Experimental [FT-IR and FT-Raman] Analysis and Theoretical [IR, Raman, NMR and UV-Visible] Investigation on Propylbenzene

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Abstract

In the present methodical study, FT-IR, FT-Raman and NMR spectra of the Propylbenzene were recorded and the fundamental vibrational frequencies were tabulated and assigned. The Gaussian hybrid computational calculations were carried out by HF and DFT (B3LYP and B3PW91) methods with 6-311+G(d,p) and 6-311++G(d,p) basis sets and the corresponding results were compared with experimental values. The change of chemical environment of present compound due to the addition of Ethyl and methyl chain was studied. Moreover, 13C NMR and 1H NMR were calculated by using the gauge independent atomic orbital (GIAO) method with B3LYP methods and the 6-311++G(d,p) basis set and their spectra were simulated and the chemical shifts related to TMS were compared. A study on the electronic and optical properties; absorption wavelengths, excitation energy, dipole moment and frontier molecular orbital energies, were performed by HF and DFT methods. The calculated HOMO and LUMO energies (kubo gap) were displayed in the figures which show that the occurring of charge transformation within the molecule. Besides frontier molecular orbitals (FMO), molecular electrostatic potential (MEP) was performed. NLO properties related to Polarizability and hyperpolarizability was also discussed. The local reactivity of the molecule has been studied using Fukui function.

Keywords: Propylbenzene; Gauge independent atomic orbital; Chemical shifts; FMO, Fukui function

Introduction

Propylbenzene is an organic compound that is based on the aromatic hydrocarbon with an aliphatic substitution. It is inflammable and colorless liquid, insoluble in water and less dense than water. The chemical is also flammmable and incompatible with strong oxidizing agents. It is stable, but may form peroxides in storage if in contact with the air. It is important to test for the presence of peroxides before heating or distilling. Other synonyms of Propylbenzene are: n-Propylbenzene; Isocumene; Propylene benzene; 1-Phenylpropane; Phenyl propane; Benzene, n-propyl. When there is contact between aromatic hydrocarbons and strong oxidizing agents it amounts to vigorous reactions sometimes amounting to explosions. They can react exothermically with bases and with diazo compounds. Substitution at the benzene nucleus occurs by halogenations (acid catalyst), nitration, sulfonation, and the Friedel-Crafts reaction. The propylbenzene is a byproduct while alkylation of benzene with propylene and it is useful a starting material for chemical synthesis [1]. Moreover, DIPB can be dehydrogenated to di-isopropenylbenzenes which can further be applied to produce plastics, elastomers and resins with valuable properties [2].

The literature survey reveals that, to the best of our knowledge, no intensive observation of spectroscopic [FT-IR and FT-Raman] and theoretical [HF/DFT] investigation has been reported so far. Therefore, the present investigation was undertaken to study the vibrational spectra, geometrical frame work review, inter and intra molecular interaction between HOMO and LUMO energy levels and first order hyperpolarizability of non linear optical (NLO) activity of the molecule.

Experimental Details

The compound Propylbenzene is purchased from Sigma–Aldrich Chemicals, USA, which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FT-IR spectrum of the compound is recorded in Bruker IFS 66V spectrometer in the range of 4000–400 cm−1. The spectral resolution is ±2 cm−1. The FT-Raman spectrum of same compound is also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 µm line widths with 200 µW power. The spectra are recorded in the range of 4000–100 cm−1 with scanning speed of 30 cm−1min−1 of spectral width 2 cm−1. The frequencies of all sharp bands are accurate to ±1 cm−1.

