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NBO, conformational, NLO, HOMO–LUMO, NMR and electronic spectral study on 1-phenyl-1-propanol by quantum computational methods



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HIGHLIGHTS

- The compound 1-phenyl-1-propanol investigated by FT-IR, FT-Raman and NMR and UV-Vis spectroscopic tool.
- The chemical shift is found in favor of its change of chemical property.
- The charge transfer in the molecule by HOMO-LUMO studied in relation with NBO analysis.
- The study of NLO property in relation with polarizability and hyperpolarizability is done.
- Chemical reactivity region have been found along with the Fukui function.

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G R A P H I C A L A B S T R A C T

1-Phneyl-1-propanol is used as intermediate for composition of fluoxetine anti-depressant drug. It is a major depression drug for pediatric depression. Though the molecule has symmetry, it has different trans–cis structure with tiny different energies. The theoretical vibrational frequencies have been found in good agreement with the corresponding experimental data. ¹H and ¹³C NMR spectra were recorded and chemical shifts of the molecule were compared to TMS by using the Gauge-Independent Atomic Orbital (GIAO) method. A study on the electronic and optical properties, absorption wavelengths, excitation energy, dipole moment and frontier molecular orbital energies are performed using HF and DFT methods.



ABSTRACT

In this study, FT-IR, FT-Raman, NMR and UV spectra of 1-phenyl-1-propanol, an intermediate of antidepressant drug fluoxetine, has been investigated. The theoretical vibrational frequencies and optimized geometric parameters have been calculated by using HF and density functional theory with the hybrid methods B3LYP, B3PW91 and 6-311+G(d,p)/6-311++G(d,p) basis sets. The theoretical vibrational frequencies have been found in good agreement with the corresponding experimental data. ¹H and ¹³C NMR spectra were recorded and chemical shifts of the molecule were compared to TMS by using the Gauge-Independent Atomic Orbital (GIAO) method. A study on the electronic and optical properties, absorption wavelengths, excitation energy, dipole moment and frontier molecular orbital energies are performed using HF and DFT methods. The thermodynamic properties (heat capacity, entropy and enthalpy) at different temperatures are also calculated. NBO analysis is carried out to picture the charge transfer between the localized bonds and lone pairs. The local reactivity of the molecule has been studied using the Fukui function. NLO properties related to polarizability and hyperpolarizability are also discussed.

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Introduction

1-Phenyl 1-propanol is an organic compound containing an aromatic hydrocarbon with an aliphatic substitution. It is a colorless liquid, soluble in water. It is used as intermediate for composition of fluoxetine anti-depressant drug. Fluoxetine is a major depression drug for pediatric depression. It is also used for obsessive disorder both for adult and pediatric as drug for diseases like bulmia nervosa, panic disorder and premenstrual dysphonic disorder. It is the third most prescribed anti-depressant after sertraline. Other synonyms of alpha-Ethylbenzyl alcohol; Benzyl alcohol, alpha-ethyl-; Benzenemethanol, alpha-ethylalpha-Ethylbenzyl alcohol; Benzyl alcohol, alpha-ethyl. Zhu et al. [1] made DFT study on the candidate molecule, and it was found that while inclusion of 1-phenyl 1-propanol in two modified cyclic decapeptides, it functions as driving force for inclusion of complex formation. This facilitates enhancement of binding affinity of 1-phenyl 1-propanol enantiomer with cyclic decapeptides. Zhoo et al. also made DFT study using B3LYP basis set of the molecule their results reveal that 1-phenyl 1-propanol could form more stable inclusion complex in cyclic decapeptide [2]. And Choi et al. [3] found in their study that 1-phenyl 1-propanol is used as chiral intermediate in the synthesis of the anti-depressant drugs. In the present study, the stable geometry of the molecule is analyzed and discussed with its bond length, bond angle and dihedral angle. The vibrational modes of the molecule is calculated and compared with the experimental values. Spectra of the ¹³C NMR and ¹H NMR is analyzed and chemical shift is calculated comparing with TMS. Electronic transition of the molecule is analyzed to know the site of chromospheres with UV-vis spectra and reactivity center is identified with Fukui function.

Experimental details

The spectra of the compound 1-phenyl 1-propanol are obtained from spectral library purchased from Sigma–Aldrich Chemicals, USA. The FT-IR spectrum of the compound is recorded using a Bruker IFS 66V spectrometer in the range of 4000–400 cm⁻¹. The spectral resolution is ± 2 cm⁻¹. The FT-Raman spectrum of the same compound is also recorded using the same instrument with an FRA 106 Raman module equipped with a Nd:YAG laser source operating at 1.064 µm line widths with 200 mW power. They are recorded in the range of 4000–100 cm⁻¹ with a scanning speed of 30 cm⁻¹ min⁻¹ of spectral width 2 cm⁻¹. The frequencies of all sharp bands are accurate to ± 1 cm⁻¹. The high resolution ¹H



Fig. 1. Conformational analysis.



Fig. 2. Optimised structure of 1-phenyl-1-propanol.

NMR and ¹³C NMR spectra are recorded using 300 MHz and 75 MHz NMR spectrometer respectively.

Computational methods

The quantum computational works of the compound are performed using HF and hybrid B3LYP and B3PW91 using the basis sets 6-31+G(d,p) and 6-311+G(d,p). All these calculations are performed using the GAUSSIAN 09W [4] program package on i7 processor in a personal computer. Becke's three-parameter hybrid function (B3) combined with the Lee–Yang–Parr correlation function constitute B3LYP [5,6]. In the same way Becke's three parameter hybrid function (B3) [7] combined with the gradient-corrected correlation functional Perdew and Wang (PW91) [8,9] constitute B3PW91 method. The optimized molecular structure of the molecule is shown in Fig. 2.

The ¹H and ¹³C NMR isotropic shielding are calculated using the GIAO method [10] supported by the TMS B3LYP 6-311+G (2d,p). ¹³C isotropic magnetic shielding (IMS) of any X carbon atoms is computed by relation $CS_x = IMS_{TMS}-IMS_x$, where IMS_{TMS} is the isotropic shielding of tetra methyl silene. The ¹H and ¹³C isotropic chemical shifts of the compound with reference to TMS in solvent phase are calculated supported by IEFPCM methods. The electronic properties, HOMO–LUMO energies, absorption wavelengths and oscillator strengths are calculated using the time-dependent selfconsistent filed theory [11,12] with B3LYP functional for solvent and gas phase. Moreover, dipole moment, nonlinear optical (NLO) properties, linear polarizabilities and first hyperpolarizabilities have also been studied. Fukui function is used to predict both the reactive centers and the possible sites of nucleophilic and electrophilic attack.

Results and discussion

Conformational analysis

Conformational analysis was carried out for 1-phenyl-1-propanol by potential energy surface scan to find all possible conformers with B3LYP method using 6-311G(d,p) basis set. The scans were obtained by minimizing the potential energy in all geometrical parameters by varying the torsion angles by steps of 10° in the range of $0-360^\circ$ rotation around the bond [13]. The rotation about C14—C12 single bond produces different conformers of the title molecule. C12 is attached with O—H and phenyl ring, C14 has a methyl substituent. Since each carbon atom has different substituent, the rotation projects an energy profile diagram with respect to the dihedral angle of O21—C14—C12—C17. The lowest energy states of the diagram corresponds to the staggered form (2a and 2b in Fig. 1), whereas the highest energy states corresponds eclipse form (1a & 1b). Among the eclipsed conformers the one with O—H group with dihedral angle O21—C14—C12—C17 of 0° degree shows highest energy. This is due to the orientation of the O—H group in which H22 is pointing away from the phenyl ring that leads the remote chance for establishment bonding between C2—H22 as a conformer mounts to maximum. The methyl and phenyl group overlap each other, due to that energy increased at 130° degree. At 250° degree the bulky groups such as phenyl and methyl group are away from each other, the conformer shows less energy.

Molecular geometry

From the conformer analysis it is found that the stable structure of the molecule is as shown in Fig. 2. The 1-phenyl 1-propanol belongs to C_1 point group symmetry. The present molecule contains one ethyl, a hydroxyl and one methyl group, which are loaded in the left moiety. The calculated bond length, bond angle and dihedral angle by HF, B3LYP and B3PW91 methods with 6-31+G(d,p), 6-311++G(d,p) basis sets are presented in Table 1. The aromaticity of the benzene ring is deformed as a result of any deviation from its original characteristics. It is found that the candidate molecules are deformed from the hexagonal structure of the benzene due the substitution. It is evident from the difference calculated in bond length between C1-C2 & C2-C3 at the point of substitution is 0.003 Å. Consequently, as these bonds are at the point substitution the property of the phenyl ring is changed with respect to the ligand (ethyl and methyl groups). Similarly the difference in bond angle between C2–C3–C4, where the substitution is attached with the C3 atom, and C1–C6–C5 is 0.774°. The values too indicate that the structure of the ring is deformed from the hexagonal structure.

