Conformational analysis, spectroscopic (FTIR, NMR and UV-Vis.), molecular docking and quantum chemical simulation studies of 1-phenylethanone-O-pyropyl oxime ether

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Abstract

The stable conformer of the synthesized 1-phenylethanone-O-pyropyl oxime ether (PEPOE) has been determined by potential energy profile analysis. All the structural parameters of PEPOE were identified by Density Functional Theory (DFT) with B3LYP method and 6-311++G(d,p) basis set. The spectroscopic properties, FTIR, NMR and UV-Vis results have been theoretically calculated and compared with experimental data. The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energies and the electron density distribution were performed by same level. The heat capacity, entropy, and enthalpy of the PEPOE have been calculated at temperature range from 100 to 1000 °C. In addition, the molecular docking studies with DNA and Human Serum Albumin (HSA) structures have been performed to find the most preferred binding mode of the ligand inside the DNA and HSA cavity. As a result of these studies, the binding free energies of DNA and HSA have been calculated as -20.92 and -26.78 kJ/mol, respectively. The results show that these calculations are valuable for providing insight into molecular properties of the oxime ether compounds.

Keywords: Oxime ether, Spectroscopy, Quantum chemical calculation, Molecular docking

1. Introduction

Cancer is the most important health threat worldwide today [1]. For this reason, new molecules exhibiting anticancer properties have been intensively studied by researchers in recent years. Oxime ether molecules are bioactive compounds, which are used as medicine and pesticide, so it is important to investigate the synthesis and properties of such molecules [2]. These type molecules had -C=N-O- and alkyl groups, are simply obtained from the reaction of ketone or aldehyde with hydroxylamine hydrochloride and alkyl halide an aqueous DMSO [3]. The excess KOH is used as a catalyst during the reaction.

On the other hand, these type molecules show interesting electronic properties because they have two heteroatoms, N and O atoms. The structures and electronic properties of these molecules are performed as theoretically and experimentally due to versatile antimicrobial activity and they exhibited high DNA binding affinity as well as significant cytotoxic activity [4-10]. But, spectroscopic properties, quantum chemical studies and the interactions with DNA and HSA of PEPOE molecule have not been presented yet in literature. In view of the biological significance of oxime ether derivatives, a detailed conformational, spectroscopic properties such as IR, NMR and UV-Vis., physicochemical properties, frontier molecular orbitals (FMOs), molecular electrostatic potential (MEP) and thermodynamic properties of PEPOE have been undertaken for the first time. In addition, the molecular docking studies were performed as theoretically to explain the interaction of PEPOE with DNA and HSA.

2. Experimental and Theoretical Methods

2.1. Materials and measurements

All chemicals used in the experiments were purchased commercially and used without further purification. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded on a Varian Infinity plus spectrometer. UV-Vis and IR spectra were measured on an Agilent Cary60 and Perkin Elmer Spectrum Two FT-IR spectrophotometers, respectively.

2.2. Synthesis of 1-phenylethanone-O-pyropyl oxime ether (PEPOE)

The PEPOE was synthesized according to the literature [3]. The PEPOE was prepared by refluxing a mixture of a acetophenone (2.50 g, 20.80 mmol), hydroxylamine hydrochloride (1.38 g, 24.95 mmol), propyl chloride (1.960 g, 24.95 mmol) in the 25 mL DMSO and 10 mL H_2O solution, and 10.00 g KOH were mixed in a flask. The reaction mixture was stirred for 2 h under reflux at 60 °C. The reaction was monitored by TLC. The organic layer was extracted three times to obtained crude oxime ether, which was subject to bulb to bulb distillation, giving PEPOE (2.09 g) as yellow oil in %57 yield. The molecular weight of molecule ($C_{11}H_{15}NO$) is 177.12 g.mol-1. FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra confirmed the molecule, and the results have been given in Table 1.

Table 1. FT-IR and NMR data of PEPOE

FT-IR, ATR, frequency (cm^{-1})
3053vw, 2965w, 2939w, 2880w, 1685m, 1498w, 1447m, 1383m, 1369w, 1317w, 1265m, 1048s, 998s, 977m, 927s, 759s, 692s, 558s, 529m
^{1}H-NMR, DMSO-d_6, chemical shifts (ppm)
7.69–7.42 (*m*, 5H), 4.19 (*t*, 2H), 2.27 (*m*, 2H), 1.75 (*s*, 3H), 1.02 (*m*, 3H)
^{13}C-NMR, DMSO-d_6, chemical shifts (ppm)
154.48, 137.12, 129.12, 128.60, 126.23, 75.98, 22.80, 12.96, 10.72

