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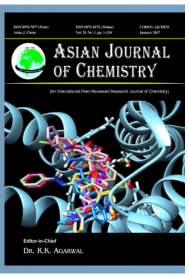

Conformational Studies with Density Functional Theory of Ethylene Glycol as Intermediate

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Ethylene glycol is an important organic compound and chemical intermediate used in a large number of industrial processes. This study focuses on the density functional theory with basis set 6-311++G(d,p) that provides a method for analyzing the reactivity of ethylene glycol in terms of local and global descriptions that account for various chemical and critical phenomena with optimized structure. A comparative study of these spectroscopic properties was attributed with reported experimental studies justifies the nature of the compound, suitability to act as an intermediate and for conjugation of metallic's and organics in particular.

Keywords: Ethylene glycol, Density functional theory, Raman and Infrared spectra.

INTRODUCTION

Ethylene glycol and its oligomers have a wide range of applications including use as pharmaceutical excipients, binders, plasticizers, *etc.* [1] used for synthesizing nanoparticles by autocombustion method or for preparing metal nanoparticles without oxidizing the particles [2]. Ethylene glycol in combination with citric acid or hydrazine is generally used in such process. This molecule has been studied both theoretically as well as experimentally by electron diffraction, infrared spectroscopy, microwave spectroscopy, nuclear magnetic resonance spectroscopy and variable temperature Raman spectroscopy.

Density functional calculations on a variety of systems have been carried out by large number of researchers due to availability of open source and proprietary software as well as increase in computational efficiency [3]. The choice of ethylene glycol gained importance due to its diffuse functions with specified basis set that are essential in density functional methods. These basis sets used in the study of medium and large size hydrogen bonded systems and further provides small basis set superposition error (BSSE) [4]. The basis set that includes both diffuse and polarization functions has already been used for several hydrogen bonded systems. Quantum chemical calculations were performed by using Gaussian 03 [5,6] package to obtain best possible and optimized results with the hybrid density functional method B3LYP with 6-311++G(d,p) basis set. This method is realized as Becke's three parameter hybrid functional combined with the Lee, Yang and Parr correlation - B3LYP functional with 6-311++G(d,p) basis set that has been selected for its accuracy and better performance as reported in several studies [7]. DFT method is (i) utilized to study the chemical reactivity and site selectivity of molecular systems that provides stability of the system. (ii) to analyze and interpret the parameters like global hardness, chemical potential and electrophilicity of that is useful in accurate description of hydrogen bonding interactions [7,8].

The present focus of work attributes optimized molecular geometry, vibrational frequencies, infrared intensities and Raman scattering activities of ethylene molecule by performing a series of self-consistent-field calculations using the LCAO-SCF method with Gaussians as the basic expansion functions.

COMPUTATIONAL METHODS

The choice of using this basis set is aimed at polarization and diffuse functions that gained importance due to low molecular weight 62.07 g/mol termed as small molecule and minimization of error. The descriptions of these electronic correlations reveal interesting properties like energy gap of orbitals, chemical potential and hardness that describe the electrophic nature of the molecule. It was concluded that this method is the best suitable method for studies involving with ethylene glycol.

Optimization of ethylene glycol is performed by Avagadro software for determining its spectroscopic properties related to bond lengths and bond angles. Further computational studies were configured by Gaussian software [5,6] with frequency optimization with chosen basis set.

RESULTS AND DISCUSSION

The optimized molecular structure is illustrated in Fig. 1 with colours of red indicating the oxygen, grey indicating carbon and hydrogen in white. The molecular distribution with associated bonding parameters contributing to bond lengths and bond angles were tabulated in Table-1 along with computed parameters from basis set are in agreement with reported values [9-11].

