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Vibrational Analysis, Electronic Transition Studies and NMR Chemical Shift Analysis on 4-Propylphenol Using DFT Methods

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ABSTRACT

The FT-IR, FT-Raman spectra of the title molecule 4-Propylphenol is recorded in the range 4000–400 cm^{-1}and 4000–500 cm^{-1} respectively. All computations were carried out by DFT methods using the B3LYP/6-311++G (d,p) basis set. The vibrational fundamental modes of the molecule identified from the spectra, in comparison with computed wave numbers, were assigned. The different possible donor and acceptor electronic molecular orbitals were determined using the NBO analysis. The HOMO-LUMO energy distribution was calculated and the oscillator strength of different bonding and anti-bonding orbitals were computed, from which the UV-visible spectrum of the molecule, recorded in the range of 200–1100 nm, was explored as to what transition have the peaks in the spectrum. The NMR chemical shift spectra were recorded in the region 0-12 ppm for hydrogen's and 0-200 ppm for carbons. The shift were also computed using the DFT methods and the values are compared and assigned for different atoms in the molecule. The reactivity of the molecule was also investigated and both the positive and negative centers of the molecule were identified using chemical descriptors and molecular electrostatic potential (MEP) analysis. The non-linear optical (NLO) properties of the title molecule was identified using the calculated values of polarizability and hyperpolarizability. The Docking of the molecule with different protein is carried out in order to understand the biological activity of the molecule.

Keywords:— *FT-IR, FR-Raman, NBO, HOMO, LUMO, Docking, NMR, etc.,*

I. INTRODUCTION

Phenols are a class of organic compounds containing a hydroxyl group and a benzene ring. Unlike normal alcohols, phenols are acidic because of the influence of the aromatic ring. It is a volatile white crystalline solid. Phenols are synthesized by fusing a sulphonic acid with sodium hydroxide to form the sodium salt of the phenol. The free phenol is liberated by adding sulphuric acid. It is used as anti-bacterial and anti-septic and also for the sterilization of surgical instrument and bandaging materials [1]. Phenol denatures protein by its ability to form hydrogen bond and thereby causes denervation. Histologic sections show nonselective nerve destruction, muscle atrophy and necrosis at the site of phenol injections. Higher concentrations of phenol are associated with greater tissue destruction.

Phenol is so in expensive that it attracts many small-scale uses. It is a component of industrial paint strippers used in the aviation industry for the removal of epoxy, polyurethane and other chemically resistant coatings. Phenol derivatives have been used in the preparation of cosmetics including sunscreens, hair colorings, skin lightening preparations, as well as in skin toners/ exfoliators. The combination of alkylation and halogenations produces phenolic micro-biocides which are used as active disinfectants and helps for the preservation of materials. Chloro-phenol is an important group of industrial chemical which got variety of uses ranging from preparation of preservatives to insecticides. But they show highoral toxicity and were almost not biologically degradable [2].

However, phenolic fluorine compounds which are physiologically inert display insignificant toxicity [3]; such low toxicity is an important factor in many applications like agricultural chemicals, pharmaceuticals, biocides and dyes. The vibrational spectrum of phenol was extensively studied and analyzed[4-6], similarly vibrational assignments for almost all the chlorinated phenols, such as isomers of mono chloro-dichloro- and tri-chloro-phenols and penta-chloro phenols were reported by various earlier investigators [7]. The vibrational spectrum of 2,4,6-trichlorophenol has been reported by Faniran and Shurwell [8]. Various spectroscopic studies of chloro and methyl phenol have been reported in literatures [9]. Recently, Singh and Rai have studied the infrared and the electronic absorption spectra of 4-chloro-2-methyl, 4-chloro-3-methyl and 6-chloro-3-methyl phenols. A complete vibrational assignment of phenol and phenol-OD has been given by Evans [5]. However, NBO analysis, Mullikan Charge analysis, NMR chemical shift analysis, and UV analysis accompanied with the complete vibrational analysis supported by DFT computations were not carried out for the title molecule 4-Propylphenol. Hence the present study has been undertaken to carry out all these analyses and report the outcomes.

II. METHODS

Experimental details

The compound 4-propylphenol of spectroscopic grade is purchased from Sigma–Aldrich Chemicals, Chennai. The FT-IR spectrum of the compound is recorded using a Bruker IFS 66V spectrometer in the range of 4000–500 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 an Nd-YAG laser source operating at 1.064 μm line widths with 200 mW power. It was recorded in the range of 4000–500 cm^{-1} with a scanning speed of 30 cm^{-1} of spectral width 2 cm^{-1}. The frequencies of all sharp bands are accurate to ±1 cm^{-1}. The NMR spectra were recorded in ($CdCl_3$) chloroform solvent phase in the range of 0-200 ppm for ^{13}C with the scanning interval of 20 ppm and ^{1}H in the range 0-12 ppm with the scanning interval of 1ppm. The UV-Visible spectrum was recorded in the range of 200-1100 nm, with the scanning interval of 100 nm, using UV-1700 series instrument.

Quantum chemical calculations

All the quantum chemical computations in the this work are performed using the Gaussian 09 (13A)software programs [10] on a Pentium IV/3.02GHz personal computer and the wave numbers and geometrical parameters were computed using B3LYP functional with 6-311++G (d, p) basis set. Density functional theory DFT has been proved to be extremely useful in handling electronic structure of molecules. The basic set 6-311++ G (d,p) was effective study on organic molecules. The potential energy distribution (PED) for each mode of vibration which identifies the purity of the modies computed using VEDA-4 program [11].

III. RESULT AND DISCUSSION

Conformational Analysis

The optimized geometry of the 4-Propylphenol is obtained by using B3LYP with 6-311++G (d,p) basis set and used for conformational analysis of the molecule. Conformational analysis is performed by potential energy surface scan function using semi empirical method PM6. The PM6 method is reported to be very reliable and faster compared to other methods [12]. The surface scan of the molecule is carried out by measuring the total energy of the molecule by varying the dihedral angle 5C-4C-11O-22H from 0 to 360^0. The graphical result, total energy verses scan coordinates of this confirmer analysis is presented in Figure 1. The graph clearly shows that there is a conformer with minimum energy lies in two areas 0 & -180^0 with total energy -425.534 hartee.

Molecular Geometry

The geometrical analysis of 4-propylphenol was carried out using B3LYP methods with 6-311++G (d, p) basis set. The structural parameters such as the bond length and bond angle calculated are presented in Table.1. The pictorial representation is shown in Figure 2.

