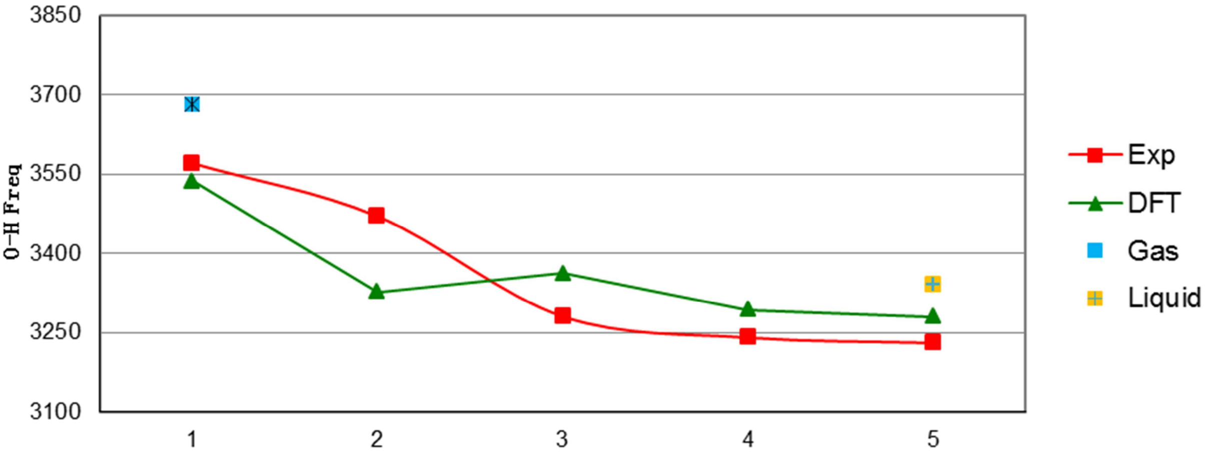


Figure 6. Vibrational frequency of (CH$_3$OH)$_5$ in gas phase, a) 5 (cyclic), b) 5ZZ, c) 5ZA, d) 5Z, and inset shows zoomed O-H Stretching frequencies with number of mode (N in table 6).

It is well-known that gaseous methanol has a higher vibrational frequency for the O-H stretch than liquid methanol (Shimanouchi, 1972). Clearly, even with the small basis set is used in this study, the OH vibrational frequency drops as the number of methanol molecules in the cluster increases. The minimum frequency is essentially attained when there are five methanol's in the cluster, which provides further evidence to support the suggestion that five or six hydrogen-bonded methanol's are sufficient to mimic liquid behavior. Figure 6 shows that results of DFT method become near to experimental values and with increasing of cluster size, frequencies shifted to liquid methanol frequency (3681 and 3340 cm^{-1} for gas and liquid molecules respectively (Buck and Huisken, 2000)) and another results is in DFT method at the latest OH frequencies are combination vibrations of CH and OH modes in most clusters (for example, 1MCBu, 1,3MCBu$_1$, 1,3MCBu$_2$, 1M$_2$CBu and 1,4MCBu, 1-M-CPe). Figure S2 is showed vibrational spectrometry for pentamer of methanol molecules that is calculated at DFT level of theory.