The structure optimization and zero point vibrational energy of the compound is 123.00 kcal/mol in HF/6-311+G(d,p), 115.69, 115.679 kcal/mol in B3LYP/6-311+/6-311+G(d,p) respectively and 116.943, and 115.89 kcal/mol in B3PW91/6-311+/6-311+G(d,p) respectively. These values indicate that B3LYP method with 6-311+/6-311+G(d,p) basis set predicts the minimum energy configuration for the molecule when compared to the other methods and basis sets.

Vibrational assignments

In order to obtain the spectroscopic significance of 1-phenyl-1propanol, the calculations are performed using HF, B3LYP, B3PW91 methods with 6-311+/6-311++G(d,p) basis sets. The molecule has C_1 point group symmetry, consists of 22 atoms. On the basis of C_1 symmetry, the molecule has 60 fundamental modes of vibrations and they can be distributed as 40 in-plane vibrations of A' species and 20 out-of-plane vibrations of A" species, i.e., $\Gamma_{vib} = 40$ A' + 20 A" as the symmetry of the molecule has a non-planar structure. observed and calculated- both scaled and unscaled FT-IR and FT-Raman frequencies for various modes of vibrations have been presented in Tables 2 and 3 and experimental and computational spectra of the compound are as shown in Figs. 3 and 4.

The calculated frequencies are scaled down to give up the rational with the observed frequencies. The scaling factors are 0.914, and 0.9067 for HF/6-311++G(d,p). For the B3LYP/6-311+/6-311++G(d,p) and B3PW91/6-31+G/6-311+G(d,p) basis sets the scaling factors are 0.9628 and 0.959.

O—*H* Vibrations

The O–H vibrations are generally measured between 3600 and 3200 cm^{-1} . Mikhail et al. [14] observed the O–H stretching vibrations of 1,2 dihydroxybenzene at 3321, 3381 cm⁻¹. In the candidate molecule, the stretching vibration is observed with strong band at 3370 cm⁻¹ which is in conformity with the literature. The in-plane bending vibration occurs between 1350 and 1200 cm⁻¹. Here too, the in-plane vibration is found at 1364 cm⁻¹ in the expected range. In the same way the out-of-plane vibrations are generally observed at 900–700 cm⁻¹ [15]. In the present molecule the out-of-plane vibrations are observed at 900 cm⁻¹, which is also found in the expected range. Thus the O–H vibrations on the whole are not affected in any way by the vibrations of phenyl ring or ethyl or methyl group of the molecule.

C-H Vibrations

The C–H stretching vibrations are normally observed in the region $3100-3000 \text{ cm}^{-1}$ for the aromatic benzene structure [16,17], which shows their uniqueness of the skeletal vibrations. In the present molecule the stretching vibrations appear at 3090, 3080, 3070, 3059, 3038, 3028, 2987, 2971, 2940, 2910 and 2900 cm⁻¹. The among presented five phenyl ring vibrations, first three band are active both in FT-Raman and FT-IR and other two are active in IR alone. And rest of the CH stretching vibrations are due to the substitutions of ethyl and methyl chain, which are suppressed below the expected range, and it is in conformity with the literature [18].

The C-H in-plane ring bending vibrations are normally observed as a number of strong to weak intensity bands in the region 1300–1000 cm⁻¹ [19]. C—H in-plane bending vibrations of the present compound are found at 1300, 1282, 1270, 1225, 1190, 1179, 1081, 1070, 1050, 1024, and 1010 cm⁻¹. All the vibrations are observed above the expected range which are affected by any other functional group vibrations. The C-H out-of-plane bending vibrations normally appear in the region 1000-800 cm⁻¹ [20]. The C—H out-of-plane bending vibrations are found at 869, 850, 782, 750, 746, 710, 705, 699, 694, 624 and 586 cm⁻¹. The out-of-plane vibrations of the phenyl ring are observed suppressed below the expected region, it is because of electron withdrawing nature of the substitutional group. The same trend is observed by Badawi in the vibrational assignments of the 2,4 dichlorophenoxyacetic [18]. Thus the stretching and in-plane bending vibrations of substitution-chain are observed in the expected range and out-ofplane vibrations are found below the expected region.

Ring vibrations

The C=C stretching vibrations are generally observed at 1600–1400 cm⁻¹ [15]. In the present compound the C=C vibrations are observed at 1620, 1590, and 1580 cm⁻¹. The vibrations are found increased from the expected range, it is due to the substitution. The stretching vibrations of C-C are expected at 1450–1250 cm⁻¹ [21]. The stretching vibrations of the candidate molecule for C-C are found at 1503, 1488, 1482, 1457, 1446 and 1374 cm⁻¹, the vibrations are in expected range the except one which is found little higher and it is due the substitutional chain. The last three vibrations are due to the C-C stretching vibrations of the substitution chain.

The in-plane vibration of C–C is observed below 1000 cm^{-1} . The in-plane vibrations are found at 1000, 990, 985, 980, 972 and 962 cm⁻¹. The observed vibrations are in the expected region and which is not affected by the any other vibrational modes. The out-of-plane vibrations are usually observed below 700 cm^{-1} , three vibrations of the chain are found at 560, 527 and 510 cm⁻¹. The three phenyl ring C–C out-of-plane bending vibrations are found mixed with other CCC vibrations of the molecule. Thus on the whole C–C vibrations are observed in the expected region.

The optimized geometrical parameters of 1-phenyl-1-propanol.