2.3. DFT studies

The potential energy profile of the PEPOE was calculated as function of the corresponding dihedral angle by employing the Becke–Lee–Yang–Parr functional (B3LYP) method with 6-311++G(d,p) basis set to find out stable conformer [11]. The obtained stable conformer was further optimization by using 6-311++G(d,p) basis set. The spectroscopic and physicochemical dates of PEPOE were calculated by using the optimized geometry. The calculated vibrational frequencies were scaled by 0.958 for 4000-1700 cm^{-1} and 0.978 for 1700-400 cm^{-1} ranges, respectively [12,13]. The ^{1}H and ^{13}C-NMR chemical shifts were performed by using the Gauge-Independent Atomic Orbital (GIAO) method with reference to tetramethylsilane (TMS). The electronic excitation to the first 12 singlet-to-singlet excited states of the PEPOE was calculated using TDDFT with the B3LYP/6-311++G(d,p) level in EtOH solution using the CPCM method. The energies of HOMO, LUMO molecular orbitals, HOMO-LUMO energy gap, molecular electrostatic potential (MEP) and thermodynamic properties were determined at same level. All theoretical calculations were performed with Gaussian 09 software packed program by using HP Z240 model workstation [14].

2.4. Molecular docking

The molecular structures of B-DNA (PDB ID: 1BNA) and HSA (PDB ID: 1H9Z) were obtained from Protein Data Bank. The PEPOE molecule file in mol2 format was converted to PDB format with the Autodock program. All docking calculations were performed using AutoDock Vina program [15]. In addition, Discovery Studio 3.5 software was used to visualize the docked systems.

3. Results and Discussion

3.1. Conformational analysis and optimized structure

Conformational analysis of the PEPOE was carried out by using B3LYP/6-311++G(d,p) method in two steps. Firstly, *E* and *Z* isomers were determined according to the sequence of the groups around the C = N double bond of oxime group, and secondly, the potential energy surface (PES) of the compound was scanned around the dihedral angles C5-C6-C7-N1 (α) and C7-N1-O1-C9 (β) from 0 to 360° at increments of 10°. The structure with the minimum potential energy in the equilibrium geometry is more stable. The structure of the *E* and *Z* isomers of PEPOE molecule are shown in Figure 1 (a), while the PES obtained from rotation C6-C7 and N1-O1 bond are seen in Figure1 (b).

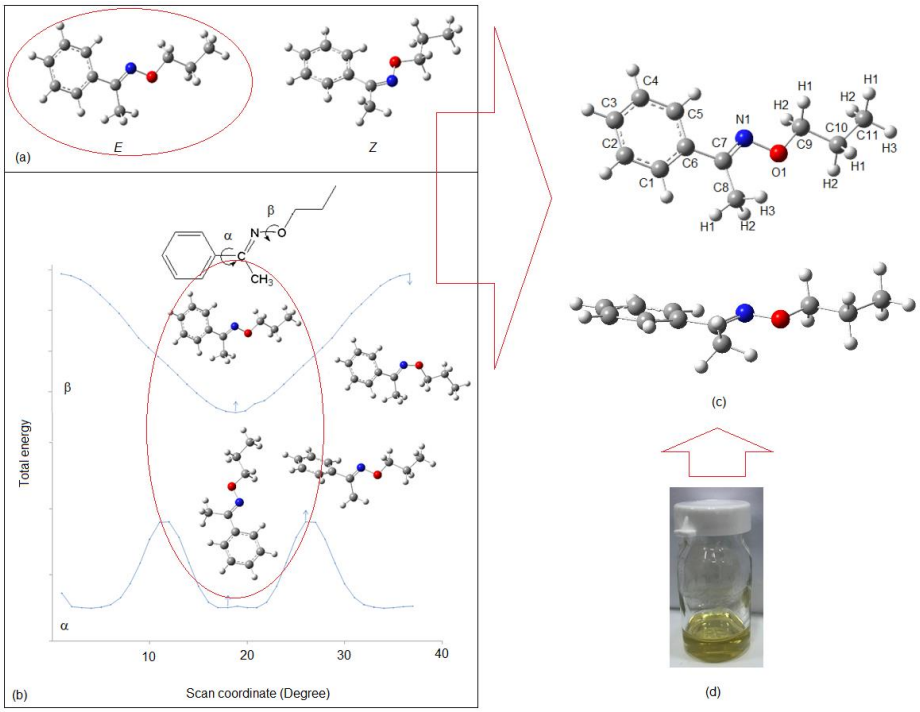

Figure 1. Conformation analysis and optimized structure of PEPOE molecule; (a) *E*- and *Z*- isomer, (b) potential energy surfaces for α and β rotations, (c) the optimized structure with atomic numbers and (d) the photo of liquid PEPOE molecule.

The *E* isomer of PEPOE molecule is more stable than the *Z* isomer by 10.84 kJ/mol. As seen in Figure 1 (b), the corresponding dihedral angles in the most stable conformer for PEPOE molecule were calculated as α = 168° and β = 177°. These results clearly indicate that the molecular structure of the PEPOE molecules is not planar, belongs to C_1 point group symmetry as seen in Figure 1 (c). The molecular structure of PEPOE (yellow oily liquid as seen in Figure 1 (d)) was re-optimized by the B3LYP / 6-311++G(d,p) level.