The computed bond length of C1-C2, C1-C2, C3-C4, C4-C5, and C5-C6 of phenyl ring are found to be around 1.39A° and that of C1-C6 1.40A°. The experimental [13] values coincide with these values except for C5-C6 which is found to be 1.38 and that of C3-C4 & C4-C5 at 1.38A°. For pure benzene ring the bond length values are expected between 1.38 and 1.39A°, which shows the OH substitution has made some influence on the bond lengths within the ring. If there is single and double bonds within the ring, the values would be 1.34A° for double bonds and 1.45A° for single bonds. But here the values are almost equal around 1.39A° which indicates the electronic conjugation is present within the ring, hence the distinction between the double and single bonds are disappeared. Whereas the CC bond lengths outside the ring C1-C12, C12-C13 and C13-C14 bonds are around 1.51, 1.54 and 1.53A° respectively.

This shows that they are purely single bonded but also a slight elongation of the bonds, may be due to repulsion because of the increased negative charges of the carbon atoms in the alkane groups.

The CH bond length of C2-H7, C3-H8, C5-H9 and C6-H10 in the phenol ring is found to be 1.085A°, the experimental value for these bonds is 1.084A° [13]. Both of them are in the expected range which shows the influence of the propyl group on these bonds is insignificant. The bond length of CH bonds in alkane group is 1.09A°, whose experimental value is also 1.09A° which indicate the hydrogen nuclei in the phenyl ring are more positive than that of propyl group.

The computed bond length of C-O and OH bonds in the phenol ring are 1.37A° and 0.962A° respectively. The experimental values of these two bonds are 1.35A° and 0.951A° respectively. The O-H bond length has a good agreement with the experimental value, whereas the bond length of C-O is found to be less experimentally, but both of them are in the expected range which shows they are not influenced by the presence of propyl group.

The bond angle of C-C-C bond in the phenol ring is estimated experimentally as 120°, except at C4 and C1 where the angles are found to be 118 and 119° respectively, these are two points where the substitution groups are attached. The bond angle computed shows variation around 120°. OH is attached at C4 and propyl group is attached at C1 which indicate the influence of OH on the ring is more when compared to that of propyl group.

The CCC bond angle formed in the alkane group makes an angle of 113° whereas its experimental bond angle is 112°. The bond angle of CCH bond in the phenol ring is 120° whose experimental angle is 120° for trigonal planar structure. The angle made by C3-C2-H7 and C5-C6-H10 atoms is reduced as 118°. This reduction is due to the attachment of the heavy alkane group to the CL atom (ie) responsible for angle of nearby atom. The CCH bond angle of alkane group is expected to be 109 A° and is found to have a comparable angle with the theoretical calculation.

The bond angle HCH bond is experimentally found as 106A° which is in good agreement with H20-C12-H21 and H18-C14-H17 bond. But H15-C14-H16, H15-C14-H17 and H16-C14-H17 is found as 107.5A°. This increase in bond angle is due the increase in bond length of C14 and C13 bond. The CCO and COH bond angle in phenol ring is 117° whose experimental value is 115° and 109.5° respectively. In general, the bond angles shows clear deviation from the expected values 120° and 109° at several points which indicate the substitutional groups have caused redistribution electronic charges on these places and formed substantial distortion in the planar structure of the molecule.

Mullikan and Natural charge analysis

The charges on the titled compound are computed using B3LYP and 6-311++G(d, p) basis set. Values are presented in Table. 2 and graphically in Figure 3. The charge analysis on benzene ring reveals that the charges of the carbon atoms in the ring is equally negative, as they draw charges from the hydrogen atoms which are attached to them. This is found to be the case here also, except the C1 and C4, where the substitutions are attached. C1 where propane group is attached is found to be highly positive (1.246) in Mullikan Population analysis (MPA) method, but almost neutral (-0.055) in Natural atomic charge (NAC) method. C4 where Hydroxyl group attached is found to be highly positive (0.307) in NAC and negative (-0.316) in MPA. Since the Oxygen is relatively greater electronegative than carbon, the prediction by NAC seems more reasonable than MPA.

Among the three carbon atoms in the propane chain, there is wider charge variation according to MPA; C12 (-0.823), C13 (-0.135) & C14 (-0.636), which may be based on the fact that C12 is attached to phenyl ring, hence it may draw more electron from the ring, C13 is attached to only two hydrogen atoms, hence the charge it can withdraw is less and C14 is attached to three hydrogen atoms, hence it can have relatively high charge. But in the case of NAC, the first two carbon atoms have almost equal charge (-0.39 & -0.37) whereas the third one is with higher charge (-0.572). This implies the first carbon C12 does not draw any charge from the phenyl ring and the last one relatively higher in charge due to three hydrogen atoms. All the hydrogen atoms bonded with the carbon atom in and out of benzene ring are found to be equally positive. The hydrogen atoms in the propane group is slightly less positive than in the phenyl ring, which means pulling power of the carbon atom in the ring is more when compared to that in the chain. H22 atom is found to be highly positive (0.261 in MPA and 0.465 in NAC) as it is bonded to oxygen.

NMR Assessment

The chemical shifts for H and C atoms of the titled compound were computed for its optimized structure, supported by GIAO functional along with B3LYP & 6-311++G(d, p) combination in both gas and chloroform ($cdcl_3$) phases. The same is also measured experimentally in chloroform phase and the values are tabulated in Table 3. The experimental and theoretical CNMR and HNMR spectra of the compound 4-propylphenol are shown in the Figure 4 (a) & (b) respectively.

In the ^{13}C NMR, Aromatic ring carbon atoms give rise to chemical shifts in the range from 120 to 130ppm [15]. In the title compound the chemical shift of aromatic carbon atoms namely C2, C3, C5 and C6 lies between 116-134 ppm. The C1 and C4 atom show considerable deviation from these value. C1 and C4 have 142 and 161 ppm shift theoretically, whereas both of them have same value 135 ppm experimentally. C1 is attached with propane group and C4 with oxygen group respectively. According to MPA, C1 should have the maximum shift and according to C4 should have the maximum shift. Thus the theoretical prediction coincides with the NCA, but the experimental shift shows equal value for both C1 and C4. The shift for the three carbon atoms in the propane group show values 42, 33, 15 ppm theoretically and 77, 37, & 24 ppm experimentally. All of them are in the expected aliphatic range, but the experimental value 77 ppm for C12 is higher than the aliphatic range which is naturally due to the attachment with the aromatic ring.

Hydrogen attached to aromatic ring have a larger chemical shift, usually from 6.5-8.0 ppm [16]. They are shielded by the large isotropic field generated by the electron in the ring structure. The computed values of 7H, 8H, 9H, and 10H in chloroform ($cdcl_3$) phase are 7.24, 7.33, 6.6 and 6.9 ppm which are in good agreement with experimental results. The aliphatic H atom outside the ring shows interesting chemical shift values. The H atoms in last C14 atom show chemical shift around 1 ppm which is the lowest values, which are lower than the expected value for methyl H atoms. The H atoms in next carbon C13 show chemical shift values around 1.5 ppm which is also less than the expected value for methylene group. The H atoms attached with C12 values shows values around 2.5 ppm which agrees with values of H atom in aliphatic carbon atoms. These variations in chemical shift values are mainly due to the charges finally settled in their respective carbon atoms, which is not uniform in this case.