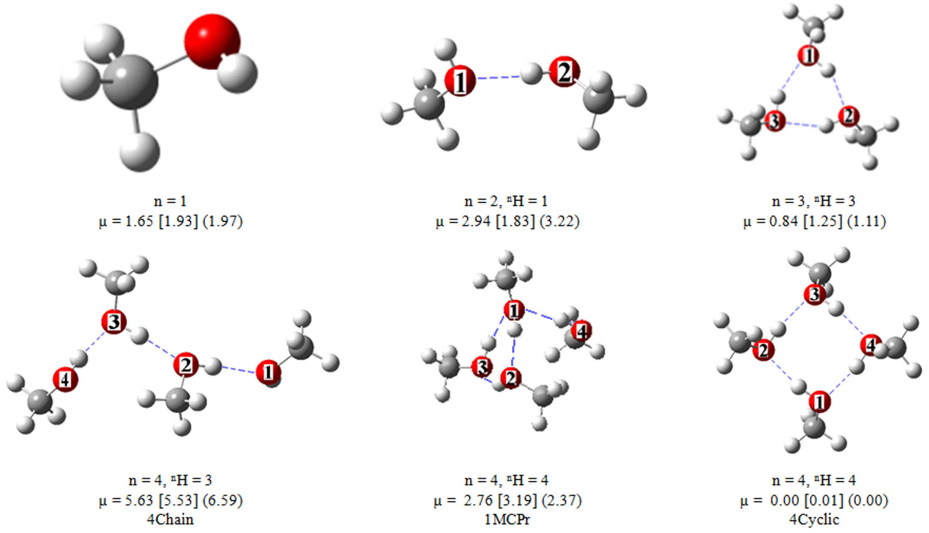
4. Conclusions

In this study, we have reported that in all of conformers with equal methanol molecule number, the cyclic structure has the most stabilization energy and DFT calculations have the more SE than HF and MP2 levels of theory. The results of this work showed the old n-mers have a slightly greater stability than the even n-mers and the average number of primary hydrogen bonds per methanol molecule increases up to n = 3 but then levels of around one as n approaches 6. The SHB roles prevailing forces opposite steric hindrance in structure of clusters and so caused more stability of them. A BSSE and ZPE correction is noted in the SE calculations. Primary and secondary hydrogen bonding was established by AIM analysis and its effects on SE were investigated. Higher $\rho_{(r)}$ values obtained by AIM analysis help to establish the nature of hydrogen bonding in the methanol clusters. The maximum $\rho_{(r)}$ values are observed in the cyclic structures even though from n=4 onwards they are uniformly around 0.048 *a.u.*. According to frequencies data, secondary hydrogen bonds lead to decreasing of intensities for inclusive oxygen atoms vibration which this effect have been seen in 1,3MCBu1 and 1,3MCBu$_2$ very clearly.

Supporting information

Supplementary data associated with this article consist of Schematic representation of the most stable geometry for (CH_3OH)n, n =1-4 (Figure S1), Vibrational spectroscopy of (CH_3OH)5 (Figure S2), Stabilization energy values for three method (Table S1), Effect of BSSE and ZPE corrections on SE (Table S2), Primary hydrogen bonding length, electron density ($\rho_{(r)}$) and laplacian of electron density at BCP in methanol clusters up 4 molecules (Table S3), Geometry properties for methanol structures in DFT level of theory (Table S4), mulliken charge table for oxygen and hydrogen atoms contains in primary hydrogen bonding (Tables S5 and S6), and stretching frequencies for O-H in (CH_3OH)n, n = 1-4 and its isomers (Table S7) is provided in the supporting information.

Supplementary data



n = 1
μ = 1.65 [1.93] (1.97)

n = 2, ^{n}H = 1
μ = 2.94 [1.83] (3.22)

n = 3, ^{n}H = 3
μ = 0.84 [1.25] (1.11)

n = 4, ^{n}H = 3
μ = 5.63 [5.53] (6.59)
4Chain

n = 4, ^{n}H = 4
μ = 2.76 [3.19] (2.37)
1MCPr

n = 4, ^{n}H = 4
μ = 0.00 [0.01] (0.00)
4Cyclic

Figure S1. Schematic representation of the most stable geometry for $(CH_3OH)_n$, n =1-4, along with the number of primary hydrogen bonds (^{n}H) and total dipole moment values in Debye as obtained from DFT calculations using the 6-31G(d) basis set. The values in brackets and parentheses correspond to μ values obtained from MP2 and HF calculations respectively.