Computational Methods

In the present work, HF and some of the hybrid methods; B3LYP and B3PW91 are carried out using the basis sets 6-31+G(d,p) and 6-311+G(d,p). All these calculations are performed using GAUSSIAN 09W [3] program package on Pentium IV processor in personal computer. In DFT methods; Becke’s three parameter hybrids function combined with the Lee-Yang-Parrcorrelation function (B3LYP) [4,5], Becke’s three parameter exact exchange-function (B3) [6] combined with gradient-corrected correlational functional of Lee, Yang and Parr (LYP) [7,8] and Perdew and Wang (PW91) [9,10] predict the best results for molecular geometry and vibrational frequencies for moderately larger molecules. The calculated frequencies are scaled down to give up the rational with the observed frequencies. The scaling factors...
are 0.959, 1.028, 1.297 for HF/6-311++G(d,p). For B3LYP/6-311++G(d,p) basis set, the scaling factors are 0.993, 0.810/0.994,1.046, 1.09. For B3PW91/6-31+G/6-311+G(d,p) basis set, the scaling factors are 0.983, 1.04, 1.08/1.01, 0.940, 0.794. The optimized molecular structure of the molecule is obtained from Gaussian 09 and Gaussview program and is shown in Figure 1. The comparative optimized structural parameters such as bond length, bond angle and dihedral angle are presented in Table 1. The observed (FT-IR and FT-Raman) and calculated vibrational frequencies and vibrational assignments are submitted in Table 2. Experimental and simulated spectra of IR and Raman are presented in the Figures 2 and 3.

The *H and *C NMR isotropic shielding are calculated with the GIAO method [11] using the optimized parameters obtained from B3LYP/6-311++G(d,p) method. *C isotropic magnetic shielding (IMS) of any X carbon atoms is made according to value *C IMS of TMS, \( CS_x = IMS_{TMS} - IMS_x \). The *H and *C isotropic chemical shifts of TMS at B3LYP methods with 6-311+G(d,p) level using the IEPCM method in DMSO, Nitromethene and CC4. The absolute chemical shift is found between isotropic peaks and the peaks of TMS [12]. The electronic properties; HOMO-LUMO energies, absorption wavelengths and oscillator strengths are calculated using B3LYP method of the time-dependent DFT (TD-DFT) [13,14] method in gas phase and solvent phase. Moreover, the dipole moment, nonlinear optical (NLO) properties, linear polarizabilities and first hyperpolarizabilities have also been studied. The local reactivity of the molecule has been studied using Fukui function. The condensed softness indices are found and it is used to predict both the reactive centers and possible sites of nucleophilic and electrophilic attacks.

**Results and Discussion**

**Molecular geometry**

The molecular structure of Propylbenzene belongs to CS point group symmetry. The optimized structure of the molecule is obtained from Gaussian 09 and Gaussview program [15] and is shown in Figure 1. The present molecule contains two ethyl and one methyl groups which are loaded in the left moiety. The hexagonal structure of the benzene is broken at the point of substitution due to the addition of heavy mass. It is also evident that, the bond length (C1-C2&C2-C3) at the point of substitution is 0.059Å is greater than rest of others in the

![Molecular Structure of Propylbenzene.](image-url)

| Geometrical parameter | HF/6-311+G(d,p) | 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                 | 1.390          | 1.390           | 1.399              | 1.399               | 1.393               | 1.397               |
| C1-C6                 | 1.385          | 1.386           | 1.393              | 1.393               | 1.388               | 1.391               |
