

## Research Article

# Stability Analysis and Frontier Orbital Study of Different Glycol and Water Complex

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Received 20 October 2012; Accepted 7 November 2012

Academic Editors: J. G. Han, T. Kar, and A. M. Koster

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A detailed theoretical study of hydrogen-bond formation in different polyethylene glycol + water complex and dipropylene glycol + water have been performed by Hartree Fock (HF) method, second-order Møller-Plesset perturbation theory (MP2), and density functional theory (DFT) using 6-31++G(d,p) basis set. B3LYP DFT-D, WB97XD, M06, and M06-2X functionals have been used to describe highly dispersive hydrogen-bond formation appropriately. Geometrical parameters, interaction energies, deformation energies, deviation of potential energy curves of hydrogen bonded O–H from that of free O–H, frontier orbitals, and charge transfer have been studied to analyze stability and nature of hydrogen bond formation of various glycol and water complexes. It is found that WB97XD is best among all the applied DFT functionals to describe hydrogen bond interaction, and intermolecular hydrogen bonds have higher covalent character and accordingly higher strength when glycol acts as proton donor for glycol + 1 water complex system.

## 1. Introduction

Polyethylene glycol and its derivatives are applied extensively as drag delivering medium in medical industry [1] and gas hydrate inhibitor in petroleum industry [2, 3]. Experimental study of ethylene glycol molecule and ethylene glycol aqueous solution has been performed using nuclear magnetic resonance (NMR) spectroscopy [4, 5], infrared spectroscopy (IR) [6–9], ultraviolet (UV) spectroscopy [9], Raman Spectroscopy [10], X-ray, and Neutron diffraction techniques [11]. Quantum chemical-based study on different conformers of ethylene glycol has revealed that the gauche form is the most stable conformer in aqueous solution [12, 13]. Hydrogen-bond, an attractive proton donor-acceptor interaction between donor (bonded combination of hydrogen with other electronegative atom) and acceptor (electron-rich region) [14, 15], plays crucial role in determining microscopic and macroscopic behaviour of glycols and water system. Since aqueous solution of glycols are used as gas hydrate

inhibitor during drilling practice in petroleum industry, detailed scientific understanding of hydrogen-bond interaction between glycol and water is essential to utilize glycols more efficiently as gas hydrate inhibitor. Quantum chemical calculation is very effective to investigate the hydrogen-bond interaction and its impact on the performance of gas hydrate inhibitors. The effect of microsolvation on ethylene glycol has been studied using density functional theory considering the contribution of many body energies by Chaudhari and Lee [16]. A polymer reference interaction site model theory-based study of polyethylene glycol-water system has been reported by Xu et al. [17]. Theoretical study of hydrogen-bond interaction in ethylene glycol cluster, carried out by Kumar et al., has revealed that the presence of water destroys the intermolecular hydrogen-bonds in ethylene glycol cluster [18]. Quantum chemical analysis of hydrogen-bond interaction in trimethylene glycol-water complex has been performed by Pal and Kundu [19]. Though literature of quantum chemical study of hydrogen-bond formation in

TABLE 1: Calculated hydrogen-bond distances ( $d_{O\cdots H}$ , Å), hydrogen-bond angles ( $A_{O\cdots H-O}$ , degree), and dipole moment ( $D$ , debye) for single EG and EG +  $n_w$  water complex ( $n_w = 1, 2$ ) using 6-31++G(d,p) basis set and various methods.

System	Parameters	Methods						
		MP2	WB97XD	B3LYP DFTD	MO62X	MO6	B3LYP	HF
EG	$D$	2.46	2.35	2.36	2.35	2.35	2.33	2.34
EG + 1 water complex (GD)	$d_{O\cdots H}$ , $O_{11} \cdots H_{10}$	1.93	1.91	1.89	1.94	1.95	1.92	2.04
	$A_{O\cdots H}$ , $O_{11} \cdots H_{10}-O_4$	174.48	175.33	176.70	160.81	159.87	176.19	178.05
	$D$	4.47	4.26	4.20	4.42	4.50	3.97	4.09
EG + 1 water complex (WD)	$d_{O\cdots H}$ , $O_1 \cdots H_{11}$	1.93	1.89	1.89	1.96	1.92	1.90	2.03
	$A_{O\cdots H}$ , $O_1 \cdots H_{11}-O_{12}$	153.39	158.14	154.63	144.61	151.63	162.56	163.87
	$D$	2.46	2.35	2.36	2.35	2.35	2.33	2.34
EG + 2 water complex	$d_{O\cdots H}$ , $O_{11} \cdots H_{10}$	1.93	1.90	1.89	1.91	1.94	1.93	2.05
	$d_{O\cdots H}$ , $O_{14} \cdots H_5$	1.94	1.91	1.89	1.93	1.94	1.94	2.05
	$A_{O\cdots H}$ , $O_{11} \cdots H_{10}-O_4$	178.40	177.47	174.49	177.35	164.04	173.9	177.04
	$A_{O\cdots H}$ , $O_{14} \cdots H_5-O_1$	176.84	178.56	178.65	165.84	163.49	173.47	176.47
	$D$	2.57	2.48	2.49	2.81	2.60	2.03	1.94
EG dimer	$d_{O\cdots H}$ , $O_1 \cdots H_{15}$	1.88	1.88	1.85	1.90	1.91	1.90	2.03
	$A_{O\cdots H}$ , $O_1 \cdots H_{15}-O_{11}$	168.91	168.50	168.40	157.80	159.41	174.87	179.88
	$D$	4.82	4.27	4.04	5.07	5.02	3.68	4.08

different complexes is vast [20–26], quantum chemical study of hydrogen-bond interaction between water and glycols other than ethylene glycol and trimethylene glycol has not been reported so far. Electronic structure-based studies on hydrogen-bond formation between water and glycol having ether functional group (C–O–C) (e.g., diethylene glycol, triethylene glycol and dipropylene glycol) have not been performed till date.

A detail theoretical analysis is reported here to comprehend the electronic nature of the hydrogen-bond formation in various polyethylene glycol-water and dipropylene glycol-water systems, and its property using Hartree Fock, Møller-Plesset is truncated at second-order (MP2), density functional theory (DFT), and density functional theory with dispersion function (DFT-D). The detail study of geometrical parameters of optimized structures, interaction energies, deformation energies, relaxation energies, many body energy contributions, charge transfer, potential energy plots, and frontier orbitals reported in this paper should provide electronic structure-based insights on hydrogen-bond formation

in glycol-water complex and scientific understanding on application of different glycols as a gas hydrate inhibitors.

## 2. Computational Detail

Geometry optimization and interaction energy calculation have been carried out using Hartree Fock (HF) [27] method, second-order Møller-Plesset perturbation theory (MP2) [28], density functional theory (DFT) [29, 30], and density functional theory with dispersion function (DFT-D) [31]. The calculations for DFT and DFT-D level of theory have been performed using different functionals, namely, B3LYP [32, 33], WB97XD [34], M06 [35], and M062X [35]. As polarity [36] of molecule has great influence on intermolecular hydrogen bonding, hydrogen-bond-forming orbitals require larger space occupation [37]. Thus diffuse and polarization functions augmented split valence 6-31++G(d,p) basis set that is used for better description of molecular orbitals for geometry optimization. Since hydrogen bonding is a kind of donor-acceptor interaction, additional dispersion

TABLE 2: Calculated hydrogen-bond distances ( $d_{O\dots H}$ , Å), hydrogen-bond angles ( $A_{O\dots H}$ , degree), and dipole moment ( $D$ , debye) for single DEG and DEG +  $n_w$  water complex ( $n_w = 1, 2$ ) using 6-31++G(d,p) basis set and various methods.