Vibrational Analysis

In order to obtain vibrational significance of 4-propylphenol,the calculations are performed to find out the normal modes of vibrations using B3LYP method with 6-311++G(d, p) basis set. The molecule contains 22 atoms and hence there are 60 normal modes of vibrations, observed both theoretically and experimentally. The theoretical wave numbers were scaled using suitable scaling factor and all the values are presented in table 4. The experimental FTIR and FT-Raman spectra of the compound are shown in Figure 5.

O–H vibration

The O-H vibrations are generally observed between 3600 and 3200 cm^{-1} [17]. In this present molecule the only one O-H stretching vibration is observed with the value 3399 cm^{-1}. This value is slightly at high end of the expected region, which happens when there is a possibility for the hydrogen bond formation. The calculated value for this band falls still very large value at 3699cm^{-1}.The in-plane and out-plane O-H bending vibrations are observed at 1352 & 894cm^{-1} in FT-Raman respectively, these are slightly low which may be due to the high number of CH stretching modes which also fall in these region.

CH vibration

The aromatic C-H appears in the range 3100 -3000 cm^{-1}[18], which is generally not affected by the substituents, as indicated by the bond lengths in structural analysis. In the present molecule 4-propylphenol, C-H stretching vibrations are observed at 3130 cm^{-1} in FT-IR spectrum and at 3180,3160 &3148 cm^{-1} in FT-Raman spectrum. All these values are slightly greater than the expected values, the reason may be due to the altered conjugation of the charges within the ring due to the substitutions hydroxyl and propanol groups. The calculated wave numbers are 3178, 3151, 3143, 3131 cm^{-1}, which agree well with the experimental values. In aliphatic chains the C-H stretching vibrations are expected within the range 3000-2900 cm^{-1}. There are seven C-H vibrations in propyl group, they are observed at 3023 and 3070, 3068, 3045, 3010, 2980 & 2900 cm^{-1} in the experimental spectra and corresponding calculated values are 3071, 3067, 3042, 3020, 3007, 3003 & 2997 cm^{-1} respectively. All these values are at the higher end of the expected region which is quite unusual and may be due to the enhanced electronic conjugation inside the ring to which the propyl group is attached. The charge distribution in the propyl chain itself is changed due to the attachment with phenol ring.

The in-plane bending and out-of-plane bending modes of both aromatic and aliphatic are generally found within ranges 1300 - 1000 cm^{-1} and 1000-750 cm^{-1} respectively, being separated without much distinction. In the present molecule, the in-plane bending vibrations are observed at 1233, 1174, 1112 cm^{-1} in FT-IR and at 1326, 1301, 1257, 1216, 1151, 1102 cm^{-1} in FT-Raman. The out of plane bending vibrations are observed at 844, 822, 767, 739, 709, 641, 549, 503, 430 cm^{-1} in FT-IR and at 836 and 408 cm^{-1}in FT-Raman. The observed values shows a Fermi resonance effect as the values are extended at both ends.

C-C vibration

Within benzene ring, though C=C and C-C distinction is not there, vibrationally the bands in the region 1600-1500 cm^{-1} are considered as C=C in character and those between 1500-1400 cm^{-1} are due to C-C in character [19].In present molecule, there are nine CC stretching modes, the calculated wave numbers of them are 1647, 1623, 1535, 1503, 1492, 1489, 1480, 1459, 1405 cm^{-1}. Out of these the first three bands 1647, 1623 & 1535cm^{-1} are due to C=C stretching within the ring, the next three bands 1503, 1492, 1489cm^{-1}are due to C-C within the ring and the other three bands 1480, 1459, 1405 cm^{-1}are due to the propyl group. These bands are observed experimentally at 1612, 1513 & 1450 cm^{-1} in FT-IR and at 1635, 1504, 1495, 1483, 1472 & 1460 cm^{-1} in FT-Raman spectra, which exactly coincide with ranges of the calculated frequency. All these values are also found enhanced generally, which is due to the same effect observed in the case of CH vibrations.

Similarly here in the bending modes, the distinction between aromatic and aliphatic CC is disappeared, the C-C in-plane and out of plane bending vibrations are expected in the region 1000-200 cm^{-1}[20]. In the present molecule, they are observed at 1024, 962, 379, 309 and 294cm^{-1}computationally.The Experimental values are observed at 1035, 1016 and 933 cm^{-1}in FT-IR and 1035 and 996 cm^{-1}in FT Raman respectively. Fermi resonance effect is obviously visible here in this mode also.

C-O vibration

The C-O vibrations are generally found mixed with CH in-plane and C-C stretching modes [21] and hence they have to be assigned based on the potential energy distribution (PED) values, here in this molecule there is only one C-O, hence the C - O stretching is observed at 1376 cm^{-1} computationally and respective experimental value is found at 1375 cm^{-1} in FT-IR, based on the PED values. The in-plane and out-plane C-O bending vibrations are found at 934 & 291 cm^{-1}respectively. They are found well within the expected region which shows they are not affected by the other modes in the molecule.

NBO Analysis

Natural bonded orbitals (NBO) analysis is carried out in order to understand the different donor and acceptor orbitals, their occupancies, stability and probability of charge transfer among them. This is useful for understanding the delocalization of electron density from lewis occupied donor to unoccupied non-lewis acceptors within the molecule. The stabilization of orbital interaction is proportional to the energy difference between interacting orbitals. Therefore the interaction having strongest stabilization takes place between effective donors and effective acceptors.

The stabilization energies of the title compound were performed by using second-order perturbation theory [22]. For each donor NBO(i) and acceptor NBO(j), the stabilization energy $E^{(2)}$ associated with electron delocalization between donor and acceptor is estimated as [23-24]

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

Where q_i is the donor orbital occupancy, ε_i, ε_j are diagonal elements (orbital energies) and F(i, j) is the off-diagonal NBO Fock matrix element. In this study, all the above NBO parameters are computed using B3LYP/6-311G++ (d, p) level of theory and the results are presented in Table 5. The larger the E $^{(2)}$ value, the more intensive is the interaction between electron donors and electron acceptors, i.e., the more donating tendency from electron donors and electron acceptors, and greater the extent of conjugation of the whole system.