| C1-H7                 | 1.076          | 1.007           | 1.085              | 1.085               | 1.085               | 1.086               |
| C2-C3                 | 1.390          | 1.390           | 1.399              | 1.399               | 1.393               | 1.397               |
| C2-C12                | 1.513          | 1.513           | 1.512              | 1.512               | 1.507               | 1.507               |
| C3-C4                 | 1.385          | 1.385           | 1.393              | 1.393               | 1.388               | 1.391               |
| C3-H8                 | 1.076          | 1.076           | 1.085              | 1.085               | 1.085               | 1.086               |
| C4-C5                 | 1.385          | 1.385           | 1.393              | 1.394               | 1.388               | 1.391               |
| C4-H9                 | 1.075          | 1.075           | 1.084              | 1.084               | 1.083               | 1.085               |
| C5-C6                 | 1.385          | 1.585           | 1.394              | 1.394               | 1.388               | 1.391               |
| C5-H10                | 1.075          | 1.075           | 1.084              | 1.084               | 1.083               | 1.085               |
| C6-H11                | 1.075          | 1.075           | 1.084              | 1.084               | 1.083               | 1.085               |
| C12-C13               | 1.535          | 1.535           | 1.541              | 1.541               | 1.533               | 1.535               |
| C12-H17               | 1.087          | 1.087           | 1.095              | 1.095               | 1.094               | 1.096               |
| C12-H18               | 1.087          | 1.087           | 1.095              | 1.095               | 1.094               | 1.096               |
| C13-H14               | 1.087          | 1.087           | 1.095              | 1.095               | 1.094               | 1.096               |
| C13-C15               | 1.527          | 1.527           | 1.530              | 1.530               | 1.524               | 1.525               |
| C13-H16               | 1.087          | 1.087           | 1.095              | 1.095               | 1.094               | 1.096               |
| C15-H19               | 1.087          | 1.087           | 1.093              | 1.093               | 1.092               | 1.093               |
| C15-H20               | 1.087          | 1.087           | 1.094              | 1.094               | 1.093               | 1.096               |
| C15-H21               | 1.087          | 1.087           | 1.094              | 1.094               | 1.093               | 1.095               |
| **Bond Angle(°)**     |                |                 |                    |                     |                     |                     |
| C2-C1-C6              | 121.024        | 121.024         | 121.059            | 121.059             | 121.010             | 121.049             |
| C2-C1-H7              | 119.540        | 119.540         | 119.350            | 119.383             | 119.350             | 119.352             |
| C6-C1-H7              | 119.434        | 119.434         | 119.638            | 119.558             | 119.638             | 119.598             |
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Table 1: The optimized geometrical parameters of propylbenzene.
### Table 2: Observed and calculated vibrational frequencies of propylbenzene using HF and DFT (B3LYP & B3PW91) at the 6-31+& 6-311+G (d, p) level.