Geometrical parameter	HF/6-311+G(d,p)	B3LYP/6-311+G(d,p)	B3LYP/6-311++G(d,p)	B3PW91/6-311+G(d,p)	B3PW91/6-311++G(d,p)
Bond length (Å)					
C1–C2	1.387	1.397	1.397	1.395	1.391
C1—C6	1.386	1.397	1.397	1.395	1.391
C1—H7	1.076	1.086	1.086	1.086	1.085
C2–C3	1.390	1.400	1.400	1.398	1.394
C2—H8	1.073	1.084	1.084	1.085	1.083
C3–C4	1.390	1.401	1.401	1.399	1.395
C3-C12	1.516	1.517	1.517	1.513	1.510
C4C5	1.386	1.396	1.396	1.394	1.390
C4—H9	1.077	1.088	1.088	1.088	1.087
C5	1.360	1.096	1.096	1.595	1.392
C5-H11	1.075	1.080	1.086	1.086	1.085
C12—H13	1.075	1 102	1 102	1 103	1 102
C12-C14	1.534	1.542	1.542	1.537	1.535
C12-021	1.407	1.432	1.432	1.423	1.423
C14—H15	1.086	1.096	1.096	1.096	1.095
C14—H16	1.086	1.097	1.097	1.097	1.095
C14–C17	1.529	1.533	1.533	1.528	1.526
C17—H18	1.085	1.094	1.094	1.094	1.093
C17—H19	1.087	1.097	1.097	1.096	1.095
C17—H20	1.086	1.097	1.097	1.096	1.095
021—H22	0.942	0.965	0.965	0.963	0.960
Bond angle (°)					
C2-C1-C6	120.458	120.386	120.386	120.384	120.389
C2-C1-H7	119.579	119.622	119.622	119.626	119.642
C6-C1-H7	119.961	119.991	119.991	119.989	119.967
C1–C2–C3	120.406	120.392	120.392	120.373	120.357
C1-C2-H8	120.110	120.443	120.443	120.555	120.537
C3-C2-H8	119.478	119.156	119.156	119.064	119.097
C2-C3-C4	118.790	118.897	118.897	118.935	118.946
C2-C3-C12	121.463	121.258	121.258	121.209	121.201
C4–C3–C12	119.723	119.811	119.811	119.822	119.818
C3-C4-C5	120.872	120.781	120.781	120.752	120.743
C3-C4-H9	110.224	110.584	110.52	119.038	119.640
C3-C4-H9	119.334	120.012	120.012	120.018	120.016
C4 - C5 - C10	120.024	120.012	110.012	120.018	110.843
C6-C5-C10	120 163	120 169	120 169	120 157	120 138
C1-C6-C5	119 446	119 527	119 527	119 533	119 544
C1-C6-H11	120 298	120 267	120 267	120 269	120 262
C5-C6-H11	120.254	120.204	120.204	120.195	120.191
C3-C12-H13	107.944	108.216	108.216	108.113	108.043
C3-C12-H14	111.457	111.534	111.534	111.214	111.180
C3-C12-O21	108.257	107.999	107.999	108.134	108.239
H13-C12-C14	108.608	108.260	108.260	108.239	108.288
H13-C12-O21	109.096	109.140	109.140	109.339	109.283
C14-C12-O21	111.392	111.613	111.613	111.725	111.725
C12-C14-H15	108.203	107.901	107.901	107.931	107.939
C12-C14-H16	108.360	108.215	108.215	108.163	108.139
C12–C14–C17	113.828	113.994	113.994	113.921	113.826
H15-C14-C16	106.953	106.800	106.800	106.717	106.688
HI5-CI4-CI7	109.223	110,367	110,367	110.262	110,565
110-014-017	110.052	110.289	110.289	110,502	110,400
C14-C17-H19	111.426	111.430	111 430	111 494	111 490
C14-C17-H20	112 032	112 195	112 195	112 259	112 260
H18-C17-H19	107 527	107 571	107 571	107 515	107 542
H18-C17-H20	106.894	106.587	106.587	106.455	106.413
H19–C17–H20	108.168	108.040	108.040	108.043	108.014
C12-021-H22	110.463	108.712	108.712	108.445	108.203
Dihadral angla					
C6-C1-C2-C3	0.078	0.05	0.05	0.03	0.04
C6-C1-C2-H8	-0.078	179.05	179.05	179.09	179.08
H7-C1-C2-C3	_179.8	_179.68	-179.68	_179.09	_179.69
H7-C1-C2-H8	-0.63	-0.68	-0.68	-0.64	-0.66
$C_{2}-C_{1}-C_{6}-C_{5}$	-0.19	-0.26	-0.26	-0.26	-0.30
C2-C1-C6-H11	-179.82	-179.84	-179.84	-179.83	-179.81
H7-C1-C6-C5	179.54	179.47	179.47	179.48	179.4
H7-C1-C6-H11	-0.08	-0.10	-0.10	-0.09	-0.06
C1-C2-C3-C4	0.43	0.34	0.34	0.36	0.37
C1-C2-C3-C12	-177.84	-177.56	-177.56	-177.52	-177.52
H8-C2-C3-C4	-178.75	-178.66	-178.66	-178.70	-178.67
Н8—С2—С3—С12	2.96	3.41	3.41	3.40	3.42

(continued on next page)

Table 1 (continued)

Geometrical parameter	HF/6-311+G(d,p)	B3LYP/6-311+G(d,p)	B3LYP/6-311++G(d,p)	B3PW91/6-311+G(d,p)	B3PW91/6-311++G(d,p)
C2-C3-C4-C5	-0.52	-0.54	-0.54	-0.54	-0.54
C2-C3-C4-H9	179.12	179.05	179.05	179.03	178.95
C12-C3-C4-C5	177.79	177.40	177.40	177.38	177.38
C12-C3-C4-H9	-2.55	-2.99	-2.99	-3.04	-3.11
C2-C3-C12-H13	-145.67	-148.26	-148.26	-146.33	-146.86
C2-C3-C12-C14	95.13	92.75	92.75	94.96	94.43
C2-C3-C12-021	-27.70	-30.23	-30.23	-28.05	-28.63
C4-C3-C12-H13	36.05	33.83	33.83	35.79	35.25
C4-C3-C12-C14	-83.13	-85.14	-85.14	-82.90	-83.44
C4-C3-C12-021	154.02	151.86	151.86	154.07	153.48
C3-C4-C5-C6	0.25	0.34	0.34	0.31	0.28
C3-C4-C5-H10	179.81	179.77	179.77	179.75	179.73
H9-C4-C5-C6	-179.40	-179.26	-179.26	-179.25	-179.21
H9-C4-C5-H10	0.16	0.17	0.17	0.18	0.23
C4-C5-C6-C1	0.11	0.07	0.07	0.09	0.14
C4-C5-C6-H11	179.74	179.65	179.65	179.66	179.65
H10-C5-C6-C1	-179.45	-179.36	-179.36	-179.34	-179.30
H10-C5-C6-H11	0.18	0.22	0.22	0.23	0.21
C3-C12-C14-H15	55.10	54.93	54.93	55.11	54.84
C3-C12-C14-H16	-60.53	-60.29	-60.29	-60.00	-60.23
C3-C12-C14-C17	176.71	176.62	176.62	176.89	176.69
H13-C12-C14-H15	-63.69	-64.02	-64.02	-63.52	-63.71
H13-C12-C14-H16	-179.32	-179.24	-179.24	-178.63	-178.78
H13-C12-C14-C17	57.92	57.66	57.66	58.27	58.14
021-C12-C14-15H	176.13	175.84	175.84	176.04	175.88
021-C12-C14-H16	60.50	60.62	60.62	60.93	60.82
021-C12-C14-C17	-62.26	-62.48	-62.48	-62.17	-62.26
C3-C12-021-H22	-171.89	178.93	178.93	178.39	176.76
H13-12C-021-H22	-54.66	-63.64	-63.64	-64.12	-65.80
C14-C12-O21-H22	65.23	55.98	55.98	55.68	54.02
C12-C14-C17-H18	-175.87	-176.79	-176.79	-176.32	-176.87
C12-C14-C17-H19	-56.34	-57.07	-57.07	-56.60	-57.09
C12-C14-C17-H20	65.00	64.23	64.23	64.79	64.26
H15-C14-C17-H18	-54.82	-55.92	-55.92	-55.39	-55.92
H15-C14-C17-H19	64.70	63.80	63.80	64.33	63.86
H15-C14-C17-H20	-173.95	-174.90	-174.90	-174.27	-174.79
H16-C14-C17-H18	62.29	61.25	61.25	61.78	61.30
H16-C14-C17-H19	-178.18	-179.03	-179.03	-178.50	-178.92
H16-C14-C17-H20	-56.83	-57.73	-57.73	-57.10	-57.57

NMR assessment

NMR spectroscopy is currently used for the structural elucidation of complex molecules. The optimized structure of 1-phenyl-1-propanol obtained by B3LYP hybrid method with 6-311++G(d,p)basis set, is used to obtain the NMR spectra. The isotropic shielding is calculated with B3LYP/6-311++G(d,p) method and shielding with respect to TMS is calculated with B3LYP/6-311+G(2d,p) GIAO method. The chemical shifts in gas phase as well as in different solvent phase are calculated by finding the difference between the above two and values are presented in Table. 4 and experimental spectra of the compound are as shown in Fig. 5.

The chemical shifts of the carbon atoms; C12, C2, C6, C4, C5, C1 and C3 are almost ranging from 44 to 87 ppm. And the chemical shifts of two carbons C14 and C17 are found considerably large whose values are 120.6499 and 175.0724 ppm respectively. In the methyl group C17 is more shifted than others due to the delocalization of σ and σ^* electrons from C12—C14. The electronegative atom withdraw the electron density around the proton and thus, causes deshielding (reverse of shielding). Due to deshielding, smaller value of applied field will be needed to bring the proton to resonance. In the same way the carbon in the ethyl group is deshielded, thus have the higher chemical shift [22].

The chemical shifts of the hydrogen atoms in the compound are found almost equal around 24 ppm, which show that the chemical environment of the hydrogen atoms are affected by oxygen or any carbon atoms. When chemical shifts are compared among different solvents phases, no appreciable difference has been observed. Hence the impact of the solvents on the chemical shifts of the compound for various atoms is negligibly small. The values are correlated with the experimental spectra of the compound and graph is as shown in Fig. 6.

Electronic and optical properties (HOMO-LUMO analysis)

When molecular orbitals are viewed in qualitative graphical representation, it can provide insight into the concepts such as reactivity, conjugation, aromaticity and lone pair. The positive and negative is represented in red and green color respectively [23]. The energies of two important molecular orbitals of 1-phe-nyl-1-propanol; highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) were calculated using B3LYP/6-311+G(d,p) method and are presented in Table 5. The energy gap between HOMO and LUMO is critical parameter in determining molecular electrical transport properties [24]. The calculated energy gap ($E_{HOMO}-E_{LUMO}$) explains the ultimate charge transfer in the molecule. The calculations of the electronic structure of 1-phenyl-1-propanol are optimized in the singlet state. The 3D plots of frontier orbitals in the optimized state, HOMO and LUMO for the molecule are shown in Fig. 7.