Based on the stabilization energy values, the top ten highly probable transitions in this molecule are O11 to C3-C4 (n- π*, 26.65 kcal/mol), C5-C6 to C3-C4(π- π*, 22.26 kcal/mol), C1-C2 to C5-C6 (π-π*, 21.74 kcal/mol), C3-C4 to C1-C2(π-π*, 21.16 kcal/mol), C1-C2 to C3-C4 (π - π*, 19.06 kcal/mol), C5-C6 to C1-C2 (π-π*, 18.36 kcal/mol), C3-C4 to C5-C6(π-π*, 17.0 kcal/mol), O11 to C3-C4 (n-σ*, 5.92 kcal/mol), C6-H10 to C1-C2 (σ-σ*, 4.53 kcal/mol), C2-H7 to C1-C6(σ- σ*,4.53 kcal/mol). In this list the last three transitions are less probable as they are not favored by the selection rules. The first of the ten transition is n- π * transition which takes place between OH group and benzene ring, which is the most probable transition in this molecule. The remaining six transitions are π-π* transitions which take place within the benzene ring, which are almost equally probable. However the intensities of these peaks in the spectrum are determined by the occupancy level of the concerned orbitals, which can be calculated from the HOMO-LUMO analysis through the parameter oscillator strength, this is carried out in the UV-Visible analysis.

UV-Visible study

The oscillator strengths (f) and HOMO – LUMO (H↔L) contribution of the top ten transitions of the compound are studied using TD-DFT+B3LYP functional with 6-311++G(d, p) basis set in gas as well as in ethanol phases, as the experimental spectrum of the compound is recorded in ethanol phase. Both experimental and theoretical UV-vis spectra of the compound are presented in Figure 6. Theoretical parameters computed along with experimental absorption wavelength are presented in Table 6.

In ethanol phase, the wave length of the ten transitions are computed to be 252.67, 233.82, 223.51, 218.73, 211.81, 205.38, 200.56, 198.21, 192.60, & 191.56 nm respectively. The corresponding energy gaps of the transitions are 4.9070, 5.3025, 5.5472, 5.6685, 5.8535, 6.0368, 6.1820, 6.2552, 6.4373 & 6.4724 eV respectively and the corresponding oscillator strength are 0.0455, 0.0024, 0.0756, 0.0439, 0.0005, 0.0018, 0.0095, 0.0052, 0.0031, 0.2730 respectively. Observation of these values indicates that only the three transitions will have the appreciable intensity of absorption. That means peaks at 252, 223 and 218nm will have greater intensity in both the spectra, the computational and UV-Vis experimental spectra. The experimental values of these peaks are found to be 278, 223 and 202 nm respectively. The first transition is clearly is in the n-π ∗ transition region in experimental spectrum, whereas this is closer to π – π ∗ transition theoretically. Based on the oscillator strength values the first and third transitions will have almost equal intensity while the second transition will have the maximum intensity, as shown in the theoretical spectrum. But this order is not followed in experimental spectrum, where the first transition has the maximum intensity.

The same ten transitions in gas phase have energy gap, 4.9068, 4.9958, 5.3500, 5.6269, 5.6909, 5.8322, 5.9900, 6.0720, 6.2650, 6.2931eV, absorption wavelengths 252.68, 248.17, 231.75, 220.24, 217.86, 212.58, 206.99, 204.19, 197.90 & 197.02 nm and oscillator strength are 0.0322, 0.0003, 0.0184, 0.0669, 0.0008, 0.0010, 0.0029, 0.0083, 0.0003 & 0.0124 respectively. This shows the solvent has the effect on determining the allowed transition and their wavelength of absorption [25].

HOMO-LUMO Analysis

The highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals(LUMO) are computed with B3LYP functional with 6-311++G(d, p) basis set and the pictorial diagram of the H-L is shown in Figure 7. The HOMO-LUMO energy gap and different reactivity descriptors of molecule in both levels are presented in Table 7.

The parameters mentioned above, which are called as descriptors of molecule, have been calculated at B3LYP/6-311++G(d,p) level. The notations used in the formula are energy gap (ΔE), the ionization potential (I), the electron affinity (A), the absolute hardness (h) and softness (S), and absolute electro negativity (c).

The energy gap between HOMO and LUMO of the title molecule in the gas phase is 0.207 eV. In our case the electro negativity is -0.125 eV. The global hardness is a good indicator of the chemical stability. The global hardness of the title molecule is found to be -0.103 eV. The global softness was -9.63 eV indicating that the global softness is very high.

The electrophilicity index is a measure of the energy lowering due to the maximal electron flow between donor (HOMO) and the acceptor (LUMO). The electrophilicity index of the title molecule is 0.07003 eV. The dipole moment is another important electronic property when a molecule has a large dipole moment, intermolecular interactions are very strong. The calculated dipole moment value for the title compound is 1.441 debye.

IV. MEP (MOLECULAR ELECTROSTATIC POTENTIAL) ANALYSIS

The molecular electrostatic potential (MEP) surface is a method of mapping electrostatic potential of the molecule. The size and shape of the molecule and dipole moment of the molecule provide a visual method to understand the relative polarity of the various points on the molecule. The MEP of the molecule are computed by using B3LYP/6-311++G (d, p) functional and basis set and is shown pictorially in Figure 8. Different values of electrostatic potential at the surfaces are represented by different colours. The MEP is often depicted using a colour scheme such as red denoting the most negative, blue the most positive and other spectrum colours intermediate values.

The electrostatic potential increase in the order red < orange < yellow < green < blue. The colour code of the maps is in the range between -5.911a.u. (deepest red) and5.911 a.u (deepest blue) in compound. The red regions in the cloud are crowded around the negative atoms oxygen and blue colour is found among the hydrogen and some of the carbon atoms. The positive regions of MEP related to electrophilic reactivity and the negative regions to nucleophilic reactivity.

Molecular Docking

Protein-ligand docking method is a new technique for predicting and understanding the biological interaction of the compound with other huge molecules. This technique determines the probable inhibitor binding energy, inter molecular energy, ligand-protein interaction and affinity values of the molecules at the binding sites. To study the binding affinity of the present molecule with several target proteins, the Auto Dock program 4.0 [26] was used. The optimized geometry of the title compound is used as ligand. The protein- ligand binding resolute is determined using Activity Spectra (PASS) [27] and other online tools for various activities.