| S. No | Symmetry Species C<sub>n</sub> | Observed Frequency (cm<sup>-1</sup>) | Methods |
|-------|-----------------------------|-----------------------------------|---------|
|       |                             | FT-IR 6-311+G (d, p) | B3LYP 6-311+G (d, p) | B3PW91 6-311+G (d, p) |
| 1     | A'                           | 3009 -                        | 3093 3097 3095 3090 3096 | (C-H) ν |
| 2     | A'                           | 3080 -                        | 3080 3084 3082 3079 3083 | (C-H) ν |
| 3     | A'                           | 3070m                         | 3071 3076 3073 3070 3075 | (C-H) ν |
| 4     | A'                           | 3060m                         | 3059 3063 3060 3057 3062 | (C-H) ν |
| 5     | A'                           | 3040s                         | 3056 3062 3059 3056 3060 | (C-H) ν |
| 6     | A″                           | 3030s                         | 2976 2997 2994 2998 3006 | (C-H) ν |
| 7     | A″                           | 3010w                         | 2973 2994 2991 2993 3001 | (C-H) ν |
| 8     | A″                           | 3005w                         | 2956 2972 2970 2973 2979 | (C-H) ν |
| 9     | A″                           | 2960s                         | 2937 2951 2949 2954 2958 | (C-H) ν |
| 10    | A″                            | 2940s                         | 2927 2937 2935 2935 2938 | (C-H) ν |
| 11    | A″                            | 2930s                         | 2920 2931 2930 2930 2931 | (C-H) ν |
| 12    | A″                            | 2870m                         | 2912 2928 2925 2927 2929 | (C-H) ν |
| 13    | A″                            | 1610w                         | 1653 1596 1596 1621 1605 | (C-C) ν |
| 14    | A″                            | 1605w                         | 1628 1578 1575 1599 1584 | (C-C) ν |
| 15    | A″                            | 1590w                         | 1524 1513 1558 1490 1478 | (C-C) ν |
| 16    | A″                            | 1500s                         | 1505 1499 1503 1461 1454 | (CH₂) δ |
| 17    | A″                            | 1495s                         | 1491 1486 1490 1448 1443 | (C-C) ν |
| 18    | A″                            | 1455m                         | 1442 1484 1442 1440 1436 | (C-C) ν |
| 19    | A″                            | 1450s                         | 1436 1476 1434 1438 1430 | (C-C) ν |
| 20    | A″                            | 1440w                         | 1428 1421 1429 1433 1428 | (C-C) ν |
| 21    | A″                            | 1380w                         | 1374 1353 1361 1363 1354 | (C-C) ν |
| 22    | A″                            | 1340w                         | 1352 1325 1333 1323 1330 | (C-C) ν |
| 23    | A″                            | 1290w                         | 1315 1305 1312 1293 1316 | (C-H) ν |
| 24    | A″                            | 1250w                         | 1277 1286 1294 1267 1306 | (C-H) ν |
| 25    | A″                            | 1200s                         | 1272 1267 1275 1253 1273 | (C-H) ν |
| 26    | A″                            | 1180w                         | 1211 1196 1193 1186 1201 | (C-H) ν |
| 27    | A″                            | 1160w                         | 1170 1175 1172 1174 1188 | (C-H) ν |
| 28    | A″                            | 1160w                         | 1150 1152 1149 1142 1157 | (C-H) ν |
| 29    | A″                            | 1105w                         | 1100 1132 1129 1117 1137 | (C-H) ν |
| 30    | A″                            | 1100w                         | 1106 1094 1075 1100 1069 | (C-H) ν |
| 31    | A″                            | 1095w                         | 1077 1078 1059 1094 1057 | (C-H) ν |
| 32    | A″                            | 1050w                         | 1051 1041 1023 1051 1019 | (C-H) ν |
| 33    | A″                            | 1040w                         | 1032 1022 1004 1036 1007 | (C-H) ν |
| 34    | A″                            | 1030w                         | 1024 1010 993 1032 1002 | (C-C) ν |
| 35    | A″                            | 1000s                         | 1018 990 972 1001 968 | (C-C) ν |
| 36    | A″                            | 910w                          | 943 974 952 997 913 | (C-C) ν |
| 37    | A″                            | 895w                          | 929 956 937 979 902 | (C-H) ν |
| 38    | A″                            | 890w                          | 882 868 886 895 896 | (C-H) ν |
| 39    | A″                            | 865w                          | 824 835 855 839 871 | (C-H) ν |
| 40    | A″                            | 840w                          | 814 821 841 815 846 | (C-H) ν |
| 41    | A″                            | 820w                          | 806 798 815 802 826 | (C-H) ν |
| 42    | A″                            | 740vs                         | 757 770 788 771 760 | (C-H) ν |
| 43    | A″                            | 705vs                         | 710 711 727 714 700 | (C-H) ν |
| 44    | A″                            | 700vs                         | 682 697 713 691 682 | (C-C) ν |
| 45    | A″                            | 610m                          | 664 665 649 666 655 | (C-H) ν |
| 46    | A″                            | 590s                          | 583 594 580 591 581 | (C-H) ν |
| 47    | A″                            | 570vs                         | 550 559 546 558 547 | (C-H) ν |
| 48    | A″                            | 530vs                         | 505 493 542 496 489 | (C-H) ν |
| 49    | A″                            | 490s                          | 418 410 442 404 398 | (CCC) δ |
| 50    | A″                            | 480s                          | 341 343 370 337 332 | (CCC) δ |
| 51    | A″                            | 470vs                         | 305 307 330 302 299 | (CCC) δ |
| 52    | A″                            | 400 m                         | 278 276 297 271 266 | (CCC) γ |
| 53    | A″                            | 370m                          | 238 227 245 225 222 | (CCC) γ |
| 54    | A″                            | 280s                          | 103 101 109 99 98 | (CCC) γ |
| 55    | A″                            | 270s                          | 84 82 89 82 80 | (C-C) γ |
| 56    | A″                            | 260s                          | 37 45 48 38 43 | (C-C) γ |
ring. Consequently, the property of the same also changed with respect to the ligand (ethyl and methyl groups). The bond angle of C1-C2-C3 is 1.306° elevated than C4-C5-C6 in the ring which also conform the breaking of hexagonal shield.