System	Parameters	Methods						
		MP2	WB97XD	B3LYP DFT-D	MO62X	MO6	B3LYP	HF
DEG	$D$	1.14	0.96	1.05	0.97	1.04	1.02	0.93
DEG + 1 water complex (GD)	$d_{O\dots H}$ , $O_{18} \dots H_{17}$	1.94	1.90	1.88	1.94	1.93	1.92	2.04
	$A_{O\dots H}$ , $O_{18} \dots H_{17}-O_7$	172.60	172.47	174.51	159.06	163.90	177.25	177.37
	$D$	3.64	3.48	3.59	3.33	3.47	3.52	3.32
DEG + 1 water complex (WD)	$d_{O\dots H}$ , $O_7 \dots H_{18}$	1.91	1.88	1.86	1.90	1.91	1.90	2.02
	$A_{O\dots H}$ , $O_7 \dots H_{18}-O_{19}$	160.25	162.39	162.09	152.65	154.61	164.61	166.90
	$D$	1.88	1.59	1.69	1.91	1.78	1.53	1.58
DEG + 2 water complex	$d_{O\dots H}$ , $O_6 \dots H_{23}$	1.91	1.89	1.86	1.90	1.90	1.89	2.02
	$d_{O\dots H}$ , $O_7 \dots H_{18}-O_{19}$	1.91	1.89	1.86	1.90	1.90	1.89	2.02
	$A_{O\dots H}$ , $O_6 \dots H_{23}-O_{22}$	160.32	165.19	162.1	152.74	154.93	164.35	166.27
	$A_{O\dots H}$ , $O_7 \dots H_{18}-O_{19}$	160.31	165.30	162.05	152.74	154.94	164.43	166.26
	$D$	0.92	3.58	0.91	0.06	0.31	1.66	1.92
DEG dimer complex	$d_{O\dots H}$ , $O_{24} \dots H_{16}$	2.08	2.07	2.04	2.09	2.07	2.04	2.11
	$d_{O\dots H}$ , $O_7 \dots H_{33}$	2.08	1.96	2.04	2.09	2.07	2.04	2.02
	$A_{O\dots H}$ , $O_{24} \dots H_{16}-O_6$	154.38	156.89	152.57	147.54	151.83	167.59	150.66
	$A_{O\dots H}$ , $O_7 \dots H_{33}-O_{23}$	154.37	157.17	152.58	147.53	151.78	167.58	173.49
	$D$	0.84	1.57	0.80	0.58	0.62	1.50	1.49

function with density functional theory, that is, DFT-D-based calculation, has also been performed. Natural energy decomposition analysis (NEDA) has been performed using WB97XD/6-31++G(d,p) method.

Interaction energy ( $\Delta E$ ) for hydrogen-bonded complex is calculated as the difference between the energy of hydrogen-bonded complex and the summation of the energies of each component monomer [38] as

$$\Delta E = E_{\text{complex}} - \sum E_{\text{component}}, \quad (1)$$

where  $E_{\text{complex}}$  and  $E_{\text{component}}$  are optimized energy of hydrogen-bonded complex and each individual component monomer, respectively. Interaction energies have corrected for the basis set superposition error (BSSE) by virtue of counterpoise method [39]. A hydrogen-bonded complex is more stable if interaction energy is more negative compared to other hydrogen-bonded configurations. In order to measure the change in conformation of glycol molecules due to presence of water, deformation energy ( $\Delta E_{\text{def}}$ ) [40] for a glycol molecule in any cluster/complex is calculated, as the

difference of total electronic energies of glycol in its complex and free state is as follows:

$$\Delta E_{\text{def}} = E_{\text{molecule\_in\_complex}} - E_{\text{molecule\_in\_free\_state}}. \quad (2)$$

Hydrogen-bond cooperativity is studied by calculating relaxation energy ( $\Delta E_{\text{relax}}$ ), two-body energy ( $\Delta E_2$ ), and three-body energy ( $\Delta E_3$ ) using the following [41, 42]:

$$\begin{aligned} \Delta E_{\text{relax}} &= \sum_{i=1}^n E(i) - \{E_G + n_w * E_W\}, \\ \Delta E_2 &= \sum_{i=1}^n \sum_{j>1}^n \Delta^2 E(ij), \end{aligned} \quad (3)$$

$$\Delta^2 E(ij) = E(ij) - \{E(i) + E(j)\},$$

$$\begin{aligned} \Delta E_3 &= \Delta^3 E(ijk) = E(ijk) - \{E(i) + E(j) + E(k)\} \\ &\quad - \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(jk)\}. \end{aligned}$$

TABLE 3: Calculated hydrogen-bond distances ( $d_{O\cdots H}$ , Å), hydrogen-bond angles ( $A_{O\cdots H-O}$ , degree), and dipole moment ( $D$ , debye) for single TEG and TEG +  $n_w$  water complex ( $n = 1, 2, 4$ ) using 6-31++G(d,p) basis set and various methods.

System	Parameters	Methods						
		MP2	WB97XD	B3LYP DFTD	MO62X	MO6	B3LYP	HF
TEG	$D$	2.58	2.34	2.43	2.31	2.46	2.41	2.42
TEG + 1 water complex (GD)	$d_{O\cdots H}$ , $O_{25}\cdots H_{15}$	1.94	1.90	1.89	1.94	1.93	1.92	2.04
	$A_{O\cdots H}$ , $O_{25}\cdots H_{15}-O_6$	173.13	172.71	175.39	159.79	164.13	177.01	178.10
	$D$	4.61	4.30	4.33	4.51	4.61	4.08	4.18
TEG + 1 water complex (WD)	$d_{O\cdots H}$ , $O_6\cdots H_{25}$	1.90	1.88	1.85	1.90	1.913	1.89	2.02
	$A_{O\cdots H}$ , $O_6\cdots H_{25}-O_{26}$	160.76	162.44	162.64	153.65	154.59	165.46	168.99
	$D$	1.72	1.56	1.5	1.76	1.77	1.56	1.94
TEG + 2 water complex	$d_{O\cdots H}$ , $O_{25}\cdots H_{15}$	1.94	1.90	1.89	1.94	1.93	1.92	2.04
	$d_{O\cdots H}$ , $O_{28}\cdots H_{23}$	1.92	1.89	1.87	1.90	1.92	1.91	2.04
	$A_{O\cdots H}$ , $O_{25}\cdots H_{15}-O_6$	173.07	174.19	175.47	160.52	164.03	176.55	178.99
	$A_{O\cdots H}$ , $O_{28}\cdots H_{23}-O_{22}$	179.34	178.75	176.76	171.22	161.78	175.54	179.45
	$D$	5.40	4.80	4.64	5.66	5.80	4.08	4.69

TABLE 4: Calculated hydrogen-bond distances ( $d_{O\cdots H}$ , Å), hydrogen-bond angles ( $A_{O\cdots H}$ , degree), dipole moment ( $D$ , debye) for DPG molecule and DPG +  $n_w$  water complex ( $n_w = 1, 2, 3$ ), DPG dimer, and water dimer using 6-31++G(d,p) basis set and various methods.

System	Parameters	Methods						
		MP2	WB97XD	B3LYP DFTD	MO62X	MO6	B3LYP	HF
DPG	$D$	5.01	4.47	4.46	4.40	4.30	4.43	4.69
DPG + 1 water complex (GD)	$d_{O\cdots H}$ , $O_{24}\cdots H_{21}$	1.93	1.90	1.88	1.91	1.93	1.93	2.05
	$A_{O\cdots H}$ , $O_{24}\cdots H_{21}-O_{20}$	178.60	176.25	175.19	176.23	164.79	174.44	177.44
	$D$	5.48	4.67	4.62	5.23	5.75	4.61	5.00
DPG + 1 water complex (WD)	$d_{O\cdots H}$ , $O_{22}\cdots H_{24}$	1.90	1.88	1.86	1.91	1.91	1.90	2.03
	$A_{O\cdots H}$ , $O_{22}\cdots H_{24}-O_{25}$	162.78	166.07	161.8	151.04	155.18	167.98	171.36
	$D$	4.03	4.17	3.68	2.99	3.17	4.29	4.99
DPG + 2 water complex	$d_{O\cdots H}$ , $O_{22}\cdots H_{24}$	1.90	1.89	1.86	1.92	1.91	1.90	2.03
	$d_{O\cdots H}$ , $O_{20}\cdots H_{28}$	1.90	1.89	1.86	1.92	1.91	1.90	2.03
	$A_{O\cdots H}$ , $O_{22}\cdots H_{24}-O_{25}$	162.54	161.59	161.55	149.65	154.93	167.89	170.64
	$A_{O\cdots H}$ , $O_{20}\cdots H_{28}-O_{27}$	162.54	161.60	161.68	149.66	154.94	167.88	170.64
	$D$	4.65	4.21	4.18	2.45	3.29	5.47	6.04
DPG dimer	$d_{O\cdots H}$ , $O_{43}\cdots H_{23}$	—	1.89	1.87	1.90	1.91	1.91	2.04
	$A_{O\cdots H}$ , $O_{43}\cdots H_{23}-O_{22}$	—	171.89	167.63	170.67	167.46	171.92	172.87
	$D$	—	7.09	5.83	6.93	7.04	5.19	5.65

