



COMPUTATIONAL CHEMISTRY: MOLECULAR STRUCTURE, SPECTROSCOPIC (UV-VISIBLE AND IR), ELECTRONIC, CHEMICAL AND THERMOCHEMICAL ANALYSIS OF 3'-PHENYL-1,2-DIHYDROSPIRO[INDENO[5,4-B]FURAN-7,2'-OXIRAN]-8(6H)-ONE

Vishnu A. Adole*¹, Vinayak R. Bagul², Satish A. Ahire³, Rajendra K. Pawar⁴, Ganesh B. Yelmame⁵, Abhijit R. Bukane¹

¹Department of Chemistry, Mahatma Gandhi Vidyamandir's Arts, Science and Commerce College, Manmad, Nashik, India (Affiliated to SP Pune University, Pune)

²Department of Chemistry, Mahatma Gandhi Vidyamandir's Arts, Science and Commerce College, Surgana, Nashik, India (Affiliated to SP Pune University, Pune)

³Department of Chemistry, Mahatma Gandhi Vidyamandir's Loknete Vyankatrao Hiray Arts, Science and Commerce College Panchavati Nashik, India (Affiliated to SP Pune University, Pune)

⁴Department of Chemistry, Mahatma Gandhi Vidyamandir's MSG Arts, Science and Commerce College, Malegaon, Nashik, (Affiliated to Savitribai Phule Pune University, Pune)

⁵Department of Chemistry, Mahatma Gandhi Vidyamandir's SPH Arts, Science and Commerce College, Nampur, Nashik, India (Affiliated to Savitribai Phule Pune University, Pune)

*Corresponding author: vishnuadole86@gmail.com

ABSTRACT

Present investigation deals with the synthesis and density functional theory study (DFT) of a new epoxide derivative; 3'-phenyl-1,2-dihydrospiro[indeno[5,4-b]furan-7,2'-oxiran]-8(6H)-one (PHIFO). The synthesis of a PHIFO has been carried out by the reaction of (E)-7-benzylidene-1,2,6,7-tetrahydro-8H-indeno[5,4-b]furan-8-one with alkaline hydrogen peroxide in ethanol at room temperature. The structure of a synthesized epoxide derivative is affirmed on the basis of a proton nuclear magnetic resonance spectroscopy. The geometry of a PHIFO is optimized by using the density functional theory method at the B3LYP/6-31G(d,p) basis set. The optimized geometrical parameters like bond length and bond angles have been computed. The absorption energies, oscillator strength, and electronic transitions have been derived at the TD-DFT method at the B3LYP/6-31G(d,p) level of theory for B3LYP/6-31G(d,p) optimized geometries. The effect of polarity on the absorption energies is discussed by computing UV-visible results in dichloromethane (DCM). The vibrational wavenumbers are assigned to various functional groups and the gas phase vibrational data is compared with vibrational data obtained in the DCM. Quantum chemical parameters have been determined and examined. Molecular electrostatic potential (MEP) surface plot analysis has been carried out at the same level of theory. Some thermodynamic functions have likewise been examined. Mulliken atomic charge study is also discussed in the present study. The thermochemical data consisting total energy, heat capacity at constant volume, total entropy, zero-point vibrational energy, and rotational constants have been evaluated from harmonic vibrational frequencies.

Keywords: 3'-Phenyl-1,2-dihydrospiro[indeno[5,4-b]furan-7,2'-oxiran]-8(6H)-one, B3LYP/6-31G(d,p), MEP, TD-DFT.

1. INTRODUCTION

The chemistry of heterocyclic compounds has been extended to a colossal degree. Several heterocyclic scaffolds frameworks have been found to apply incredible pharmacological properties. Due to their diverse applications in medicinal chemistry and chemical biology, the research has been explored tremendously [1-4]. Numerous new heterocyclic compounds have

been synthesized in view of their remedial applications [5-7]. Dihydrofuran ring, the 2-arylidene indanone, and the chalcone skeleton have been found to exert good biological applications [8-13]. To understand the biological activity, it is very much necessary to know their physical and chemical properties. DFT is a method that can provide a good deal of information regarding the physical and chemical behavior of the molecules [14-

18]. The properties like bond lengths, bond angles, dipole moment, charge distribution, reactive sites, etc. could be examined based on the basis of computation study by using the DFT method [19-21].

Different spectroscopic investigations like IR, UV/Visible spectra, Raman, and NMR is possible by means of a computational study [22-31]. Besides, DFT computations can also predict frontier molecular orbital energies and thereby the electronic excitation energy also. The comparative analysis between theoretical experiments and experimental results provides a good deal of information for the prediction of correct vibrational assignments. Importantly, the study of the reaction mechanisms is made easier due to computation calculations based on DFT. In light of various important aspects discussed above, here in this paper, we wish to report the synthesis and density functional theory investigation of 3'-Phenyl-1,2-dihydrospiro[indeno[5,4-*b*]furan-7,2'-oxiran]-8(6*H*)-one (PHIFO). To the best of our knowledge, this is the first report on the synthesis and computational study of the title molecule. In the current examination, we have emphasized the crucial aspects like structural, electronic, and chemical parameters for a better understanding of the physical and chemical behaviour of the title molecule.