The Kubo gap, global chemical hardness, electronegativity and global electrophilicity index are calculated and their values are shown in Table 5. The average chemical hardness from gas to solvent phase is 3.16 eV which considerably high and hence the compound is chemically stable. Similarly, the electro negativity is observed to be increased from 3.5265 up to 6.6768 eV. The electronegativity is a measure of attraction of an atom for electrons in a covalent bond. When two unlike atoms are covalently bonded,

Table 2	
Experimental and calculated scaled frequencies of 1-phenyl-1-propanol using HF/DFT(B3LYP&B3PW91) with 6-31+(d,p) and 6-311+G(d,p) basis sets.	

S. no.	Symmetry species C ₁	Observed	l frequency	Calculated frequency			Vibrational assignments		
				HF	B3LYP	B3LYP B3PW91			
		FT-IR	FT-Raman	6-311+G(d,p)	6-31+G(d,p)	6-311+G(d,p)	6-31+G(d,p)	6-311+G(d,p)	
1	A'	3370s	-	3374	3354	3354	3350	3573	ν О—Н
2	A'	3090m	3090w	3098	3098	3098	3095	3090	ν С—Н
3	A′	3080s	3080w	3078	3083	3083	3083	3078	ν С—Н
4	A'	3070s	3070w	3065	3071	3071	3070	3065	ν C—Η
5	A'	3059s	_	3054	3061	3061	3060	3055	ν С—Н
6	A'	3038s	_	3042	3048	3048	3046	3042	ν С—Н
7	A'	3028s	_	2998	2992	2992	3000	2993	v C—H
8	Α′	29875	_	2997	2982	2982	2989	2983	v C—H
9	Δ′	29075 2971s	_	2973	2961	2961	2968	2961	v C—H
10	Δ/	20/13 20/0c		20/8	2001	2001	2000	2007	v с -н
10	A'	23403	2010w	2020	2016	2016	2014	2012	v с -н
11	A	-	2910W	2929	2910	2910	2914	2915	V C—H
12	A	-	2900W	2916	2805	2805	2859	2800	V C—H
13	A'	1620W	-	1634	1593	1593	1599	1598	V C = C
14	A'	1590W	-	1608	1572	1572	15/8	15/8	VC=C
15	Α'	-	1580w	1505	1475	1475	14/1	14/1	v C = C
16	Α′	1503w	-	1479	1459	1459	1448	1448	v C—C
17	A'	1488w	-	1468	1447	1447	1435	1435	v C—C
18	A'	1482w	-	1457	1431	1431	1426	1427	v C—C
19	A'	1457m	-	1453	1426	1426	1414	1413	ν C—C
20	A'	1446m	-	1414	1373	1373	1368	1370	ν C—C
21	A'	1374w	-	1393	1359	1359	1349	1348	ν C—C
22	Α′	1364m	-	1375	1327	1327	1325	1323	β О—Н
23	A'	-	1300w	1332	1309	1309	1316	1312	β С—Н
24	A′	1282m	-	1310	1299	1299	1290	1294	β С—Н
25	A'	_	1270w	1267	1276	1276	1266	1270	, в С—Н
26	Α′	1225m	_	1236	1241	1241	1233	1237	в C—Н
27	Α'	-	1190w	1193	1190	1190	1187	1191	в С —Н
28	Α′	1179m	_	1182	1158	1158	1154	1157	в С —Н
29	Α′	1081m	_	1120	1143	1143	1141	1145	рс н в С—Н
30	Δ′	1070m	_	1073	1138	1138	1133	1134	вс-н
31	Δ′	-	1050w	1059	1096	1096	1095	1095	вс-н
22	A'	- 1024m	105000	1035	1050	1050	1055	1055	
22	A'	1024III 1010m	-	1045	1009	1005	1073	1074	βC-11 8C-11
24	A	101011	10105	1019	1055	1055	1034	1020	рС— н
24	A	-	1000vs	990	1015	1015	1024	1020	β C C
35	A'	-	9905	975	1012	1012	1012	1014	βCC
36	A'	-	985W	975	977	977	973	978	β ((
37	A″	980w	-	961	964	964	961	961	β CC
38	A″	972w	-	942	954	954	960	960	β C—C
39	A″	962w	-	931	947	947	943	947	β C—C
40	A″	900w	-	902	897	897	893	896	δ Ο—Η
41	A″	869w	-	833	859	859	861	863	δ C—H
42	A‴″	-	850w	829	827	827	824	825	δ C—H
43	A″	782w	-	769	795	795	794	796	δ C—H
44	A″	750w	750w	733	746	746	741	744	δ C—H
45	Α″	746m	-	712	729	729	727	730	δ С—Н
46	A″	710s	-	673	685	685	682	685	δ C—H
47	A″	705s	-	621	609	609	603	607	δ C—H
48	A″	699s	-	619	606	606	602	606	δ C—H
49	Α″	694s	-	533	515	515	510	513	δ C —H
50	Α″	624m	_	498	487	487	484	485	δ С—Н
51	Α″	586w	_	414	399	399	395	395	δ C—H
52	Α″	-	560w	369	358	358	359	360	δ C—C
52	A″	5271	_	313	308	308	305	306	δ (—C
54	Α″	5101		265	272	272	264	260	δ C—C
55	Λ//	51000	4500	205	272	272	204	200	\$ CCC
55	/\ \//	-	450%	200	230	230	240	241/ 224	
20	A"	-	2505	218	240	240	234	234	
5/	A"		240s	208	206	206	202	205	
58	A''	-	230s	105	103	103	101	102	
59	A''	-	150w	91	91	91	90	91	ι-ι-ι τ
60	A'	-	125W	32	35	35	34	35	ι-ι-ι τ

v – stretching, β – in-plane bending, δ – out-of-plane bending, α – deformation, τ – Torsional bending.

the shared electrons will be more strongly attracted to the atom of greater electronegativity. The electrophilicity index is a measure of energy lowering due to the maximal electron flow between the donor [HOMO] and the acceptor [LUMO]. From Table 5, it is found that the electrophilicity index of 1-phenyl-1-propanol is 1.9673 eV in the gas phase and 2.136 eV in solvent, which is moderate, and this value ensures the strong energy transformation between

HOMO and LUMO. The dipole moment in a molecule is another important electronic property. Whenever the molecule has larger dipole moment, the intermolecular interactions are very strong. The calculated dipole moment value for the title compound is 1.9389 in the gas phase and 2.5450 Debye in the solvent phase. This shows that the 1-phenyl-1-propanol molecule has strong intermolecular interactions.

