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A Theoretical Study of Hydrogen-Bonded Complexes of Ethylene Glycol, Thioglycol and Dithioglycol with Water

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In the present study, a theoretical analysis of hydrogen bond formation of ethylene glycol, thioglycol, dithioglycol with single water molecule has been performed based on structural parameters of optimized geometries, interaction energies, deformation energies, orbital analysis and charge transfer. *ab initio* molecular orbital theory (MP2) method in conjunction with 6-31+G* basis set has been employed. Twelve aggregates of the selected molecules with water have been optimized at MP2/6-31+G* level and analyzed for intramolecular and intermolecular hydrogen bond interactions. The evaluated interaction energies suggest aggregates have hydrogen bonds of weak to moderate strength. Although the aggregates are primarily stabilized by conventional hydrogen bond donors and acceptors, yet C-H···O, S-H···O, O-H···S, *etc*. untraditional hydrogen bonds also contribute to stabilize many aggregates. The hydrogen bonding involving sulfur in the aggregates of thioglycol and dithioglycol is disfavoured electrostatically but favoured by charge transfer. Natural bond orbital (NBO) analysis has been employed to understand the role of electron delocalizations, bond polarizations, charge transfer, *etc*. as contributors to stabilization energy.

Keywords: Ethylene glycol, Thioglycol, Dithioglycol, Hydrogen bonding, Molecular orbital theory, Natural bond orbital.

INTRODUCTION

A hydrogen bond is an attractive donor-acceptor interaction, in which generally, the donor atoms are electronegative compared to hydrogen and acceptor atoms have unshared lone pair of electrons [1,2]. The role of hydrogen bonding in solvation, diffusion through membranes, adsorption on to the surfaces and in directing structure of polypeptides and double helices of polynucleotides is well recognized [3-5].

The hydrogen bond plays crucial role in the formation of clathrate hydrate in marine sediments and below permafrost region, which is considered to be significant future energy source [6,7]. The decomposition of methane hydrate and hazards in petroleum industry owing to formation of gas in oil pipe line are of great concern. Controlled inhibition of gas hydrate formation is thus very important and various thermodynamic and kinetic inhibitors can break hydrogen bonded network of clathrate structure by itself forming comparatively stronger hydrogen bond with water molecules of clathrate. Since glycols are used as gas hydrate inhibitors [8,9], the electronic structure based understanding of hydrogen bond formation can help in designing and scientific comprehension of use of various molecules as gas hydrate inhibitors. Explicit study of interactions between 1,2-ethanediol (ethylene glycol), 2-mercaptoethanol (thioglycol), 1,2-ethane dithiol (dithioglycol) with single water molecule has been carried out with the objective to reveal the effect of molecules having two vicinal hydroxyl, one thiol vicinal to hydroxyl and two vicinal thiol groups on intermolecular and intramolecular hydrogen bond formation possibilities. These molecules are the simplest molecules with functional groups to serve as a simple model for biological molecules like sugars and as a prototype for intramolecular hydrogen bonding [10]. Ethylene glycol and other molecules are the rotor molecules with existence in a number of possible conformations [11]. Ten unique conformers of ethylene glycol and dithioglycol have been described [12,13]. Experimental study of ethylene glycol molecule and its aqueous solution has been performed using nuclear magnetic resonance spectroscopy [14,15], infrared [16-19], ultraviolet spectroscopies [19], Raman spectroscopy [20], X-ray and neutron diffraction techniques [21]. Dithio-glycol has been studied extensively both from experimental [22-25] and theoretical point of view [26-29]. Theoretical studies by Klein [30] and Mandado *et al*. [31] questioned the presence of intramolecular hydrogen bonding in ethylene glycol but weak intramolecular interactions are identified in ethylene glycol by vapour phase OH-stretching overtone spectroscopy by Howard *et al.* [10]. Overtone spectra of 2-mercaptoethanol and 1,2-ethanedithiol has been studied by Kjaergaard *et al.* [32]. It is anticipated that there exists a competition between intra- and intermolecular hydrogen bonding interactions in deciding the conformation of ethylene glycol, ethylene thioglycol and 1,2-ethane dithiol. The objective of this study is to report the analysis of hydrogen bond formation in ethylene glycol-water, thioglycol-water, 1,2-ethane dithiol-water system using Moller-Plesset second order perturbation theory. The study will help us to conceptualize the nature of hydrogen bond formation and its effect on electronic structure and bond orbitals of ethylene glycol-water, thioglycol-water, 1,2-ethane dithiol-water systems.

COMPUTATIONAL METHODS

The geometries of ethylene glycol (EG), thioglycol (EGS, EGS2), dithioglycol (EGSS) and their corresponding hydrogen bonded aggregates with single water molecule have been optimized employing Moller-Plesset perturbation theory (MP2) with 6-31+G* level. The MP2 theory takes into account the dispersion forces and charge transfer effects required for accurate description of hydrogen bonded complexes. The stability of various aggregates is examined by harmonic vibrational frequency calculations and characterized each stationary point as a minimum. Gaussian 2003 set of program has been used to perform all the calculations for monomers and the complexes [33]. The stabilization energy (S.E.) was estimated by taking the difference of energy of the complex and the sum of the energies of the separated monomers (eqn. 1):

$$\text{Stabilization energy (S.E.)} = E_{ab} - \{E_a + E_b\} \qquad (1)$$

where E_{ab} is electronic energy of aggregate, E_a and E_b refer to energies of component subunits of aggregate [34]. Basis set superposition error (BSSE) in the aggregates is corrected by standard counterpoise (CP) method proposed by Boys & Bernardi [35]. The CP method uses mixed basis sets with 'ghost orbitals'. A hydrogen bonded complex is said to be more stable if interaction energy is more negative as compared to other hydrogen bonded configurations. The distortion (deformation) energy that estimates the relaxation of monomers upon complexation was calculated using eqn. 2:

$$E_{Dis} = (E_{M1} + E_{M2}) - (E_{M1,Dis} + E_{M2,Dis}) \qquad (2)$$

where E_{M1} and E_{M2} are energies of individual monomeric forms in gas phase and $E_{M1,Dis}$ and $E_{M2,Dis}$ are single point energies obtained for the distorted isolated monomer geometry upon complexation [36]. Natural bond orbital (NBO) analysis has been employed to evaluate the second order delocalization energies ($E^{(2)}$ values) and hence find the amount of charge transferred from proton donor to proton acceptor [37,38]. The natural atomic charges that inform about bond polarizations and hence help understand the nature of hydrogen bonding have been determined employing natural population analysis (NPA) incorporated within NBO at MP2 level of theory and 6-31+G* basis set.

RESULTS AND DISCUSSION

Structural and energetic analysis: Full geometry optimization has been carried out on gauche conformation of ethylene glycol, thioglycol, dithioglycol at MP2/6-31+G* level and it resulted in eight minima on the potential energy surface. Quantum chemical based study on different conformers of ethylene glycol revealed that gauche conformation is more stable in aqueous solution [39,40]. Four of the optimized molecules (EG, EGS, EGS2, EGSS) are stabilized inherently by intramolecular hydrogen bonding (IHB) while other four structures are non-hydrogen bonded and are labeled as EG′, EGS′, EGS2′ and EGSS′. The optimized structures are shown in Fig. 1. The difference in relative energies of intramolecularly hydrogen bonded and non-hydrogen bonded structures ranges from 2-4 kcal/mol at MP2/6-31+G* (Table-1). The present study analyzes the nature and strength of hydrogen bonds formed by ethylene glycol, thioglycol and dithioglycol with single water molecule.

TABLE-1
ABSOLUTE AND RELATIVE ENERGIES OF HYDROGEN BONDED AND NON-HYDROGEN BONDED [DENOTED BY (′) ROTAMERS OF ETHYLENE GLYCOL, THIOGLYCOL AND DITHIOGLYCOL AT MP2/6-31+G*

Molecule	Absolute energies	ZPVE	Relative energies (kcal/mol)
EG	-229.5642994	57.79650	0
EG′	-229.5578034	57.51990	4.08
EGS	-552.158572	54.28602	0
EGS′	-552.1549622	54.23095	2.27
EGS2	-552.160352	54.38260	0
EGS2′	-552.1549384	54.07867	3.40
EGSS	-874.7539467	50.81376	0
EGSS′	-874.7504954	50.74515	2.17

The hydrogen bonded structures EG, EGS, EGS2, EGSS are 4.08, 2.27, 3.40 and 2.17 kcal/mol more stable at MP2/6-31+G* than their respective non-hydrogen bonded forms EG′, EGS′, EGS2′, EGSS′, respectively. The geometrical parameters of ground state of all the optimized molecules are reported in Tables 2 and 3. The hydrogen bonded forms EG, EGS, EGS2, EGSS differ from non-hydrogen bonded forms in dihedral angle H5-O1-C2-C3 being 44.8°, 50.1°, 54.8°, 58.2° *versus* 177.2°, 198.2°, 162.5°, 210.9°, respectively in EG′, EGS′, EGS2′, EGSS′ at MP2/6-31+G*. The requisite parameters for describing IHB in EG, EGS, EGS2, EGSS and their aggregates with water are listed in Table-4. The non-bonded distances between different hydrogen bond donors and hydrogen bond acceptors have been scrutinized and the non-bonded distances that are less than the sum of van der Waal radii are also recorded along with angle at bridging hydrogen. The sum of van der Waal radii is also included for comparison. The shorter the