2. MATERIAL AND METHODS

2.1. General remarks

The chemicals with high purity were purchased from sigma laboratory Nashik. The chemicals were used as received without any further purification. Melting point was determined in open capillary and uncorrected. ¹H NMR spectra was recorded with a Bruker using CDCl₃ as solvent. Reaction was monitored by thin-layer chromatography using aluminium sheets with silica gel 60 F254 (Merck).

2.2. Synthesis of PHIFO

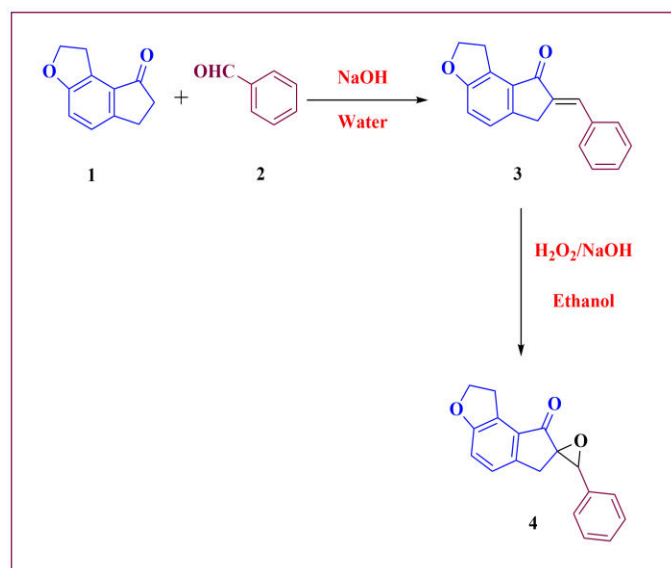
Table 1: Physicochemical and Spectral data of title compound

Systematic Name of the Product	3'-phenyl-1,2-dihydrospiro[indeno[5,4- <i>b</i>]furan-7,2'-oxiran]-8(6 <i>H</i>)-one
Abbreviation used	PHIFO
Physicochemical data	Yield: 70%, Colour: white
¹ H NMR (500 MHz, CDCl ₃)	2.87 (d, <i>J</i> = 17.8 Hz, 1H), 3.18 (d, <i>J</i> = 17.8 Hz, 1H), 3.58 (t, <i>J</i> = 8.9 Hz, 2H), 4.00 (s, 1H), 4.69 (t, <i>J</i> = 8.9 Hz, 2H), 7.04 (m, 2H), 7.32 (dd, <i>J</i> = 6.8, 2.0 Hz, 2H), 7.40 (m, 3H)

2.3. Computational work

DFT calculations were performed on an Intel (R) Core (TM) i5 computer using Gaussian-03(W) program

The title molecule PHIFO is synthesized is synthesized from (*E*)-7-benzylidene-1,2,6,7-tetrahydro-8*H*-indeno[5,4-*b*]furan-8-one. The synthesis method is depicted in Scheme 1. The compound (*E*)-7-benzylidene-1,2,6,7-tetrahydro-8*H*-indeno[5,4-*b*]furan-8-one is synthesized as per our previously reported method [8]. For the synthesis of PHIFO, the compound 3 (10mmol) was dissolved in ethyl alcohol. To this, appropriate amount of 6% H₂O₂ solution was added. Then 1mL 5% NaOH solution was added slowly and the solution was stirred on magnetic stirred at room temperature. The reaction was continuously monitored using thin layer chromatography (n-hexane/EtOAc [7:3]). The crude product was obtained by adding crushed ice. The obtained crude product was dried naturally and recrystallized from hot ethanol. The synthesized product was characterized using ¹H NMR spectroscopic method. The physicochemical and spectral data of the title compound is given in Table 1.



Scheme 1 Synthesis of title compound

package without any constraint on the geometry [32]. The geometry of the molecules studied in this is optimized by DFT/B3LYP method using 6-31G(d,p)

basis set. The FMO analysis and quantum chemical study has been performed using same basis set. Absorption energies (λ in nm), oscillator strength (f), and transitions of title molecule have been calculated at TD-B3LYP/6-31G(d,p) level of theory for B3LYP/6-31G(d,p) optimized geometries in gas phase and dichloromethane (DCM). To investigate the reactive sites of the title molecules, the molecular electrostatic potential (MEP) was computed using the same method. All the calculations were carried out for the optimized structure in the gas phase.

3. RESULTS AND DISCUSSION

3.1. Chemistry

The title compound has been synthesized by oxidation reaction of (*E*)-7-benzylidene-1,2,6,7-tetrahydro-8*H*-indeno [5,4-*b*] furan-8-one with alkaline hydrogen peroxide solution. The structure of the title compound is confirmed on the basis of proton magnetic resonance spectroscopy. The compound has two characteristic peaks at 2.87 ppm (d, $J = 17.8$ Hz, 1H) and 3.18 (d, $J = 17.8$ Hz, 1H). These two protons are "diastereotopic" and couples with each other by a germinal coupling. This coupling is evidence for the formation of the epoxide. Other signals are appeared as expected and exactly match with the structure of the title molecule.