The bond lengths and angles of the PEPOE molecule are given in Table S1, while the optimized structure with atomic numbers is shown in Figure 1 (c). The average C-C bond length of aromatic ring of PEPOE is 1.397 Å. Bond lengths of C6-C7, C9-C10 and C10-C11 were calculated 1.507, 1.520 and 1.532 Å, respectively. The CN and NO bonds of oxime group were determined as 1.287 and 1.096 Å, respectively. These bond lengths are compatible with the data of other oxime molecules in the literature [16, 17]. The C-C-C bond angles of benzene ring in the PEPOE molecule are in range of 119.2-121.0°. The oxime bond angles C7-N1-O1 and N1-O1-C9 were calculated as 112.2 and 109.7°, respectively. In addition, C9-C10-C11 and O1-C9-C10 bond angles of propyl group were performed at 112.0 and 107.8°, respectively. These results indicate that the central atoms of these bond angles make sp^2 hybridization.

3.2. Spectroscopic properties

The experimental and theoretical infrared spectra of PEPOE are given in Figure 2. The calculated frequencies with intensities, observed FTIR wave numbers and probable assignments of PEPOE using B3LYP / 6-311++G(d,p) level are listed in Table S2. The calculated values are generally higher than the experimental values, so the scale factors were used to compute the calculated and experimental wave numbers [12,13].

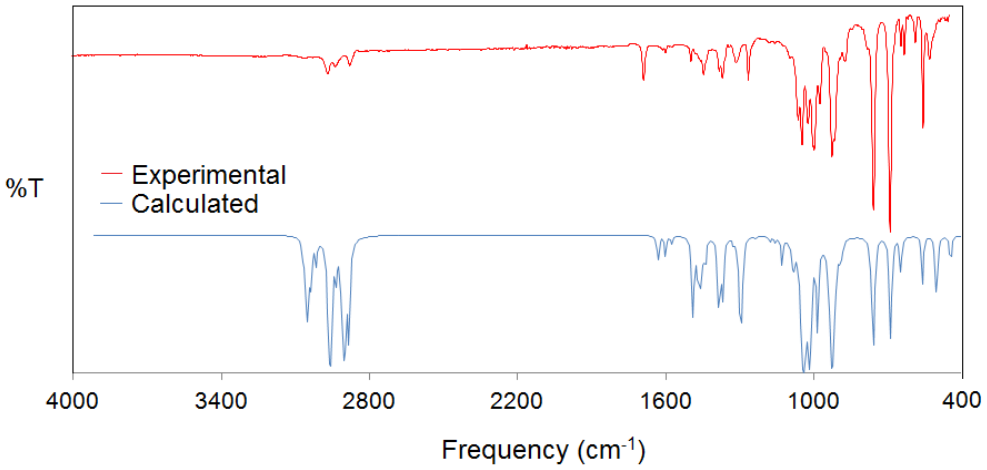

Figure 2. Experimental (red) and simulated (blue) infrared spectra of PEPOE.

The aromatic C-H stretching vibrations are observed in the region 3000-3100 cm^{-1} [18]. The aromatic C-H stretching vibration of PEPOE was measured as weak band at 3053 cm^{-1} (calcd. 3050 cm^{-1}). The aliphatic C-H vibrations were observed at 2965, 2939 and 2880 cm^{-1} as weak bands, while they were calculated between 2966 and 2883 cm^{-1}. The substitution sensitive C-H in-plane and the out of plane bending vibrations were performed at 1492-648 cm^{-1} and 1402-560 cm^{-1}, respectively. The experimental CN band of oxime group for title compound was measured at 1685 cm^{-1} as medium band and calculated at 1631 cm^{-1}. The aromatic CC stretching vibrations usually occur in the region 1625-1400 cm^{-1} [19]. The CC bands are of variable intensity and were measured at 1601 and 1369 cm^{-1}. These stretching bands were calculated at 1600-1371 cm^{-1}. The NO stretching vibration, which is significant characteristic band for the oxime molecules, is usually independent of the rest of the modes in the molecule. The NO stretching for PEPOE was observed at 927 cm^{-1} as sharp bands, while this vibration mode was calculated at 928 cm^{-1}. The other vibration modes are listed in Table S2.