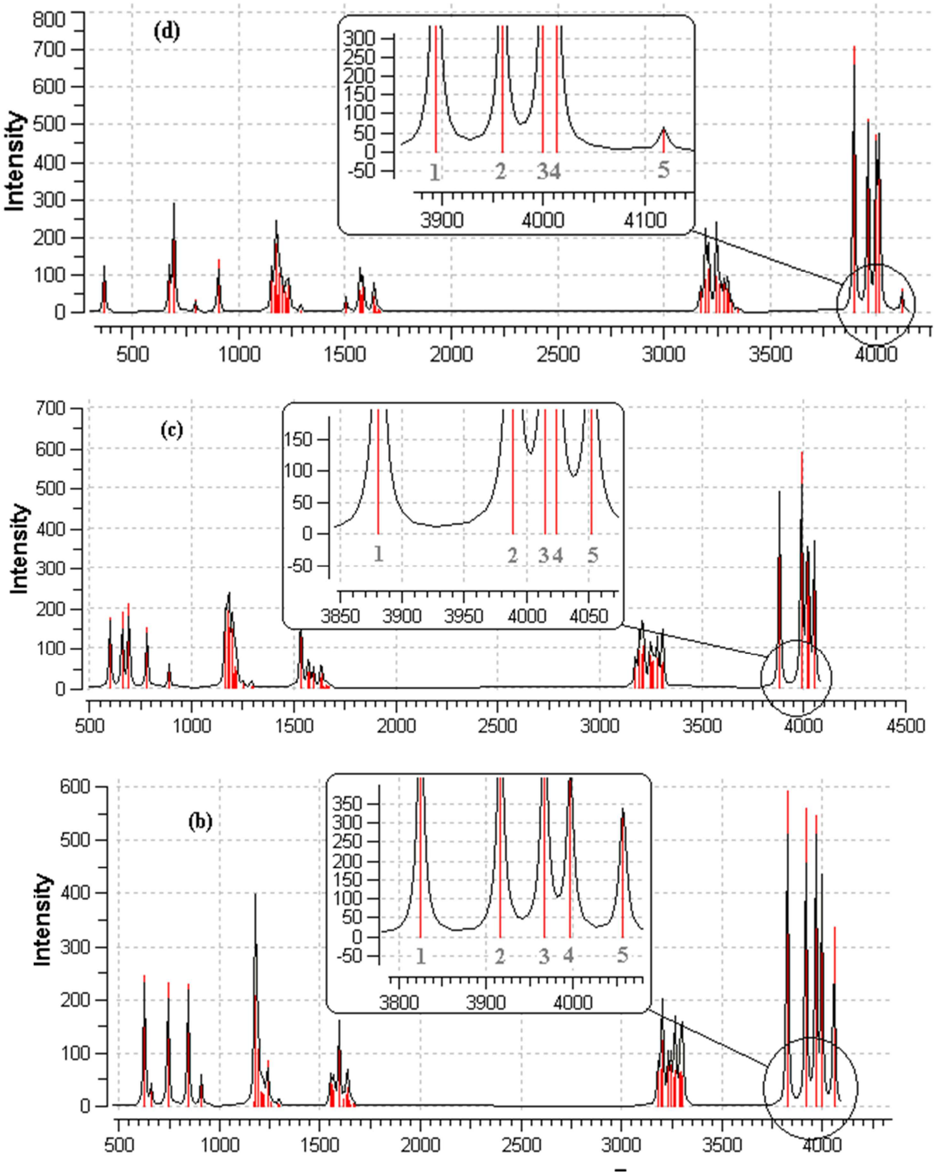


Figure S2. Vibrational spectroscopy of $(CH_3OH)_5$ in gas phase, a) 5Cyclic, b) 1MCBu, c) $1M_2CPr$, d)5Chain, and inset shows zoomed O-H Stretching frequencies.

Table S1. Stabilization energy in kcal/mol at the HF, DFT and MP2 methods for $(CH_3OH)_n$, n=2-6.

		-SE	
Structure	**HF**	**DFT**	**MP2**
2	5.5	7.5	4.9
3Cyclic	16.8	24.2	15.3
4Chain	20.3	28	18.7
1MCPr	22.8	33.3	20.8
4Cyclic	28.4	39.9	26.2
5Chain	28.9	40.7	26.3
1M2CPr	30.4	43.7	27.9
1MCBu	33.8	48.6	30.6
5Cyclic	37.1	51.3	34.1
1M3CPr	38	54.6	34.5
1,3MCBu1	39.7	57.2	35.8
1,3MCBu2	40.8	58.1	37.1
1,4MCBu	40.7	58.3	37
1M2CBu	41.6	59.6	37.2
1MCPe	43.1	60.5	38.6
6Boat	45.3	62.8	41.4
6Chair	45.8	62.5	42.2

Table S2. Effect of BSSE and ZPE corrections on SE (kcal/mol) at the DFT/6-31G(d) level for $(CH_3OH)_n$, n=2-5.