The structure optimization and zero point vibrational energy of the compound in HF and DFT(B3LYP/B3PW91) with 6-311+/6-311+G(d,p) are 123.00, 115.69, 115.679, 116.943, and 115.89 Kcal/Mol, respectively. The calculated value of HF is greater than the values of DFT method because the assumption of ground state energy in HF is greater than the true energy. Though, both C loaded by CH2, the bond length values between C2-C12 and C12-C13 are differed 0.0290 Å since further weighted by CH3 in the chain. The entire C-H bonds in the chain and methyl group having almost equal inter nuclear distance. Form the optimized molecular structure; it is observed that there is no arithmetical change in the chain. So there is no further change in geometrical property.

Vibrational assignments

In order to obtain the spectroscopic signature of the propylbenzene, the computational calculations are performed for frequency analysis. The molecule, has Cs point group symmetry, consists of 21 atoms, so it has 57 normal vibrational modes. On the basis of Cs symmetry, the 57 fundamental vibrations of the molecule can be distributed as 39

| S. No. | Observed frequency | HF  | B3LYP | B3PW91 |
|--------|-------------------|-----|-------|--------|
|        |                   | 6-311G (d,p) | 6-31G (d,p) | 6-311G (d,p) | 6-31G (d,p) |
| 1      | 3090w             | 3347 | 3187  | 3211   | 3198   |
| 2      | 3080m             | 3333 | 3174  | 3199   | 3185   |
| 3      | 3070m             | 3323 | 3166  | 3165   | 3190   |
| 4      | 3060m             | 3310 | 3152  | 3152   | 3176   |
| 5      | 3040s             | 3307 | 3151  | 3151   | 3175   |
| 6      | 3030s             | 3220 | 3084  | 3084   | 3115   |
| 7      | 3010w             | 3217 | 3081  | 3081   | 3110   |
| 8      | 3005w             | 3199 | 3059  | 3058   | 3089   |
| 9      | 2960s             | 3178 | 3037  | 3037   | 3069   |
| 10     | 2940s             | 3167 | 3023  | 3023   | 3050   |
| 11     | 2930s             | 3160 | 3017  | 3017   | 3044   |
| 12     | 2910m             | 3151 | 3012  | 3012   | 3071   |

Table 3: Calculated unscaled frequencies of propyl benzene using HF/DFT (B3LYP/B3PW91) with 6-311+(d,p) and 6-311+G(d,p) basis sets.
in-plane vibrations of $A'$ species and 18 out of plane vibrations of $A^*$ species, i.e., $\Gamma_{\text{vo}} = 39 A' + 18 A^*$. In the CS group symmetry of molecule is non-planar structure and has the 57 vibrational modes span in the irreducible representations.

The harmonic vibrational frequencies (unscaled and scaled) calculated at HF, B3LYP and B3PW91 levels using the triple split valence basis set along with the diffuse and polarization functions, 6-31+G(2d,p) and observed FT-IR and FT-Raman frequencies for various modes of vibrations have been presented in Tables 2 and 3. Comparison of frequencies calculated at HF and B3LYP/B3PW91 with the experimental values reveal the over estimation of the calculated vibrational modes due to the neglect of a harmonicity in real system. Inclusion of electron correlation in the density functional theory to certain extends make the frequency values smaller in comparison with the HF frequency data. Reduction in the computed harmonic vibrations, although basis set sensitive is only marginal as observed in the DFT using 6-311+G(d,p).

C-H Vibrations: The C–H stretching vibrations are normally observed in the region 3100–3000 cm$^{-1}$ for aromatic benzene structure [16,17] which shows their uniqueness of the skeletal vibrations. The bands appeared at 3090, 3070, 3065, 3060 and 3040 cm$^{-1}$ in the Propylbenzene have been assigned to C–H ring stretching vibrations. The C–H in-plane ring bending vibrations are normally occurred as a number of strong to weak intensity bands in the region 1300-1000 cm$^{-1}$ [18]. In the present case, four C–H in-plane bending vibrations of the present compound are identified at 1290, 1280, 1250 and 1200 cm$^{-1}$. The calculated frequencies for B3LYP/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods for C–H in-plane bending vibrations showed excellent agreement with recorded spectrum as well as literature data. The C–H out-of-plane bending vibrations are normally observed in the range 1000–809 cm$^{-1}$ [19]. The C–H out-of-plane bending vibrations is observed at 895, 890, 865, 840 and 820 cm$^{-1}$. The entire C–H stretching and bending vibrations are located at the top end of the expected region which is because of these vibrations have not affected by ethyl and methyl group in the molecule. Whereas, all the out of plane bending vibrations are suppressed to the lower end of the expected region.