In present studies, the docking was found to happen with protein 4BNF with a hydrogen bond of length 1.9Åwhich results in the formation of residue GLU 27. The docking indicates that the molecule by docking with the protein, it can indulgein anticancer activity. This details of the ligand-protein interaction is shown in Table.8, and the graphical representation is shown in Figure 9. In vitro anticancer activity of the molecule with a panel of tumor cell lines shows a wide potency range. –

V. FIGURES AND TABLES

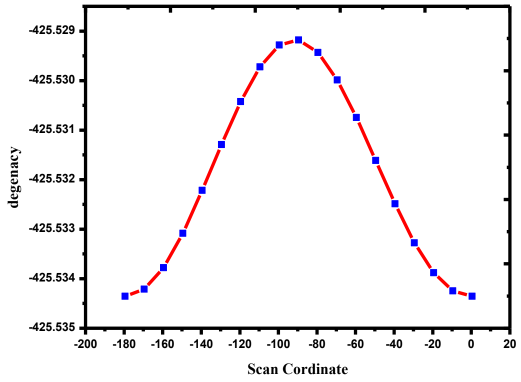


Figure 1. Potential energy surface scan of 4-Propylphenol

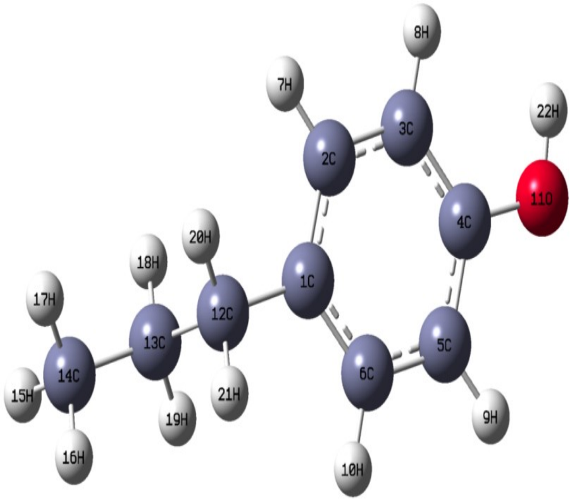


Figure 2: Molecule structure of 4-propyl phenol

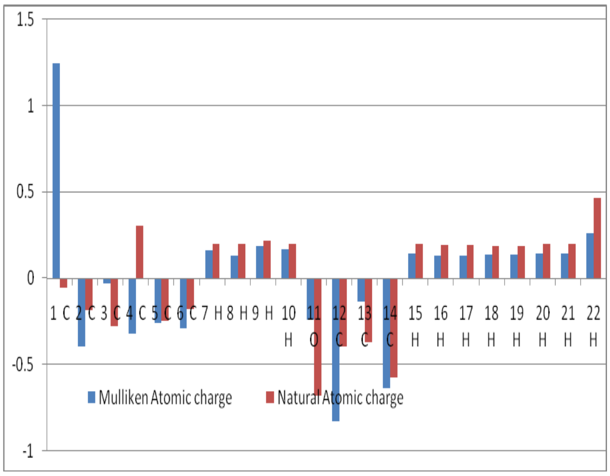
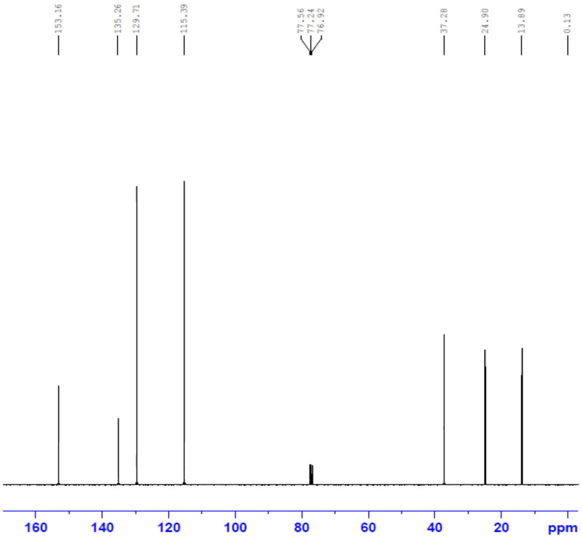