		-SE		
Structure	**BSSE**	**Uncorrected for BSSE and ZPE**	**BSSE corrected**	**ZPE corrected**
2	-2.7	7.5	4.7	5.8
3Cyclic	-7.2	24.2	17.0	20.0
4Chain	-7.8	28	20.2	23.3
1MCPr	-11.3	33.3	21.9	27.4
4Cyclic	-10.2	39.9	29.6	21.8
5Chain	-11.6	40.7	29.1	34.1
1M2CPr	-13.4	43.7	30.3	36.5
1MCBu	-14.0	48.6	34.6	41.1
5Cyclic	-10.9	51.3	40.3	44.4

Table S3. Primary hydrogen bonding length, electron density ($\rho_{(r)}$) and laplacian of electron density at BCP ($\nabla^2_{\rho BCP}$) in methanol clusters up to 4 molequels at the DFT/6-31G(d) method. $\nabla^2_{\rho BCP}$ is in negative values.

Structure	**(H…O)$_{1,2}$/RHO/ $\nabla^2_{\rho BCP}$**	**(H…O)$_{2,3}$/RHO/ $\nabla^2_{\rho BCP}$**	**(H…O)$_{3,4}$/RHO/ $\nabla^2_{\rho BCP}$**	**(H…O)$_{4,1}$/RHO/ $\nabla^2_{\rho BCP}$**
Dimer	1.898/0.032/0.023			
3Cyclic	1.828/0.037/0.026	1.845/0.035/0.026	1.825/0.037/0.027	
4Chain	1.951/0.037/0.027	1.886/0.044/0.033	1.944/0.039/0.027	
1MCPr	1.739/0.045/0.032	1.871/0.033/0.024	1.906[a]/0.030/0.022	1.902/0.031/0.022
4Cyclic	1.721/0.046/0.033	1.721/0.046/0.033	1.721/0.046/0.033	1.721/0.046/0.033

[a] for primary hydrogen bonding between (H…O)$_{1,3.}$

Table S4. Geometry properties for methanol structures in DFT level of theory.

Structure	**geometry properties**				
	O-H	**O---H**	**<COH**	**C-O**	**<OHO**
2	0.9736	1.89818	107.88294	1.42241	158.026
3Cyclic	0.9861533	1.83278	108.40606	1.42158333	152.267
4Chain	0.98082	1.800845	108.077403	1.4227525	171.886
1MCPr	0.98443	1.8547275	108.57802	1.42495	153.983
4Cyclic	0.99424	1.71876	108.2106	1.42168	169.254
5Chain	0.984322	1.7610075	108.113344	1.42434	173.454
1M2CPr	0.985612	1.828136	108.55289	1.424502	159.627
1MCBu	0.990954	1.763616	108.158856	1.424906	166.672
5Cyclic	0.994994	1.699272	108.008122	1.420564	176.253
1M$_3$CPr	0.987075	1.8101833	108.625712	1.42489167	160.923
1,3MCBu$_1$	0.9888917	1.7821833	108.297633	1.42622333	165.956
1,3MCBu$_2$	0.9889183	1.7796483	108.288955	1.425895	167.026
1,4MCBu	0.9884333	1.7868667	108.223645	1.42631	165.818
1M$_2$CBu	0.9918117	1.7492167	108.657178	1.424275	167.49
1MCPe	0.9925917	1.7350867	107.9706	1.42378667	173.913
6Boat	0.9946767	1.7017917	108.02079	1.42107667	175.008
6Chair	0.9949367	1.6916133	107.867408	1.42052833	174.534

Table S5. Mulliken charge for oxygen and hydrogen atoms contains in primary hydrogen bonding up 4 methanol clusters at DFT/6-31G(d) method. Oxygen charge is in negative values and cluster names arrangement by the stability.