3.1.1. Computational study

3.1.1.1. Structural investigation

The structure of the title molecule **PHIFO** with optimized molecular geometry is given in Fig. 1. The molecule PHFO is having C1 point group symmetry and the dipole moment is 2.6731 Debye. The E(RB3LYP) energy of the title molecule is -920.0012 a.u. which indicates its stability. The data of bond lengths and bond angles of the title molecule PHIFO are presented in Table 2 and Table 3. The carbonyl (C16-O20) bond length is 1.2189 Å in the title molecule. The epoxide skeleton has bond lengths 1.4991 (C21-C22), 1.4262 (C21-O34), and 1.4271 Å (C22-O34). The C21-C22-C23 bond angle is 126.7535° and the C23-C22-O34 bond angle is 113.7126°. The other data in regards to bond lengths and bond angles in the title molecule is ideally matching with the structural arrangement.

3.1.1.2. Frontier molecular orbital and electronic absorption studies

The HOMO-LUMO representation of the title molecule is delineated in Fig. 2. The HOMO-LUMO

study gives data in regard to the charge transfer phenomenon within the molecule. The HOMO-LUMO energy gap in the title molecule is 4.21 eV which demonstrates the inevitable charge transfer occurring inside the molecule. The HOMO-LUMO energies are exceptionally indispensable for evaluating the chemical reactivity of the molecules. Based on HOMO-LUMO energies, we have examined different electronic and chemical parameters of the title molecule. These parameters of the title molecule are discussed and presented in Tables 4 and 5.

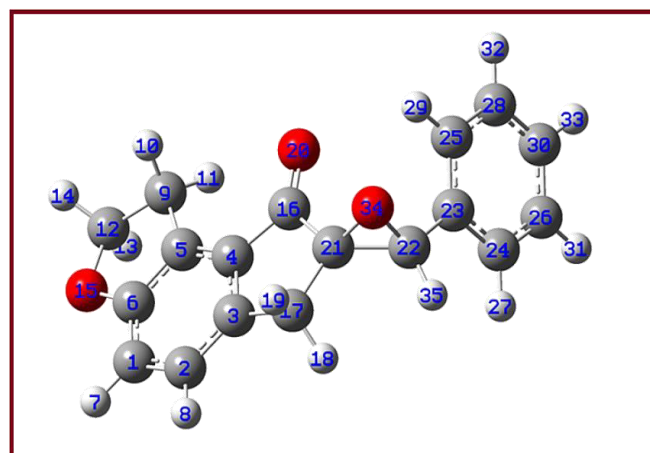


Fig. 1: Optimized Molecular Structure of the title molecule

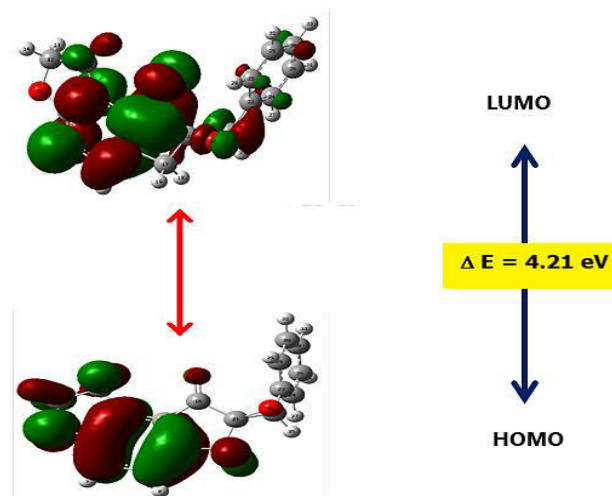


Fig. 2: HOMO-LUMO of title molecule

The properties like ionization potential (I), electronegativity (χ), electron affinity (A), hardness (η), softness (σ), chemical potential (μ), electrophilicity

index (ω), and charge transfer have been built up (ΔN_{max}). The softness and hardness values show the polarizability and in this manner chemical reactivity also. The electrophilicity value of the title molecule is 3.52 eV which recommends that it is a decent electrophile. The charge transfer value in the title

molecule is 1.83 eV. The important electronic absorption band in the title molecule PHIFO is 362.22 nm ($f = 0.0061$) with excitation energy of 3.4229 eV. The UV-spectra of the title compound in gas phase and DCM computed by TD-DFT method at B3LYP/6-31G (d,p) basis set is given in Fig. 3 and Fig. 4 respectively.

Table 2: Optimized bond lengths of title molecule at B3LYP/6-31(d,p)

Bond lengths (Å)					
C1-C2	1.401	C9-C12	1.5504	C22-H35	1.0938
C1-C6	1.3973	C12-H13	1.0957	C23-C24	1.4015
C1-H7	1.0847	C12-H14	1.0919	C23-C25	1.4001
C2-C3	1.3943	C12-O15	1.4566	C24-C26	1.3939
C2-H8	1.0865	C16-O20	1.2189	C24-H27	1.0877
C3-C4	1.4076	C16-C21	1.524	C25-C28	1.394
C3- C17	1.5158	C17-H18	1.0956	C25-H29	1.0824
C4- C5	1.3908	C17-H19	1.0975	C26-C30	1.396
C4-C16	1.4758	C17-C21	1.5315	C26-H31	1.0861
C5- C6	1.3936	O20-H29	2.6072	C28-C30	1.3963
C5- C9	1.5069	C21-C22	1.4991	C28-H32	1.0861
C6- O15	1.3629	C21-O34	1.4262	C30-H33	1.0862
C9-H10	1.096	C22-C23	1.4903	C23-C24	-
C9-H11	1.0932	C22-O34	1.4271	C23-C25	-

Table 3: Optimized bond angles of title molecule at B3LYP/6-31(d,p)