The chemical shifts in the NMR spectrum information are considered as an integral part. These are valuable because of their spectral interpretation of their susceptibility to structural changes. The combined use of experimental and theoretical NMR methods is important in predicting the structure of biological molecules especially oximes [20]. The observed ^{1}H and ^{13}C-NMR spectra of compound PEPOE in DMSO solvent are given in Figure 3, while the ^{1}H and ^{13}C-NMR theoretical and experimental chemical shifts and the assignments of PEPOE are listed in Table S3. The PEPOE molecule has five aromatics and ten aliphatic hydrogens. The aromatic protons were observed as multiple peaks at 7.62 and 7.42 ppm. These chemical shifts were determined by DFT between 8.28 and 7.56 ppm. The aliphatic protons belong to methyl and propyl groups were measured as 2.27 ppm in methyl group and 4.19, 1.75 and 1.02 ppm in propyl group, while they were calculated between 4.14 and 0.85 ppm. The ^{13}C-NMR spectrum of PEPOE shows eleven different carbon atoms. The signal of C7 atom was observed at 154.48 ppm, while this chemical shift was calculated at 161.28 ppm. The measured chemical shifts between 137.12 and 126.23 ppm are assigned to phenyl carbon atoms and they are in harmony with calculated values as seen in Table S3. The four signals of aliphatic carbon atoms were measured in the range of 75.98-10.72 ppm (calcd. range 80.09-9.53 ppm). The ^{1}H and ^{13}C-NMR results of PEPOE molecule are well agreed with the chemical shifts reported for similar oxime molecules [16,17].

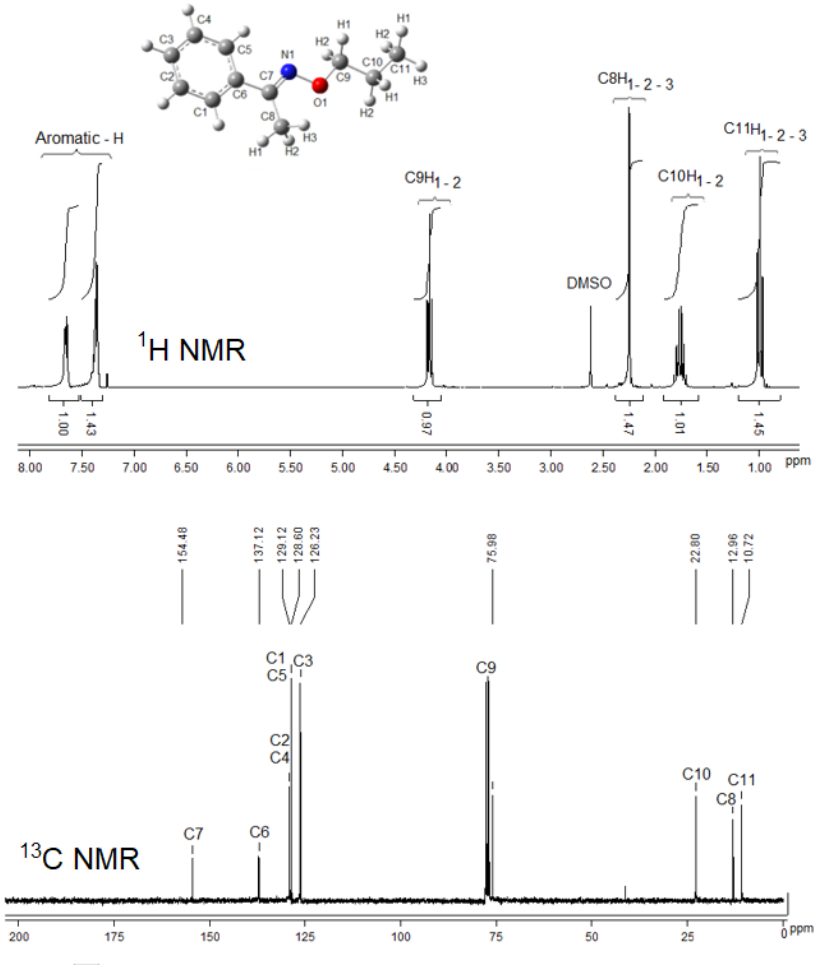

Figure 3. ^{1}H and ^{13}C-NMR spectra of PEPOE.

The absorption wavelength, excitation energies and oscillator strength (*f*) of PEPOE were determined by TDDFT/B3LYP method in EtOH solvent and summarized in Table S4. The first 12 lowest singlet-singlet spin allowed excited states were taken into account for the TDDFT calculation. The experimental UV-Vis. electronic spectra of PEPOE was investigated at the range of 800-200 nm in EtOH solution and compared with the theoretical spectrum given in Figure 4. The strong absorption bands were experimentally measured at 250 and 200 nm, while these absorption bands were calculated at 280 and 200 nm, respectively. It was determined that these absorption bands can be ascribed to the $\pi \rightarrow \pi^*$ transitions when the frontier molecular orbitals are examined by visual inspection.

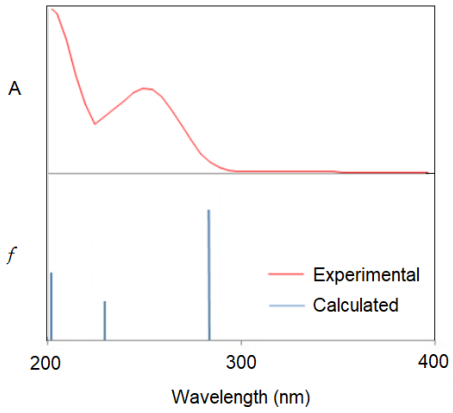

Figure 4. Experimental (red) and theoretical (blue) UV-Vis. spectra of PEPOE.