Calculated unscaled frequencies	of 1-phenyl-1-propano	l using HF/DFT(B3LYP&B3PW91) with 6-31+(d,p) and 6	-311+G(d,p) basis sets.
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S. no.	Observed fre	equency	Calculated frequency				
			HF	B3LYP		B3PW91	
	FT-IR	FT-Raman	6-311+G(d,p)	6-31+G(d,p)	6-311+G(d,p)	6-31+G(d,p)	6-311+G(d,p)
1	3646w		4204	3837	3837	3869	3871
2	3090m	3090w	3389	3218	3218	3228	3209
3	3080s	3080w	3368	3202	3202	3215	3197
4	3070s	3070w	3353	3189	3189	3202	3184
5	3059s		3341	3179	3179	3191	3173
6	3038s		3328	3166	3166	3177	3160
7	3028s		3245	3107	3107	3128	3109
8	2987s		3243	3098	3098	3117	3098
9	2971s		3218	3075	3075	3095	3075
10	2940s		3191	3041	3041	3054	3041
11		2910w	3170	3028	3028	3039	3025
12		2900w	3156	2976	2976	2982	2971
13	1620w		1802	1654	1654	1668	1660
14	1590w		1773	1633	1633	1646	1639
15		1580w	1660	1532	1532	1534	1528
16	1503w		1631	1515	1515	1510	1504
17	1488w		1619	1502	1502	1497	1490
18	1482w		1607	1486	1486	1487	1482
19	1457m		1603	1481	1481	1475	1468
20	1446m		1560	1427	1427	1427	1423
21	13/4w		1536	1411	1411	1406	1400
22	1364m	1200	1517	1378	1378	1382	1374
23	1202	1300W	1469	1359	1359	1372	1362
24	1282m	1270	1445	1349	1349	1345	1344
25	100Em	1270W	1397	1323	1323	1320	1319
20	1225111	11001	1316	1269	1209	1230	1200
27	1170m	115000	1203	1203	1203	1203	1207
20	1081m		1290	1188	1188	1190	1189
30	1070m		1236	1182	1182	1181	1178
31	107011	1050w	1220	1139	1139	1142	1137
32	1024m	100011	1204	1111	1111	1119	1115
33	1010m	1010s	1174	1096	1096	1099	1066
34		1000vs	1141	1054	1054	1068	1065
35		990s	1123	1051	1051	1055	1053
36		985w	1123	1014	1014	1014	1016
37	980w		1107	1001	1001	1002	998
38	972w		1085	991	991	1001	997
39	962w		1073	983	983	984	984
40	900w		1039	931	931	931	930
41	869w		960	892	892	897	896
42		850w	955	859	859	859	857
43	782w	750	886	826	826	828	827
44	/50W	/50W	845	//5	//5	//3	//2
45	746m 710a		820	/5/	/5/	/58	/58
40	710s 705c		677	/11	/11	/11	/12
47	7035		675	620	620	629	620
40	0995 604c		591	525	525	522	522
	624m		543	506	506	505	503
51	5861		J4J 452	415	J00 /15	JUJ /12	/10
52	30000	560w/	402	372	372	374	373
53	527w	50010	341	320	320	318	318
54	510w		289	282	282	275	270
55	51000	450w	278	259	259	257	257
56		250s	238	249	249	244	243
57		240s	227	214	214	211	212
58		230s	115	107	107	106	105
59		150w	99	94	94	94	94
60		125w	35	36	36	35	36

The low energy electronic excited states of the molecule are calculated at the B3LYP/6-311++G(d,p) level using the TD-DFT approach based on the previously optimized ground-state geometry of the molecule. The calculations are performed for 1-phenyl-1-propanol in the gas phase and with the solvent phase. The calculated excitation energies, oscillator strength (*f*) and wavelength (λ) and spectral assignments are given in Table 6.

Global softness and local region-selectivity

Besides the traditional reactivity descriptors, such as HOMO & LUMO, there are certain other chemical reactivity descriptors such as global hardness (η), global softness (S) local softness (ΔS), Fukui function (f) global electrophilicity (ω) and local electrophilicity ($\Delta \omega$) [25–28] which are defined by Koopman's theorem [29,30] as follows.



Fig. 3. Experimental (D) and calculated (A, B, C) FT-IR spectrum of 1-phenyl-1-propanol.

Electronegativity (χ) is a measure of the power of an atom or a group of atoms to attract electrons [31] and can be calculated from HOMO–LUMO as

$$\chi = -\frac{1}{2}(E_{\rm HOMO} + E_{\rm LUMO}) \tag{1}$$

Global hardness (η) is a measure the resistance of an atom to charge transfer [32] and it can calculated as

$$\eta = -\frac{1}{2}(E_{\rm HOMO} - E_{\rm LUMO}) \tag{2}$$

The global softness (*S*) describes the capacity of an atom or a group of atoms to receive electrons [33] and is equal to reciprocal of global hardness.

$$S = \frac{1}{\eta} = -2(E_{\rm HOMO} - E_{\rm LUMO}) \tag{3}$$

The global electrophilicity (ω) can be calculated from the electronegativity and chemical hardness using the relation

$$\omega = \frac{\chi^2}{2\eta} \tag{4}$$

Fukui indices (f_k) are the indicator of the reactive regions and the nucleophilic and electrophilic behaviors of the molecule. If f_k for any given site is positive then it is a preferred site for nucleophilic attack, in contrast the negative value implies electrophilic attack.

The Fukui function is calculated using the relation [34,35]:



Fig. 4. Experimental (D) and calculated (A, B, C) FT-Raman spectrum of 1-phenyl-1-propanol.

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\delta N}\right)_{\nu(\mathbf{r})}$$
(5)

where $\rho(r)$ is the electron density.

The phenyl ring gets activated at the *ortho* and *para* positions as there are electron releasing substituents such as -OH, -NH2, -OR, and R. A propanol substituent in fact is an electron withdrawing substituent, consequently promotes the *ortho* and *para* positions for nucleophilic attack, a common reactivity trend observed in phenyl compounds. Local reactivity descriptors such as fk+, fk-, Δf , and $\Delta \omega$ for the different sites of the phenyl ring are in conformity with the observed reactivity trend of the candidate molecule. The values are shown in Table 7.

fk+, fk-, Δf and $\Delta \omega$ unambiguously reveal the order of the nucleophilic attack to be in the decreasing sequence as C4 > C2 and that of the electrophilic attack is found to be C1 > C3 > C5 > C6 in the phenyl ring. Though the trend for the attack of the electrophile is in conformity with that of ΔS and $\Delta \omega$ for C4 and C2, the carbon atom C6 is deviated from the usual trend of the phenyl ring being electrophile, rather it is observed to be nucleophile. It is due to the electron releasing center of O–H group. A graphical representation of the nucleophile and electrophile of the compound is plotted between electrophilicity index and corresponding carbon atoms, it is as shown in Fig. 8.

Molecular electrostatic potential (MEP) maps

The molecular electrical potential surfaces from Fig. 9 illustrate the charge distributions of molecules three dimensionally. This map allows us to visualize variably charged regions of a

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Table 4	
Experimental and calculated ¹ H and ¹³ C NMR chemical shifts	(ppm) of 1-phenyl-1-propanol.

Atom	im Gas			Solvent								
position				CCl ₄			DMSO			Methanol		
	B3LYP/6- 311+G(d,p) (ppm)	B3LYP/6- 311+G(2d,p) GIAO (ppm)	Shift (ppm)	B3LYP/6- 311+G(d,p) (ppm)	B3LYP/6- 311+G(2d,p) GIAO (ppm)	Shift (ppm)	B3LYP/6- 311+G(d,p) (ppm)	B3LYP/6- 311+G(2d,p) GIAO(ppm)	Shift (ppm)	B3LYP/6- 311+G(d,p) (ppm)	B3LYP/6- 311+G(2d,p) GIAO (ppm)	Shift (ppm)
C1	67.7189	114.747	47.0281	65.2415	117.224	51.9825	67.7086	114.757	47.0484	65.2559	117.21	51.9541
C2	70.8574	111.608	40.7506	68.9682	113.497	44.5288	71.9945	110.471	38.4765	69.6506	112.815	43.1644
C3	49.3034	133.162	83.8586	47.7877	134.678	86.8903	48.3755	134.09	85.7145	47.2653	135.2	87.9347
C4	69.9249	112.541	42.6161	67.385	115.081	47.696	69.6379	112.828	43.1901	67.2612	115.204	47.9428
C5	68.9169	113.549	44.6321	66.1252	116.34	50.2148	68.0957	114.37	46.2743	65.6372	116.828	51.1908
C6	70.4897	111.976	41.4863	68.0551	114.41	46.3549	69.7243	112.741	43.0167	67.5483	114.917	47.3687
C12	112.848	69.6172	43.2308	112.189	70.2766	41.9124	113.257	69.2089	44.0481	112.443	70.0226	42.4204
C14	153.192	29.2735	123.9185	151.644	30.8215	120.8225	153.017	29.4488	123.5682	151.558	30.9081	120.6499
C17	179.691	2.7745	176.9165	178.504	3.9621	174.5419	180.142	2.3239	177.8181	178.769	3.6966	175.0724
H7	24.1085	7.7736	16.3349	23.9672	7.9149	16.0523	23.9686	7.9135	16.0551	23.8891	7.993	15.8961
H8	23.646	8.2361	15.4099	23.6529	8.2292	15.4237	23.7063	8.1758	15.5305	23.6781	8.204	15.4741
H9	24.4463	7.4358	17.0105	24.2608	7.6213	16.6395	24.1917	7.6904	16.5013	24.1142	7.7679	16.3463
H10	24.2319	7.6502	16.5817	24.0627	7.8194	16.2433	24.0337	7.8484	16.1853	23.9485	7.9336	16.0149
H11	24.2562	7.6259	16.6303	24.0847	7.7974	16.2873	24.0939	7.7882	16.3057	23.9922	7.8899	16.1023
H13	26.9932	4.8889	22.1043	23.6529	5.0498	18.6031	26.8104	5.0717	21.7387	26.7281	5.154	21.5741
H15	30.146	1.7361	28.4099	29.9818	1.9003	28.0815	29.9516	1.9305	28.0211	29.8892	1.9929	27.8963
H16	30.1649	1.7172	28.4477	30.1829	1.6992	28.4837	30.2332	1.6489	28.5843	30.2326	1.6495	28.5831
H18	30.429	1.4531	28.9759	30.3528	1.5293	28.8235	30.4195	1.4626	28.9569	30.3629	1.5192	28.8437
H19	30.8272	1.0549	29.7723	30.7357	1.1464	29.5893	30.6866	1.1955	29.4911	30.6587	1.2234	29.4353
H20	30.6707	1.2114	29.4593	30.559	1.3231	29.2359	30.5439	1.3472	29.1967	30.495	1.3871	29.1079
H22	30.0473	1.8348	28.2125	29.9439	1.9382	28.0057	29.5434	2.3387	27.2047	29.6439	2.2382	27.4057