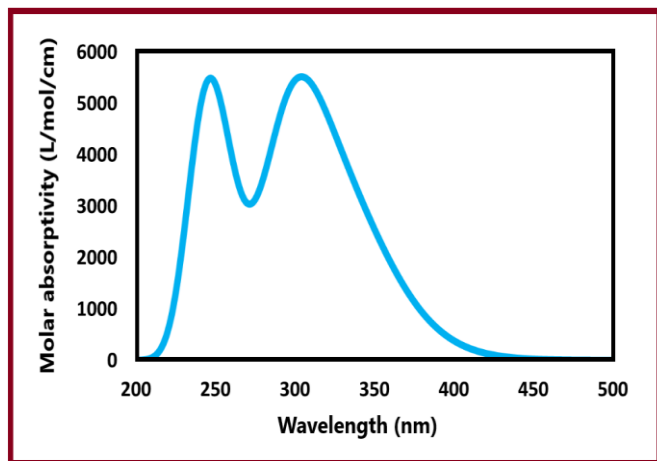
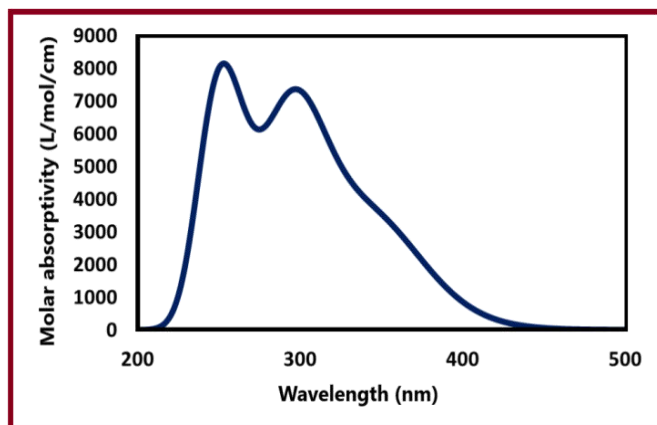
Bond angles (°)					
C2-C1-C6	118.6545	H11-C9-C12	112.5448	C21-C22-H35	113.5225
C2-C1-H7	121.256	C9-C12-H13	111.7677	C23-C22-H35	119.4578
C6-C1-H7	120.0895	C9-C12-H14	113.703	C23-C22-O34	113.7126
C1-C2-C3	119.9991	C9-C12-O15	107.3076	C23-C22-H35	113.6407
C1-C2-H8	119.4249	H13-C12-H14	108.7959	C34-C22-H35	118.4942
C3-C2-H8	120.576	H13-C12-O15	107.5756	C22-C23-C24	122.0955
C2-C3-C4	120.0448	H14-C12-C15	107.4165	C22-C23-C25	119.3815
C2-C3-C17	128.9282	C6-O15-C12	107.5602	C23-C24-C26	120.5252
C4-C3-C17	111.0135	C4-C16-O20	127.3723	C23-C24-H27	119.6578
C3-C4-C5	120.7167	C4-C16-C21	105.7042	C26-C24-H27	119.8167
C3-C4-C16	110.4315	O20-C16-C21	126.9204	C23-C25-C28	119.9576
C5-C4-C16	128.8508	C3-C17-H18	112.8484	C23-C25-H29	119.0377
C4-C5-C6	118.191	C3-C17-H19	111.6245	C28-C25-H29	121.0015
C4-C5-C9	133.127	C3-C17-C21	103.3559	C24-C26-C30	119.8817
C6-C5-C9	108.6586	H18-C17-H19	107.1026	C24-C26-H31	119.8673
C1-C6-C5	122.3918	H18-C17-C21	112.68	C30-C26-H31	120.2484
C1-C6-O15	124.253	H19-C17-C21	109.2544	C25-C28-C30	120.4714
C5-C6-O15	113.3548	C16-C21-C17	107.673	C25-C28-H32	119.5419
C5-C9-H10	110.9142	C16-C21-C22	123.0193	C30-C28-H32	119.9868
C5-C9-H11	113.0869	C16-C21-O34	119.0472	C26-C30-C28	119.7763
C5-C9-C12	101.2604	C17-C21-C22	122.1392	C26-C30-H33	120.0745
H10-C9-H11	106.8072	C17-C21-O34	119.3887	C28-C30-H33	120.1484
H10-C9-C12	112.3245	C21-C22-C23	126.7535	-	-

Table 4: Electronic parameters of PHIFO

Entry	E (a.u.)	E _{HOMO} (eV)	E _{LUMO} (eV)	I (eV)	A (eV)	E _g (eV)
PHIFO	-920.0012	-5.96	-1.75	5.96	1.75	4.21

Table 5: Global reactivity parameters of PHIFO

Entry	χ (eV)	η (eV)	σ (eV ⁻¹)	ω (eV)	μ (eV)	ΔN_{max} (eV)	Dipole Moment (Debye)
PHIFO	3.85	2.10	0.48	3.52	-3.85	1.83	2.6731

**Fig. 3: UV spectrum by TD-DFT method at 6-31G (d,p) basis set in gas phase****Fig. 4: UV spectrum by TD-DFT method at 6-31G (d,p) basis set in DCM**