Figure 3: The graphical plot of MAC and NAC in 4-propylphenol



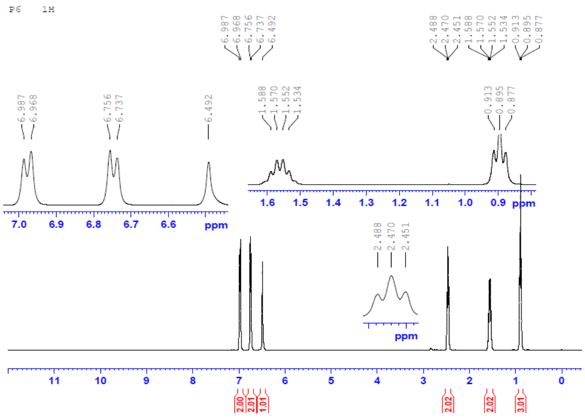


Figure 4.(a) ^{13} C&^{1}H NMR Experimental spectrum for 4-propylphenol

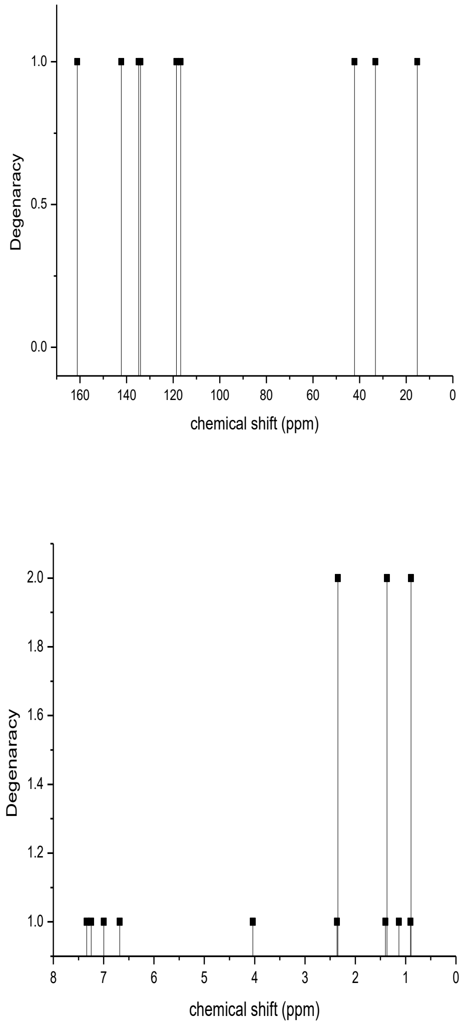


Figure 4(b) ^{13}C &^{1}H NMR theoretical spectrum for 4-propylphenol

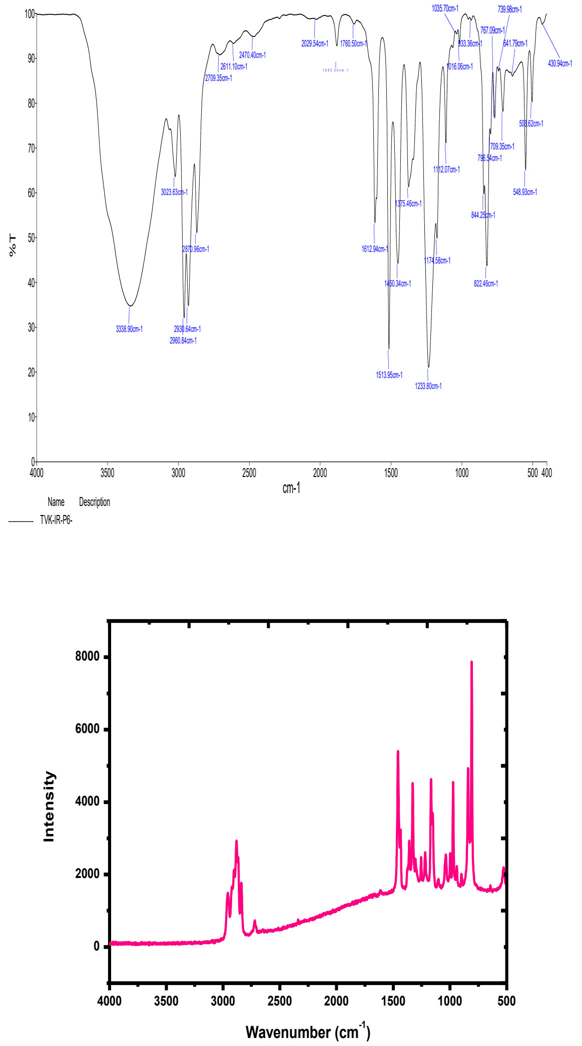


Figure 5. Experimental FT-IR and FT-Raman spectra of 4-propylphenol

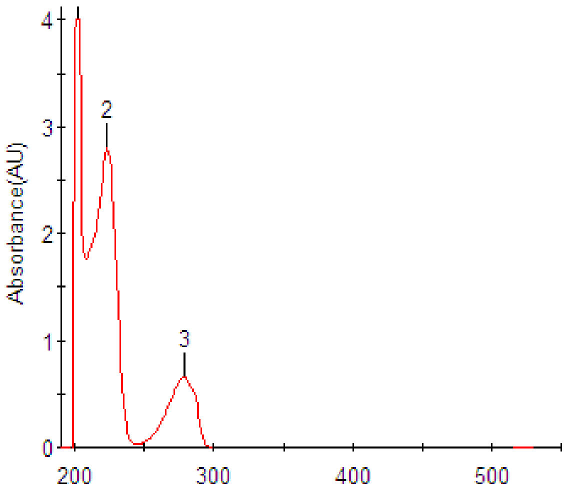


Figure 6. Experimental and Theoretical and UV-Vis Spectra of using 4-propylphenol

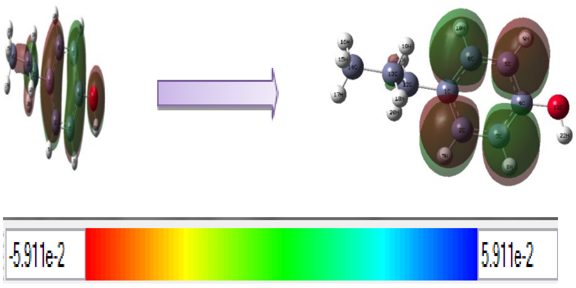


Figure 7. Frontier molecular orbitals of 4-propylphenol

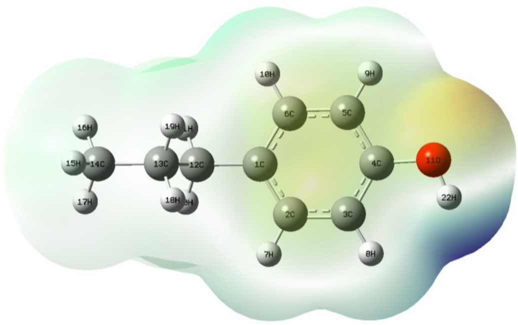


Figure 8. Molecular electrostatic potential

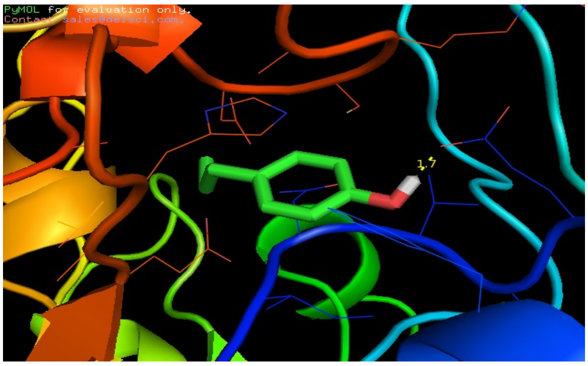


Figure 9. Molecular binding pose

VI. CONCLUSION

The structural analysis of the molecule indicates that the hydroxyl group has considerably altered the conjugation within the ring and also the charge distribution along the propane chain. The charge and NMR chemical shift analysis showed that the charges on the atoms C1 and C4 is drastically altered by the substitutional groups and thereby these atoms show considerable deviation in chemical shift from the expected value; C1 and C4 are found have 142 and 161 ppm shift

Table 1: Optimized Geometrical parameter for 4-Propyl phenol Computed at B3LPY/6-311++G(d,p).

Bond Length (Å)	B3LYP	XRD *	Bond Angle (°)	B3LYP	XRD *
	6-311++G (d,p)			6-311++G (d,p)	
Benzene ring (CC)			Benzene ring (CCC)		
C1-C2	1.3973	1.39	C1-C2-C3	121.51	120.3
C1-C2	1.3942	1.39	C2-C3-C4	119.83	120.3
C3-C4	1.3944	1.41	C3-C4-C5	119.69	118.8
C4-C5	1.3947	1.41	C4-C5-C6	119.67	120.7
C5-C6	1.3907	1.38	C1-C6-C5	121.76	120.0
C1-C6	1.4007	1.39	C2-C1-C6	117.52	119.5
Out of ring (CC)			Out of ring (CCC)		
C1-C12	1.5123	1.51	C2-C1-C15	121.26	
C12-C13	1.5409	1.54	C6-C1-C12	121.18	120.2
C13-C14	1.5309	1.53	C1-C12-C13	113.50	111.5
Benzene ring (CH)			C13-C12-C20	108.93	
C2-H7	1.0856	1.08	C12-C13-C14	112.96	113.9
C3-H8	1.0864	1.08	Benzene ring (CCH)		
C5-H10	1.0835	1.08	C1-C2-H7	119.5709	119.99
C6-H10	1.0857	1.08	C3-C2-H7	118.9124	119.62
Out of ring (CH)			C4-C3-H8	120.1197	119.15
C12-H20	1.096		C2-C3-H8	120.0428	120.44
C12-H21	1.0961		CCO ring		
C13-H18	1.0958	1.09	C3-C4-O11	122.7833	
C13-H19	1.0958	1.09	C5-C4-O11	117.5241	
C14-H15	1.0935	1.09	C4-O11-H22	109.6596	
C14-H16	1.0947	1.09	CCH ring		
C14-H17	1.0947	1.09	C4-C5-H9	119.0803	119.63
Benzene ring (CO)			C6-C5-H9	121.2456	119.58
C4-O11	1.3718	1.35	C1-C6-H10	119.375	120.16
Benzene ring (OH)			C5-C6-H10	118.8635	119.81
O11-22H	0.9627	0.951	C1-C12-H20	109.4883	
			C1-C12-H21	109.469	
			C13-C12-H21	108.9061	
			H20-C12-H21	106.2878	
			C12-C13-H18	108.9614	108.21
			C12-C13-H19	108.9845	108.21
			C14-C13-H18	109.8282	109.36
			C14-C13-H19	109.8056	110.28
			H18-C13-H19	106.0586	106.8
			C13-C14-H15	111.2785	110.77
			C13-C14-H16	111.2595	111.43
			C13-C14-H17	111.2717	112.19
			H15-C14-H16	107.6476	107.57
			H15-C14-H17	107.6515	106.58
			H16-C14-H17	107.5434	108.04

Table 2: Mulliken Charges of 4-Propylphenol with B3LYP/6-311++G(d, p) basis set.