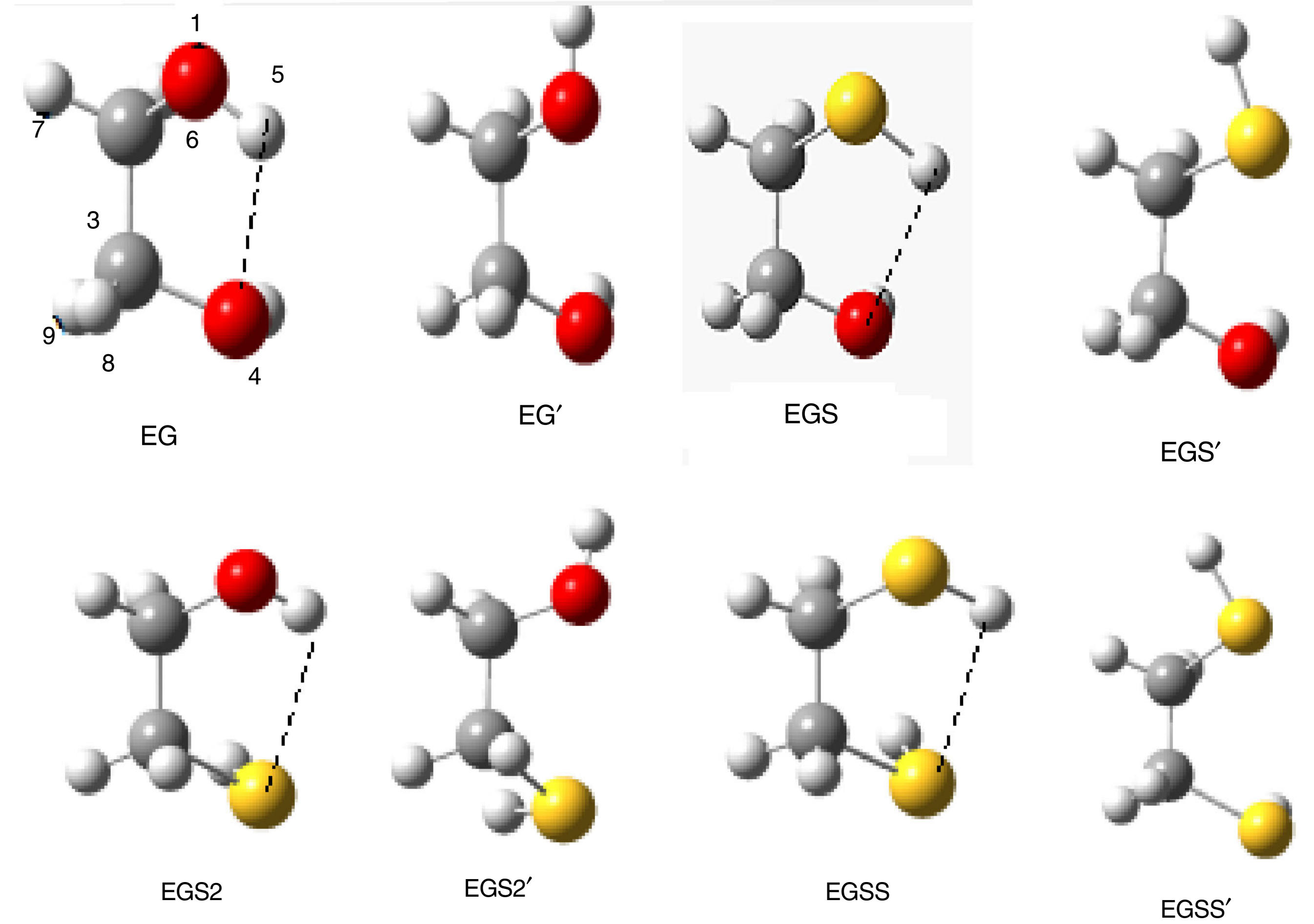


Fig. 1. Optimized hydrogen bonded and non-hydrogen bonded rotamers (′) of ethylene glycol, thioglycol and dithioglycol

TABLE-2
GEOMETRICAL PARAMETERS OF H-BONDED ETHYLENE GLYCOL, THIOGLYCOL, DITHIOGLYCOL AT MP2/6-31+G* THEORETICAL LEVEL. ALL THE BOND DISTANCES ARE IN Å, ANGLES AND DIHEDRAL ARE IN °

EG	EG	EGS	EGS	EGS2	EGS2	EGSS	EGSS
C2-O1	1.425	C2-S1	1.817	C2-O1	1.424	C2-S1	1.817
C3-C2	1.516	C3-C2	1.521	C3-C2	1.522	C3-C2	1.525
O4-C3	1.439	O4-C3	1.433	S4-C3	1.822	S4-C3	1.820
H5-O1	0.977	H5-S1	1.341	H5-O1	0.977	H5-S1	1.342
H6-C2	1.094	H6-C2	1.095	H6-C2	1.094	H6-C2	1.096
H7-C2	1.101	H7-C2	1.096	H7-C2	1.100	H7-C2	1.095
H8-C3	1.092	H8-C3	1.092	H8-C3	1.094	H8-C3	1.094
H9-C3	1.098	H9-C3	1.099	H9-C3	1.095	H9-C3	1.095
H10-O4	0.974	H10-O4	0.974	H10-S4	1.343	H10-S4	1.343
C3-C2-O1	110.67	C3-C2-S1	112.89	C3-C2-O1	112.33	C3-C2-S1	114.70
O4-C3-C2	110.11	O4-C3-C2	112.21	S4-C3-C2	112.72	S4-C3-C2	114.74
H5-O1-C2	106 .30	H5-S1-C2	95.41	H5-O1-C2	107.30	H5-S1-C2	96.02
H6-C2-O1	106.57	H6-C2-S1	106.18	H6-C2-O1	105.45	H6-C2-S1	104.98
H7-C2-O1	110.56	H7-C2-S1	110.48	H7-C2-O1	110.86	H7-C2-S1	110.27
H8-C3-C2	110.10	H8-C3-C2	110.48	H8-C3-C2	109.33	H8-C3-C2	109.89
H9-C3-C2	111.26	H9-C3-C2	109.75	H9-C3-C2	110.70	H9-C3-C2	109.48
H10-O4-C3	108.67	H10-O4-C3	108.50	H10-S4-C3	96.27	H10-S4-C3	96.05
O4-C3-C2-O1	-57.1	O4-C3-C2-S1	-62.2	S4-C3-C2-O1	-61.0	S4-C3-C2-S1	-67.0
H5-O1-C2-C3	44.8	H5-S1-C2-C3	50.1	H5-O1-C2-C3	54.8	H5-S1-C2-C3	58.2
H6-C2-O1-C3	120.5	H6-C2-S1-C3	119.9	H6-C2-O1-C3	119.3	H6-C2-S1-C3	119.2
H7-C2-O1-C3	237.9	H7-C2-S1-C3	236.1	H7-C2-O1-C3	236.1	H7-C2-S1-C3	234.4
H8-C3-C2-O1	58.2	H8-C3-C2-S1	54.7	H8-C3-C2-O1	56.0	H8-C3-C2-S1	51.6
H9-C3-C2-O1	179.2	H9-C3-C2-S1	174.6	H9-C3-C2-O1	175.2	H9-C3-C2-S1	169.9
H10-O4-C3-C2	283.2	H10-O4-C3-C2	287.9	H10-S4-C3-C2	292.2	H10-S4-C3-C2	293.9

TABLE-3
GEOMETRICAL PARAMETERS OF NON H-BONDED ETHYLENE GLYCOL, THIOGLYCOL, DITHIOGLYCOL AT MP2/6-31+G* THEORETICAL LEVEL. ALL THE BOND DISTANCES ARE IN Å, ANGLES AND DIHEDRALS ARE IN °

EG’	EG’	EGS’	EGS’	EGS2’	EGS2’	EGSS’	EGSS’
C2-O1	1.428	C2-S1	1.825	C2-O1	1.430	C2-S1	1.828
C3-C2	1.513	C3-C2	1.520	C3-C2	1.516	C3-C2	1.522
O4-C3	1.427	O4-C3	1.490	S4-C3	1.820	S4-C3	1.819
H5-O1	0.973	H5-S1	1.342	H5-O1	0.972	H5-S1	1.342
H6-C2	1.100	H6-C2	1.095	H6-C2	1.100	H6-C2	1.095
H7-C2	1.101	H7-C2	1.096	H7-C2	1.098	H7-C2	1.095
H8-C3	1.092	H8-C3	1.092	H8-C3	1.094	H8-C3	1.094
H9-C3	1.100	H9-C3	1.099	H9-C3	1.094	H9-C3	1.095
H10-O4	0.973	H10-O4	0.974	H10-S4	1.343	H10-S4	1.343
C3-C2-O1	108.32	C3-C2-S1	109.49	C3-C2-O1	107.2	C3-C2-S1	111.07
O4-C3-C2	113.78	O4-C3-C2	112.81	S4-C3-C2	114.32	S4-C3-C2	114.56
H5-O1-C2	108.87	H5-S1-C2	95.57	H5-O1-C2	109.32	H5-S1-C2	95.44
H6-C2-O1	111.07	H6-C2-S1	110.20	H6-C2-O1	110.17	H6-C2-S1	109.11
H7-C2-O1	110.87	H7-C2-S1	110.31	H7-C2-O1	111.15	H7-C2-S1	110.04
H8-C3-C2	109.43	H8-C3-C2	110.57	H8-C3-C2	108.27	H8-C3-C2	110.03
H9-C3-C2	108.70	H9-C3-C2	109.19	H9-C3-C2	110.21	H9-C3-C2	109.26
H10-O4-C3	108.74	H10-O4-C3	108.86	H10-S4-C3	96.18	H10-S4-C3	96.08
O4-C3-C2-O1	-64.8	O4-C3-C2-S1	-54.6	S4-C3-C2-O1	-69.0	S4-C3-C2-S1	-58.6
H5-O1-C2-C3	177.2	H5-S1-C2-C3	198.2	H5-O1-C2-C3	162.5	H5-S1-C2-C3	210.9
H6-C2-O1-C3	119.2	H6-C2-S1-C3	119.3	H6-C2-O1-C3	118.6	H6-C2-S1-C3	119.2
H7-C2-O1-C3	239.4	H7-C2-S1-C3	238.7	H7-C2-O1-C3	239.0	H7-C2-S1-C3	237.7
H8-C3-C2-O1	52.6	H8-C3-C2-S1	62.4	H8-C3-C2-O1	49.2	H8-C3-C2-S1	59.7
H9-C3-C2-O1	171.0	H9-C3-C2-S1	181.7	H9-C3-C2-O1	166.7	H9-C3-C2-S1	177.8
H10-O4-C3-C2	302.4	H10-O4-C3-C2	300.2	H10-S4-C3-C2	278.1	H10-S4-C3-C2	298.5

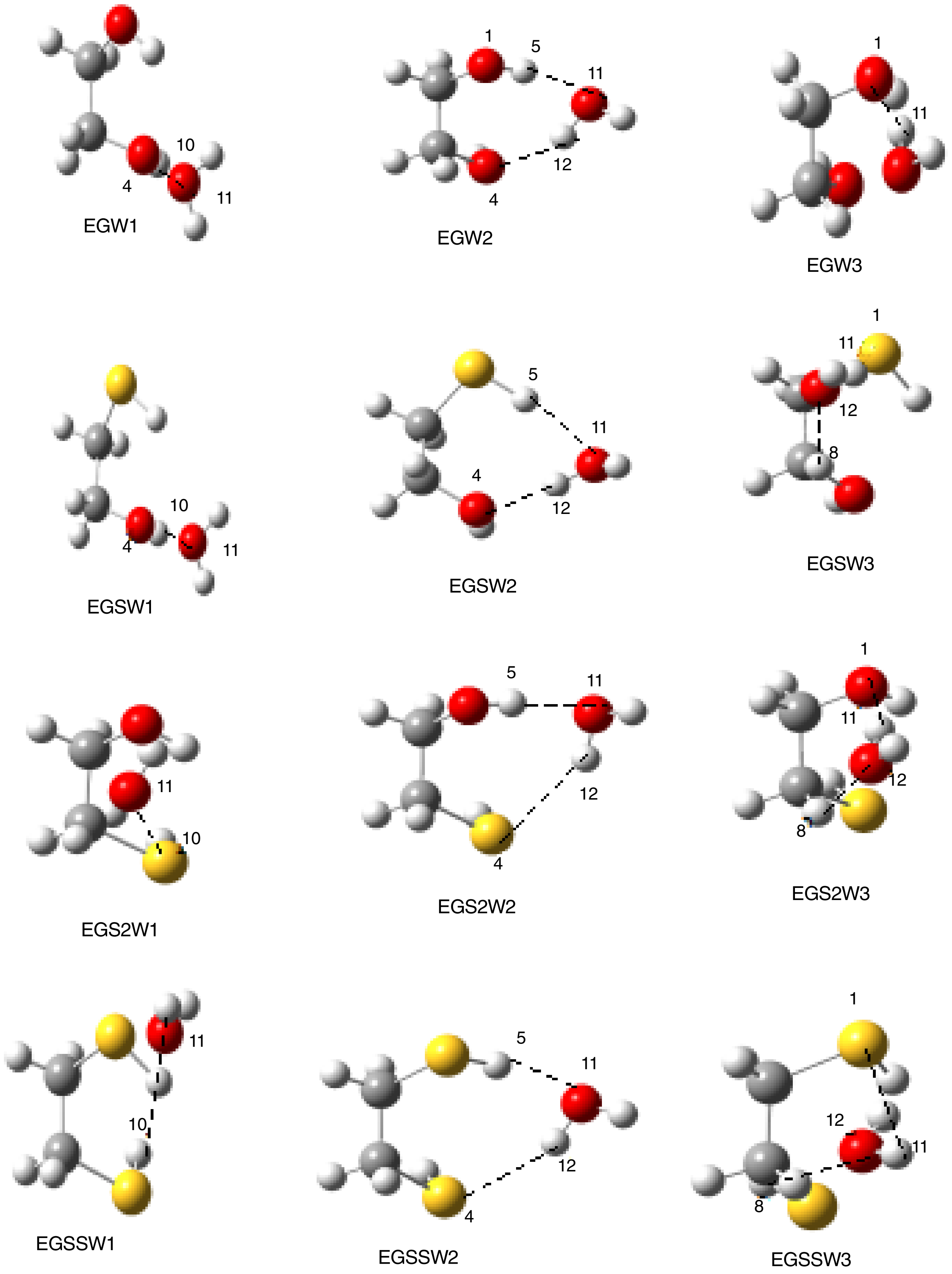
TABLE-4
IMPORTANT INTRAMOLECULAR HYDROGEN BONDING PARAMETERS; HYDROGEN BOND DISTANCES, HYDROGEN BOND ANGLES, DIPOLE MOMENT IN MONOMERS AND AGGREGATES OF ETHYLENE GLYCOL, THIOGLYCOL, DITHIOGLYCOL WITH WATER AT MP2/6-31+G* THEORETICAL LEVEL