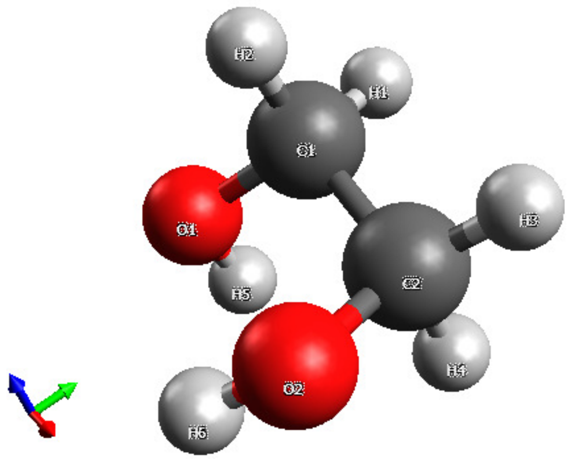


Fig. 1. Optimized structure of ethylene glycol

Vibration spectroscopy performed with FTIR is one of the most useful experimental tools to study the hydrogen-bonded clusters. Generally, the stronger the hydrogen bond, the more the O-H stretching frequency is shifted to lower frequency. Vibration spectroscopy is one of the most useful experimental tools to study the hydrogen-bonded clusters. The effect of hydrogen bond formation is to increase the infrared intensity and to low the O-H stretching frequency. Generally, the stronger the hydrogen bond, the more the O-H stretching frequency is shifted to lower frequency. The corresponding FTIR [12] wave numbers and intensities with Raman active intensities corresponding to assigned functional groups with stretching and bending modes were tabulated in Table-2. These computed results signify that the infrared and Raman spectra are in good

TABLE-2
SPECTROSCOPIC PARAMETERS OF ETHYLENE GLYCOL

IR wave numbers	Raman active intensities	IR intensities	Functional group
159.3152	0.0892	10.6400	–
301.3092	0.5938	80.1675	C-C-O torsion
324.0939	0.5448	7.4921	C-C-O bending
452.0080	1.4755	166.8194	C-C-O bending
535.6803	0.7114	31.8332	C-C-O bending
862.5359	6.4784	27.0920	C-C stretching
881.3394	3.6038	20.1859	CH_2 rocking
1048.7831	1.9230	74.2947	C-O stretching
1055.4197	3.1193	10.4025	C-O and C-C stretching
1093.7407	3.3468	102.6838	C-O stretching
1194.8234	4.0258	18.7250	NH_3/CH_2 bending
1231.5974	3.4790	23.6646	CH_2 twisting
1365.7311	9.7407	2.0076	CH_2 wagging
1370.0081	4.4116	8.5282	CH_2 wagging
1398.6205	3.0480	21.6502	CH_2 wagging
1427.2272	4.7695	43.3485	CH_2 scissoring
1491.0606	7.3833	4.8152	OC_2H_4 bending
1499.5359	6.3671	1.4367	CH_2 bending
2956.3131	136.7726	69.2323	C-H stretching anti-sym
3009.5727	146.5904	53.4086	C-H stretching anti-sym
3070.8199	107.1670	32.7378	NH stretching
3096.4412	71.5060	29.3036	NH stretching
3794.7245	53.3801	44.7379	O-H stretching local mode
3826.5380	72.3450	29.1496	O-H stretching local mode