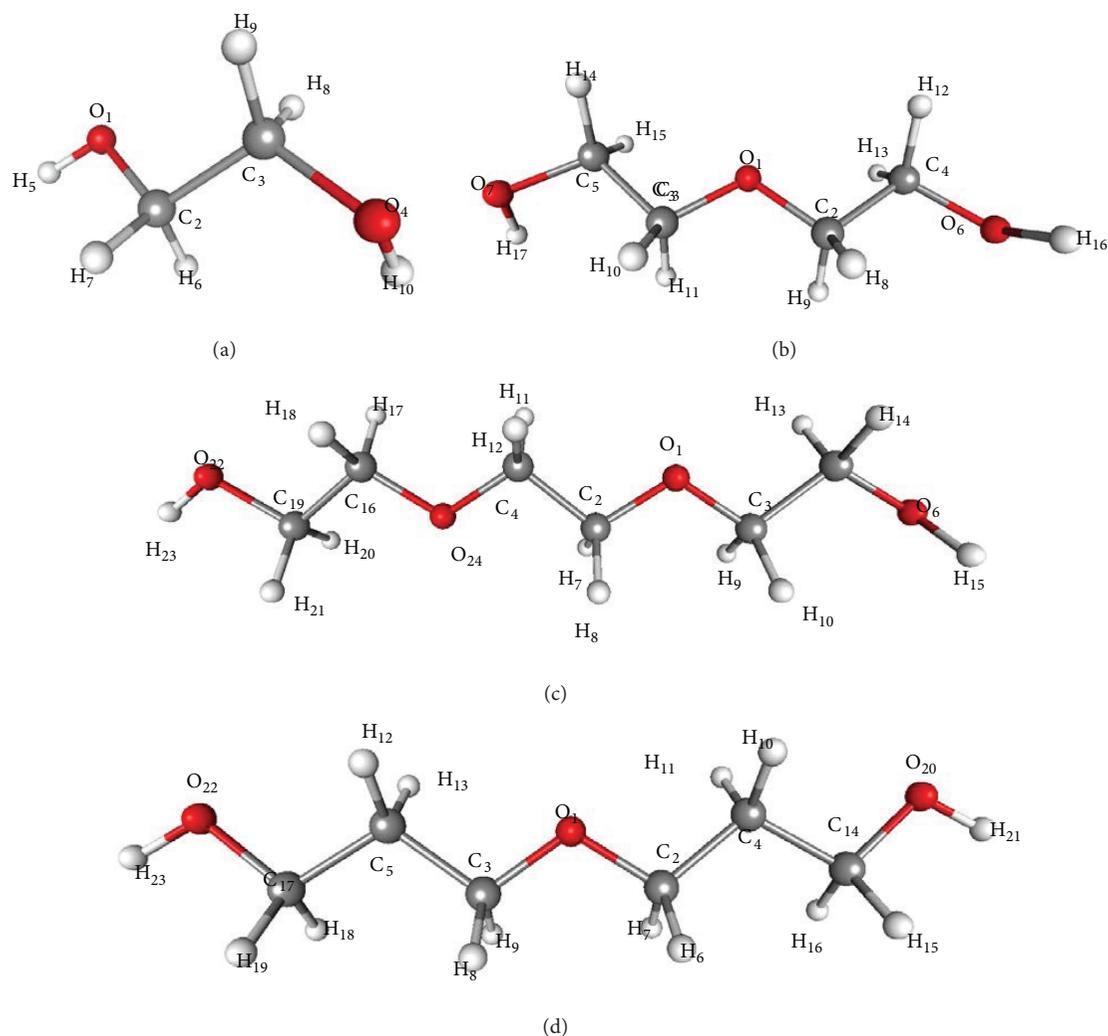


FIGURE 1: Optimized structures using WB97XD/6-31++G(d,p) of (a) ethylene glycol (EG), (b) diethylene glycol (DEG), (c) triethylene glycol (TEG), and (d) dipropylene glycol molecule (DPG) (colour legend: red = oxygen, black = carbon, and whitish grey = hydrogen).

Here,  $E(i)$ ,  $E(ij)$ , and  $E(ijk)$  are the energies of the monomer, dimer, and trimer in complex or cluster,  $E_G$  and  $E_W$  are the energies of glycols, water in free state and  $n$  is number of component molecule in complex ( $n = 3$ , one glycol and two water molecules), and  $n_w$  is number of water molecule ( $n_w = 2$ ) in complex. Gaussian 09 software package has been used to perform all the calculations reported here [43].

### 3. Results and Discussion

The optimized structures of ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), and dipropylene glycol (DPG) molecule, their dimer, their complex with one and two water molecules have been obtained by HF, MP2, and DFT methods using 6-31++G(d,p) basis set and B3LYP DFT-D, WB97XD, M06, and M06-2X functionals, and the corresponding structures obtained by using WB97XD functional DFT method are shown in Figures 1, 2, 3, and 4, respectively. For present study, two cases like glycol acts

as proton donor (referred by GD) and water act as proton donor (referred by WD) are considered for different glycols, and one water complex and their optimized structures are presented in Figure 3. The calculated geometrical parameters using 6-31++G(d,p) basis set and different levels of theory are summarized in Tables 1, 2, 3, and 4. The calculated hydrogen-bond distances obtained using MP2, WB97XD, B3LYP DFT-D, and parameterized functional (M06, M06-2X) based methods are less than hydrogen-bond distances obtained from HF method for all the systems studied here. The calculated hydrogen-bond distance for EG dimer using MP2 and DFT methods corresponds well with experimental value, that is, 1.80 Å [11]. The calculated hydrogen-bonded O–H bond distance and free O–H bond distance for EG dimer using MP2 and DFT methods is equal to 0.97 Å and 0.96 Å, respectively, and is in good agreement with experimental value, that is, 0.96 Å [11]. It is also observed that hydrogen-bond angle values for intermolecular hydrogen bonds in all the glycol +  $n_w$  water and their dimer are greater

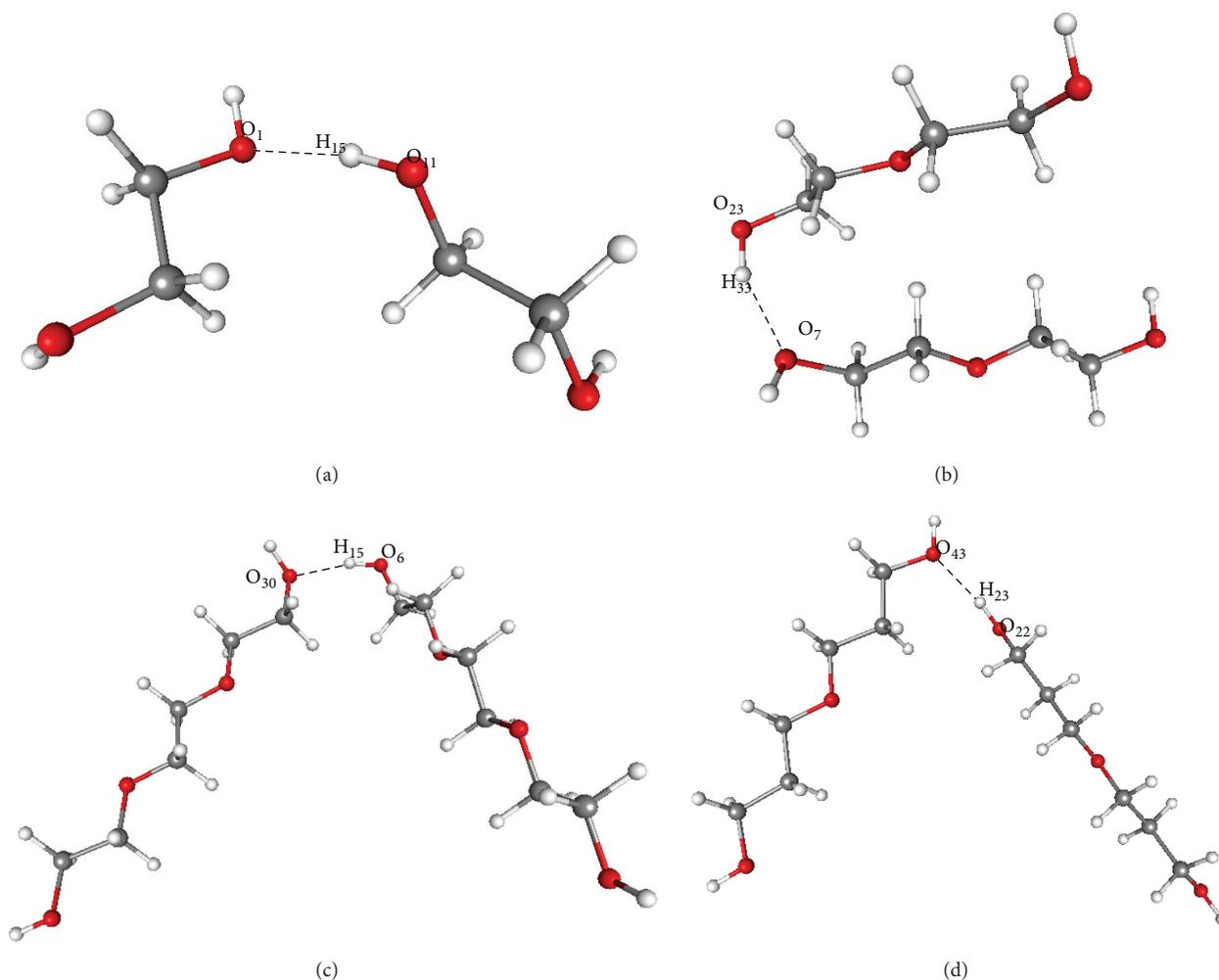


FIGURE 2: Optimized structures using WB97XD/6-31++G(d,p) of (a) ethylene glycol (EG) dimer, (b) diethylene glycol (DEG) dimer, (c) triethylene glycol (TEG) dimer, and (d) dipropylene glycol (DPG) dimer (colour legend: red = oxygen, black = carbon, whitish grey = hydrogen, and black-dotted line is hydrogen-bond).