Methyl groups vibrations: With the aromatic ring, for the substitution of CH$_3$ group, the vibrational frequencies for nine fundamental vibrations such as three stretching, in plane and out of plane bending vibrations normally observed in the region of 3000-2750 cm$^{-1}$, 1250-950 cm$^{-1}$ and 950-720 cm$^{-1}$ [19,20], respectively.

Accordingly, the stretching vibrational peaks are observed at 3030, 3010 and 3005 cm$^{-1}$, in plane bending vibrational bands are found at 1180, 1160, and 1105 cm$^{-1}$ and out of plane bending signals are identified at 740, 705 and 700 cm$^{-1}$. All the CH$_3$ stretching vibrations are located in asymmetric range which shows the enhancement of CH$_3$ group vibrations in the present molecule. Except, two out of plane vibrations, the entire bending signals are received within the expected region. The ethyl group in the chain influences the bending vibrations of CH$_3$. The above assignments go along with the literature of R.N. Singh and Varsanyi [19,20].

Ethyl group vibrations: The aliphatic chain substitution CH$_2$ ethyl group with the aromatic ring will have eight fundamental vibrations such as four stretching, in plane and out of plane bending vibrations normally found in the region of 3000-2850, 1300-1000 cm$^{-1}$ and 810-722 cm$^{-1}$ [21,22], respectively. In the present study of propylbenzene the stretching vibrations are found at 2960,2930, 2910, 2870 cm$^{-1}$, the in-plane bending vibrations are found at 1100, 1095, 1050, 1040 cm$^{-1}$ and subsequently out of plane vibrations are at 610, 590, 570 and 530 cm$^{-1}$. All the stretching and bending vibrational bands are found within the region.

C-C vibrations: The bands due the C-C stretching vibrations are called skeletal vibrations normally observed in the region 1430–1650 cm$^{-1}$ for the aromatic ring compounds [23,24]. Socrates [25] mentioned that, the presence of conjugate substituent suchs C=C causes stretching peaks around the region 1625-1575 cm$^{-1}$. As predicted in the earlier references, in this title compound, the prominent peaks are found with strong and medium intensity at 1610, 1605 and 1590 cm$^{-1}$ due to C=C stretching vibrations. The C-C stretching vibrations are appeared at 1495, 1455 and 1450 cm$^{-1}$. The CCCin-plane and out of plane bending vibrations are appeared at 490, 480 and 470 cm$^{-1}$ and 400, 370 and 280 cm$^{-1}$. Similar to the ring C-H vibrations, these skeletal CC stretching and bending vibrations are found within the expected region and also make a good agreement with literature [26].

NMR assessment: NMR spectroscopy is currently used for structure elucidation of complex molecules. The combined use of experimental and computational tools offers a powerful gadget to interpret and predict the structure of bulky molecules. The optimized structure of Propylbenzene is used to calculate the NMR spectra at B3LYP method with 6-311++G(d,p) level using the GIAO method and the chemical shifts of the compound are reported in ppm relative to TMS for $^1$H and $^{13}$C NMR spectra which are presented in Table 4. The corresponding spectra are shown in Figure 4.

In view of the range of $^{13}$C NMR chemical shifts for similar organic molecules usually is >100 ppm [27,28], the accuracy ensures reliable interpretation of spectroscopic parameters. In the present work, $^{13}$C NMR chemical shifts of some carbons in the chain are >100 ppm, as they would be expected in Table 5. In the case of Propylbenzene, the chemical shift of C1, C3, C3/C4, C5 and C6 are 81.21, 77.35, 86.13, 78.60, and 85.31 ppm, respectively. The shift is higher in C2, C12, C13 and C15 than rest of others.

The C3 in the chain has more shifted than other due to the delocalization of $\sigma$ and $\pi$ electrons. The shift of the entire carbons of the ring is found increased when going from gas to solvent due to the solvent effect. The shift values of carbons in DMSO phase are greater than Chloroform phase. The chemical shift values of oxygen have not changed due to the solvent effect. The experimental and theoretical $^1$H and $^{13}$C NMR chemical shift of Propylbenzene are presented in Table 5. This effect of isolation is the main cause to change the chemical property from benzene to Propylbenzene.