3.3. Physicochemical properties

For organic derivatives, the HOMO and LUMO are important for determining electron transfer and movements of electrons. This is useful for many reactions and the organic semiconductors of which HOMO-LUMO band gap is most important. The molecules with large HOMO-LUMO band gaps are generally found to be stable and not reactive. The HOMO and LUMO energies of PEPOE were performed as -6.229 and -1.278 eV, respectively. The band gap was calculated as 4.951 eV. The HOMO and LUMO molecular orbitals are presented in Figure 5 (a). In a molecule, the ionization potential (IP) is related to HOMO energy while the electron affinity (EA) is determined by the LUMO energy. Therefore, The IP and EA are determined as below equations [21],

$$IP = -E_{HOMO},\ EA = -E_{LUMO}$$

Using the IP and EA, the global chemical reactivity descriptors belong to a molecule were calculated by below equations [21]:

hardness, $\eta = (IP-EA) / 2 = 2.475$,

electronegativity, $\chi = (IP+EA) / 2 = 3.754$,

chemical potential, $\mu = -(IP+EA) / 2 = -3.754$,

softness $S= 1/2\eta = 1.238$ and

electrophilicity index $\omega= \mu^2/2\ \eta =2.847$.

The chemical reactivity of a molecule can be visualized with the help of three-dimensional MEP surfaces. To determine the reactivity of the PEPOE molecule, the MEP surface was plotted using B3LYP/6-311++G(d,p) as presented in Figure 5 (b). The color code of this map ranges from $-3.486e^{-2}$ and $+3.486e^{-2}$ a.u., where blue shows the strongest attraction and red indicates repulsion. From MEP surface, the negative potential areas are on the nitrogen and oxygen atoms of the oxime group while positive potential areas are on the phenyl hydrogen atoms. These results provide information about the region where the compounds may have inter-molecular interactions, especially with biological molecules [22].

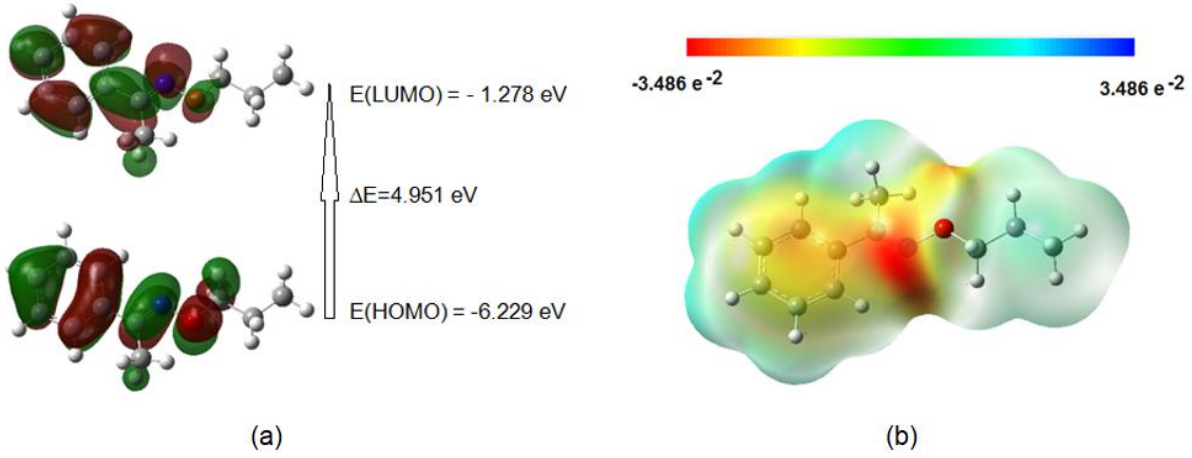

Figure 5. (a) HOMO and LUMO orbitals, (b) MEP of PEPOE.

The standard thermodynamic functions were obtained theoretically by B3LYP/6-311++G(d,p) level from the harmonic frequencies are presented in Figure 6. Thermodynamic functions such as heat capacity (C), entropy (S) and enthalpy (H) increase with rising temperature due to molecular vibrations densities [23]. The disorder increases with thermal agitation, so the entropy increases with increasing temperature. The slope of this increase is higher than the other thermodynamic parameters (C and H), as seen Figure 6.

The correlation equations with temperatures between C, S and H were determined with quadratic formulas as given below:

$C\ (J/mol.K) = -16.2090 + 0.7768\ T - 0.0003\ T^2$ $(R^2 = 0.9985)$

$S\ (J/mol.K) = 238.6800 + 0.7016\ T - 0.0001\ T^2$ $(R^2 = 0.9868)$

$H\ (kJ/mol) = 612.6200 + 0.0509\ T + 0.0002\ T^2$ $(R^2 = 0.9982)$

The corresponding fitting factors (R^2) for C, S and H were calculated as 0.9985, 0.9868 and 0.9982, respectively.