TABLE-1
LINEAR AND ANGULAR BONDING PARAMETERS OF ETHYLENE GLYCOL

Nature of bond	Bond angle	Nature of bond	Bond angle	Nature of bond	Bond angle	Nature of bond	Bond angle
O2-O1-C3	68.785	O1-H10-H6	119.3529	H7-C4-H8	112.8713	H5-C4-H7	107.0334
O1-O2-C4	86.2164	C4-H10-H6	64.2928	O2-O1-H9	148.041	O1-H6-H7	97.2394
O1-C3-C4	108.0576	H7-C3-H10	114.205	H5-O1-H9	69.8338	H6-C4-H7	76.9629
O2-C4-C3	95.5811	H7-H6-H10	84.4679	H6-O1-H9	102.6367	O1-C3-H8	110.0084
O2-O1-H5	86.3539	H8-C3-H10	97.04	H8-H5-H9	116.4193	O2-C4-H8	106.4907
O1-C3-H5	123.7206	H6-H10-H8	82.2306	O2-H10-C3	96.056	O2-H8-H5	93.2632
O2-C3-H5	144.6507	O2-H10-H9	160.2163	C4-C3-H10	94.9663	H6-C3-H8	120.4931
O1-H5-C4	66.5216	H5-H10-H9	73.0194	H5-C3-H10	129.4439	O2-H8-H7	71.094
O2-C4-H5	120.2419	O2-O1-H6	74.003	O2-H10-H6	92.774	H5-H8-H7	79.8816
C4-C3-H5	111.3016	O1-C3-H6	103.8718	H5-H6-H10	61.8276	C3-O1-H9	91.2485
O2-H7-H6	79.3909	O2-C3-H6	98.7172	H7-C4-H10	133.8733	C3-H5-H9	82.974
H5-H6-H7	80.753	O1-H6-C4	70.3357	O1-H10-H8	158.2618	H6-H5-H9	97.6558
O2-H8-C3	65.4005	O2-C4-H6	97.874	H8-C4-H10	110.4819	O1-H10-O2	117.4922
C3-C4-H8	111.2326	C4-C3-H6	96.6642	H7-H8-H10	80.0455	O1-H10-C4	164.7548
H5-C3-H8	90.145	O1-H6-H5	69.4458	C3-H10-H9	95.1592	O1-H10-H5	129.1203
H6-C4-H8	143.5144	H5-C3-H6	109.6145	H6-H10-H9	106.0789	C4-H10-H5	66.0149
C3-H8-H7	66.4361	C4-H6-H5	64.3013	O1-C3-H7	125.3143	H6-C3-H10	109.1529
H6-H7-H8	101.9166	O1-O2-H7	100.4575	O2-H7-C3	62.7149	H7-O2-H10	86.3531
C4-O1-H9	118.2701	H6-C3-H7	72.7119	O1-C4-H7	133.7153	H7-H5-H10	70.3171
C4-H5-H9	114.0384	O1-O2-H8	93.9982	O2-C4-H7	118.0183	H8-O2-H10	79.9306
H7-H5-H9	130.8546	O1-C4-H8	111.8283	C3-C4-H7	111.3687	H8-H5-H10	68.0919
O1-H10-C3	142.9286	O1-H5-H8	78.9261	O1-H5-H7	81.362	H9-O1-H10	107.0741
C4-O2-H10	70.9184	H5-C4-H8	88.3758	O2-H7-H5	82.5777	C4-H10-H9	136.6574
O2-H10-H5	113.3097	H6-H5-H8	85.1102	H5-C3-H7	107.4221	H8-H10-H9	121.4423

TABLE-3
COMPUTATIONAL PARAMETERS OF ETHYLENE GLYCOL

HOMO-LUMO (eV)	Dipole moment (μ) Debye	Global hardness $\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2$	Chemical potential $\mu = (\varepsilon_{LUMO} + \varepsilon_{HOMO})/2$	Electrophilicity index $\omega = \frac{\mu^2}{2\eta}$
7.113	2.6011	3.556	-4.021	2.27

agreement with the experimental and theoretical values reported [9-11]. In this study, we have performed a frequency calculation to obtain the spectroscopic signature of ethylene glycol monomer. According to the theoretical calculations, this ethylene glycol species has a planar structure of C1 point group symmetry.

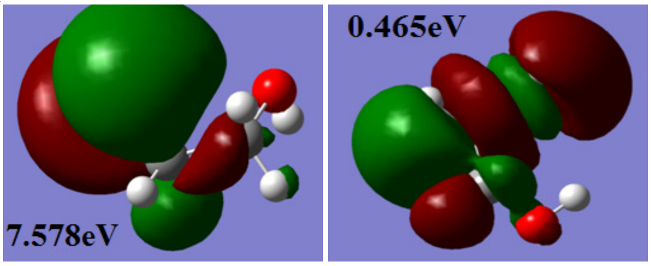
Contribution to properties that gained importance in using ethylene glycol in the synthesis mechanism of materials were tabulated in Table-3 along with their corresponding thermodynamic properties are listed in Table-4.