Fig. 5. ¹³C NMR experimental spectrum.

molecule. The knowledge of the charge distributions can be used to determine how molecules interact with one another and it is also used to determine the nature of the chemical bond. Molecular electrostatic potential is calculated at the B3LYP/6-311+G(d,p) optimized geometry [36,37]. The figure shows the negative charges are more concentrated more at the top of the oxygen atoms, whereas the blue region is spread at the top of the hydrogen atoms of the O–H group and other region found to be neither red nor blue [38], so almost neutral. Greater regions of intermediary potential, yellow and green, and smaller or no regions of extreme potential, red and blue, are key indicators of smaller electronegativity.

The color code of these maps is in the range between -6.15 a.u. (deepest red) and 6.15 a.u. (deepest blue) in the compound. The positive (blue) regions of MEP are related to electrophilic reactivity and the negative (green) regions to nucleophilic reactivity (Fig. 6). From the MEP map of the candidate molecule, it can be observed that the red regions of the molecule were found to be ready for electrophilic attack, and especially in the phenyl ring the atoms are clouded with red color.

Polarizability and first order hyperpolarizability calculations

In order to investigate the relationships among molecular structures and non-linear optic properties (NLO), the polarizabilities and first order hyperpolarizabilities of the 1-phenyl-1-propanol compound were calculated using the DFT-B3LYP method and the 6-311+G(d,p) basis set, based on the finite-field approach.

The polarizability and hyperpolarizability tensors (α_{xx} , α_{xy} , α_{yy} , α_{xz} , α_{yz} , α_{zz} and β_{xxx} , β_{xxy} , β_{yyy} , β_{yxz} , β_{yyz} , β_{yyz} , β_{yzz} , β_{yzz} , β_{zzz}) can be obtained by a frequency job output file of Gaussian. However, α and β values of the Gaussian output are in atomic units (a.u.), so they have been converted into electronic units (esu)) (α ; 1 a.u. = 0.1482 × 10⁻²⁴ esu, β ; 1 a.u. = 8.6393 × 10⁻³³ esu). The calculations of the total molecular dipole moment (μ), linear polarizability (α) and first-order hyperpolarizability (β) from the Gaussian output have been explained in detail previously [39,40], and DFT has been extensively used as an effective method to investigate the organic NLO materials [41–45].

$$\begin{split} \alpha_{\text{tot}} &= \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \\ \Delta \alpha &= \frac{1}{\sqrt{2}} \Big[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2 \Big]^{\frac{1}{2}} \\ \langle \beta \rangle &= \Big[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yzx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \Big]^{\frac{1}{2}} \end{split}$$



Fig. 6. ¹H NMR experimental spectrum.

Table 5				
HOMO, LUMO, Kubo gap, global electronegativity, globa	al hardness	and so	oftness	and
global electrophilicity index.				

Parameters	Gas	Ethenol	Methanol	DMSO
E _{HOMO} (eV)	6.6882	6.8384	6.8417	6.8437
E_{LUMO} (eV)	0.3700	0.5036	0.5069	0.5099
$\Delta E_{\text{HOMO-LUMO gap}}$ (eV)	6.3182	6.3348	6.3380	6.3269
Electronegativity (χ)	3.5265	3.6710	3.6743	3.6768
Chemical hardness (η)	3.1565	3.1674	3.1674	3.1646
Global softness (σ)	234.57	233.77	233.77	233.97
Electrophilicity index (ω)	1.9673	2.1252	2.1311	2.1360
Dipolemoment (µ- Debye)	1.9389	2.5217	2.5334	2.5450

In Table 8, the calculated parameters described above and the electronic dipole moment { μ_i (i = x, y, z)} and total dipole moment μ_{tot} for the title compound are listed. The total dipole moment is calculated using the following equation [46]:

$$\mu_{tot} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}}$$

The first hyperpolarizability (β) and the components of hyperpolarizability β_x , β_y and β_z of 1-phenyl-1-propanol along with related properties (μ_{total} , α_{total} , and $\Delta \alpha$) are reported in Table 8. The calculated value of the dipole moment is found to be 1.9489 Debye. The highest value of the dipole moment is observed for component μ_x , which is equal to 1.4680D and the lowest value of the dipole moment of the molecule for the component μ_Y is -1.2336 D. The calculated average polarizability and anisotropy of the polarizability is -8.6554×10^{-24} esu and 1.248×10^{-24} esu, respectively. The magnitude of the molecular hyperpolarizability β is one of the important key factors in an NLO system. The B3LYP/6-311+G(d,p) calculated first hyperpolarizability value (β) is 216.333 × 10⁻³³ esu. From the values of dipole moment, polarizability and hyper polarizability, it is evident that the molecule constitute a better NLO material.

NBO analysis

NBO analysis has been performed using B3LYP/6-31+G(d,p) method. The analysis provides an efficient method to study the inter and intra molecular interactions among the bond pairs and also convenient basis for investigation of the charge transfer or conjugative interaction in molecular system. Some electron donor



Fig. 7. HOMO-LUMO of 1-phenyl-1-propanol.

Theoretical electronic absorption spectra of 1 Phenyl 1 Propanol (absorption wavelength λ (nm), excitation energies E(eV) and oscillator strengths (f)) using the TD-DFT/B3LYP/6-311++G(d,p) method.

λ (nm)	<i>E</i> (eV)	(f)	Major contribution	Assignment	Region	Bands
Gas 234.77 212.03 209.71	5.2811 5.8474 5.9121	0.0004 0.0443 0.0014	$H \rightarrow L (10\%)$ $H \rightarrow L (100\%)$ $H \rightarrow L (15\%)$	$n \to \pi^{*}$ $\pi \to \pi^{*}$ $n \to \pi^{*}$	Quartz UV Quartz UV Quartz UV	R-band (German, radikalartig)
DMSO 234.45 212.56 201.61	5.2884 5.8329 6.1496	0.0007 0.0705 0.0011	$H \to L (3\%)$ $H \to L (95\%)$ $H \to L-1 (5\%)$	$n \to \pi^*$ $\pi \to \pi^*$ $n \to \pi^*$	Quartz UV Quartz UV Quartz UV	R-band (German, radikalartig)
Methanol 234.42 212.40 201.67	5.2890 5.8373 6.1478	0.0006 0.0665 0.0008	$H \rightarrow L-1 (2\%)$ $H \rightarrow L (100\%)$ $H \rightarrow L-1 (2\%)$	$n \to \pi^{*}$ $\pi \to \pi^{*}$ $n \to \pi^{*}$	Quartz UV Quartz UV Quartz UV	R-band (German, radikalartig)
Ethanol 234.44 212.47 201.80	5.2885 5.8355 6.1440	0.0006 0.0678 0.0008	$\begin{split} H &\rightarrow L (2\%) \\ H &\rightarrow L (100\%) \\ H &\rightarrow L (2\%) \end{split}$	$n \to \pi^*$ $\pi \to \pi^*$ $n \to \pi^*$	Quartz UV Quartz UV Quartz UV	R-band (German, radikalartig)

H: HOMO; L: LUMO.