Species	H-bond distance (Å)		H-bond angle (°)		$\Delta r = r_{vW}$-r (Å)	Dipole moment (Debye)
EG	H5···O4	2.317	O1-H5···O4	111.29	0.403	2.900
EGS	H5···O4	2.531	S1-H5···O4	106.73	0.189	2.923
EGS2	H5···S4	2.668	O1-H5···S4	112.52	0.332	2.288
EGSS	H5···S4	2.876	S1-H5···S4	109.19	0.124	2.345
EGW1	H5···O4	2.241	O1-H5···O4	114.13	0.479	5.094
EGW2	H5···O4	2.808 Rupture	O1-H5···O4	95.12	-0.088	2.916
EGW3	H5···O4	2.258	O1-H5···O4	112.65	0.462	3.446
EGSW1	H5···O4	2.463	S1-H5···O4	109.19	0.257	5.157
EGSW2	H5···O4	2.813 Rupture	S1-H5···O4	98.80	-0.093	3.281
EGSW3	H5···O4	2.454	S1-H5···O4	109.14	0.266	1.515
EGS2W1	H5···S4	2.629	O1-H5···S4	114.46	0.371	4.896
EGS2W2	H5···S4	3.171 Rupture	O1-H5···S4	91.41	-0.171	1.759
EGS2W3	H5···S4	2.623	O1-H5···S4	113.67	0.377	2.465
EGSSW1	H5···S4	2.679	S1-H5···S4	117.19	0.321	2.244
EGSSW2	H5···S4	3.229 Rupture	S1-H5···S4	97.48	-0.229	2.259
EGSSW3	H5···S4	2.829	S1-H5···S4	110.57	0.171	1.223

Sum of van der Waal radii = $r_{vW} = r_O + r_H = 2.72$Å, $r_H + r_S = 3.0$ Å

distance from the sum of van der Waal’s radii and closer the angle to 180º suggest stronger is the hydrogen bond interaction. The intramolecular hydrogen bonds formed are bent with bond angles ranging from 106.73º to 117.19º, hence are of weak nature. The IHB leads to formation of five-membered pseudo ring structures in EG, EGS, EGS2, EGSS.

The molecules are also capable of forming intermolecular hydrogen bonds as their structures contain a number of active hydrogen bond donor and acceptor sites. As the non-hydrogen bonded forms are much higher in energy in comparison to their respective hydrogen bonded conformers, only the latter are selected for studying the aggregation with water molecule. To understand the nature of intermolecular hydrogen bonding interactions, the aggregates of single water molecule with each of the four intramolecularly hydrogen bonded molecules have been optimized at MP2/6-31+G* level for different relative positions of H_2O with respect to EG, EGS, EGS2 and EGSS and twelve aggregates which are observed to be minima on the potential energy surface are shown in Fig. 2. The data for geometrical parameters of aggregates of selected molecules



EGW1 EGW2 EGW3

EGSW1 EGSW2 EGSW3

EGS2W1 EGS2W2 EGS2W3

EGSSW1 EGSSW2 EGSSW3

Fig. 2. Optimized aggregates of ethylene glycol, thioglycol and dithioglycol with water at MP2/6-31+G*

with H_2O are reported in Tables 5 and 6. The O-H,C-H,S-H of ethylene glycol, thioglycol, dithioglycol act as potential hydrogen bond donor towards O of H_2O, while O-H of H_2O act as potential hydrogen bond donor towards these molecules. The interaction between H_2O and these molecules result in different hydrogen bonding regimes like O-H···O, C-H···O, S-H···O, O-H···S, *etc*.

The analysis of geometrical parameters (Table-4) of aggregates indicates that in almost all the aggregates except EGW2, EGSW2, EGS2W2, EGSSW2, there exist intramolecular X1-H5···Y4 interaction (X,Y = O,S). The H5···Y4 (Y = O,S) distance is increased to 2.808 Å, 2.813 Å, 3.171 Å, 3.229 Å in aggregates EGW2, EGSW2, EGS2W2, EGSSW2 from initial values of 2.317 Å, 2.531 Å, 2.668 Å, 2.876 Å in EG, EGS, EGS2, EGSS respectively at MP2/6-31+G* level indicating loss of intramolecular hydrogen bonding interaction upon aggregate formation. With the hydrogen bond distance longer than sum of van der Waals radii of the respective atoms ($r_H + r_O = 2.72$ Å, $r_H + r_S = 3.00$ Å) only dispersive interactions between the two atoms can prevail.

The Δr values which refer to differences between sum of van der Waals radii of Y (Y; H-bond acceptor) and H atom of H bond contact and H···Y distances for X-H···Y hydrogen bond are also presented in Table-4. These values can be taken as reflective of hydrogen bond strength when hydrogen bond angles are comparable. The Δr value for IHB O1-H5···O4 is 0.403 Å in EG and 0.479 Å in EGW1 while these values for IHB S1-H5···O4 is 0.189 Å in EGS and 0.257 Å in EGSW1. For conformer EGS2, Δr is 0.332 Å and EGS2W1, Δr is 0.371 Å and these values for EGSS and EGSSW1 are 0.124 Å & 0.321 Å, respectively. Thus intermolecular hydrogen bonding with water affects the geometry and strength of intramolecular hydrogen bonding. The increased Δr values show strengthening of IHB upon forming intermolecular hydrogen bonding with water, thus the phenomena of cooperativity is invoked. The results also indicate that strength of IHB decrease in the order EG > EGS2 > EGS > EGSS, the nature of bonds being O-H···O, O-H···S, S-H···O, S-H···S, respectively. In EGSS, the S-H···S is weaker than O-H···S/S-H···O of EGS, EGS2 because of unfavourable/lower electronegativity and bigger size of two interacting sulfur atoms which prevent IHB.

As seen from Table-4, there is large increase in dipole moment on aggregation for aggregates EGW1, EGSW1, EGS2W1 relative to their monomers EG, EGS, EGS2. The large dipole moment increase occurs in aggregates with glycol, thioglycol acting as hydrogen bond donor towards water. The stronger intermolecular hydrogen bond formation enhances the dipole moment

TABLE-5
GEOMETRICAL PARAMETERS OF AGGREGATES OF ETHYLENE GLYCOL, THIOGLYCOL AND DITHIOGLYCOL WITH WATER AT MP2/6-31+G* THEORETICAL LEVEL. ALL THE BOND DISTANCES ARE IN Å, ANGLES AND DIHEDRALS ARE IN °

EGW1	EGW1	EGW2	EGW2	EGW3	EGW3	EGSW1	EGSW1
C2-O1	1.428	C2-O1	1.419	C2-O1	1.436	C2-S1	1.820
C3-C2	1.517	C3-C2	1.519	C3-C2	1.516	C3-C2	1.523
O4-C3	1.434	O4-C3	1.447	O4-C3	1.441	O4-C3	1.427
H5-O1	0.978	H5-O1	0.982	H5-O1	0.979	H5-S1	1.342
H6-C2	1.094	H6-C2	1.095	H6-C2	1.093	H6-C2	1.095
H7-C2	1.101	H7-C2	1. 102	H7-C2	1.099	H7-C2	1.095
H8-C3	1.093	H8-C3	1.092	H8-C3	1.092	H8-C3	1.093
H9-C3	1.099	H9-C3	1.098	H9-C3	1.097	H9-C3	1.100
H10-O4	0.980	H10-O4	0.974	H10-O4	0.974	H10-O4	0.980
O11-H10	1.893	O11-H5	1.911	H11-O1	1.892	O11-H10	1.903
H12-O11	0.973	H12-O11	0.982	O12-H11	0.981	H12-O11	0.973
H13-O11	0.972	H13-O11	0.971	H13-O12	0.970	H13-O11	0.973
C3-C2-O1	110.24	C3-C2-O1	113.23	C3-C2-O1	109.77	C3-C2-S1	112.54
O4-C3-C2	109.78	O4-C3-C2	112.85	O4-C3-C2	109.46	O4-C3-C2	112.08
H5-O1-C2	105.35	H5-O1-C2	109.37	H5-O1-C2	105.89	H5-S1-C2	94.94
H6-C2-O1	106.80	H6-C2-O1	105.98	H6-C2-O1	106.54	H6-C2-S1	106.33
H7-C2-O1	110.41	H7-C2-O1	111.33	H7-C2-O1	109.65	H7-C2-S1	110.49
H8-C3-C2	110.01	H8-C3-C2	109.72	H8-C3-C2	110.03	H8-C3-C2	110.47
H9-C3-C2	110.90	H9-C3-C2	110.57	H9-C3-C2	111.22	H9-C3-C2	109.12
H10-O4-C3	108.24	H10-O4-C3	108.24	H10-O4-C3	108.87	H10-O4-C3	107.83
O11-H10-O4	178.0	O11-H5-O1	163.03	H11-O1-C2	101.16	O11-H10-O4	175.12
H12-O11-H10	118.88	H12-O11-H5	87.11	O12-H11-O1	158.65	H12-O11-H10	115.76
H13-O11-H12	105.70	H13-O11-H12	106.75	H13-O12-H11	106.16	H13-O11-H12	105.67
O4-C3-C2-O1	-54.9	O4-C3-C2-O1	-71.4	O4-C3-C2-O1	-55.6	O4-C3-C2-S1	-61.3
H5-O1-C2-C3	40.8	H5-O1-C2-C3	67.7	H5-O1-C2-C3	43.9	H5-S1-C2-C3	45.2
H6-C2-O1-C3	120.9	H6-C2-O1-C3	119.0	H6-C2-O1-C3	120.4	H6-C2-S1-C3	120.2
H7-C2-O1-C3	238.6	H7-C2-O1-C3	235.9	H7-C2-O1-C3	238.0	H7-C2-S1-C3	236.9
H8-C3-C2-O1	61.1	H8-C3-C2-O1	45.4	H8-C3-C2-O1	59.9	H8-C3-C2-S1	56.5
H9-C3-C2-O1	181.8	H9-C3-C2-O1	165.6	H9-C3-C2-O1	181.0	H9-C3-C2-S1	175.8
H10-O4-C3-C2	281.8	H10-O4-C3-C2	285.4	H10-O4-C3-C2	279. 3	H10-O4-C3-C2	291.5
O11-H10-O4-C3	-74.1	O11-H5-O1-C2	-55.2	H11-O1-C2-H6	44.9	O11-H10-O4-C3	69.6
H12-O11-H10-O4	-175.6	H12-O11-H5-O4	-11.5	O12-H11-O1-C2	16.9	H12-O11-H10-O4	45.1
H13-O11-H12-H10	-132.0	H13-O11-H12-H5	118.1	H13-O12-H11-H6	223.9	H13-O11-H12-H10	-133.5