Structure	**Mol. 1**		**Mol. 2**		**Mol. 3**		**Mol. 4**	
	O	**H**	**O**	**H**	**O**	**H**	**O**	**H**
Monomer	0.605	0.390						
Dimer	0.657	0.416	0.609	0.407				
3Cyclic	0.658	0.428	0.654	0.429	0.655	0.429		
4Chain	0.613	0.412	0.676	0.437	0.665	0.443	0.656	0.429
1MCPr	0.669	0.442	0.662	0.429	0.646	0.427	0.646	0.418
4Cyclic	0.672	0.442	0.672	0.442	0.672	0.442	0.672	0.442

Table S6. Mulliken charge for oxygen and hydrogen atoms contains in primary hydrogen bonding from 5 to 6 methanol clusters at DFT/6-31G(d) method. Oxygen charge is in negative values and cluster names arrangement by the stability.

Structure	**Mol. 1**		**Mol. 2**		**Mol. 3**		**Mol. 4**		**Mol. 5**		**Mol. 6**	
	O	**H**	**O**	**H**	**O**	**H**	**O**	**H**	**O**	**H**	**O**	**H**
5Chain	0.653	0.427	0.665	0.452	0.682	0.445	0.666	0.444	0.624	0.407		
1M$_2$CPr	0.673	0.447	0.668	0.430	0.645	0.425	0.661	0.435	0.655	0.433		
1MCBu	0.679	0.454	0.676	0.446	0.671	0.438	0.660	0.440	0.654	0.420		
5Cyclic	0.678	0.449	0.679	0.450	0.672	0.450	0.677	0.449	0.677	0.449		
1M$_3$CPr	0.673	0.447	0.668	0.429	0.647	0.426	0.672	0.443	0.666	0.442	0.646	0.433
1,3MCBu$_1$	0.679	0.453	0.672	0.443	0.685	0.457	0.668	0.439	0.656	0.420	0.651	0.424
1,3MCBu$_2$	0.676	0.452	0.675	0.437	0.678	0.455	0.678	0.439	0.652	0.423	0.641	0.428
1,4MCBu	0.683	0.459	0.682	0.440	0.665	0.434	0.677	0.446	0.647	0.431	0.654	0.424
1M$_2$CBu	0.695	0.463	0.580	0.443	0.670	0.442	0.664	0.437	0.659	0.442	0.650	0.427
1MCPe	0.682	0.456	0.678	0.452	0.678	0.450	0.675	0.452	0.673	0.440	0.651	0.426
6Boat	0.676	0.452	0.676	0.448	0.670	0.453	0.676	0.453	0.674	0.450	0.679	0.452
6Chair	0.680	0.452	0.680	0.452	0.680	0.452	0.680	0.452	0.680	0.452	0.680	0.452

Table S7. Stretching frequencies calculated at DFT/6-31G(d) optimized geometry for O-H in $(CH3OH)_n$, n = 1-4 and its isomers. Frequencies are scaled in cm^{-1} and and IMV (intensity of molecule's vibration) denotes to O-H intensities at any molecule.

Structure	**Frequency**	**Intensity**	**IMV**	**Structure**	**Frequency**	**Intensity**	**IMV**
Monomer	3608	11.2	1	4Chain	3610	30.2	1
					3422	663.9	2>>3
					3363	618.4	4>>2=3
					3259	956.5	3>>2=4
Dimer	3601	24.7	1>>2	1MCPr	3477	436.6	4>>3>2
	3472	387.2	2>>1		3425	510.7	3>>2=4
					3373	410.5	2>>1=3>4
					3151	636.3	1>>2=3=4
3Cylic	3357	824.7	1=2>>3	4Cylic	3255	247.8	1=2=3=4
	3350	888.2	1=3>2		3207	1845.1	2=4>1=3
	3271	9.1	1=2=3		3207	1845.5	1=3>2=4
					3093	0.0	1=2=3=4

Acknowledgements

We gratefully acknowledge the financial support of this work by the Drug Applied Research Center, Tabriz University of Medical Sciences. We are very grateful to Dr. Solimannejad of the Arak University and Dr. Massahi of the Ilam University for helpful discussions.

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