than  $160^\circ$  except for EG + 1 water (WD) complex according to all the calculation methods used. Thus intramolecular hydrogen bonds of these complex are almost linear and strong. Dipole moments of different glycols +  $n_w$  water systems along with dimer have been given in Tables 1–4. As hydrogen-bond formation helps in superposition of  $O \cdots H$  moment and delocalization of  $\pi$  electrons in hydrogen-bonded molecular cluster, the dipole moment is increased by stronger intermolecular hydrogen-bond formation [44]. The dipole moment values are higher and consequently forming stronger intermolecular hydrogen-bond when glycols are acting as proton donor compared to when water is acting as proton donor in different glycols + 1 water complex as evident in Tables 1–4.

Interaction energies for glycols (including dimers) and water systems with and without BSSE correction have been summarized in Tables 5–8. The complex formed by hydrogen bonding with more negative interaction energy should have

better stability compared to the hydrogen-bonded complex having less negative interaction energy. Accordingly the stability order for EG and water complex, as observed from Table 5 is water dimer < EG + 1 water complex (GD) < EG + 1 water complex (WD) < EG dimer < EG + 2 water complex from MP2 and WB97XD functional-based calculation. On the other hand the stability order found by B3LYP, B3LYP DFT-D, M06, and M06-2X functional-based calculation is water dimer < EG + 1 water complex (GD) < EG dimer < EG + 1 water complex (WD) < EG + 2 water complex and the stability order obtained by HF theory based calculation as: EG dimer < EG + 1 water complex (WD) < water dimer < EG + 1 water complex (GD) < EG + 2 water complex. The stability order for DEG and water complex as evident from Table 6 is DEG + 1 water complex (GD) < DEG + 1 water complex (WD) < DEG dimer < DEG + 2 water complex as per MP2 method and WB97XD, B3LYP DFT-D, M06, M06-2X, and B3LYP functional-based calculation,

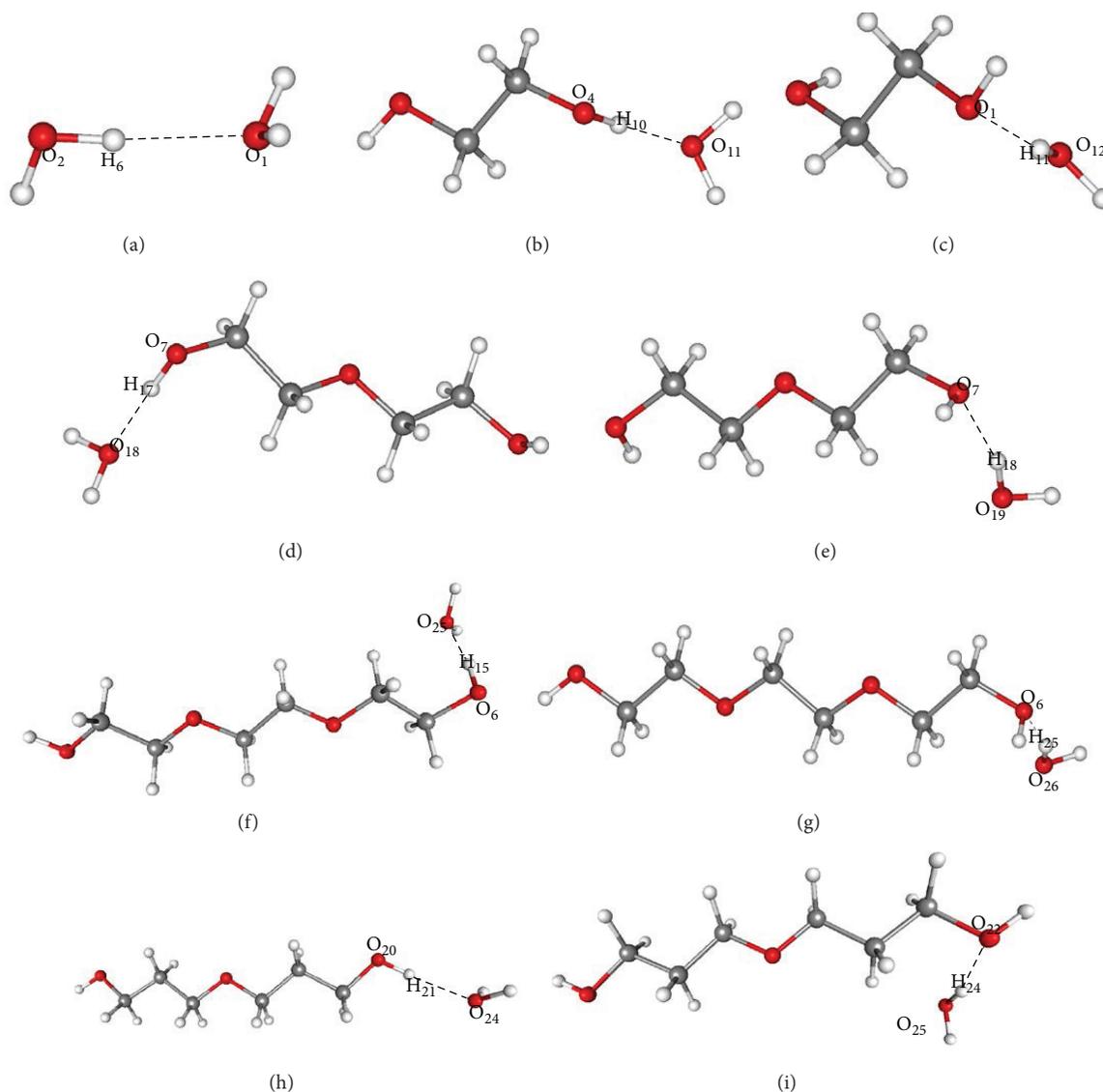


FIGURE 3: Optimized structures using WB97XD/6-31++G(d,p) of (a) water dimer [19], (b) ethylene glycol (EG) + 1 water (GD), (c) ethylene glycol (EG) + 1 water (WD), (d) diethylene glycol (DEG) + 1 water (GD), (e) diethylene glycol (DEG) + 1 water (WD), (f) triethylene glycol (TEG) + 1 water (GD), (g) triethylene glycol (TEG) + 1 water (GD), (h) dipropylene glycol (DPG) + 1 water (GD), and (i) dipropylene glycol (DPG) + 1 water (WD) (colour legend: red = oxygen, black = carbon and whitish grey = hydrogen and black-dotted line is hydrogen-bond).

differing with the stability order obtained using HF theory, that is, DEG dimer < DEG + 1 water complex (WD) < DEG + 1 water complex (GD) < DEG + 2 water complex. Similarly from Table 7, the observed stability order is TEG + 1 water complex (GD) < TEG + 1 water complex (WD) < TEG + 2 water complex as per MP2 method and WB97XD, B3LYP DFT-D, M06, M06-2X, and B3LYP functional-based calculation, contrasting the stability order determined using HF theory, that is, TEG + 1 water complex (WD) < TEG + 1 water complex (GD) < TEG + 2 water complex. It is also found from Table 8 that the stability order in ascending sense is: DPG + 1 water complex (GD) < DPG + 1 water complex (WD) < DPG + 2 water complex as per MP2

method and WB97XD, B3LYP DFT-D, M06, M06-2X, and B3LYP functional-based calculation, contrasting the stability order determined using HF theory, that is, DPG + 1 water complex (WD) < DPG + 1 water complex (GD) < TEG + 2 water complex. The interaction energies are overestimated by HF theory-based calculation as found in Tables 5–8, because HF theory does not include or consider electron correlation factor. HF theory is found to be inappropriate for describing hydrogen-bond interaction, as results obtained using HF method differ significantly from the results of MP2 method, one of the most reliable ways to describe hydrogen bonding [45, 46]. It can be inferred based on the comparison of different DFT methods with MP2 method with respect