TABLE-6
GEOMETRICAL PARAMETERS OF AGGREGATES OF ETHYLENE GLYCOL, THIOGLYCOL AND DITHIOGLYCOL WITH WATER AT MP2/6-31+G* THEORETICAL LEVEL. ALL THE BOND DISTANCES ARE IN Å, ANGLES AND DIHEDRALS ARE IN °

EGSW2	EGSW2	EGSW3	EGSW3	EGS2W1	EGS2W1	EGS2W2	EGS2W2
C2-S1	1.817	C2-S1	1.822	C2-O1	1.427	C2-O1	1.419
C3-C2	1.520	C3-C2	1.521	C3-C2	1.522	C3-C2	1.525
O4-C3	1.440	O4-C3	1.436	S4-C3	1.823	S4-C3	1.824
H5-S1	1.344	H5-S1	1.342	H5-O1	0.977	H5-O1	0.981
H6-C2	1.096	H6-C2	1.094	H6-C2	1.094	H6-C2	1.096
H7-C2	1.096	H7-C2	1.095	H7-C2	1.098	H7-C2	1.099
H8-C3	1.091	H8-C3	1.090	H8-C3	1.094	H8-C3	1.094
H9-C3	1.099	H9-C3	1.098	H9-C3	1.095	H9-C3	1.095
H10-O4	0.975	H10-O4	0.974	H10-S4	1.344	H10-S4	1.343
O11-H5	2.251	H11-S1	2.500	O11-H10	2.178	O11-H5	1.886
H12-O11	0.980	O12-H11	0.977	H12-O11	0.973	H12-O11	0.977
H13-O11	0.971	H13-O12	0.971	H13-O11	0.973	H13-O11	0.972
C3-C2-S1	114.56	C3-C2-S1	112.63	C3-C2-O1	112.22	C3-C2-O1	112.74
O4-C3-C2	112.78	O4-C3-C2	111.99	S4-C3-C2	112.44	S4-C3-C2	115.38
H5-S1-C2	97.53	H5-S1-C2	95.52	H5-O1-C2	106.72	H5-O1-C2	109.61
H6-C2-S1	105.54	H6-C2-S1	106.42	H6-C2-O1	105.42	H6-C2-O1	106.02
H7-C2-S1	110.62	H7-C2-S1	109.68	H7-C2-O1	110.94	H7-C2-O1	111.36
H8-C3-C2	110.78	H8-C3-C2	110.69	H8-C3-C2	109.50	H8-C3-C2	108.47
H9-C3-C2	109.98	H9-C3-C2	109.35	H9-C3-C2	110.35	H9-C3-C2	110.47
H10-O4-C3	108.46	H10-O4-C3	108.56	H10-S4-C3	95.45	H10-S4-C3	96.67
O11-H5-S1	157.10	H11-S1-C2	83.76	O11-H10-S4	162.73	O11-H5-O1	169.29
H12-O11-H5	77.12	O12-H11-S1	144.40	H12-O11-H10	122.78	H12-O11-H5	93.23
H13-O11-H12	106.38	H13-O12-H11	105.98	H13-O11-H12	105.38	H13-O11-H12	106.42
O4-C3-C2-S1	-68.0	O4-C3-C2-S1	-60.1	S4-C3-C2-O1	-60.6	S4-C3-C2-O1	-70.9
H5-S1-C2-C3	61.4	H5-S1-C2-C3	44.2	H5-O1-C2-C3	52.3	H5-O1-C2-C3	84.6
H6-C2-S1-C3	119.5	H6-C2-S1-C3	119.8	H6-C2-O1-C3	119.5	H6-C2-O1-C3	117.9
H7-C2-S1-C3	234.9	H7-C2-S1-C3	236.5	H7-C2-O1-C3	236.6	H7-C2-O1-C3	234.8
H8-C3-C2-S1	49.4	H8-C3-C2-S1	57.6	H8-C3-C2-O1	57.1	H8-C3-C2-O1	47.2
H9-C3-C2-S1	169.7	H9-C3-C2-S1	177.1	H9-C3-C2-O1	176.3	H9-C3-C2-O1	165.4
H10-O4-C3-C2	292.8	H10-O4-C3-C2	286.6	H10-S4-C3-C2	293.5	H10-S4-C3-C2	288.3
O11-H5-S1-C2	-75.2	H11-S1-C2-H6	52.5	O11-H10-S4-C3	11.7	O11-H5-O1-C2	-65.2
H12-O11-H5-O4	-13.6	O12-H11-S1-C2	-7.2	H12-O11-H10-S4	95.5	H12-O11-H5-O1	7.8
H13-O11-H12-H5	125.2	H13-O12-H11-H6	208.1	H13-O11-H12-H10	-150.3	H13-O11-H12-H5	119.1
EGS2W3	EGS2W3	EGSSW1	EGSSW1	EGSSW2	EGSSW2	EGSSW3	EGSSW3
C2-O1	1.435	C2-S1	1.824	C2-S1	1.817	C2-S1	1.821
C3-C2	1.521	C3-C2	1.525	C3-C2	1.526	C3-C2	1.526
S4-C3	1.822	S4-C3	1.822	S4-C3	1.822	S4-C3	1.820
H5-O1	0.979	H5-S1	1.344	H5-S1	1.344	H5-S1	1.342
H6-C2	1.093	H6-C2	1.095	H6-C2	1.096	H6-C2	1.095
H7-C2	1.098	H7-C2	1.093	H7-C2	1.095	H7-C2	1.095
H8-C3	1.093	H8-C3	1.094	H8-C3	1.093	H8-C3	1.093
H9-C3	1.094	H9-C3	1.095	H9-C3	1.095	H9-C3	1.095
H10-S4	1.343	H10-S4	1.344	H10-S4	1.343	H10-S4	1.343
H11-O1	1.897	O11-H10	2.484	O11-H5	2.191	H11-S1	2.502
O12-H11	0.981	H12-O11	0.975	H12-O11	0. 976	O12-H11	0.977
H13-O12	0.970	H13-O11	0.972	H13-O11	0.972	H13-O12	0.971
C3-C2O-1	111.95	C3-C2-S1	114.73	C3-C2-S1	115.70	C3-C2-S1	115.14
S4-C3-C2	112.41	S4-C3-C2	114.44	S4-C3-C2	115.87	S4-C3-C2	114.70
H5-O1-C2	106.98	H5-S1-C2	95.42	H5-S1-C2	98.06	H5-S1-C2	96.22
H6-C2-O1	105.37	H6-C2-S1	105.48	H6-C2-S1	104.87	H6-C2-S1	105.02
H7-C2-O1	109.79	H7-C2-S1	109.84	H7-C2-S1	110.19	H7-C2-S1	109.33
H8-C3-C2	109.41	H8-C3-C2	110.68	H8-C3-C2	109.88	H8-C3-C2	110.40
H9-C3-C2	110.34	H9-C3-C2	108.34	H9-C3-C2	109.51	H9-C3-C2	108.74
H10-S4-C3	96.43	H10-S4-C3	95.99	H10-S4-C3	96.48	H10-S4-C3	96.30
H11-O1-C2	101.90	O11-H10-S4	135.66	O11-H5-S1	164.63	H11-S1-C2	88.80
O12-H11-O1	155.82	H12-O11-H10	108.90	H12-O11-H5	83.49	O12-H11-S1	146.35
H13-O12-H11	106.42	H13-O11-H12	105.83	H13-O11-H12	106.07	H13-O12-H11	106.18
S4-C3-C2-O1	-59.4	S4-C3-C2-S1	-63.2	S4-C3-C2-S1	-71.9	S4-C3-C2-S1	-64.6
H5-O1-C2-C3	53.8	H5-S1-C2-C3	39.7	H5-S1-C2-C3	74.6	H5-S1-C2-C3	54.9
H6-C2-O1-C3	119.4	H6-C2-S1-C3	119.6	H6-C2-S1-C3	118.6	H6-C2-S1-C3	119.4
H7-C2-O1-C3	236.1	H7-C2-S1-C3	235.9	H7-C2-S1-C3	233.3	H7-C2-S1-C3	234.4
H8-C3-C2-O1	58.1	H8-C3-C2-O1	56.2	H8-C3-C2-O1	47.3	H8-C3-C2-S1	55.1
H9-C3-C2-O1	177.2	H9-C3-C2-O1	174.3	H9-C3-C2-O1	165.5	H9-C3-C2-S1	173.0
H10-S4-C3-C2	291.7	H10-S4-C3-C2	311.6	H10-S4-C3-C2	295.5	H10-S4-C3-C2	294.8
H11-O1-C2-H6	54.7	O11-H10-S4-C3	72.58	O11-H5-S1-C2	-95.2	H11-S1-C2-H6	65.6
O12-H11-O1-C2	20.1	H12-O11-H10-S4	-6.2	H12-O11-H5-S4	-13.4	O12-H11-S1-2	1.4
H13-O12-H11-H6	227.0	H13-O11-H12-H10	-198.6	H13-O11-H12-H5	122.7	H13-O12-H11-H6	208.3

as hydrogen bond formation helps superposition of O···H moment and delocalization of p electrons in hydrogen bonded molecular complex [41]. In other words, bond polarizations in aggregates where oxygen atom of water acts as hydrogen bond acceptor are enhanced. On the other hand, significant decrease in dipole moment is observed in aggregates EGSW3, EGS2W2, EGSSW3 involving sulfur of thioglycol/dithioglycol as hydrogen bond acceptor.