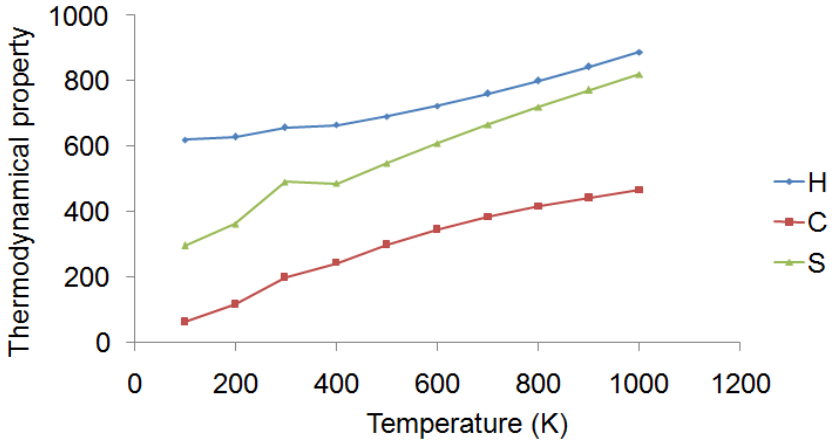

Figure 6. Graphs representing dependence of C, S and H on temperatures.

3.4. Molecular docking

The molecular docking studies are very important for experimental anti-cancer studies due to prevent loss of time and money. It is also important to give direction to experimental work. Therefore, PEPOE-DNA (PDB code: 1BNA) interactions were examined to find prefer binding mode and binding energy. The interaction energy was calculated as molecular mechanic method with AutoDock Vina program. The structure of the selected DNA of which PDB code was 1BNA is dodecamer with a d(CGCGAATTCGCG) sequence. The aromatic ring of the PEPOE and DNA base pair was found to exhibit hydrophobic interaction. In addition, the hydrogen bonding was observed between the O atom of PEPOE and the H atom of DG4 base pair. The length of this hydrogen bond was calculated as 2.257 Å. The most favorable conformation of the docked poses, which is highest binding energy, revealed that PEPOE fitted closely in to the cavity of the target DNA in the minor groove within G-C rich region, as seen in Figure 7 (a). The binding free energy of PEPOE was calculated to be -20.92 kJ/mol. The stable binding of the molecule to DNA groove also provides non-binding interactions, which are often described as van der Waals and hydrophobic interactions besides the hydrogen bonding.

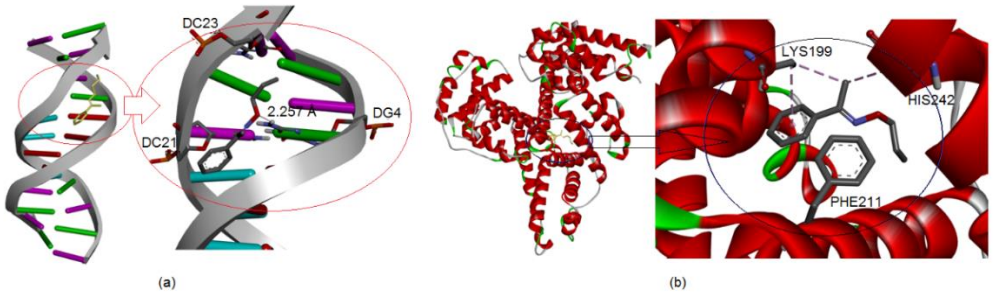

Figure 7. (a) Computational docking models illustrating the interactions between DNA and PEPOE, b) Molecular docking of the most favorable docked structure for PEPOE in subdomain IIA of HSA.

Molecular docking between PEPOE and Human Serum Albumin (HSA) is playing an important role because it allows the duration and intensity of pharmacological and toxicological properties to be examined [24,25]. Human Serum Albumin (HSA), PDB code is 1H9Z, was selected for molecular docking. This protein consists of three homologous domains (I-III), and each domain has two sub-domains (A and B). The best energy ranked result of PEPOE binding with HSA is given in Figure 7 (b). The modelling result suggested that this drug interacts with the protein in sub-domain IIA. The binding free energy of PEPOE with 1H9Z was calculated as -26.78 kJ/mol. The PEPOE molecule is mainly surrounded by Lys199, Phe211 and His242 etc. in its vicinity. The hydrophobic interaction plays the major role as indeed predicted by AutoDock Vina calculations.

4. Conclusion

In this work, the structural, spectroscopic and physicochemical properties of PEPOE molecule were calculated with using DFT/B3LYP method and 6-311++G(d,p) basis set. The molecular docking properties were investigated using AutoDock Vina program. In addition, FTIR, NMR and UV-Vis. spectroscopic properties were studied as experimentally. In summary, the conclusions are as follows.

(i) In the most stable geometry of PEPOE, *E* isomer is more stable than *Z* isomer and α, β dihedral angles are calculated as 168 and 177°, respectively.

(ii) The spectroscopic data such as vibrational and NMR were calculated B3LYP/6-311++G(d,p) level and compared with the experimental values.