The electronic absorption studies for the title compound were computed in gas phase and DCM. The properties like absorption wavelength (λ in nm), coefficient, oscillator strength (f), and electronic transitions were simulated up to four singlet excited states (S_1 , S_2 , S_3 and S_4). The absorption data in gas phase revealed that first

singlet excited state in gas phase comprises of three electronic transitions namely 70 to 74, 71 to 74 and 72 to 74. On the other hand, the electronic transitions for the first excited state in DCM are four (70 to 74, 71 to 74, 72 to 74 and 73 to 74). The absorption maximum in gas phase is located at 362.22 nm which is shifted to lower wavelength in DCM (at 354.38 nm). This information uncovered that there is strong hypsochromic shift observed for the first singlet excited state in the polar medium. This is attributed to the stabilization of excited state as compared to the ground state in the title molecule. However, the results are contrasting for the second singlet excited state. The absorption wavelength has been found to increase from 337.23 nm (gas phase) to 348.84 nm (DCM). This outcome infers that the ground state is more stabilized than this excited state. The second singlet excited state in the gas phase consists of two configurations and in DCM consists of four configurations. Both gas phase and DCM in the third singlet excited have three configurations and bathochromic shift has been linked from gas phase to DCM. Likewise, the data have been collected for fourth, fifth and sixth singlet excited states. The sixth singlet excited state contains only one configuration in both gas phase and DCM.

3.1.1.3. Mulliken atomic charges and MEP analysis

The pictorial representation of Mulliken charge density in the title molecule is given in Fig. 5 and the data are given in Table 7. The data presented in this indicate all hydrogen atoms in the molecule PHIFO are having positive charge density and therefore electropositive in nature. Amongst all carbon atoms the C6 is the most positive (0.238699) and C9 is the most negative (-0.167357) in nature. On the other hand, O34 is the most electronegative (-0.474476) oxygen atom amongst all three oxygen atoms. The graphical representation of the Mulliken charges is depicted in Fig. 6. The MEP surface analysis Fig. 7 indicates that the maximum

electron density is situated at the epoxide ring and out of two benzene rings; the benzene ring which is fused

with the other rings is having maximum electron density.

Table 6: Absorption wavelength (λ in nm), coefficient, oscillator strength (f), and electronic transitions computed at TD-DFT B3LYP/6-31G (d,p) level of theory

State	Gas Phase				DCM			
	Configuration	Coefficient	f	λ , nm	Configuration	Coefficient	f	λ , nm
I	70 -> 74	0.33234	0.0061	362.22	70 -> 74	0.31078	0.0638	354.38
	71 -> 74	0.33479			71 -> 74	0.33177		
	72 -> 74	0.50509			72 -> 74	0.45157		
II	69 -> 76	-0.10975	0.0497	337.23	70 -> 74	-0.13458	0.0638	348.84
	73 -> 74	0.69183			71 -> 74	-0.13196		
					-72 -> 74	0.19024		
III	70 -> 74	-0.28061	0.0443	299.88	73 -> 74	0.64451	0.1672	297.52
	71 -> 74	-0.43660			70 -> 74	-0.26950		
	72 -> 74	0.47621			71 -> 74	-0.42107		
IV	70 -> 74	0.54699	0.7223	283.08	72 -> 74	0.49637	0.1883	278.44
	71 -> 74	-0.43452			70 -> 74	0.54639		
V	68 -> 74	-0.10176	0.1269	247.10	71 -> 74	-0.43197	0.0103	252.12
	69 -> 74	0.64154			69 -> 74	0.66800		
	73 -> 76	0.23910			73 -> 77	0.16603		
VI	68 -> 74	0.67708	0.0087	240.18	73 -> 75	0.69476	0.0103	239.11

Table 6: Mulliken atomic charges of PHIFO

Atom	Charge	Atom	Charge
1 C	-0.063438	21 C	0.202035
2 C	-0.071060	22 C	0.056354
3 C	-0.138021	23 C	0.119774
4 C	-0.031269	24 C	-0.123776
5 C	-0.146792	25 C	-0.089135
6 C	0.238699	26 C	-0.094523
7 H	0.106805	27 H	0.076965
8 H	0.083850	28 C	-0.092887
9 C	-0.167357	29 H	0.117842
10 H	0.142645	30 C	-0.080785
11 H	0.146102	31 H	0.084644
12 C	-0.012783	32 H	0.088444
13 H	0.123688	33 H	0.084358
14 H	0.123675	34 O	-0.474476
15 O	-0.354584	35 H	0.125827
16 C	0.229659	-	-
17 C	-0.098668	-	-
18 H	0.148561	-	-
19 H	0.142213	-	-
20 O	-0.313665	-	-

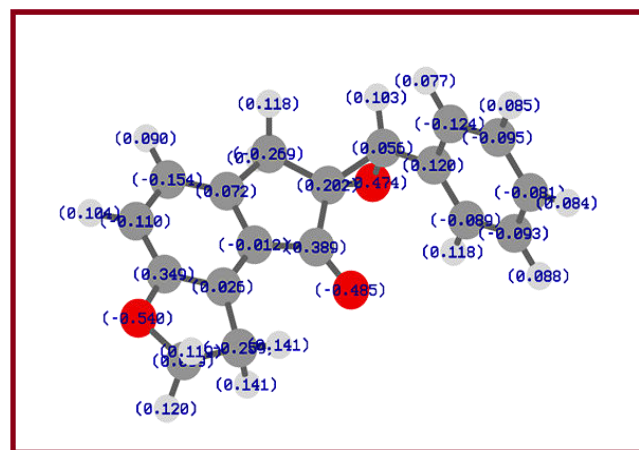


Fig. 5: Mulliken atomic charge distribution

3.1.1.4. Vibrational assignments

The structure of PHIFO with ring labeling is given in Fig. 8. The theoretical IR spectra in the gas phase and DCM were figured by the DFT method at 6-31G(d,p) basis set. The theoretical IR images are portrayed in Fig. 9 and Fig. 10. Fig. 9 is IR spectrum by DFT method at 6-31G(d,p) basis set in the gas phase whereas Fig. 10 is IR spectrum by DFT method at 6-31G(d,p) basis set in