Table-7 summarizes important structural parameters required for describing intermolecular hydrogen bonding. These include non-bonded contact distances between atoms of interacting subunits of aggregates that are lesser than sum of van der Waals radii. Except for EGW1, EGW3, EGSW1, EGS2W1 and EGSSW1 all the other aggregates involve formation of two hydrogen bonds, with water simultaneously participating as hydrogen bond donor and hydrogen bond acceptor. The angle at the bridging hydrogen is another important parameter governing strength of hydrogen bonding and thus their values are also reported in Table-7. The values of angles at bridging hydrogen (∠X-H···Y) in optimized aggregates fall in the range (129.3º to 178.0º) and this puts them in category of hydrogen bonds of weak (θ = 90-150º) to moderate strength (θ = 130-180º). One of the IUPAC report lists criterion of important geometric feature of hydrogen bonding that angle X-H···Y (X is hydrogen bond donor and Y is hydrogen bond acceptor) should preferably be above 110º and close to 180º. It is observed from Tables 4 and 7 that hydrogen bond angle values of intramolecular hydrogen bonds of molecules under study are less than hydrogen bond angle of intermolecular hydrogen bonds between title molecules with water. It is inferred that the strength of IHB is less than intermolecular hydrogen bonds of glycol and its sulfur analogues with water. Hydrogen bonded aggregates with single hydrogen bond exhibit more linear hydrogen bridging angle than aggregates with two hydrogen bonds.

The intermolecular interactions of two monomeric units upon complexation leads to structural changes in the geometry of both the subunits and are marked in the form of distortion energies. The values have been evaluated as the difference of the monomer conformation in gas phase and the conformation in the aggregate and are reported in Table-7. The distortion energies are comparatively much smaller in comparison to stabilization energies and range from 0.11-1.57 kcal/mol. The positive values of distortion energy indicate that subunits are destabilized in aggregate form than their free state. The stabilization energy resulting from aggregation consist of three components (a) deformation/distortion energy (b) interaction energy upon hydrogen bonding with water (c) loss of intramolecular stabilization. As the distortion leads to loss of intramolecular stabilization, hence these two are difficult to separate from each other but loss of IHB energy is significant when water shields IHB without distortion of the molecule. Since stabilization energy is contaminated with BSSE, the values of BSSE corrected stabilization energies and BSSE upon complexation are reported in Table-7. The true stabilization energy arising from hydrogen bonding in complexes is the sum of BSSE corrected stabilization energy and distortion energy.

The aggregates EGSW3, EGS2W3 and EGSSW3 contain at least one of the two hydrogen bonds as an unconventional C-H···O interaction. C-H···O hydrogen bonds in these aggregates range from 2.350 to 2.542 Å, characteristic of weak hydrogen bond (Table-7). The hydrogen bonds involving unconventional C-H···O interaction show considerable deviation from linearity, the value of C-H···O hydrogen bond angle in these complexes lies in the range 129.3° to 143.6°. The variation in different bond lengths of hydrogen bond donor and acceptor on aggregation with water are also presented in Table-4 as Δd values. Results indicate that lengthening of hydrogen bond donor occurs in the red shifting cases (O-H, S-H) and blue

TABLE-7
IMPORTANT INTERMOLECULAR HYDROGEN BONDING PARAMETERS; HYDROGEN BOND DISTANCES, HYDROGEN BOND ANGLES, CHARGES ON HYDROGEN BOND ACCEPTOR AND HYDROGEN, BSSE CORRECTED STABILIZATION ENERGIES (S.E.), BSSE, DISTORTION ENERGIES (E_{Dis}) AND VARIATION IN BOND LENGTHS OF ATOMS INVOLVED IN HYDROGEN BONDING IN AGGREGATES OF ETHYLENE GLYCOL, THIOGLYCOL, DITHIOGLYCOL AT MP2/6-31+G* THEORETICAL LEVEL

Species	Hydrogen bond distances (Å)		Hydrogen bond angles (°)		Atomic charges		S.E. (kcal/mol)	BSSE (kcal/mol)	E_{Dis} (kcal/mol)	Δd
EGW1	O11···H10	1.893	O4-H10···O11	178.0	$q_H(q_O)$	0.533 (-1.018)	-5.86	2.55	0.11	0.006
EGW2	H12···O4	1.895	O11-H12···O4	149.8	$q_H(q_O)$	0.536 (-0.848)	-8.39	3.75	1.46	0.011
	O11···H5	1.911	O1-H5···O11	163.0	$q_H(q_O)$	0.537 (-1.040)				0.005
EGW3	H11···O1	1.892	O12-H11···O1	158.7	$q_H(q_O)$	0.526 (-0.845)	-6.24	2.19	0.18	0.010
EGSW1	O11···H10	1.903	O4-H10···O11	175.1	$q_H(q_O)$	0.529 (-1.018)	-5.77	2.64	0.11	0.006
EGSW2	H12···O4	1.906	O11-H12···O4	154.5	$q_H(q_O)$	0.529 (-0.842)	-5.75	2.83	0.51	0.009
	O11···H5	2.251	S1-H5···O11	157.1	$q_H(q_O)$	0.166 (-1.037)				0.003
EGSW3	H11···S1	2.500	O12-H11···S1	144.4	$q_H(q_S)$	0.508 (-0.068)	-4.10	1.63	0.13	0.006
	O12···H8	2.542	C3-H8···O12	130.2	$q_H(q_O)$	0.241 (-1.021)				-0.002
EGS2W1	O11···H10	2.178	S4-H10···O11	162.7	$q_H(q_O)$	0.161 (-1.015)	-3.09	1.59	0.05	0.001
EGS2W2	H12···S4	2.545	O11-H12···S4	140.3	$q_H(q_S)$	0.518 (-0.060)	-6.44	3.07	1.57	0.006
	O11···H5	1.886	O1-H5···O11	169.3	$q_H(q_O)$	0.538 (-1.024)				0.004
EGS2W3	H11···O1	1.897	O12-H11···O1	155.8	$q_H(q_O)$	0.520 (-0.843)	-6.38	2.39	0.17	0.010
	O12···H8	2.522	C3-H8···O12	129.3	$q_H(q_O)$	0.282 (-1.038)				0.001
EGSSW1	O11···H10	2.484	S4-H10···O11	135.7	$q_H(q_O)$	0.153 (-1.022)	-4.15	2.08	0.96	0.001
EGSSW2	H12···S4	2.528	O11-H12···S4	150.4	$q_H(q_S)$	0.510 (-0.048)	-3.38	2.15	0.68	0.005
	O11···H5	2.191	S1-H5···O11	164.6	$q_H(q_O)$	0.167 (-1.021)				0.002
EGSSW3	H11···S1	2.502	O12-H11···S1	146.4	$q_H(q_S)$	0.509 (-0.058)	-4.08	1.93	0.12	0.006
	O12···H8	2.350	C3-H8···O12	143.6	$q_H(q_O)$	0.286 (-1.022)				-0.001

shift is observed from contraction of hydrogen bond donor C-H bonds.

The stabilization energies for the aggregates of ethylene glycol span a range from 5.86-8.39 kcal/mol. For thioglycol, range of stabilization is 3.09-6.44 kcal/mol. For dithioglycol, similar range of stabilization from 3.38-4.15 kcal/mol. Results suggests hydrogen bonding ability to decrease from ethylene glycol to thioglycol to dithioglycol. Minimum stabilization for aggregates of dithioglycol is also due to repulsive interactions of two heavy sulfur atoms at distance less than sum of their van der Waal radii.

The hydrogen bonded aggregates with larger negative value of stabilization energy is more stable than other hydrogen bonded aggregates. The aggregates labeled EGW2, EGSW2, EGS2W2 and EGSSW1 are most stabilized aggregates of ethylene glycol, thioglycol and dithioglycol with water among the other aggregates. EGW2 with highest stabilization energy of 8.39 kcal/mol has two O-H···O hydrogen bonds involving water as hydrogen bond acceptor towards O-H bond of EG and hydrogen bond donor to O atom of EG resulting in pseudo seven membered ring structure. The BSSE calculated for this aggregate is largest and amounts to 3.75 kcal/mol. The distortion energy for this aggregate is quite substantial and calculated to be 1.5 kcal/mol. This is understandable as this aggregate formation is accompanied by rupture of IHB, varied conjugative interactions along with other changes. The next most stable aggregate is EGS2W2 with S.E. of 6.44 kcal/mol has also closed ring structure with water molecule inserted into the intramolecular hydrogen bond. It is stabilized by O-H···S and O-H···O hydrogen bond. BSSE has also large value *i.e.* 3.07 kcal/mol. Deformation energy calculated for this aggregate is 1.6 kcal/mol. For thioglycol, EGSW1 and EGSW2 have comparable S.E. of 5.8 kcal/mol, although former aggregate is stabilized by one intermolecular O···H-O and one intramolecular S-H···O hydrogen bond and the later is stabilized by two intermolecular O-H···O and O···H-S hydrogen bonds. The deformation energies are 0.11 and 0.51 kcal/mol, respectively for these aggregates. The lowest stabilization energy for aggregate of dithioglycol is of EGSSW2 despite of two hydrogen bonds ascribed to the weak nature of these hydrogen bonds, as this aggregate is stabilized by O-H···S and S-H···O bonds, since sulphur has poor hydrogen bonding ability than oxygen. The aggregate labeled as EGS2W1 has least S.E. of only 3.09 kcal/mol among all optimized aggregates. The value of BSSE and deformation energy is 1.59 and 0.05 kcal/mol, respectively for this aggregate.

Interestingly the aggregates EGW1 with one short, strong and near linear intermolecular hydrogen bond and EGW3 with intact intramolecular hydrogen bond have comparatively smaller stabilization than EGW2 upon aggregation with water. For thioglycol also, EGSW1 and EGSW3 with preserved intramolecular hydrogen bonding have lesser stabilization than EGSW2 with no intramolecular hydrogen bond stabilization. These results also hold true for other conformation of thioglycol where EGS2W2 with no intra hydrogen bond is more stable than EGS2W1 and EGS2W3. The stabilization of EGW2, EGSW2 and EGS2W2 aggregates (Table-7) lacking intramolecular hydrogen bonding clearly indicates that intermolecular interactions between water and the molecules are stronger than intramolecular interactions. It can be rationalized in terms of shorter van der Waal non-bonded distances and greater linearity of hydrogen bonds during intermolecular hydrogen bond formation relative to intramolecular hydrogen bond formation.

In aggregates EGW1 and EGW3, the intramolecular hydrogen bond is strengthened on interaction with water as evident from shorter hydrogen bond lengths and more linear hydrogen bond angles as compared to EG. This is true too for EGSW1, EGSW3 and EGSSW1, EGSSW3 aggregates (Table-4). With similar hydrogen bond donor and acceptor atoms in EGW1 and EGSW1, the stabilization energy is little less for EGSW1. The angular property suggests that deviation from linearity is comparatively larger in EGSW1 than EGW1. The stabilization energy of EGW1 is 5.86 kcal/mol when compared to water dimer at MP2/6-31+G* (S.E.= 4.93 kcal/mol) shows ethylene glycol forms stronger intermolecular hydrogen bonds than water. The smaller length of intermolecular hydrogen bonds in EGW1 (1.893 Å) compared to 1.934 Å in water dimer and the higher dipole moment of EGW1 to be 5.094 Debye relative to 4.155 Debye in water dimer, supports stronger hydrogen bonding formed by ethylene glycol than water.