(iii) The UV-Vis. spectra were measured range of 800-200 nm in EtOH solution, and calculated by using TDDFT method, so the all electronic transitions of PEPOE can be $\pi \rightarrow \pi^*$ transitions.

(iv) The HOMO-LUMO band gap was calculated as 4.951 eV.

(v) The total electron density lies in the range $-3.486e^{-2}$ and $+3.486e^{-2}$ a.u. The negative potential sites are on oxime group.

(vi) The enthalpy (H), entropy (S) and heat capacity (C) values are increasing with rising temperature due to the increasing molecular vibrations intensities.

(vii) The binding free energies were calculated as -20.92 kJ/mol for DNA and -26.78 kJ/mol for HSA.

(viii) The PEPOE molecule was docked to DNA through minor groove within G-C rich region, while the molecule was linked to protein via hydrophobic interactions in subdomain IIA

Supporting Information

The supporting information is available at the end of the manuscript. The selected bond distances and angles of PEPOE molecule were listed in Table S1. The calculated and observed IR frequencies with probable assignments were given in Table S2, the theoretical and experimental ^{1}H and ^{13}C-NMR chemical shifts and the assignments were presented in Table S3 and the absorption wavelength, excitation energies and oscillator strength (*f*) were summarized in Table S4.

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Supporting Information

Table S1. Selected geometric parameters of PEPOE molecule

Bond Length (Å)	DFT	Bond Angles (°)	DFT
C6-C1	1.402	C8-C7-C6	122.7
C1-C2	1.395	C7-C6-C5	120.3
C2-C3	1.390	C6-C5-C4	121.0
C3-C4	1.397	C5-C4-C3	120.5
C4-C5	1.388	C4-C3-C2	119.2
C5-C6	1.408	C3-C2-C1	120.4
C6-C7	1.489	C2-C1-C6	121.1
C7-C8	1.507	C8-C7-N1	121.3
C7-N1	1.287	C7-N1-O1	112.2
N1-O1	1.096	N1-O1-C9	109.7
O1-C9	1.096	C6-C7-N1	116.0
C9-C10	1.520	C1-C6-C7	121.9
C10-C11	1.532	C1-C6-C5	117.8
C3-H	1.084	H1-C8-H2	108.8
C4-H	1.084	H1-C8-H3	108.8
C5-H	1.081	H2-C8-H3	106.4
C1-H	1.082	H1-C9-H2	108.2
C2-H	1.084	H1-C10-H2	106.8
C8-H1	1.394	H1-C11-H2	107.7
C8-H2	1.434	H1-C11-H3	107.6
C8-H3	1.086	H2-C11-H3	107.6
C9-H1	1.093	O1-C9-C10	107.8
C9-H2	1.093	C5-C4-C4H	119.5
C10-H1	1.095	C4H-C4-C3	120.0
C10-H2	1.095	C4-C5-C5H	120.2
C11-H1	1.094	C4-C3-C3H	120.4
C11-H2	1.094	C3H-C3-C2	120.4
C11-H3	1.092	C3-C2-C2H	120.2
		C2H-C2-C1	119.4
		C2-C1-C1H	118.2
		C1H-C1-C6	120.6
		C9-C10-C11	112.0
		C7-C8-C8H1	113.1
		C7-C8-C8H2	109.7
		C7-C8-C8H3	109.8

Table S2. Experimental and calculated vibrational wavenumbers of PEPOE with their assignment (wavenumber in cm^{-1})