Table 7	
Fukui function and global and local softness, and electrophilicity index of 1-phenyl-1-propanol	

Atoms	$f\!\!+\!=(q+1)-q$	f - = q - (q - 1)	$\Delta f = (f+) - (f-)$	$\Delta S = \Delta f \sigma_{gs}$	$\Delta \omega = \Delta f \omega_{gei}$
1 C	0.038965	1.119852	-1.08089	-0.29158	-1.15462
2 C	0.076121	-2.69677	2.772889	0.748012	2.962031
3 C	-0.00596	1.43428	-1.44024	-0.38852	-1.53848
4 C	0.031474	-3.88396	3.915436	1.056224	4.182512
5 C	0.022561	3.607259	-3.5847	-0.967	-3.82921
6 C	0.094266	0.226146	-0.13188	-0.03558	-0.14088
7 H	0.070759	0.016164	0.054595	0.014727	0.058319
8 H	0.060816	0.003125	0.057691	0.015563	0.061626
9 H	0.065247	-0.01513	0.080379	0.021683	0.085862
10 H	0.070211	-0.00063	0.070845	0.019111	0.075677
11 H	0.081764	0.011998	0.069766	0.01882	0.074525
12 C	0.058498	1.211255	-1.15276	-0.31097	-1.23139
13 H	0.061225	0.005377	0.055848	0.015066	0.059657
14 C	-0.00983	1.172581	-1.18241	-0.31897	-1.26307
15 H	0.023893	0.006809	0.017084	0.004609	0.018249
16 H	0.028337	0.0198	0.008537	0.002303	0.009119
17 C	0.031202	-1.08467	1.115876	0.301018	1.191991
18 H	0.041251	0.012245	0.029006	0.007825	0.030985
19 H	0.022039	-0.00113	0.023166	0.006249	0.024746
20 H	0.028723	-0.00712	0.035843	0.009669	0.038288
21 0	0.068328	-0.19646	0.264791	0.07143	0.282853
22 H	0.040115	0.038992	0.001123	0.000303	0.0012

 ΔS = local softness, σ_{gs} – global softness; $-\Delta \omega$ local electrophilic index, ω_{gei} – global electrophilic index.



Fig. 8. Electrophilicity index of the carbon atoms.

orbital, electron acceptor orbital and interacting stabilization energy resulting from the second order micro disturbance theory are reported [47,48] in Table. 9. The result of interaction is a loss of occupancy from concentration of the NBO of idealized Lewis structure into empty non-Lewis orbital. For each donor (*i*) and acceptor (*j*), the stabilization energy E(2) associated with the delocalization $i \rightarrow j$ is estimated as

$$E_2 = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies) and F(i, j) is the off-diagonal NBO Fock matrix element [49].

The π - π^* conjugation of the double bonds in the phenyl ring and its extension of the conjugation is realized outside the ring through π_{C2-C3} - $\sigma^*_{C12-H13}$ hyper conjugation. Normally π_{C-X} to σ_{C-H} donor-acceptor interaction is known as negative hyperconjugation which is signature of blue shift hydrogen bonding. From the lone pair of oxygen (O21) hyperconjugation it is observed that there is interaction through nO21- σ^*_{C3-C12} , $\sigma^*_{C12-H13}$ and $\sigma^*_{C12-C14}$. In the



Fig. 9. MEP map of 1-phenyl-1-propanol.

Table 8

The electronic dipole moment (μ) (Debye), polarizability (α) and first hyperpolarizability (β) of 1-phenyl-1-propanol.

Parameter	a.u.	Parameter	a.u.
α_{xx}	-51.7862	β_{xxx}	12.9608
α_{xy}	0.0472	β_{xxy}	5.9150
α_{vv}	-59.6866	β_{xyy}	-0.9302
α_{xz}	-1.8507	β _{γγγ}	1.3945
α_{vz}	3.0115	β _{xxz}	0.1793
α _{zz}	-63.7389	β_{xyz}	-5.4161
α_{tot}	$-8.6554 imes 10^{-24}$ esu	β_{yyz}	0.4328
Δα	$1.248 \times 10^{-24} \text{ esu}$	β_{xzz}	11.7318
μ_x	1.4680	β_{yzz}	0.4199
μ_y	-1.2336	β_{ZZZ}	-2.2363
μ_z	0.3485	β_{tot}	216.333×10^{-33} esu
μ_{tot}	1.9489		

Second order perturbation theory of Fock matix in NBO basis of 1-phenyl-1-propanol.

Donor	Type of bond	Occupancy	Acceptor	Type of bond	Occupancy	Energy E(2) kcal/ mol	Energy difference <i>E</i> (<i>j</i>)– <i>E</i> (<i>i</i>) a.u.	Polarized energy <i>F</i> (<i>i</i> , <i>j</i>) a.u.
C1–C2	σ	1.98002	C1-C6	σ^{*}	0.01582	2.22	1.26	0.047
			C1—H7	σ^{*}	0.01214	0.96	1.16	0.030
			C2-C3	σ^{*}	0.02385	2.70	1.26	0.052
			C1—H8	σ^{*}	0.01342	1.14	1.18	0.033
			C3-H12	σ^{*}	0.03063	3.44	1.10	0.055
			C6-H11	σ^{*}	0.01210	2.40	1.16	0.047
C1–C6	σ	1.98118	C1-C2	σ^{*}	0.01451	2.21	1.27	0.047
			C1-H7	σ^{*}	0.01214	0.99	1.17	0.047
			C2—H8	σ^{*}	0.01342	2.31	1.18	0.047
			C5–C6	σ^{*}	0.01568	2.18	1.26	0.047
			C5-H10	σ^{*}	0.01196	2.45	1.16	0.048
			C6-H11	σ^{*}	0.01210	0.99	1.17	0.030
	π	1.66608	C2-C3	π	0.33731	19.43	0.29	0.067
			C4—C5	π	0.33676	20.66	0.28	0.068
C1—H7	σ	1.98252	C1–C2	σ	0.01451	0.77	1.10	0.026
			C1–C6	σ	0.01582	0.74	1.09	0.025
			C2–C3	σ	0.02385	3.76	1.09	0.057
			C5–C6	σ	0.01568	3.65	1.09	0.056
C2-C3	σ	1.97436	C1-C2	σ^{*}	0.01451	0.84	1.09	0.027
			C1-H7	σ [*]	0.01214	3.72	1.09	0.057
			C2—H8	σ^{*}	0.01342	1.02	1.18	0.031
			C3–C4	σ^{*}	0.02111	3.12	1.26	0.056
			C3-C12	σ^{*}	0.03063	1.39	1.10	0.035
			C4—H9	σ^{*}	0.01357	2.46	1.15	0.048
			C12-H13	σ^{*}	0.03257	0.60	1.09	0.023
	π	1.64342	C1–C6	π [°]	0.01582	21.05	0.27	0.068
			C4–C5	π	0.33676	20.45	0.27	0.068
			C12-H13	σ^{*}	0.03257	1.13	0.64	0.026
			C12–C14	σ^{*}	0.03357	2.76	0.60	0.040
			C12-021	σ^{*}	0.02419	0.99	0.52	0.022
C2—H8	σ	1.97977	C1-C2	σ	0.01451	0.84	1.09	0.027
			C1-C6	σ^{*}	0.01582	3.72	1.09	0.027
			C2-C3	σ^{*}	0.02385	1.07	1.08	0.030
			C3–C4	σ^{*}	0.02111	4.71	1.08	0.064
$C_{2}-C_{4}$	σ	1 97530	(2 - (3))	σ [*]	0.02385	3 16	1 27	0.056
62 61	0	1107000	C2—H8	ر م	0.01342	2 32	1 18	0.047
			$C_{3}-C_{12}$	ۍ م	0.03063	129	1 10	0.034
			C4C5	σ [*]	0.33676	2.39	1.27	0.049
			C4—H9	σ^*	0.01357	0.97	1.16	1.030
			C5-H10	σ^*	0.01196	2.18	1.16	0.045
			C12-021	σ^*	0.02419	1.13	0.97	0.030
C3–C12	σ	1.97418	C1-C2	σ^{*}	0.01451	2.14	1.20	0.045
			C2–C3	σ^{*}	0.02385	1.76	1.20	0.041
			C3–C4	σ^{*}	0.02111	1.52	1.19	0.038
			C4–C5	σ^{*}	0.33676	2.25	1.20	0.047
			C12–C14	σ^{*}	0.03357	0.81	0.99	0.025
			C14–C17	σ^{*}	0.00846	2.04	1.00	0.040
			021–H22	σ	0.00688	1.87	1.09	0.041
C4–C5	σ	1.98010	C3–C4	σ	0.02111	2.77	1.26	0.053
			C3–C12	σ	0.03063	3.25	1.10	0.054
			C4—H9	σ_{*}	0.01357	1.11	1.16	0.032
			C5–C6	σ_{*}	0.01568	2.22	1.27	0.047
			C5-H10	σ	0.01196	0.98	1.16	0.030
			C6-H11	σ	0.01210	2.38	1.17	0.047
	π	1.67489	C1–C6	π	0.01582	19.43	0.28	0.066
			C2–C3	π	0.02385	20.48	0.29	0.069
C4—H9	σ	1.98097	C2-C3	ਰ	0.02385	4.61	1.09	0.063
			C3–C4	σ	0.02111	0.90	1.09	0.028
			C4–C5	σ	0.33676	0.79	1.10	0.026
			C5–C6	σ	0.01568	3.61	1.09	0.056
C5–C6	σ	1.98077	C1-C6	σ	0.01582	2.17	1.27	0.047
			C1—H7	σ	0.01214	2.41	1.17	0.047
			C4–C5	σ	0.33676	2.28	1.27	0.048
			C4—H9	σ	0.01357	2.48	1.16	0.048
			C5-H10	σ	0.01196	1.00	1.16	0.030
			C6—H11	σ	0.01210	0.98	1.17	0.030
C5-H10	σ	1.98262	C1-C6	σ	0.01582	3.57	1.10	0.056
			C3–C4	σ	0.02111	3.78	1.09	0.057
			C4–C5	σ	0.33676	0.77	1.10	0.026