H_2S-H_2O dimer has been optimized as a model to compare strength of hydrogen bonds formed by thioglyol with water. Two H_2S-H_2O dimers have been optimized, one with S-H of H_2S as hydrogen bond donor to oxygen of water (S-H···O interaction) and other with O-H of H_2O as hydrogen bond donor to S of H_2S as acceptor. The S.E. for S-H···O in EGS2W1 is -3.09 kcal/mol and S.E. for S-H···O in EGSSW1 is -4.15 kcal/mol relative to -2.55 for same interaction in H_2S-H_2O dimer, calculated at MP2/6-31+G*. This again indicates that thioglycol and dithioglycol forms stronger hydrogen bonds to water than formed by H_2S with water. The stabilization energy for the other H_2S-H_2O dimer with O-H···S is -1.75 kcal/mol and the stabilization energy is minimum for H_2S dimer (-0.85 kcal/mol).

Natural bond orbital (NBO) and Frontier molecular orbital (FMO) analysis: The electron delocalizations which are important for hydrogen bond formation in aggregates of selected molecules at MP2/6-31+G* are recorded in Table-8 while all other delocalizations are shown in Table-9. The second order interaction energy $E^{(2)}$ values indicate energy lowering and are used to estimate the relative strength of hydrogen bonds. The $E^{(2)}$ values for aggregates with water suggest strong intermolecular hydrogen bond interactions resulting from charge transfer. Table-9 shows that some of the internal delocalizations get affected upon the onset of intermolecular hydrogen bonding interactions with water. The most stable aggregate EGW2 show enhancement of $n_{O1} \rightarrow \sigma^*_{C2\text{-}C3}$ delocalization relative to EG. The change in $E^{(2)}$ value for this delocalization is from 4.43 to 8.87 kcal/mol. Similar increase in $E^{(2)}$ for $n_{S1} \rightarrow \sigma^*_{C2\text{-}C3}$ delocalization is from 3.49 to 5.08 for EGSW2. The variation in $E^{(2)}$ for $n_{O1} \rightarrow \sigma^*_{C2\text{-}C3}$ interaction is 4.03 kcal/mol in EGS2W2 relative to EGS2.

In addition complete elimination of the delocalization responsible for intramolecular hydrogen bond occurs in water aggregate EGW2, EGSW2, EGS2W2 and EGSSW2 because of rupture of IHB upon aggregation. On the other hand, in rest

TABLE-8

ORBITAL INTERACTIONS AND SECOND ORDER DELOCALIZATION ENERGIES $E^{(2)}$ (kcal/mol) AND OCCUPANCIES OF ACCEPTOR ANTIBONDING ORBITALS IMPORTANT FOR THE HYDROGEN BONDS PRESENT IN THE AGGREGATES OF ETHYLENE GLYCOL, THIOGLYCOL AND DITHIOGLYCOL WITH WATER AT MP2/6-31+G* THEORETICAL LEVEL

Species	Donor EG	Acceptor H_2O	$E^{(2)}$	Donor H_2O	Acceptor EG	$E^{(2)}$	Occupancies Acceptor EG		Acceptor H_2O	
EGW1	–		–	nO11 →	σ^*O4-H10	16.89	σ^*O4-H10	0.022	–	–
EGW2	nO4 →	σ^*O11-H12	11.96	nO11 →	σ^*O1-H5	15.76	σ^*O1-H5	0.024	σ^*O11-H12	0.018
EGW3	nO1 →	σ^*O11-H12	12.05	–		–	–	–	σ^*O11-H12	0.018

Species	Donor EGS	Acceptor H_2O	$E^{(2)}$	Donor H_2O	Acceptor EGS	$E^{(2)}$	Occupancies Acceptor EGS		Acceptor H_2O	
EGSW1	–		–	nO11 →	σ^*O4-H10	16.43	σ^*O4-H10	0.022	–	–
EGSW2	nO4 →	σ^*O11-H12	10.15	nO11 →	σ^*S1-H5	4.99	σ^*S1-H5	0.013	σ^*O11-H12	0.016
EGSW3	nS1 →	σ^*H11-O12	7.66	–		–	–	–	σ^*H11-O12	0.015

Species	Donor EGS2	Acceptor H_2O	$E^{(2)}$	Donor H_2O	Acceptor EGS2	$E^{(2)}$	Occupancies Acceptor EGS2		AcceptorH_2O	
EGS2W1	–		–	nO11 →	σ^*S4-H10	6.61	σ^*S4-H10	0.014	–	–
EGS2W2	nS4 →	σ^*H11-O12	7.28	nO11 →	σ^*O1-H5	17.48	σ^*O1-H5	0.025	σ^*O11-H12	0.015
EGS2W3	nO1 →	σ^*O11-H12	11.82	nO12 →	σ^*C3-H8	1.25	σ^*C3-H8	0.011	σ^*O11-H12	0.018

Species	Donor EGSS	Acceptor H_2O	$E^{(2)}$	Donor H_2O	Acceptor EGSS	$E^{(2)}$	Occupancies Acceptor EGSS		Acceptor H_2O	
EGSSW1	–		–	nO11 →	σ^*S4-H10	1.94	–	–	σ^*S4-H10	0.008
EGSSW2	nS4 →	σ^*O11-H12	7.49	nO11 →	σ^*S1-H5	6.56	σ^*S1-H5	0.015	σ^*O11-H12	0.015
EGSSW3	nS1 →	σ^*H11-O12	8.12	nO12 →	σ^*C3-H8	2.96	σ^*C3-H8	0.013	σ^*H11-O12	0.016

TABLE-9

IMPORTANT DELOCALIZATIONS AND SECOND ORDER INTERACTION ENERGY VALUES IN MONOMERS AND AGGREGATES OF ETHYLENE GLYCOL, THIOGLYCOL, DITHIOGLYCOL AT MP2/6-31+G*

System	nO1→σ^*C2-C3	nO1→σ^*C2-H7	nO4→σ^*O1-H5	nO4→σ^*C2-C3	nO4→σ^*C3-H9
EG	4.43	9.70	1.78	7.04	5.28
EGW1		9.84	2.55	7.36	5.44
EGW2	8.87	7.01	-		6.53
EGW3	4.11	8.40	2.37	7.02	4.75
System	**nS1→σ^*C2-C3**	**nS1→σ^*C2-H7**	**nO4→σ^*S1-H5**	**nO4→σ^*C2-C3**	**nO4→σ^*C3-H9**
EGS	3.49	5.59	0.88	8.07	5.48
EGSW1		5.61	1.29	8.06	6.48
EGSW2	5.08	4.71	-	4.55	7.31
EGSW3		5.89	1.26	7.92	5.36
System	**nO1→σ^*C2-C3**	**nO1→σ^*C2-H7**	**nS4→σ^*O1-H5**	**nS4→σ^*C2-C3**	**nS4→σ^*C3-H9**
EGS2	6.55	8.56	3.14	4.74	3.91
EGS2W1	6.00	8.53	3.76	4.59	3.97
EGS2W2	10.58	4.15+3.69	-	4.15	3.90
EGS2W3	4.71	8.39	4.02	4.71	3.84
System	**nS1→σ^*C2-C3**	**nS1→σ^*C2-H7**	**nS4→σ^*S1-H5**	**nS4→σ^*C2-C3**	**nS4→σ^*C3-H9**
EGSS	4.73	4.84	1.63	5.41	3.67
EGSSW1		5.27	3.73	3.52	5.17
EGSSW2	6.61	3.18	-		4.36
EGSSW3		5.49	2.10	5.29	3.70

of the aggregates with preserved IHB, the strength of IHB is enhanced on aggregation. The delocalization $n_{X4}\rightarrow\sigma^*_{Y1-H5}$ (X=O, S, Y=O, S) contribute towards intramolecular hydrogen bond formation. With $E^{(2)}$ value for this delocalization is 1.78 kcal/mol in EG, 0.88 kcal/mol in EGS, 3.14 kcal/mol in EGS2 and 1.63 in EGSS at MP2/6-31+G*. The $E^{(2)}$ for $n_{O4}\rightarrow\sigma^*_{O1-H5}$ get enhanced from 1.78 in EG to 2.55 and 2.37 kcal/mol in EGW1 and EGW3, respectively. Similar increase of $E^{(2)}$ for $n_{O4}\rightarrow\sigma^*_{S1-H5}$ is 0.41 and 0.38 kcal/mol in EGSW1 and EGSW3 respectively relative to EGS. Thus intermolecular hydrogen bond impacts intramolecular hydrogen bond. Out of EGS and EGS2, intramolecular hydrogen bond S···H-O in EGS2 is stronger than O···H-S in EGS as can be seen from larger $E^{(2)}$ of 3.14 relative to 0.88 kcal/mol in EGS. It concludes O-H to be stronger hydrogen bond donor than S-H. EGW2, the most stable aggregate has strong covalent component (Table-8) of two hydrogen bonds as evidenced by $E^{(2)}$ of 11.96 kcal/mol for $n_{O4}\rightarrow\sigma^*_{O11-H12}$ and $E^{(2)}$ of 15.76 kcal/mol for $n_{O11}\rightarrow\sigma^*_{O1-H5}$. The occupancies of the acceptor antibonding orbitals of water upon aggregate formation are fairly high and range from 0.011 to 0.025 a.u. NBO analysis (Table-10) shows that occupancy of hydrogen bond acceptor oxygen and sulfur lone pair electrons

TABLE-10
ORBITAL OCCUPANCIES OF LONE PAIRS OF HYDROGEN BOND ACCEPTOR AND HYDROGEN BOND DONOR ORBITALS AT MP2/6-31+G*

Water	LP (1)OW	2.000	$\sigma^*_{\text{O1-H2}}$	0.000					
	LP(2)OW	1.999	$\sigma^*_{\text{O1-H3}}$	0.000					
EG	LP(1)O1	1.987	$\sigma^*_{\text{O4-H10}}$	0.006	EGS2	LP(1)O1	1.986	$\sigma^*_{\text{S4-H10}}$	0.006
	LP(2)O1	1.972	$\sigma^*_{\text{O1-H5}}$	0.009		LP(2)O1	1.971	$\sigma^*_{\text{O1-H5}}$	0.013
	LP(1)O4	1.988				LP(1)S4	1.994	$\sigma^*_{\text{C3-H8}}$	0.011
	LP(2)O4	1.972				LP(2)S4	1.970		
					EGS2W1	LP(1)OW	1.999	$\sigma^*_{\text{S4-H10}}$	0.014
						LP(2)OW	1.991		
EGW1	LP(1)OW	1.999	$\sigma^*_{\text{O4-H10}}$	0.022	EGS2W2	LP(1)S4	1.992	$\sigma^*_{\text{O-HW}}$	0.015
	LP(2)OW	1.982				LP(2)S4	1.965		
EGW2	LP(1)O4	1.984	$\sigma^*_{\text{O1-H5}}$	0.024		LP(1)OW	1.999	$\sigma^*_{\text{O1-H5}}$	0.025
	LP(2)O4	1.965	$\sigma^*_{\text{O-H(W)}}$	0.018		LP(2)OW	1.979		
	LP(1)OW	1.999			EGS2W3	LP(1)O1	1.983	$\sigma^*_{\text{O-HW}}$	0.018
	LP(2)OW	1.980				LP(2)O1	1.962		
EGW3	LP(1)O1	1.984	$\sigma^*_{\text{O-H(W)}}$	0.018		LP(1)OW	1.999	$\sigma^*_{\text{C3-H8}}$	0.011
	LP(2)O1	1.962				LP(2)OW	1.998		
EGS	LP(1)O4	1.988	$\sigma^*_{\text{O4-H10}}$	0.008	EGSS	LP(1)S1	1.993	$\sigma^*_{\text{S4-H10}}$	0.006
	LP(2)O4	1.972	$\sigma^*_{\text{S1-H5}}$	0.008		LP(2)S1	1.974	$\sigma^*_{\text{S1-H5}}$	0.011
	LP(1)S1	1.994	$\sigma^*_{\text{C3-H8}}$	0.015		LP(1)S4	1.994	$\sigma^*_{\text{C3-H8}}$	0.012
	LP(2)S1	1.975				LP(2)S4	1.971		
EGSW1	LP(1)OW	1.999	$\sigma^*_{\text{O4-H10}}$	0.022	EGSSW1	LP(1)OW	1.999	$\sigma^*_{\text{S4-H10}}$	0.008
	LP(2)OW	1.982				LP(2)OW	1.996		
EGSW2	LP(1)O4	1.981	$\sigma^*_{\text{O-HW}}$	0.016	EGSSW2	LP(1)S4	1.991	$\sigma^*_{\text{O-HW}}$	0.015
	LP(2)O4	1.968				LP(2)S4	1.965		
	LP(1)OW	1.999	$\sigma^*_{\text{S1-H5}}$	0.013		LP(1)OW	1.999		
	LP(2)OW	1.992				LP(2)OW	1.990	$\sigma^*_{\text{S1-H5}}$	0.015
EGSW3	LP(1)S1	1.992	$\sigma^*_{\text{O-HW}}$	0.015	EGSSW3	LP(1)S1	1.991	$\sigma^*_{\text{O-HW}}$	0.016
	LP(2)S1	1.964				LP(2)S1	1.963		
	LP(1)OW	1.999	$\sigma^*_{\text{C-H}}$	0.015		LP(1)OW	1.999	$\sigma^*_{\text{C3-H8}}$	0.013
	LP(2)OW	1.998				LP(2)OW	1.996		