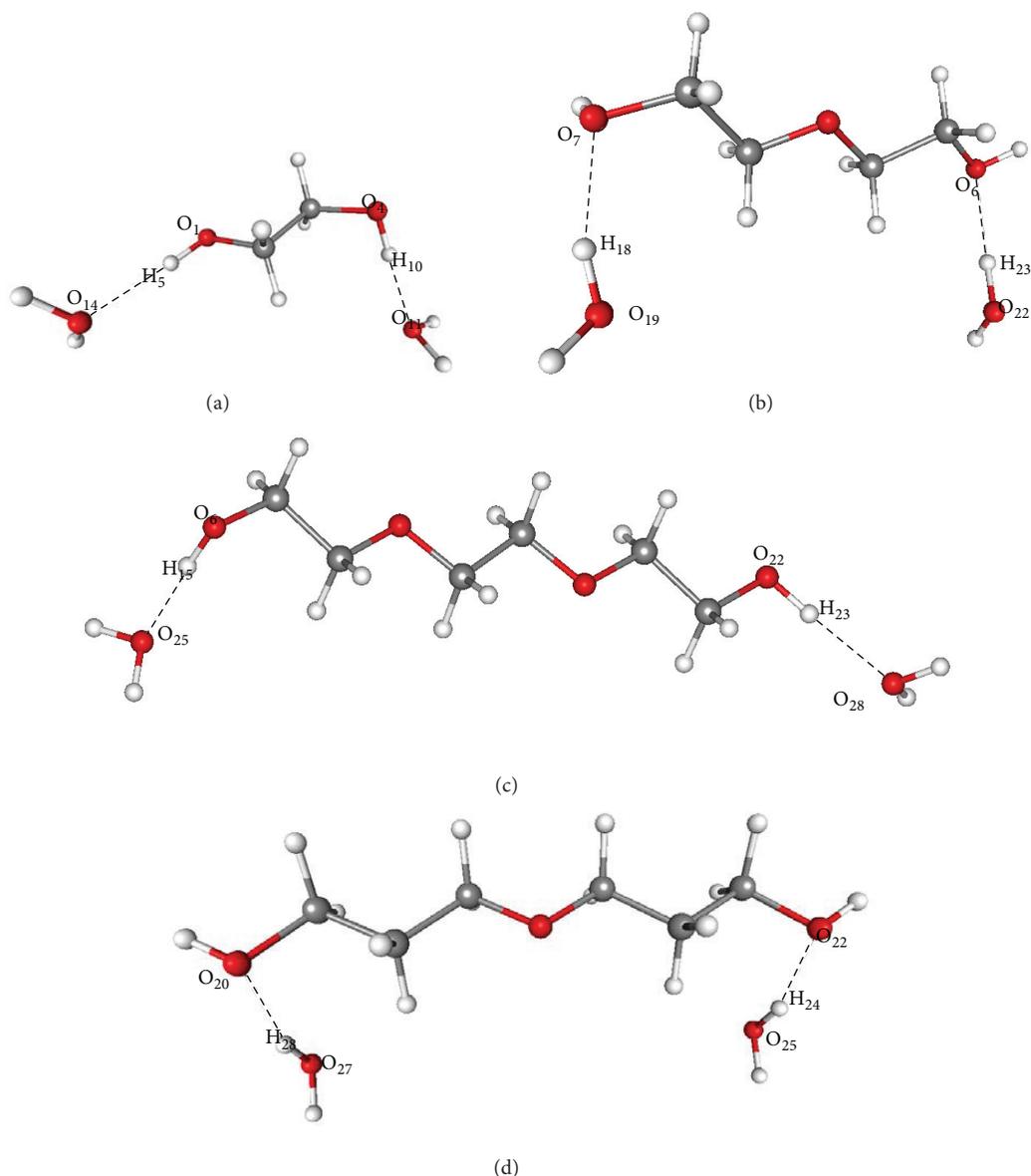


FIGURE 4: Optimized structures using WB97XD/6-31++G(d,p) of (a) ethylene glycol (EG) + 2 water, (b) diethylene glycol (DEG) + 2 water, (c) triethylene glycol (TEG) + 2 water, and (d) dipropylene glycol (DPG) + 2 water, (colour legend: red = oxygen, black = carbon, whitish grey = hydrogen, and black-dotted line is hydrogen-bond).

to the values of interaction energies and stability trends of hydrogen-bonded complexes that WB97XD is the best among all the applied DFT functionals to describe hydrogen-bond interaction. Stronger hydrogen-bond is formed in glycols + water complex compared to the hydrogen-bond formed in water dimer system according to all the quantum chemical calculation methods applied as evident in Tables 5–8. Relaxation energies and deformation energies for various glycols and water system are summarized in Tables 9, 10, 11, and 12. The positive values of both deformation energy and relaxation energy depict that the molecules or ligands in their complex form become destabilized compared to their free state form. Many body energies for glycols + 2

water complex calculated at WB97XD/6-31++G(d,p) level of theory have been summarized in Table 13. Two-body energy is found to be negative and consequently attractive in nature, whereas three-body energy is found to be positive and consequently repulsive in nature for all the glycols + 2 water system studied. It is found that two-body energy contribution is maximum (compared to relaxation and three-body energy) toward interaction energy, and consequently two-body energy is most significant for the stability of such hydrogen-bonded complexes.

The potential energy curves for a free O–H bond of single DEG, TEG, and DPG molecule are represented in Figures 5(a), 5(c), and 5(e), respectively. The potential energy