Atoms	Mullikan Atomic Charge	Natural atomic Charge
	B3LYP/6-311+G(d,p)	B3LYP/6-311+G(d,p)
1 C	1.246	-0.055
2 C	-0.395	-0.181
3 C	-0.031	-0.277
4 C	-0.316	0.307
5 C	-0.255	-0.244
6 C	-0.288	-0.179
7 H	0.163	0.200
8 H	0.130	0.198
9 H	0.186	0.216
10 H	0.166	0.200
11 O	-0.236	-0.676
12 C	-0.823	-0.390
13 C	-0.135	-0.370
14 C	-0.636	-0.572
15 H	0.145	0.200
16 H	0.130	0.192
17 H	0.129	0.191
18 H	0.136	0.189
19 H	0.136	0.189
20 H	0.141	0.197
21 H	0.142	0.198
22 H	0.261	0.465

Table 3: Calculated ^{1}H and ^{13} C NMR Chemical shifts (ppm) of 4-propylphenol

Atom	Gas	CdCl$_3$	Exp.	Atom	Gas	CdCl$_3$	Exp.
1C	141.5	142.2	153.1	7H	7.1	7.24	6.91
2C	133.4	133.9	135.2	8H	6.43	6.68	6.75
3C	116.1	116.7	115.3	9H	6.96	6.99	6.96
4C	161.4	161.2	153.1	10H	7.23	7.33	6.97
5C	119.3	118.6	129.7	15H	1.13	1.13	1.55
6C	134.9	134.8	135.2	16H	0.88	0.9	0.91
12C	42.7	42.19	77.21	17H	0.87	0.89	0.89
13C	33.2	33.18	37.28	18H	1.36	1.37	1.57
14C	15.61	15.28	24.9	19H	1.4	1.4	1.58
				20H	2.28	2.34	2.47
				21H	2.31	2.36	2.48
				22H	3.47	4.03	6.73

Table 4a: Observed method DFT/B3LYP with 6-311++G(d,p) level calculated vibrational frequencies of 4-Propylphenol

Experimental frequency cm-^{1}		B3LYP/6-311++G (d,p)	Assignment	PED %
FT-IR	FT-RAMAN	Scaled (cm^{-1})		
3699		3820	ν OH	ν OH 100
	3180	3178	ν CH	ν CH 98
	3160	3151	ν CH	ν CH 98
	3148	3143	ν CH	ν CH 93
3130		3131	ν CH	ν CH 99
	3070	3071	ν CH	ν CH 98
	3068	3067	ν CH	ν CH 95
	3045	3042	ν CH	ν CH 99
3023		3020	ν CH	ν CH 95
	3010	3007	ν CH	ν CH 49
	2980	3003	ν CH	ν CH 89
	2900	2997	ν CH	ν CH 98
	1635	1647	ν CC	ν CC 51, β CCC 1
1612		1623	ν CC	ν CC 59
1513		1535	ν CC	ν CC 10 , β HCC 364
	1504	1503	ν CC	β HCH 7
	1495	1492	ν CC	β HCH 75 γ CHCH 12,
	1483	1489	ν CC	β HCH 74
	1472	1480	ν CC	β HCH 89
	1460	1459	ν CC	β HCC 48
1450		1405	ν CC	β HCC 32, β HCH 29
1375		1376	ν CO	τ HCCC 34 τ HCCH 31,
	1359	1352	β OH	β HCC 45, β HOC 18
	1326	1344	β CH	β HCC 21
		1315	β CH	β HCC 37
	1301	1310	β CH	τ HCCC 41
	1257	1268	β CH	ν OC 50
1233		1243	β CH	β HCC 14, τ HCCC 11, τ HCCC 11
	1216	1222	β CH	ν CC 38
1174		1189	β CH	β HCC 73
	1151	1182	β CH	β HOC 36, ν CC 16
1112		1130	β CH	ν CC 21 β HCC 10,
	1102	1103	β CH	ν CC 21, β CCC 13, β HCC 18, γ CHCH 22
		1075	β CH	ν CHCH 11
1035	1035	1033	β CC	ν CC 26
1016		1024	β CC	β CCC 57, ν CC 24
	996	962	β CC	τ HCCC 27, γ CCCH 56
933		934	β CO	γ CCCH 61, τ HCCC 16
	898	894	γ OH	ν CC 45, β HCC 17
		873	γ CH	β HCC 15, β HCH 11 ,τ HCCC 28,
844		853	γ CH	ν CC 22
	836	834	γ CH	τ HCCC 35 γ CCCH 19, γ OCCC 10
822		808	γ CH	γ CCCH 18, τ HCCC 57

Table 4b: Observed method DFT/B3LYP with 6-311++G(d,p) level calculated vibrational frequencies of 4-Propylphenol

Experimental frequency cm-^{1}		B3LYP/6-311++G(d,p)	Assignment	PED %
FT-IR	FT-RAMAN	Scaled (cm^{-1})		
767		771	γ CH	ν OC 13, ν CC 15
739		742	γ CH	β HCC 21, τ HCCH 34
709		717	γ CH	τ CCCC 56
641		653	γ CH	β CCO 10, β CCC 63, ν CC 10
549		552	γ CH	β CCC 10, τ CCCC 15 γ OCCC 13,
503		503	γ CH	β CCC 28, γ OCCC 19
430		425	γ CH	β CCO 50, β CCC 15
	408	418	γ CH	τ CCCC 74
-	-	379	γ CC	β CCC 12, τ CCCC 27, γ OCCC 23,
-	-	309	γ CC	β CCC 52, β CCO 17
-	-	294	γ CC	β CCC 49, ν CC 12
-	-	291	γ CO	τ HOCC 91
-	-	234	τ CCC	τ HCCH 22 τ HCCC 61,
-	-	201	τ CCC	β CCC 28, τ CCCC 43
-	-	80	τ CCC	τ CCCC 83
-	-	78	τ CCC	β CCC 22, τ CCCC70
-	-	43	τ CCC	τ CCCC 81

ν–stretching; β–in–plane bending; δ–deformation; γ–out of plane bending; ω–wagging and τ-torsion.