TABLE-4
THERMODYNAMIC PARAMETERS

Moment of inertia 1×10^{-46} Kg m^2			Energy 1×10^4 eV	Enthalpy (Kcal/mol)	Entropy (cal/mol K)
I_x	I_y	I_z			
5.51	15.32	18.42	6.26	56.67	69.87

The computed parameters like energy gap, susceptibility (negative of chemical potential) and hardness indicate tendency to homogenize at all concentrations. Electrophilic index measures the stabilization in the process of accepting electrons from local environment and tendency to exchange electronic charge reveal the nature of ethylene glycol to act as intermediate.

Vibration analysis require the bonding between orbital's that arise due to highest unoccupied and lowest occupied orbital's separated by gap of 7.113 eV along with schematic illustration of contour maps indicating the HUMO and LOMO energies are illustrated in Fig. 2. Infrared and Raman spectra have been determined by using the same basis set and is shown in Figs. 3 and 4. On observation of both these spectra the OH regions are approximately equal with increased intensity indicating ethylene glycol to act as intermediate that necessities molecular interactions in forming complex. Thermodynamic parameters are in acceptable range to act as intermediate to form binary mixtures [13].



HOMO LUMO

Fig. 2. Schematic illustration of energies

Conclusions

- Ethylene glycol was studied using DFT method with basis set 6-311 ++G(d,p).
- The observed and calculated frequencies are found to be in very good agreement with reported works both experimental and theoretical.
- Assignment of various groups to infrared and Raman spectra are functional revealing the contribution of molecules in bonding
- The spectroscopic and thermodynamic parameters are in acceptable limit that forms a basis to act as intermediate with electron accepting capability in formation of complex.
- Vibration studies of the molecule reveal changes in bond angles of involved molecules with specified angles differed by 100°.
- Fingerprint regions contribution if more than the functional group of molecules with endothermic activity with less disorder.

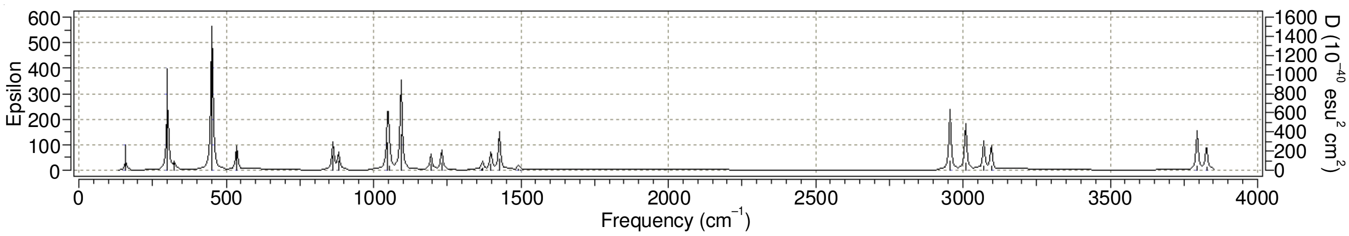


Fig. 3. IR spectrum

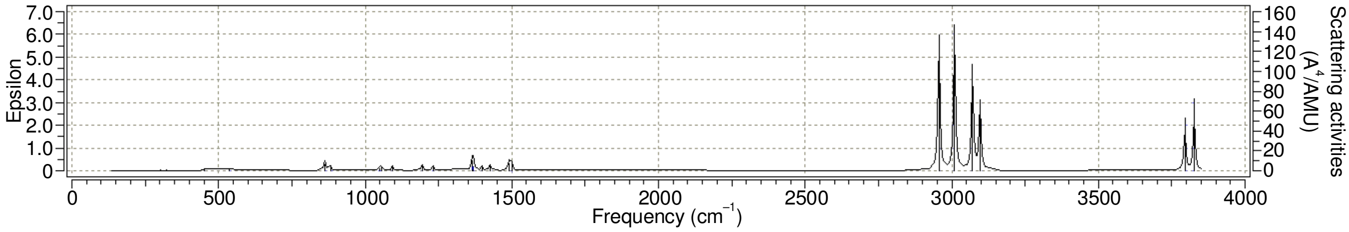


Fig. 4. Raman spectrum

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