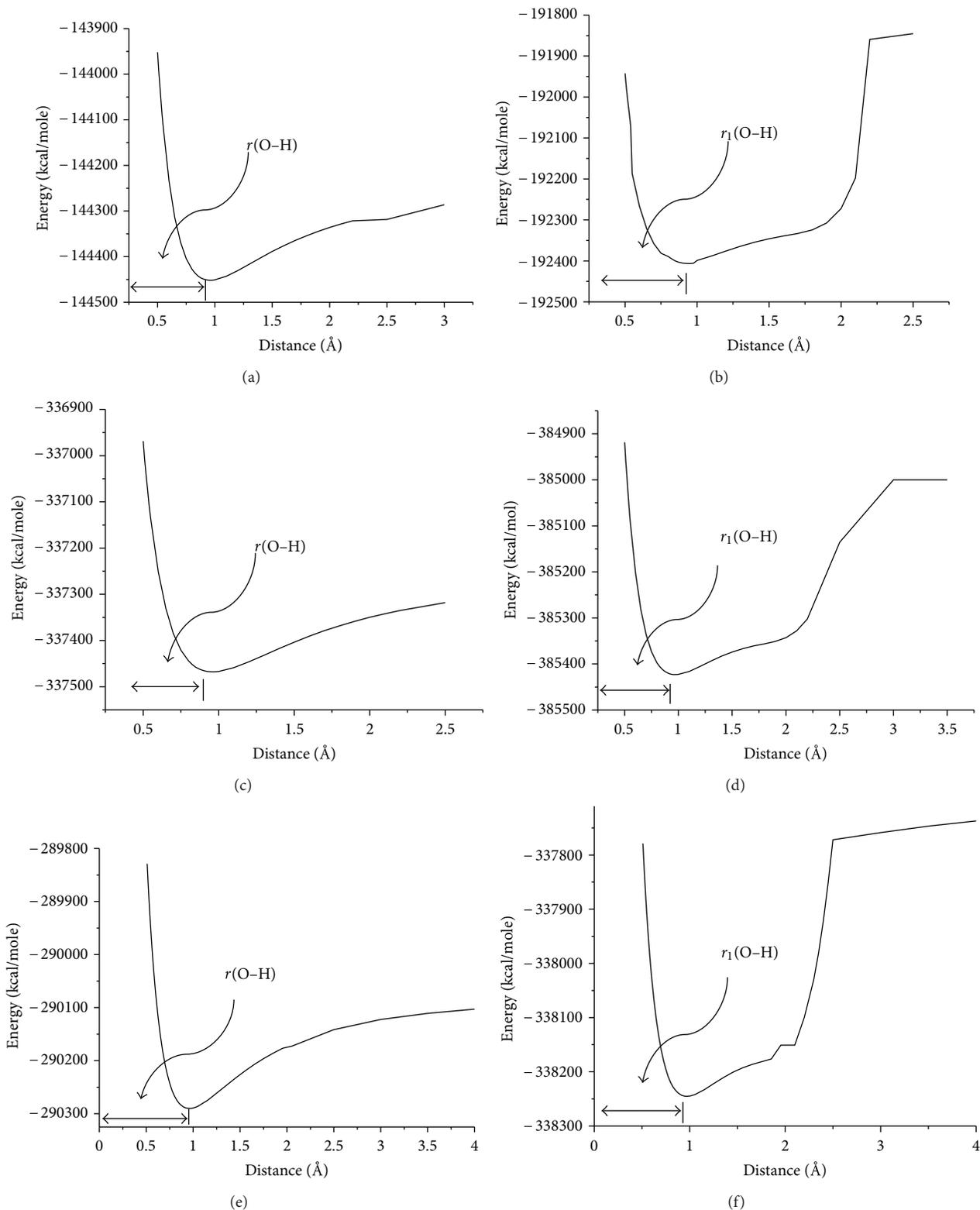


FIGURE 5: Calculated energy (kcal/mol) curve using WB97XD/6-31++G(d,p) of for (a) a free bond of O-H ( $O_4-H_{10}$ ) group of DEG, (b) hydrogen-bonded O-H ( $O_4-H_{10}$ ) group of DEG + 1 water complex (GD), (c) a free bond of O-H ( $O_6-H_{15}$ ) group of triethylene glycol (TEG), (d) hydrogen-bonded O-H ( $O_6-H_{15}$ ) group of triethylene glycol + 1 water complex (GD), (e) a free bond of O-H ( $O_{20}-H_{21}$ ) group of dipropylene glycol (DPG), and (f) hydrogen-bonded O-H ( $O_{20}-H_{21}$ ) group of DPG + 1 water complex (GD).

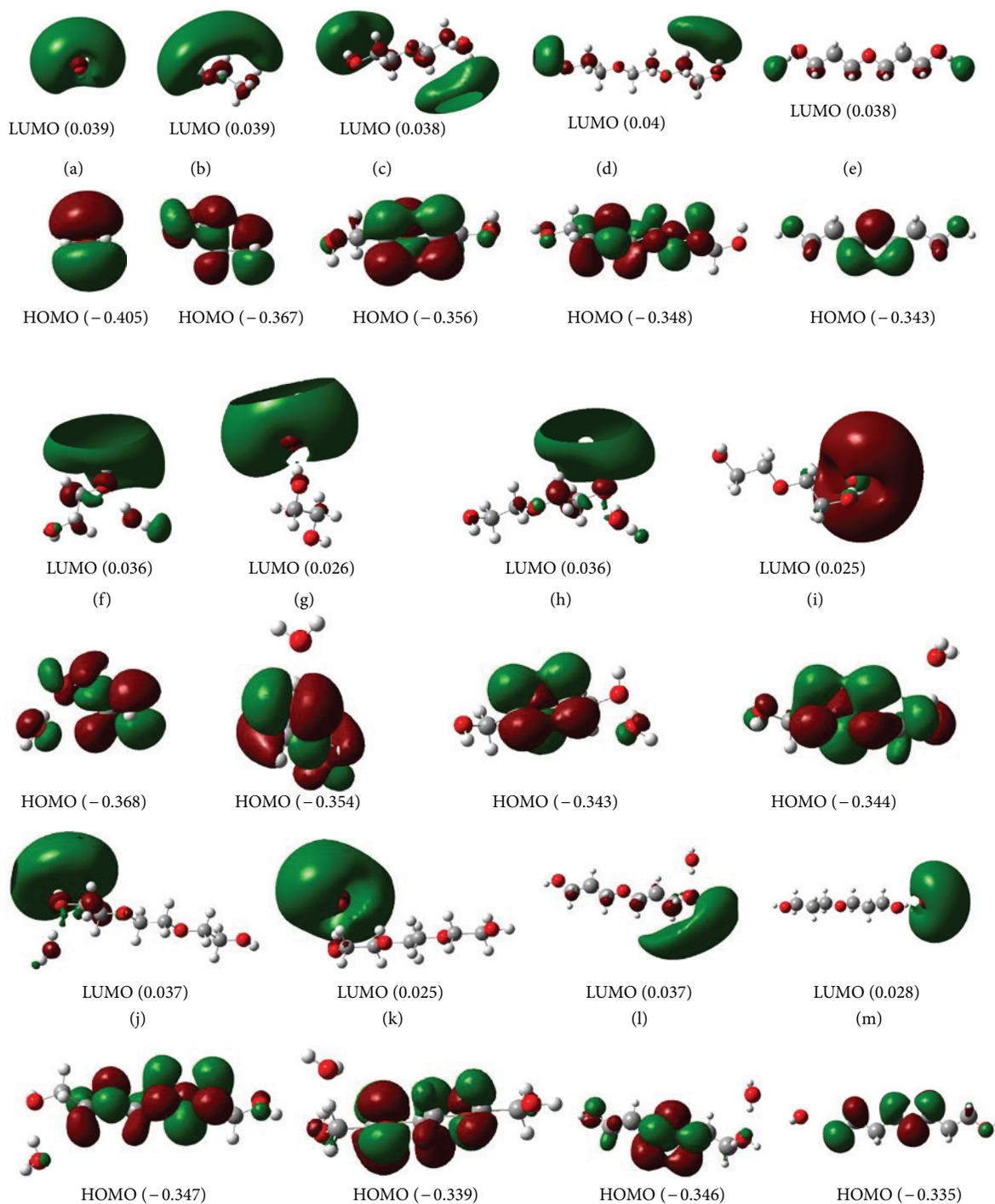


FIGURE 6: Frontier orbitals (HOMO, LUMO energies are atomic unit) simulated by WB97XD/6-31++G(d,p) theory for (a) water molecule, (b) EG molecule, (c) DEG molecule, (d) TEG molecule, (e) DPG molecule, (f) EG + 1 water complex (WD), (g) EG + 1 water complex (GD), (h) DEG + 1 water complex (WD), (i) DEG + 1 water complex (GD), (j) TEG + 1 water complex (WD), (k) TEG + 1 water complex (GD), (l) DPG + 1 water complex (WD), and (m) DPG + 1 water complex (GD).

TABLE 5: Calculated energy of interaction energy without correction ( $\Delta E$ , kcal/mole), BSSE corrected energy of hydrogen-bond formation using counterpoise correction ( $\Delta E_{CP}$ , kcal/mole) for EG +  $n$  water complex ( $n = 1, 2$ ), EG dimer, and water dimer [19] using 6-31++G(d,p) basis set and various methods.

Systems	Calculation methods	$\Delta E$	$\Delta E_{CP}$
EG + 1 water complex (GD)	MP2	-7.01	-4.94
	WB97XD	-6.78	-5.86
	B3LYP DFT-D	-7.09	-6.10
	M062X	-7.14	-6.18
	M06	-6.72	-5.82
	B3LYP	-5.92	-4.99
	HF	-5.08	-4.38
EG + 1 water complex (WD)	MP2	-7.55	-5.49
	WB97XD	-7.50	-6.72
	B3LYP DFT-D	-8.38	-7.49
	M062X	-8.06	-7.23
	M06	-7.28	-6.50
	B3LYP	-6.14	-5.34
	HF	-4.94	-4.35
EG + 2 water complex	MP2	-13.40	-9.40
	WB97XD	-12.96	-11.19
	B3LYP DFT-D	-13.62	-11.72
	M062X	-13.43	-11.49
	M06	-12.41	-10.66
	B3LYP	-11.47	-9.67
	HF	-9.72	-8.35
EG dimer	MP2	-7.69	-4.98
	WB97XD	-7.62	-6.78
	B3LYP DFT-D	-8.36	-7.38
	M062X	-7.50	-6.60
	M06	-7.05	-6.26
	B3LYP	-5.55	-4.77
	HF	-4.60	-3.95
Water dimer	MP2	-6.39	-4.83
	WB97XD	-6.71	-5.95
	B3LYP DFT-D	-5.97	-5.19
	M062X	-6.58	-5.80
	M06	-5.99	-5.25
	B3LYP	-6.35	-5.61
	HF	-5.01	-4.36

curves for hydrogen-bonded O–H of DEG + 1 water complex (GD), TEG + 1 water complex (GD), and DPG + 1 water complex (GD) are also shown in Figures 5(b), 5(d), and 5(f), respectively. The broadening in potential energy curve of hydrogen-bonded O–H reveals that a strong intermolecular hydrogen-bond is formed in DEG + 1 water complex (GD), TEG + 1 water complex (GD), and DPG + 1 water complex (GD) complexes [47]. The broadening width of potential

TABLE 6: Calculated energy of interaction energy without correction ( $\Delta E$ , kcal/mole), BSSE corrected energy of hydrogen-bond formation using counterpoise correction ( $\Delta E_{CP}$ , kcal/mole) for DEG +  $n_w$  water complex ( $n_w = 1, 2$ ), and DEG dimer using 6-31++G(d,p) basis set and various methods.