Table 5: Second order perturbation theory of Fock matrix in NBO basis of 4-propylphenol

Donor	Type of bond	Occupancy	Acceptor	Type of bond	Occupancy	Energy E(2) kcal/mol
O 11	n	1.88423	C 3 - C 4	π *	0.02696	26.65
C 5 - C 6	π	1.69996	C 3 - C 4	π *	0.02696	22.26
C 1 - C 2	π	1.66304	C 5 - C 6	π*	0.33478	21.74
C 3 - C 4	π	1.66279	C 1 - C 2	π *	0.35322	21.16
C 1 - C 2	π	1.66304	C 3 - C 4	π*	0.39274	19.06
C 5 - C 6	π	1.69996	C 1 - C 2	π *	0.35322	18.36
C 3 - C 4	π	1.66279	C 5 - C 6	π *	0.33478	17
O 11	n	1.97964	C 3 - C 4	s*	0.02696	5.92
C 6 - H 10	s	1.97932	C 1 - C 2	s*	0.0242	4.53
C 2 - H 7	s	1.97925	C 1 - C 6	s*	0.02456	4.53
C 2 - C 3	s	1.97418	C 4 - O 11	s*	0.025	4.44
C 3 - C 4	s	1.97825	C 4 - C 5	s*	0.02475	4.27
O 11 - H 22	s	1.98751	C 4 - C 5	s*	0.02475	4.24
C 5 - H 9	s	1.97818	C 3 - C 4	s*	0.02696	4.07
C 4 - C 5	s	1.973	C 3 - C 4	s*	0.02696	4.05
C 3 - H 8	s	1.97883	C 4 - C 5	s*	0.02475	3.92
C 12 - H 20	s	1.97797	C 1 - C 6	s*	0.02456	3.83
C 5 - C 6	s	1.97818	C 4 - O 11	s*	0.025	3.82
C 12 - H 21	s	1.97751	C 1 - C 2	s*	0.0242	3.71
C 5 - H 9	s	1.97818	C 1 - C 6	s*	0.02456	3.68
C 2 - C 3	s	1.97418	C 1 - C 12	s*	0.02097	3.59
C 5 - C 6	s	1.97818	C 1 - C 12	s*	0.02097	3.56
C 3 - H 8	s	1.97883	C 1 - C 2	s*	0.0242	3.54
C 2 - H 7	s	1.97925	C 3 - C 4	s*	0.02696	3.4
C 2 - C 3	s	1.97418	C 1 - C 2	s*	0.0242	3.39
C 5 - C 6	s	1.97818	C 1 - C 6	s*	0.02456	3.37
C 6 - H 10	s	1.97932	C 4 - C 5	s*	0.02475	3.36
C 1 - C 6	s	1.97302	C 1 - C 2	s*	0.0242	3.3
C 1 - C 2	s	1.97292	C 1 - C 6	s*	0.02456	3.29
C 1 - C 2	s	1.97292	C 2 - C 3	s*	0.01425	3.18
C 1 - C 2	π	1.66304	C 12 - C 13	s*	0.01845	3.05
C 3 - C 4	s	1.97825	C 2 - C 3	s*	0.01425	3.02

Table6: Theoretical electronic absorption spectra of 4-propylphenol (absorption wavelength λ (nm)), excitation energies E (ev) and oscillator strengths (f) using TD-DFT/B3LYP/6-311++G(d, p) method.

λ (nm)		E(eV)	(f)	Major contribution
Theoretical	Experimental			
Gas				
252.68		4.906	0.0322	HOMO->LUMO (84%)
248.17		4.995	0.0003	HOMO->L+1 (95%)
231.75		5.350	0.0183	HOMO->L+2 (81%)
220.24		5.629	0.0669	H-1->LUMO (16%)
217.86		5.690	0.0008	HOMO->L+4 (97%)
212.58		5.832	0.0010	HOMO->L+5 (89%)
206.99		5.990	0.0029	H-1->L+1 (97%)
204.19		6.072	0.0083	HOMO->L+6 (90%)
197.90		6.265	0.0003	HOMO->L+7 (85%)
197.02		6.293	0.0124	H-1->L+2 (73%)
Ethanol				
252.66	278	4.907	0.045	HOMO->LUMO (86%)
233.82		5.302	0.002	HOMO->L+1 (31%)
223.51	223	5.547	0.075	HOMO->L+1 (50%)
218.73	202	5.668	0.043	H-1->LUMO (11%)
211.81		5.853	0.0005	HOMO->L+4 (95%)
205.38		6.036	0.001	HOMO->L+5 (88%)
200.56		6.182	0.009	HOMO->L+6 (93%)
198.21		6.255	0.005	H-1->L+1 (39%)
192.60		6.437	0.003	HOMO->L+7 (89%)
191.56		6.472	0.027	H-1->L+1 (45%)

Table 7: Homo, Lumo, Kubo gap, global electronegativity, global hardness and softness, global electrophilicity index of 4-Propyl phenol.

Parameters	Gas
E_{HOMO} (ev)	0.22942
E_{LUMO} (ev)	0.02181
$\Delta E_{HOMO\text{-}LUMO\ gap}$ (ev)	0.20761
Elecronegativity (χ) (ev)	-0.12561
Global hardness (η)(ev)	-0.10380
Global softness (S)(ev)	-9.63347
Electrophilicity index (ω)(ev)	0.07003
Dipole Moment (m) (debye)	1.44171

Table 8: Details of the ligand-protein interaction

Protein (PDB ID)	No. of hydrogen bond	Bonded Residues	Bond Distance
4BNF	1	GLU 27	1.7

theoretically, whereas both of them have same value 135 ppm experimentally. These higher value in chemical shift serve as an indicator of the elevated biological activity of the molecule. The vibrational analysis showed that the CH and CC stretching vibrations are boosted and they are found to vibrate at the higher end of the expected region, which may be due to the enhanced electronic conjugation inside the ring. The charge distribution in the propyl chain itself is changed due to the attachment with phenol ring. The UV transitions are found to take place in the molecule betweenO11 to C3-C4 (n- π*, 26.65 kcal/mol), C1-C2 to C5-C6 (π-π*, 21.74 kcal/mol), and C3-C4 to C1-C2(π-π*, 21.16 kcal/mol). The docking of the molecule as a ligand with different proteins indicated that the docking is possible with protein 4BNF with a single hydrogen bond formation with length 1.9Å, which results in the formation of residue GLU 27. The docking also indicates that the molecule by docking with the protein, it can indulgein anticancer activity.

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