DCM. The title molecule has 99 fundamental modes of vibrations as it is a non-linear molecule with possesses C1 point group symmetry. The selected theoretical vibrational numbers are scaled and used for the assignments of vibrational bands. The scaled vibrational bands in the gas phase and DCM with vibrational assignments are given in Table 7. The Gauss-view program was used to assign the calculated harmonic vibrational wavenumbers. The aromatic C-H vibrations in the gas phase were located at 3114.1632 and 3088.416 cm⁻¹. Similar vibrational bands in DCM were observed at 3110.8608 and 3110.8608 and 3089.2704 cm⁻¹. The first band is assigned to C25-H (mode 99) stretching and the second, is composed of two stretching vibrations; C21-H and C2-H (mode 98). The asymmetric stretching vibrations (mode 89) of C27-H2 were found at 2957.1456 and 2961.072 cm⁻¹ in the gas phase and DCM respectively. The symmetric stretching vibrations (mode 86) for the same bond are located at 2920.9344 and 2922.2784 cm⁻¹ in the gas phase and DCM respectively. The carbonyl group stretching (mode 85) is present at 1725.9456 cm⁻¹ in the gas phase and at 1723.6992 cm⁻¹ in DCM. The various aromatic C=C bonds are found in the range of 1600 to 1576 cm⁻¹. The in-plane bending vibrations of the C-H group of ring D (mode 80) are situated at 1479.936 cm⁻¹ in the gas phase and at 1479.6672 cm⁻¹ in DCM. The

out-of-plane bending vibrations of the C-H group of ring D (mode 46) are situated at 958.752 cm⁻¹ in the gas phase and at 964.0128 cm⁻¹ in DCM. The scissoring vibrations of C12-H2 (mode 79) and C9-H2 (mode 75) bonds in the gas phase are present at 1477.2384 and 1432.08 cm⁻¹. The same vibrations in DCM are at 1471.0368 and 1426.6752 cm⁻¹. The C21-C22 stretching (mode 73) is located at 1388.3712 and 1389.8304 cm⁻¹ in the gas phase and DCM respectively. The wagging vibrations of C9-H2 (mode 67) and C12-H2 (mode 65) are observed at 1257.3024 and 1228.4832 cm⁻¹ in the gas phase. The similar signals in DCM are at 1257.0336 and 1226.8704 cm⁻¹. The vibrations at 1181.1456 in the gas phase and at 1182.5056 in DCM are due to twisting vibrations of the C12-H2 bond (mode 64). While vibrations at 971.1552 in the gas phase and at 969.5904 in DCM are due to twisting vibrations of the C17-H2 bond (mode 48). In this, the vibration bands and vibrational wavenumbers are in accordance with the various types of groups present in the title molecule. The solvent effect of DCM is not regular. In some vibrations, the frequencies have been found to augment and in some cases, it is declined. This theoretical data computed by means of DFT calculations infers that the effect of DCM on vibrational frequencies in the title molecule is not regular.