in aggregates decreases on aggregation. The occupancy of antibonding O-H, S-H and C-H orbitals accepting the charge increases on hydrogen bonding.

The natural atomic charges on hydrogen bond acceptor and hydrogen of hydrogen bond donor atoms of ethylene glycol, thioglycol, dithioglycol and H_2O in the aggregates are listed in Table-7 and charges on all atoms of EG, EGS/EGS2, EGSS are listed in Tables 11 and 12. The analysis of natural atomic charges obtained using NBO method at MP2/6-31+G* theoretical level indicates that in the aggregates, charge density of S of thioglycol and thioglycol range from -0.041 to -0.079 and -0.031 to -0.066 units, respectively. The polarization of S-H and C-S bond is reduced considerably in EGS, EGS2, EGSS in comparison to O-H and C-O bond in EG as expected from the small electronegativity difference between carbon and sulfur and low charge on sulfur than oxygen. Thus, the electrostatic component of hydrogen bond involving sulfur as hydrogen bond acceptor is anticipated to be weak, also supported by the hard and soft acid base (HSAB) principle, there is poorer match between the hard proton and soft sulfur.

The higher are the charges on interacting atoms, the more is the attractive electrostatic force between two atoms. Hydrogen attached to oxygen of water or ethylene glycol carry high positive charge and hydrogen attached to sulfur of thioglycol/dithioglycol has very low positive charge. The hydrogen atom H5 attached to O1 carries positive charge of 0.511 units in EG while

TABLE-11
ATOMIC CHARGES (NPA) ON ATOMS OF ETHYLENE GLYCOL, THIOGLYCOL AND THEIR AGGREGATES WITH WATER AT MP2/6-31+G* THEORETICAL LEVEL

Species	O1	C2	C3	O4	H5	H6	H7	H8	H9	H10
EG	-0.822	-0.077	-0.086	-0.827	0.511	0.212	0.180	0.219	0.192	0.497
EGW1	-0.829	-0.075	-0.082	-0.862	0.512	0.206	0.181	0.211	0.191	0.533
EGW2	-0.848	-0.077	-0.082	-0.848	0.537	0.211	0.182	0.222	0.194	0.507
EGW3	-0.845	-0.083	-0.093	-0.830	0.525	0.224	0.188	0.237	0.195	0.499
Species	S1	C2	C3	O4	H5	H6	H7	H8	H9	H10
EGS	-0.043	-0.615	-0.062	-0.819	0.143	0.251	0.233	0.223	0.193	0.495
EGSW1	-0.059	-0.611	-0.057	-0.852	0.145	0.245	0.238	0.215	0.191	0.529
EGSW2	-0.054	-0.620	-0.058	-0.842	0.166	0.253	0.236	0.224	0.197	0.508
EGSW3	-0.068	-0.610	-0.069	-0.823	0.156	0.263	0.234	0.241	0.195	0.495

TABLE-12
ATOMIC CHARGES (NPA) ON ATOMS OF ETHYLENE THIOGLYCOL (EGS2), DITHIOGLYCOL AND THEIR AGGREGATES WITH WATER AT MP2/6-31+G* THEORETICAL LEVEL

Species	O1	C2	C3	S4	H5	H6	H7	H8	H9	H10
EGS2	-0.820	-0.058	-0.613	-0.042	0.505	0217	0.187	0.257	0.246	0.120
EGS2W1	-0.825	-0.060	-0.607	-0.079	0.504	0.211	0.196	0.251	0.245	0.161
EGS2W2	-0.851	-0.056	-0.602	-0.060	0.538	0.211	0.189	0.259	0.243	0.126
EGS2W3	-0.843	-0.063	-0.622	-0.041	0.517	0.226	0.195	0.282	0.247	0.118
Species	S1	C2	C3	S4	H5	H6	H7	H8	H9	H10
EGSS	-0.036	-0.598	-0.596	-0.027	0.136	0.254	0.242	0.259	0.248	0.118
EGSSW1	-0.066	-0.597	-0.592	-0.049	0.142	0.251	0.259	0.253	0.249	0.153
EGSSW2	-0.056	-0.601	-0.587	-0.048	0.167	0.254	0.245	0.260	0.247	0.128
EGSSW3	-0.058	-0.590	-0.606	-0.031	0.146	0.260	0.243	0.286	0.248	0.116

the magnitude is reduced to 0.143 in EGS. The hydrogen H10 attached to S4 has charge of 0.120 units in EGS2 and 0.118 units in EGSS and H5 attached to S1 has just 0.136 units charge. Hence these values conclude that electrostatic interactions involving S as donor/acceptor are considerably weaker for EGS, EGS2, EGSS than that for EG, therefore electrostatic component of hydrogen bonding is higher in EG in comparison to EGS, EGS2, EGSS. Biggest value of charge is observed on hydrogen involved in hydrogen bonding. Increase in charge on hydrogen atom participating in hydrogen bonding clearly corroborates hydrogen bonding.

Upon aggregate formation, charges on all atoms undergo variations but largest change occurs on atoms participating in intermolecular hydrogen bond formation *i.e.* in almost all aggregates, the positive charge on hydrogen bond donor increases and negative charge on hydrogen bond acceptor decreases. The high positive and negative charges on the atoms involved in formation of hydrogen bond in EG clearly suggest that electrostatics also play an important role towards interaction energy while low positive and low negative charge suggest hydrogen bonds to sulfur as hydrogen bond acceptor and hydrogen bond donor are electrostatically disfavoured. Quadrupole moments Q_{XX}, Q_{YY}, Q_{ZZ} are -30.99, -23.32, -23.33 in EG, in EGS values are -36.86, -31.75,-32.21, in EGS2 values are -40.89, -31.52, -31.49, while in case of EGSS are -48.44, -38.46, -40.48. Larger quadrupolar moments of thioglycol, dithioglycol than ethylene glycol indicate hydrogen bonds are driven by charge-dipole and charge quadrupole interaction while in EG are dominated by dipole-dipole interaction.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of EG, EGS, EGS2, EGSS and their most stable water aggregate systems optimized at MP2/6-31+G* are presented in Fig. 3. The positive phase is red and negative one is green. Further, the frontier molecular orbitals (FMO) indicate charge transfer within the molecule. The calculated HOMO and LUMO energies and low value of gap show that charge transfer interactions occur within studied complexes (Table-13). From Fig. 3, it is observed that HOMO LUMO energy gap in EGW2 and EGSW2, is found to be lower than HOMO LUMO gap of their monomers EG, EGS and water also. Generally if energy gap of HOMO and LUMO decreases, it is easier for electron of HOMO to be excited and easier for LUMO to accept electrons. Relative to ethylene glycol and its complexes with water, the FMO gap is smaller for thioglycol, dithioglycol and their water aggregates. The molecules having small FMO gap is polarizable and is generally associated with high chemical reactivity and low kinetic stability. It is in accordance to the observed stabilization energy trend also. The HOMO LUMO band gap of EG and its aggregates with water is larger than thioglycol, dithioglycol and their aggregates with water.

TABLE-13
HOMO LUMO GAP OF ETHYLENE GLYCOL, THIOGLYCOL, DITHIOGLYCOL AND THEIR WATER AGGREGATES OPTIMIZED AT MP2/6-31+G*

System	HOMO	LUMO	$\Delta E_{HOMO/LUMO}$ (a.u.)	$\Delta E_{HOMO/LUMO}$ (eV)
EG	-0.439	0.075	0.364	13.98
EGW1	-0.420	0.089	0.331	13.85
EGW2	-0.428	0.075	0.353	13.68
EGW3	-0.450	0.073	0.377	14.23
EGS	-0.355	0.071	0.284	11.59
EGSW1	-o.344	0.082	0.262	11.59
EGSW2	-0.352	0.069	0.283	11.45
EGSW3	-0.365	0.072	0.293	11.89
EGS2	-0.374	0.072	0.302	12.13
EGS2W1	-0.355	0.082	0.273	11.89
EGS2W2	-0.373	0.075	0.298	12.19
EGS2W3	-0.374	0.071	0.303	12.10
EGSS	-0.359	0.064	0.295	11.51
EGSSW1	-0.354	0.072	0.282	11.59
EGSSW2	-0.352	0.064	0.288	11.31
EGSSW3	-0.363	0.069	0.294	11.75
H_2O	-0.508	0.146	0.362	17.79
H_2O-H_2O	-0.475	0.123	0.352	16.27
H_2O-H_2S	-0.362	0.090	0.272	12.29
H_2O-H_2S_2	-0.405	0.063	0.342	12.73

Conclusion

Intramolecularly hydrogen bonded gauche rotamers of ethylene glycol, thioglycol, dithioglycol are more stable than non-hydrogen bonded rotamers. Intermolecular hydrogen bonding of molecules with single water ruptures intramolecular hydrogen bond (IHB) in some aggregates and in other aggregates, it strengthen IHB as evident from bond lengths, bridging hydrogen bond angle and Δr values. Largest stabilization energy results on aggregation of ethylene glycol with water, followed by thioglycol and minimum stabilization energy obtained for aggregates of dithioglycol. While the most stable aggregate of ethylene glycol is stabilized by two intermolecular O-H···O