Mod	Assignments	Experimental	Unscaled	Scaled	Intensity
15	$\delta CO_{C9-O1} + \tau CH_{C8-H1-2-3}$		458	448	6
17	$\delta CN_{C7-N1} + \tau CH_{C11-H1-2-3} + \gamma CH_{C8-H2}$	529m	515	504	20
18	$\gamma CH_{fen} + \gamma CH_{C8-H2}$	558s	573	560	11
20	$\delta CC_{fen} + \delta NO_{N1-O1}$		663	648	10
21	γCH_{fen}	692s	705	689	41
23	γCH_{fen}	759s	776	759	40
24	$\delta CC_{fen} + \delta CC_{C7-C8}$		786	769	11
27	$\delta CC_{fen} + \gamma CH_{C11-H3}$		913	893	5
28	γCH_{fen}		932	911	5
29	νNO_{N1-O1}	927s	949	928	146
32	$\gamma CH_{C8-H1} + \gamma CH_{C8-H3}$	977m	1008	986	28
34	$\nu CC_{C9-C10} + \delta CC_{C10-C11} + \delta CH_{C8-H}$	998s	1041	1018	108
37	$\nu CO_{C9-O1} + \delta CC_{C7-C8}$	1048s	1066	1043	235
39	$\delta CH_{fen} + \delta CH_{C8-H1} + \delta CH_{C8-H2}$		1110	1086	7
40	$\nu CC_{C9-C10} + \delta CH_{fen}$		1155	1130	5
46	$\nu CC_{C6-C7} + \delta CC_{fen} + \delta CH_{C9-H} + \delta CH_{C10-H}$	1265m	1321	1292	26
47	$\delta CH_{C9-H} + \delta CH_{C10-H}$	1317w	1330	1301	16
50	$\nu CC_{fen} + \gamma CH_{C8-H1} + \gamma CH_{C8-H2} + \gamma CH_{C8-H3}$	1369w	1402	1371	18
51	$\gamma CH_{C8-H} + \gamma CH_{C9-H}$		1413	1382	8
52	$\gamma CH_{C8-H} + \gamma CH_{C9-H}$	1383w	1419	1388	19
53	$\delta CH_{C8-H1} + \delta CH_{C8-H2} + \delta CH_{C8-H3}$		1473	1441	7
55	$\gamma CH_{C8-H1} + \gamma CH_{C8-H2} + \gamma CH_{C8-H3}$	1447m	1493	1460	11
57	$\gamma CH_{C11-H1} + \gamma CH_{C11-H2} + \gamma CH_{C11-H3}$		1502	1469	8
59	$\gamma CH_{C9-H} + \gamma CH_{C10-H} + \gamma CH_{C11-H1}$	1498w	1524	1490	23
60	$\nu CC_{fen} + \delta CH_{fen}$		1526	1492	5
62	νCC_{fen}	1601w	1636	1600	5
63	νCN_{C7-N1}	1685m	1668	1631	7
64	$\nu CH_{C9-H1} + \nu CH_{C9-H2}$	2880w	3009	2883	36
65	$\nu CH_{C11-H1} + \nu CH_{C11-H2} + \nu CH_{C11-H3}$		3024	2897	33
66	$\nu CH_{C10-H1} + \nu CH_{C10-H2}$		3031	2904	46
67	$\nu CH_{C8-H1} + \nu CH_{C8-H2} + \nu CH_{C8-H3}$		3033	2906	8
68	$\nu CH_{C9-H} + \nu CH_{C10-H}$		3042	2914	9
69	$\nu CH_{C9-H} + \nu CH_{C10-H} + \nu CH_{C11-H1} + \nu CH_{C11-H2}$		3064	2935	9
70	$\nu CH_{C10-H1} + \nu CH_{C10-H2} + \nu CH_{C11-H1} + \nu CH_{C11-H2}$	2939w	3088	2958	73
71	νCH_{C11-H3}	2965w	3093	2963	36

72	νCH_{C8-H1}		3096	2966	14
73	νCH_{C8-H3}		3148	3016	6
75	νCH_{fen}		3171	3038	10
76	νCH_{fen}	3053vw	3184	3050	24
77	νCH_{fen}		3192	3058	13

s: strong, m: medium, w: weak, vw: very weak; ν: stretching, δ: in-plane bending,
γ: out-of- plane bending, τ: torsion, Scaled factor: 0,958 for 4000-1700 cm^{-1}; 0,978 for 1700-400 cm^{-1}.

Table S3. Experimental and calculated ^{1}H and ^{13}C NMR chemical shifts (ppm) of PEPOE

Atoms	Experimental	DFT/GIAO	Atoms	Experimental	DFT/GIAO
^{1}H-NMR			^{13}C-NMR		
C2H		7.65	C1	128.60	131.52
C3H	7.42	7.57	C2	128.60	133.39
C4H		7.56	C3	129.12	134.01
C1H	7.69	7.75	C4	129.12	132.56
C5H		8.28	C5	126.23	129.23
C8H1		1.85	C6	137.12	143.17
C8H2	2.27	2.06	C7	154.48	161.28
C8H3		3.08	C8	12.96	11.41
C9H1	4.19	4.14	C9	75.98	80.09
C9H2		4.07	C10	22.80	24.52
C10H1	1.75	1.77	C11	10.72	9.53
C10H2		1.76			
C11H1		0.85			
C11H2	1.02	0.86			
C11H3		1.19			

Table S4. Experimental and calculated electronic transitions, oscillator strengths and their assignments for PEPOE

Experimental			Calculated				
λ_{max} (nm)	$\varepsilon * 10^{-5}$ ($dm^3mol^{-1}cm^{-1}$)	ΔE (eV)	λ_{max} (nm)	ΔE (eV)	f_{os}	Assignment (CI coeff)	Character
250	1.8186	4.79	280	4.27	0.5027	H→L (%97)	π(phen/oxime)→π*(phen /oxime)
			227	5.27	0.1579	H→L+6 (%44)	π(phen /oxime)→π*(phen /oxime)
						H-1→L +1(%45)	π(phen)→π*(phen)
200	3.5811	5.98	200	5.98	0.1937	H-1→L (%30)	π(phen)→π*(phen /oxime)
						H→L+1 (%61)	π(phen /oxime)→π*(phen)

f_{os} = Oscillator strength, H = Highest occupied molecular orbital, L = Lowest unoccupied molecular orbital, phen. = phenyl