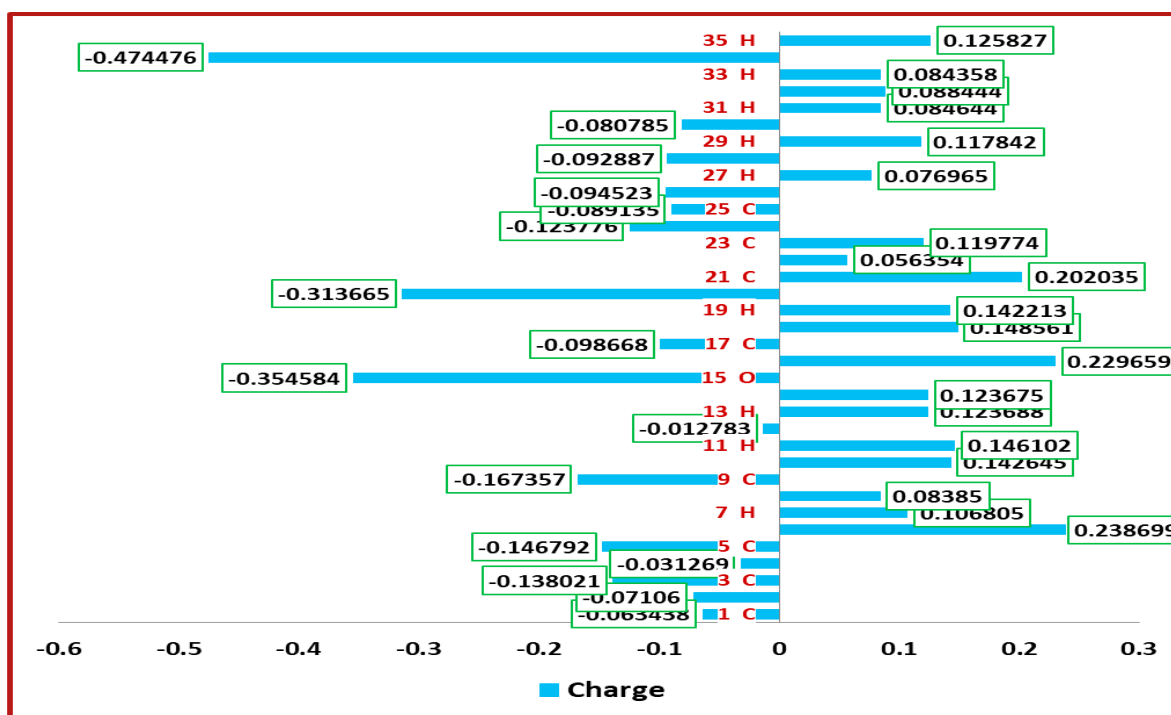


Fig. 6: Graphical representations of the Mulliken charges

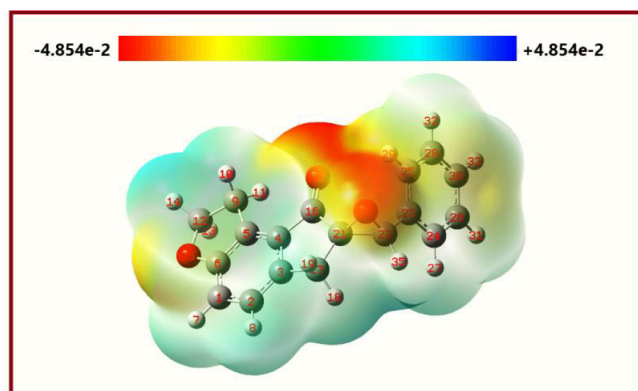


Fig.7: MEP surface plot of the title molecule

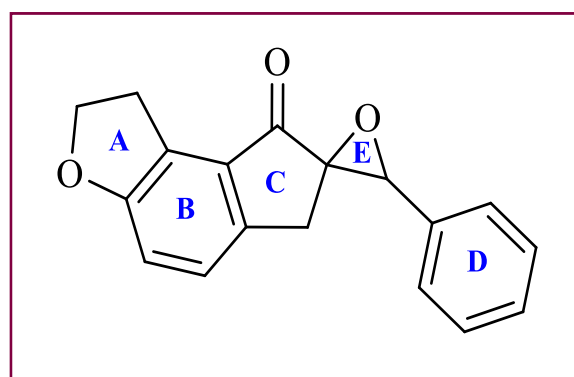


Fig. 8: Structure of PHIFO with ring labeling

Table 7: Selected theoretical vibrational assignments calculated at B3LYP/6-31G(d, p) level in gas phase and DCM

Mode	Computed scaled Frequencies(cm^{-1}) Gas Phase	Computed scaled Frequencies(cm^{-1}) DCM	Vibrational Assignments
99	3114.1632	3110.8608	ν C25-H
98	3088.416	3089.2704	ν C1-H, ν C2-H
92	3003.264	3003.9072	ν C-H (ring D)
90	2962.3104	2966.8224	asymC12-H ₂
89	2957.1456	2961.072	asymC17-H ₂
88	2937.696	2937.3984	symC9-H ₂
86	2920.9344	2922.2784	symC17-H ₂
85	1725.9456	1723.6992	ν C=O
84	1599.3216	1597.2384	ν C1=C2, ν C4=C5
83	1596.3552	1595.5392	ν C24=C26, ν C25=C28
82	1583.4624	1582.56	ν C1=C6, ν C3=C4
81	1575.8112	1575.5712	ν C23=C24, ν C28=C30
80	1479.936	1479.6672	β C-H (Ring D)
79	1477.2384	1471.0368	scis C12-H ₂
75	1432.08	1426.6752	scis C9-H ₂
73	1388.3712	1389.8304	ν C21-C22
67	1257.3024	1257.0336	ω C9-H ₂
65	1228.4832	1226.8704	ω C17-H ₂
64	1181.1456	1182.5056	t C12-H ₂
48	971.1552	969.5904	ρ C17-H ₂
46	958.752	964.0128	γ C-H (Ring D)

ν - stretching; sym- symmetric; asym- asymmetric; β - in-plane bending; γ - out of plane bending; t- twisting; ω - wagging; scis- scissoring and ρ - rocking