Table 9 (continued)

Donor	Type of bond	Occupancy	Acceptor	Type of bond	Occupancy	Energy <i>E</i> (2) kcal/ mol	Energy difference <i>E</i> (<i>j</i>)– <i>E</i> (<i>i</i>) a.u.	Polarized energy <i>F</i> (<i>i</i> , <i>j</i>) a.u.
			С5—С6	σ^{*}	0.01568	0.76	1.09	0.026
C6—H11	σ	1.98276	C1—C2 C1—C6 C4—C5 C5—C6	ດ໌ ດ໌ ດ໌	0.01451 0.01582 0.33676 0.01568	3.66 0.77 3.67 0.76	1.10 1.09 1.10 1.09	0.057 0.026 0.057 0.026
C12—H13	σ	1.97629	C2–C3 C2–C3 C3–C12 C14–H16	σ [*] π* σ [*] σ [*]	0.02385 0.02385 0.03063 0.01434	3.63 1.12 0.51 2.64	1.08 0.55 0.92 0.94	0.056 0.024 0.019 0.044
C12—C14	σ	1.97629	C2—C3 C2—C3 C3—C12 C17—H18	σ [*] π* σ [*] σ	0.02385 0.02385 0.03063 0.00492	0.58 2.45 0.97 1.35	1.17 0.64 1.01 1.04	0.023 0.039 0.028 0.034
C12-021	σ	1.99336	C3—C4 C14—H15	σ [*] σ	0.02111 0.03357	1.89 0.94	1.39 1.24	0.046 0.030
C14—H15	σ	1.97542	C12—O21 C17—H20	σ* σ*	0.02419 0.00878	4.67 2.97	0.78 0.92	0.054 0.047
C14—H16	σ	1.98039	C12—H13 C17—H19	σ [*] σ	0.03257 0.00832	2.44 2.78	0.90 0.92	0.042 0.045
C14—C17	σ	1.99070	C3–C12 C12–C14	σ [*] σ	0.03063 0.03357	1.70 2.92	1.02 0.87	0.037 0.045
C17—C19 C17—C20	σ σ	1.99076 1.98999	C14—H16 C14—H15	σ^{*} σ^{*}	0.01434 0.03357	2.55 2.42	0.94 0.94	0.044 0.042
021 021 021 021 021 021 021	n n n n n	1.97846 1.95997	C3–C12 C12–H13 C12–C14 C12–H13 C12–C14 C12–C14 C14–H15	ດ ດ ດ ດ ດ ດ	0.03063 0.03257 0.03357 0.03257 0.03357 0.03357	1.13 0.82 1.76 6.38 4.87 0.69	1.01 1.00 0.96 0.71 0.67 0.73	0.030 0.026 0.037 0.060 0.051 0.020

second lone pair there is relatively higher perturbation energy of 6.38 and 4.87 kcal/mol due to realization of the conjugation with $\sigma_{C12-H13}$ and $\sigma_{C12-H14}^{*}$, π_{C4-C5} shows strong stabilization energies of 19.43 kcal/mol and 20.48 kcal/mol with π_{C1-C6}^{*} and π_{C2-C3}^{*} respectively. And π_{C1-C6} shows comparable stabilization energy of 19.43 kcal/mol and 20.66 kcal/mol with π_{C2-C3}^{*} and π_{C4-C5}^{*} respectively. This reveals that C1–C6 prefers to be acceptor than to be a donor with C4–C5. Conversely π_{C2-C3} involves interaction with π_{C1-C6}^{*} and π_{C4-C5}^{*} with stabilization energy 21.05 kcal/mol and 20.45 kcal/mol indeed it gives the explanation that C1–C6 prefers to be an accepter with C2–C3.

Thermodynamical parameters

On the basis of vibrational analysis, the statically thermodynamic functions: heat capacity *C* entropy *S* and enthalpy changes ΔH for the title molecule were obtained from the theoretical harmonic frequencies and listed in Table 10. From Table 10, it can

 Table 10

 Thermodynamic properties at different temperatures at the B3LYP/6-311+G(d,p) level of 1-phenyl-1-propanol.

T (K)	$C^\circ_{p,m}(\operatorname{cal} \operatorname{mol}^{-1} \operatorname{K}^{-1})$	S_m° (cal mol ⁻¹ K ⁻¹)	ΔH_m° (cal mol ⁻¹ K ⁻¹)
100	119.725	10.730	64.916
200	121.228	19.903	76.354
300	123.799	31.771	87.419
400	127.586	43.798	98.805
500	132.500	54.136	110.170
600	138.347	62.508	121.170
700	144.948	69.279	131.638



Fig. 10. Correlation graph of heat capacity, entrophy and enthalpy with respect to temperature.

be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 700 K due to the fact that the molecular vibrational intensities increase with temperature. The correlation equations between heat capacity, entropy, enthalpy, and temperatures were fitted by quadratic formulae and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.99987, 0.9973, 0.9999 respectively. The corresponding fitting equations are as follows and the correlation graphics of those show in Fig. 10 $C_{p,m}^{\circ} = 0.20522 + 0.00118T + 1.43685 \times 10^{-6}T^2 \quad (R^2 = 0.99987)$

$$S_{\rm m}^{\circ} = 2.17424 + 0.01246T + 1.52227 \times 10^{-5}T^2$$
 ($R^2 = 0.9973$)

 $\Delta H_m^{\circ} = 0.331299 + 0.33129 + 2.31949 \times 10^{-6} T^2 \quad (R^2 = 0.9999)$

Conclusion

A complete geometrical parameter of the compound is carried out. The bonds where substitutional group is attached is stretched higher compared to the bond lengths of the other bond lengths of the phenyl ring, due to that the hexagonal structure of the phenyl ring is deformed. And thorough study on vibrational modes of the molecule is performed experimentally using FT-IR and FT-Raman spectra of the compound and computational by HF. B3LYP and B3PW91 with 6-31+G(d,p)/6-311++G(d,p) basis sets. It is found that C-H out plane vibrations, C=C stretching vibrations are affected by the substitutional group. O-H vibrations are not affected by any other group vibrations. The chemical shifts of all the carbon and hydrogen atoms are calculated, it is found that the two carbon atoms C14 and C17 have higher shifts compared to the other carbon atoms. It is due to the delocalization of σ - σ^* transitions from C12-C14 to C14-C17. The electronegative oxygen atom withdraw electron density around the carbon atoms thus causing more shifts.

UV–Vis and HOMO–LUMO of the compound are carried out and possible three centers of π – π^* transition are identified. Using the reactive descriptors like Fukui, local and global softness, hardness, electronegativity and local and global electrophilicity index, the centers of nucleophilic and electrophilic are indentified. The total and partial dipole moment. polarizability and hyperpolarizability of the compound are calculated and it is found that the molecule is candidate NLO material. The natural bond orbital analysis of the compound indicates that there is strong inter and intra-molecular interactions among the bond pairs. The thermodynamical parameters like heat capacity, entropy and enthalpy are found increasing with the increase of the temperature.

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