Systems	Calculation methods	$\Delta E$	$\Delta E_{CP}$
DEG + 1 water complex (GD)	MP2	-7.24	-5.13
	WB97XD	-7.00	-6.09
	B3LYP DFT-D	-7.28	-6.28
	M062X	-7.41	-6.44
	M06	-6.90	-6.01
	B3LYP	-6.06	-5.14
	HF	-5.20	-4.51
DEG + 1 water complex (WD)	MP2	-7.56	-5.53
	WB97XD	-7.51	-6.75
	B3LYP DFT-D	-8.35	-7.51
	M062X	-7.85	-7.05
	M06	-7.07	-6.32
	B3LYP	-6.19	-5.44
	HF	-5.13	-4.59
DEG + 2 water complex	MP2	-15.08	-11.04
	WB97XD	-14.12	-12.60
	B3LYP DFT-D	-16.64	-14.98
	M062X	-15.61	-13.99
	M06	-14.15	-12.65
	B3LYP	-12.33	-10.83
	HF	-10.23	-9.15
DEG dimer complex	MP2	-13.93	-8.53
	WB97XD	-9.69	-8.71
	B3LYP DFT-D	-16.08	-14.71
	M062X	-14.80	-13.41
	M06	-13.85	-12.55
	B3LYP	-6.44	-5.32
	HF	-5.04	-4.39

energy curve due to hydrogen bonding is highest for DEG + 1 water complex (GD), and consequently the hydrogen-bond between DEG and water is the strongest compared to other complexes (Figure 5). Appearance of prominent asymmetrical double minimum and high energy barrier in potential energy curve of hydrogen-bonded O–H for trimethylene glycol (TMG) + 1 water complex (TMG as proton donor) has been reported earlier [19]. These attributes (asymmetrical double minimum and high energy barrier) in the potential energy curves for hydrogen-bonded O–H of DEG + 1 water complex (GD), TEG + 1 water complex (GD), and DPG + 1 water complex (GD) are not present. This depicts that glycols having ether group (DEG, TEG, and DPG) have stronger hydrogen-bond interaction with water molecule compared to glycols without ether group (TMG).

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of different glycol

TABLE 7: Calculated energy of interaction-energy without correction ( $\Delta E$ , kcal/mole), BSSE corrected energy of hydrogen-bond formation using counterpoise correction ( $\Delta E_{CP}$ , kcal/mole) for TEG +  $n_w$  water complex ( $n_w = 1, 2$ ) using 6-31++G(d,p) basis set and various methods.

Systems	Calculation methods	$\Delta E$	$\Delta E_{CP}$
TEG + 1 water complex (GD)	MP2	-7.16	-5.03
	WB97XD	-6.95	-6.03
	B3LYP DFT-D	-7.19	-6.19
	M062X	-7.34	-6.37
	M06	-6.80	-5.90
	B3LYP	-5.98	-5.07
	HF	-5.12	-4.43
TEG + 1 water complex (WD)	MP2	-7.45	-5.39
	WB97XD	-7.43	-6.67
	B3LYP DFT-D	-8.22	-7.38
	M062X	-7.73	-6.92
	M06	-6.93	-6.19
	B3LYP	-6.09	-5.35
	HF	-5.05	-4.51
TEG + 2 water complex	MP2	-13.95	-9.84
	WB97XD	-13.51	-11.69
	B3LYP DFT-D	-14.11	-12.15
	M062X	-14.11	-12.18
	M06	-12.97	-11.24
	B3LYP	-11.89	-10.06
	HF	-10.07	-8.69

molecules and glycols + 1 water systems (both GD and WD complex), simulated by WB97XD/6-31++G(d,p) method, have been shown in Figure 6. The LUMO energies of different glycol + 1 water complexes are less compared to that of respective single glycol and water molecule. The LUMO of glycol + 1 water complex (GD) originates essentially from the LUMO of water with negligible contribution of antibonding orbital of respective glycol, but the HOMO of the same complex arises largely from the HOMO of respective glycol. On the other hand, for glycol + 1 water complex (WD), LUMO evolves mainly from the LUMO of the respective glycol, and HOMO is from the intermixing of lone pairs of both the respective glycol and water molecules. It is seen from frontier orbital analysis that the intermolecular hydrogen-bond of glycol + 1 water complex (GD) has more covalent characters compared to the intermolecular hydrogen-bond of glycol + 1 water complex (WD).

The charge transfer (CT) energies calculated using natural energy decomposition analysis (NEDA) for different glycol + 1 water complex and glycol dimer are summarized in Table 14. Charge transfer (CT) is a part of the interaction energy of molecular cluster, representing electron delocalization interaction between occupied molecular orbital of one molecule and unoccupied molecular orbital of another molecule, and it helps to elucidate intermolecular interaction

TABLE 8: Calculated interaction-energy without correction ( $\Delta E$ , kcal/mole), BSSE corrected energy of hydrogen-bond formation using counterpoise correction ( $\Delta E_{CP}$ , kcal/mole) for DPG +  $n_w$  water complex ( $n_w = 1, 2$ ), and DPG dimer using 6-31++G(d,p) basis set and various methods.

Systems	Methods	$\Delta E$	$\Delta E_{CP}$
DPG + 1 water complex (GD)	MP2	-6.69	-4.78
	WB97XD	-6.49	-5.59
	B3LYP DFT-D	-6.83	-5.87
	M062X	-6.67	-5.74
	M06	-6.05	-5.19
	B3LYP	-5.89	-4.89
	HF	-4.90	-4.20
DPG + 1 water complex (WD)	MP2	-7.39	-5.28
	WB97XD	-7.39	-6.61
	B3LYP DFT-D	-8.10	-7.23
	M062X	-7.55	-6.71
	M06	-6.77	-6.02
	B3LYP	-6.09	-5.31
	HF	-5.03	-4.43
DPG + 2 water complex	MP2	-14.67	-10.45
	WB97XD	-14.53	-12.97
	B3LYP DFT-D	-16.07	-14.33
	M062X	-14.94	-13.26
	M06	-13.49	-11.97
	B3LYP	-12.11	-10.53
	HF	-9.95	-8.74
DPG dimer	WB97XD	-8.14	-7.33
	B3LYP DFT-D	-8.85	-7.93
	M062X	-7.53	-6.67
	M06	-6.81	-6.07
	B3LYP	-5.78	-5.05
	HF	-4.97	-4.26

like hydrogen bonding or electron donor-acceptor interaction [48–50]. The charge transfer value of EG dimer is found to be much lower than the charge transfer values of both type of EG + 1 water complexes. Similarly, the charge transfer value for DEG dimer is also much lower than the charge transfer values of both type DEG + 1 water complexes. But the charge transfer values for DPG dimer and TEG dimer are higher (less negative) than the charge transfer values of DPG + 1 water complex (WD) and TEG + 1 water complex (WD), respectively, as evident in Table 14. According to the charge transfer values, DPG and TEG molecules form stronger intermolecular hydrogen-bond with water molecule when water acts as a proton donor, compared to the hydrogen-bond of their dimer complex where EG and DEG molecules form weaker intermolecular hydrogen-bond with water molecule compared to the hydrogen-bond of their dimer complex. It is advisable to use both of EG and DEG solution for inhibiting water cluster formation at low concentration, such

TABLE 9: Calculated deformation energy ( $\Delta E_{\text{def}}$ , kcal/mole) of glycol and relaxation energy ( $\Delta E_{\text{relax}}$ , kcal/mole) for EG +  $n_w$  water complex ( $n_w = 1, 2$ ), EG dimer, using 6-31++G(d,p) basis set and various methods (for dimer two values of  $\Delta E_{\text{def}}$  are given for individual EG molecule).

Systems	Calculation methods	$\Delta E_{\text{def}}$	$\Delta E_{\text{relax}}$
EG + 1 water complex (GD)	WB97XD	0.09	0.09
	B3LYP DFT-D	0.08	0.09
	M062X	0.13	0.12
	M06	0.12	0.12
	B3LYP	0.08	0.09
	HF	0.04	0.04
EG + 1 water complex (WD)	WB97XD	0.14	0.21
	B3LYP DFT-D	0.21	0.29
	M062X	0.42	0.47
	M06	0.20	0.28
	B3LYP	0.13	0.20
	HF	0.11	0.13
EG + 2 water complex	WB97XD	0.10	0.10
	B3LYP DFT-D	0.12	0.13
	M062X	0.11	0.09
	M06	0.17	0.18
	B3LYP	0.11	0.11
	HF	0.05	0.05

TABLE 10: Calculated deformation energy ( $\Delta E_{\text{def}}$ , kcal/mole) and relaxation energy ( $\Delta E_{\text{relax}}$ , kcal/mole) for DEG +  $n_w$  water complex ( $n_w = 1, 2$ ), DEG dimer using 6-31++G(d,p) basis set and various methods (for dimer two values of  $\Delta E_{\text{def}}$  are given for individual DEG molecule).