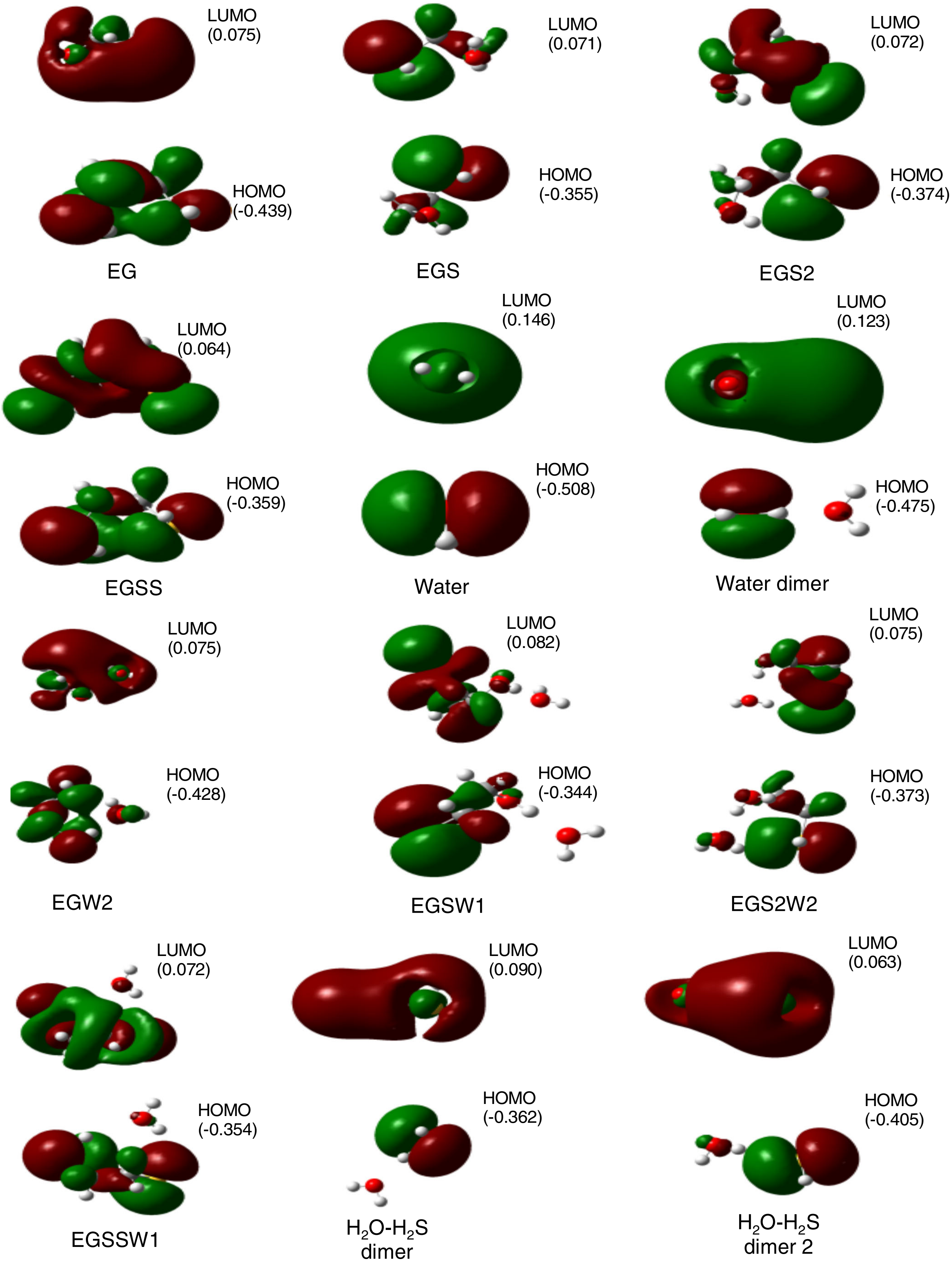


Fig. 3. Frontier orbitals (HOMO, LUMO energies in atomic units)

interactions with water, the most stable aggregate of thioglycol is stabilized by O-H···S and O-H···O interaction and for dithioglycol, the most stable aggregate of dithioglycol is stabilized by O-H···S interaction. Intermolecular hydrogen bond affects strength of hydrogen bonds by affecting bond lengths, bond polarizations, charges, charge transfer, electron delocalizations, *etc*. Larger stabilization of aggregates without IHB indicates that intermolecular interactions between water and molecule are stronger than intramolecular interaction and decide preferred orientation of rotamers in aqueous medium. Intermolecular hydrogen bonds of ethylene glycol to water are favoured both electrostatically and by charge transfer, while intermolecular hydrogen bonds of thioglycol and dithioglycol are electrostatically disfavoured and mainly stabilized by charge transfer. Stronger intermolecular hydrogen bonds are formed by ethylene glycol, thioglycol and dithioglycol with water as compared to hydrogen bonds formed by H_2O dimer, H_2S-H_2O dimer and H_2S-H_2S dimer optimized as model molecules.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. P. Schuster and P. Wolschann, *Monatsh. Chem.*, **130**, 947 (1999); https://doi.org/10.1007/PL00010280
2. G. A. Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press: New York, NY, USA (1997).
3. F.T.T. Huque and J.A. Platts, *Org. Biomol. Chem.*, **1**, 1419 (2003); https://doi.org/10.1039/b300598d
4. D.E. Leahy, J.J. Morris, P.J. Taylor and A.R. Wait, *J. Chem. Soc. Perkin. Trans. II*, 705 (1992); https://doi.org/10.1039/P29920000705
5. S. Spange and A. Reuter, *Langmuir*, **15**, 141 (1999); https://doi.org/10.1021/la980991i
6. A. Demirbas, Methane Gas Hydrate, Springer: London, UK, (2010).
7. T.S. Collett, *AAPG Bull.*, **86**, 1971 (2002).
8. J. Fink, Petroleum Engineer's Guide to Oil Field Chemicals and Fluids, Elsevier: Oxford, UK (2012).
9. A. Wehner, R. Miller, G. Fenyvesi, J.W. DeSalvo and M. Joerge, Heat Transfer Compositions Comprising Renewably-based Biodegradable 1,3-Propanediol, US Patent 2007/0200088 A1 (2007).
10. D.L. Howard, P. Jørgensen and H.G. Kjaergaard, *J. Am. Chem. Soc.*, **127**, 17096 (2005); https://doi.org/10.1021/ja055827d
11. A. Jindal and S. Vasudevan, *J. Phys. Chem. B*, **121**, 5595 (2017); https://doi.org/10.1021/acs.jpcb.7b02853
12. B.J.C. Cabral, L.M.P.C. Albuquerque and F.M.S.S. Fernandes, *Theor. Chim. Acta*, **78**, 271 (1991); https://doi.org/10.1007/BF01112850
13. P. Bultinck, A. Goeminne and D. Van de Vondel, *J. Mol. Struct. THEOCHEM*, **334**, 101 (1995); https://doi.org/10.1016/0166-1280(94)04102-X
14. K.J. Liu and J.L. Parsons, *Macromolecules*, **2**, 529 (1969); https://doi.org/10.1021/ma60011a015
15. S. Lusse and K. Arnold, *Macromolecules*, **29**, 4251 (1996); https://doi.org/10.1021/ma9508616
16. M.W.A. Skoda, R.M.J. Jacobs, J. Willis and F. Schreiber, *Langmuir*, **23**, 970 (2007); https://doi.org/10.1021/la0616653
17. P. Buckley and P.A. Giguere, *Can. J. Chem.*, **45**, 397 (1967); https://doi.org/10.1139/v67-070
18. E.L. Hommel, J.K. Merle, G. Ma, C.M. Hadad and H.C. Allen, *J. Phys. Chem. B*, **109**, 811 (2005); https://doi.org/10.1021/jp046715w
19. J.B. Zhang, P.Y. Zhang, K. Ma, F. Han, G.H. Chen and X.H. Wei, *Sci. China Ser. B-Chem.*, **51**, 420 (2008); https://doi.org/10.1007/s11426-008-0045-0
20. C. Murli, N. Lu, Z. Dong and Y. Song, *J. Phys. Chem. B*, **116**, 12574 (2012); https://doi.org/10.1021/jp306220q
21. I. Bako, T. Grosz, G. Palinkas and M.C. Bellissent-Funel, *J. Chem. Phys.*, **118**, 3215 (2003); https://doi.org/10.1063/1.1536163
22. R.N. Nandi, C.F. Su and M.D. Harmony, *J. Chem. Phys.*, **86**, 5224 (1987); https://doi.org/10.1063/1.452789
23. G. Schultz and I. Hargittai, *Acta Chir. Acad. Sci. Hung.*, **75**, 381 (1973).
24. I. Hargittai and G. Schultz, *J. Chem. Phys.*, **84**, 5220 (1986); https://doi.org/10.1063/1.450645
25. S.L. Barkowski, L. Hedberg and K. Hedberg, *J. Am. Chem. Soc.*, **108**, 6898 (1986); https://doi.org/10.1021/ja00282a010
26. M. Ohsaku, *J. Mol. Struct. THEOCHEM*, **138**, 283 (1986); https://doi.org/10.1016/0166-1280(86)80020-3
27. T. Shida and T. Monose, *J. Mol. Struct.*, **126**, 159 (1985); https://doi.org/10.1016/0022-2860(85)80112-5
28. S.L. Barkowski and K. Hedberg, *J. Am. Chem. Soc.*, **109**, 6989 (1987); https://doi.org/10.1021/ja00257a014
29. H. Takeuchi and M. Tasumi, *Chem. Phys.*, **77**, 21 (1983); https://doi.org/10.1016/0301-0104(83)85062-9
30. R.A. Klein, *J. Comput. Chem.*, **23**, 585 (2002); https://doi.org/10.1002/jcc.10053
31. M. Mandado, A.M. Grana and R.A. Mosquera, *Phys. Chem. Chem. Phys.*, **6**, 4391 (2004); https://doi.org/10.1039/B406266C
32. B.J. Miller, M. Yekutiel, A.H. Sodergren, D.L. Howard, M.E. Dunn, V. Vaida and H.G. Kjaergaard, *J. Phys. Chem. A*, **114**, 12692 (2010); https://doi.org/10.1021/jp9112798
33. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Jr, Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, Gaussian 03, Revision C.01, Gaussian, Inc, Wallingford CT (2004).
34. D. Kaur and R. Kohli, *Struct. Chem.*, **23**, 161 (2012); https://doi.org/10.1007/s11224-011-9840-x
35. S.F. Boys and F. Bernardi, *Mol. Phys.*, **19**, 553 (1970); https://doi.org/10.1080/00268977000101561
36. C. Aleman, *J. Phys. Chem. A*, **105**, 6717 (2001); https://doi.org/10.1021/jp010198p
37. A.E. Reed, R.B. Weinstock and F. Weinhold, *J. Chem. Phys.*, **83**, 735 (1985); https://doi.org/10.1063/1.449486
38. A.E. Reed, L.A. Curtiss and F. Weinhold, *Chem. Rev.*, **88**, 899 (1988); https://doi.org/10.1021/cr00088a005
39. M.A. Murcko and R.A. DiPaola, *J. Am. Chem. Soc.*, **114**, 10010 (1992); https://doi.org/10.1021/ja00051a038
40. C.J. Cramer and D.G. Truhlar, *J. Am. Chem. Soc.*, **116**, 3892 (1994); https://doi.org/10.1021/ja00088a027
41. A.E. Lutskii and N.I. Gorokhova, *Theor. Exp. Chem.*, **4**, 532 (1971); https://doi.org/10.1007/BF00527035