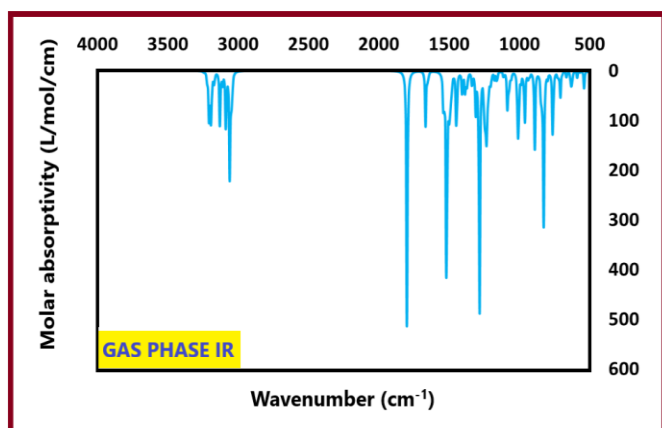
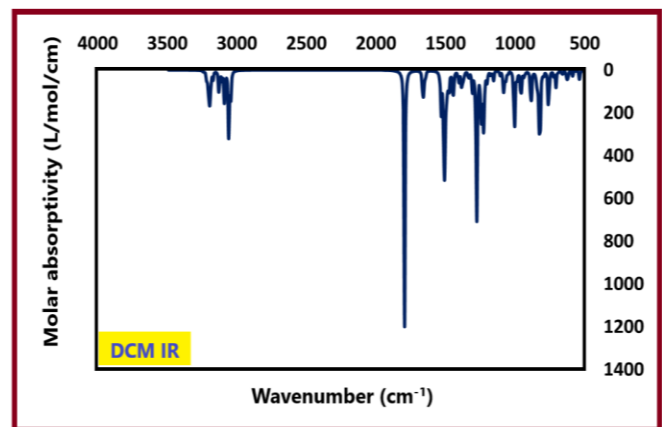
3.1.1.5. Thermochemical investigation

The thermochemical information obtained for the title molecule from the DFT method at B3LYP/6-31G(d,p) level is presented in Table 8. The thermochemical data has been established both in gas phase and DCM. In the current study, total energy (E_{total}), heat capacity at constant volume (C_v), Total entropy (S), zero point vibrational energy (E_{v_0}) and rotational constants have been evaluated from harmonic vibrational frequencies.

The thermochemical data furnished in this infers that there is no significant effect of DCM on thermochemical entities when compared with the gas phase data. The value of total entropy suggests slight augmentation in the randomness in the DCM as compared to gas phase entropy. The information uncovered in this could be helpful for the further evaluation of the other thermodynamic properties.

Table 8: Thermochemical data of title molecule in gas phase

Parameter	Gas Phase	DCM
E total (kcal mol ⁻¹)	183.345	183.334
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	181.568	181.556
Heat Capacity at constant volume, Cv (cal mol ⁻¹ K ⁻¹)	64.684	64.721
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	58.723	58.759
Total entropy, S (cal mol ⁻¹ K ⁻¹)	131.180	132.386
Translational	42.767	42.767
Rotational	34.135	34.135
Vibrational	54.278	55.484
Zero point Vibrational Energy, Ev ₀ (Kcal mol ⁻¹)	173.17259	173.12092
	0.62069	0.62069
Rotational constants (GHZ)	0.18305	0.18305
	0.15999	0.15999

**Fig. 9: IR spectrum by DFT method at 6-31G (d,p) basis set in gas phase****Fig. 10: IR spectrum by DFT method at 6-31G (d,p) basis set in DCM**

4. CONCLUSIONS

Taking everything into account, different aspects of the title molecule PHIFO have been explored by using the DFT method at B3LYP/6-31G(d,p) and TD-DFT at B3LYP/6-31G(d,p) basis sets. The effect of DCM on the absorption wavelength, vibrational frequencies, and thermochemical parameters is compared with the gas phase data. The results of our examination are talked about underneath:

- The geometry of the title molecule PHIFO is optimized B3LYP/6-311G (d, p) basis set. The molecule PHIFO is having C1 point group symmetry and the dipole moment is 2.6731 Debye. The E(RB3LYP) energy of the title molecule is -920.0012 a.u. which indicates its stability. The other data in regards to bond lengths and bond angles in the title molecule is ideally matching with the structural arrangement.
- The analysis of HOMO-LUMO energies suggests that the inevitable charge transfer is taking place within the molecule. The charge transfer value in the title molecule is 1.83 eV. The important electronic absorption band in the title molecule PHIFO is 362.22 nm (f=0.0061) with an excitation energy of 3.4229 eV. The absorption maximum for the first singlet excited state in the gas phase is located at 362.22 nm which is shifted to a lower wavelength in DCM at 354.38 nm. This information uncovered that there is a strong

hypsochromic shift observed for the first singlet excited state in the polar medium.

- In the present study, the various vibrational bands and vibrational wavenumbers are examined and it suggests the information obtained is in accordance with the various types of groups present in the title molecule. The solvent effect of DCM on vibrational frequencies is not regular.
- Amongst all carbon atoms the C6 is the most positive (0.238699) and C9 is the most negative (-0.167357) in nature. On the other hand, O34 is the most electronegative (-0.474476) oxygen atom amongst all three oxygen atoms. The MEP surface from the optimized geometry at the B3LYP/6-31G (d,p) set for the analysis of reactivity sites in the title molecule.
- In the current study, total energy, heat capacity at constant volume, total entropy, zero-point vibrational energy, and rotational constants have been evaluated from harmonic vibrational frequencies. The thermochemical data furnished in this infers that there is no significant effect of DCM on thermochemical entities when compared with the gas phase data.

5. ACKNOWLEDGEMENT

The authors are thankful to Principal, Mahatma Gandhi Vidyamandir's Arts, Science and Commerce College, Manmad, MS, India for providing laboratory facility. CIF, SPPU, Pune is acknowledged for the spectral analysis. Authors are grateful to Prof. (Dr.) A.B. Sawant for his generous help in the Gaussian study. Dr. Aapoorva P. Hiray, Coordinator, MG Vidyamandir Institute, is gratefully acknowledged for Gaussian package.

Funding information

No funding was received to carry out the present research work.

Declaration of interest

The authors declare that there is no conflict of interest for this work.

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