Systems	Calculation methods	$\Delta E_{\text{def}}$	$\Delta E_{\text{relax}}$
DEG + 1 water complex (GD)	WB97XD	0.05	0.05
	B3LYP DFT-D	0.10	0.10
	M062X	0.08	0.06
	M06	0.17	0.17
	B3LYP	0.09	0.09
	HF	0.04	0.05
DEG + 1 water complex (WD)	WB97XD	0.07	0.14
	B3LYP DFT-D	0.11	0.20
	M062X	0.10	0.14
	M06	0.16	0.24
	B3LYP	0.08	0.15
	HF	0.05	0.07
DEG + 2 water complex	WB97XD	0.09	0.23
	B3LYP DFT-D	0.22	0.39
	M062X	0.24	0.32
	M06	0.25	0.40
	B3LYP	0.16	0.29
	HF	0.09	0.13

TABLE 11: Calculated deformation energy ( $\Delta E_{\text{def}}$ , kcal/mole) and relaxation energy ( $\Delta E_{\text{relax}}$ , kcal/mole) for TEG +  $n_w$  water complex ( $n_w = 1, 2$ ) using 6-31++G(d,p) basis set and various methods.

Systems	Calculation methods	$\Delta E_{\text{def}}$	$\Delta E_{\text{relax}}$
TEG + 1 water complex (GD)	WB97XD	0.02	0.02
	B3LYP DFT-D	0.09	0.09
	M062X	0.04	0.02
	M06	0.17	0.17
	B3LYP	0.08	0.09
	HF	0.04	0.05
TEG + 1 water complex (WD)	WB97XD	0.03	0.10
	B3LYP DFT-D	0.11	0.19
	M062X	0.05	0.09
	M06	0.13	0.20
	B3LYP	0.07	0.14
	HF	0.04	0.06
TEG + 2 water complex	WB97XD	0.10	0.10
	B3LYP DFT-D	0.16	0.17
	M062X	0.12	0.10
	M06	0.32	0.32
	B3LYP	0.15	0.15
	HF	0.07	0.07

that possibilities of their dimer formation would become very less.

## 4. Conclusion

A thorough analysis of hydrogen-bond formation in polyethylene glycol +  $n_w$  water complex ( $n = 1, 2$ ) and dipropylene glycol +  $n_w$  water complex ( $n_w = 1, 2$ ) has been performed based on interaction energies, relaxation energies, deformation energies, potential energy curve for hydrogen-bonded O–H, frontier orbitals, structural parameters of optimized geometry, and charge transfer. Different polyethylene glycol + 2 water complexes are found to be most stable compared to polyethylene glycol + 1 water complexes, polyethylene dimer and water dimer as per calculated interaction energies. DPG + 2 water complex is also found to be most stable compared to DPG + 1 water complexes, DPG dimer and water dimer as per calculated interaction energies. The broadening of potential energy curve of hydrogen-bonded O–H reveal that the intermolecular hydrogen-bond formed between different glycol and water is strong. Intermolecular hydrogen bonds for different glycol + 1 water complex (glycol as proton donor) has higher covalent character and accordingly higher strength compared to that of glycol + 1 water complex (water as proton donor) according to frontier orbital analysis. WB97XD functional-based DFT is found to provide similar stability trends of hydrogen-bonded complexes as that of MP2 method. Theoretical analysis of hydrogen-bond formation in different glycols and water complexes applying

TABLE 12: Calculated deformation energy ( $\Delta E_{\text{def}}$ , kcal/mole) and relaxation energy ( $\Delta E_{\text{relax}}$ , kcal/mole) for DPG +  $n_w$  water complex ( $n_w = 1, 2$ ), DPG dimer using 6-31++G(d,p) basis set and various methods (for dimer two values of  $\Delta E_{\text{def}}$  are given for individual DPG molecule).

Systems	Methods	$\Delta E_{\text{def}}$	$\Delta E_{\text{relax}}$
DPG + 1 water complex (GD)	WB97XD	0.07	0.07
	B3LYP DFT-D	0.07	0.07
	M062X	0.05	0.04
	M06	0.15	0.16
	B3LYP	0.06	0.06
	HF	0.03	0.03
DPG + 1 water complex (WD)	WB97XD	0.01	0.02
	B3LYP DFT-D	0.11	0.19
	M062X	0.10	0.15
	M06	0.14	0.22
	B3LYP	0.10	0.16
	HF	0.05	0.07
DPG + 2 water complex	WB97XD	0.17	0.31
	B3LYP DFT-D	0.22	0.38
	M062X	0.27	0.36
	M06	0.29	0.46
	B3LYP	0.15	0.27
	HF	0.10	0.14
DPG dimer	WB97XD	0.05	0.01
		0.06	
	B3LYP DFT-D	0.11	0.26
		0.16	
	M062X	0.06	0.11
		0.05	
	M06	0.13	0.31
		0.18	
	B3LYP	0.08	0.16
		0.08	
	HF	0.05	0.08
		0.03	

TABLE 13: Calculated two-body energy  $\Delta E_2$  (kcal/mole) and three-body energy  $\Delta E_3$  (kcal/mole) of glycols + 2 water complex using WB97XD/6-31++G (d, p).

System	$\Delta E_2$	$\Delta E_3$
EG + 2 water complex	-13.33	2.04
DEG + 2 water complex	-15.03	2.20
TEG + 2 water complex	-13.67	1.88
DPG + 2 water complex	-14.83	1.85

natural bond orbital analysis, bond order, and frequency calculation-based study would be of great help, and the same would be our future endeavour. The elucidation of electronic structure property correlation-based study of different glycol in aqueous solution carried out in this paper can significantly

TABLE 14: Calculated Charge transfer (CT, kcal/mol) for glycol + 1 water complex and glycol dimers using WB97XD/6-31++G(d,p).

System	CT
EG + 1 water complex (GD)	-31.55
EG + 1 water complex (WD)	-35.98
DEG + 1 water complex (GD)	-30.38
DEG + 1 water complex (WD)	-36.93
TEG + 1 water complex (GD)	-14.83
TEG + 1 water complex (WD)	-17.85
DPG + 1 water complex (GD)	-10.57
DPG + 1 water complex (WD)	-39.47
EG dimer	-44.14
DEG dimer	-48.59
TEG dimer	-15.78
DPG dimer	-17.12

help in designing inhibitors for water cluster/clathrate system like methane hydrate.

## Acknowledgments

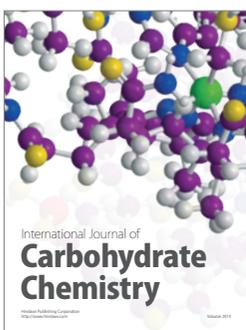
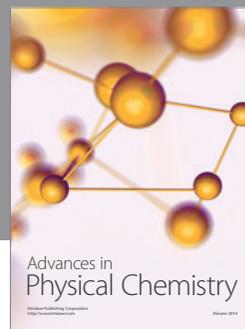
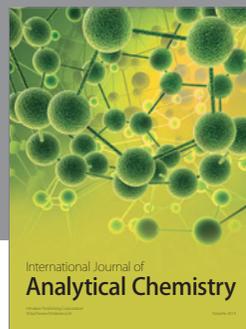
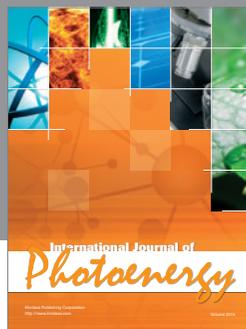
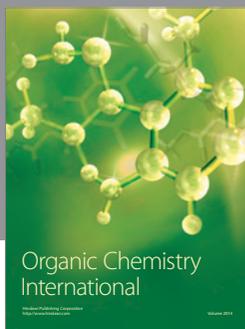
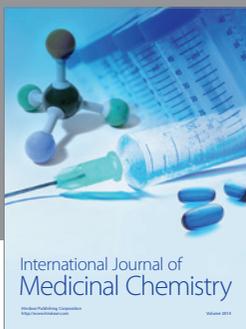
This work is financially supported by Ministry of Earth Science, India (Project no. MoES/16/48/09—RDEAS (MRDM5)). The authors also acknowledge accelrys Inc. for providing free Discovery Studio 3.1 visualization tool.

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