Optical properties (HOMO-LUMO analysis)

The UV and visible spectroscopy is used to detect the presence of chromophores in the molecule and whether the compound has NLO properties or not. The calculations of the electronic structure of Propylbenzene are optimized in singlet state. 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 on the previously optimized ground-state geometry of the molecule. The calculations are performed for Propylbenzene in gasphase and with the solvent of DMSO, CC14, and Nitromethane. The calculated excitation energies, oscillator strength ($f$) and wavelength ($\lambda$) and spectral assignments are given in Table 6.

TD-DFT calculations predict three transitions in the quartz ultraviolet region. In the case of gas phase, the strong transition is at 234.96, 210.53 and 205.88nm with an oscillator strength $f$=0.0048.
Theoretical electronic absorption spectra of propylbenzene (absorption wavelength \( \lambda \) (nm), excitation energies \( E \) (eV) and oscillator strengths (f) obtained using the TD-DFT/B3LYP/6-311++G(d,p) method.

| Atom position | Gas | Chloroform | Solvent | DMSO |
|---------------|-----|------------|---------|------|
|               | B3LYP/6-311+G(d,p) (ppm) | B3LYP/6-311+G(d,p) GIAO (ppm) | Shift (ppm) | B3LYP/6-311+G(d,p) (ppm) | B3LYP/6-311+G(d,p) GIAO (ppm) | Shift (ppm) | B3LYP/6-311+G(d,p) (ppm) | B3LYP/6-311+G(d,p) GIAO (ppm) | Shift (ppm) |
| C1            | 50.6257 | 131.84 | 81.2143 | 50.6257 | 131.84 | 81.2143 | 50.2521 | 132.214 | 81.9619 |
| C2            | 35.1536 | 147.312 | 112.1584 | 35.1536 | 147.312 | 112.1584 | 33.6205 | 148.845 | 115.2245 |
| C3            | 52.5577 | 129.908 | 77.3503 | 52.5577 | 129.908 | 77.3503 | 52.2505 | 130.215 | 77.9645 |
| C4            | 48.1658 | 134.3 | 86.1342 | 48.1658 | 134.3 | 86.1342 | 48.155 | 134.31 | 86.155 |
| C5            | 51.9287 | 130.537 | 78.6083 | 51.9287 | 130.537 | 78.6083 | 50.2138 | 130.234 | 78.0022 |
| C6            | 48.5706 | 133.89 | 85.3194 | 48.5706 | 133.89 | 85.3194 | 48.5497 | 133.916 | 85.3663 |
| C12           | 142.636 | 39.8297 | 102.8063 | 142.636 | 39.8297 | 102.8063 | 142.899 | 39.5661 | 103.3329 |
| C13           | 167.62 | 14.846 | 152.774 | 167.62 | 14.846 | 152.774 | 167.836 | 14.6298 | 153.2062 |
| C15           | 169.06 | 13.4059 | 155.6541 | 169.06 | 13.4059 | 155.6541 | 169.613 | 12.8531 | 156.7599 |
| 7H            | 24.3718 | 7.5103 | 16.6815 | 24.3718 | 7.5103 | 16.6815 | 24.1899 | 7.6922 | 16.4977 |
| 8H            | 24.1444 | 7.7377 | 16.4067 | 24.1444 | 7.7377 | 16.4067 | 23.9782 | 7.9039 | 16.0743 |
| 9H            | 24.286 | 7.5961 | 16.8899 | 24.286 | 7.5961 | 16.8899 | 24.1354 | 7.7467 | 16.3887 |
| 10H           | 24.4747 | 7.4074 | 17.0673 | 24.4747 | 7.4074 | 17.0673 | 24.3433 | 7.5388 | 16.8045 |
| 11H           | 24.2974 | 7.5847 | 16.7127 | 24.2974 | 7.5847 | 16.7127 | 24.1466 | 7.7375 | 16.4071 |
| 14H           | 30.66 | 1.2221 | 29.4379 | 30.66 | 1.2221 | 29.4379 | 30.628 | 1.2541 | 29.3739 |
| 16H           | 31.0626 | 0.8195 | 30.2431 | 31.0626 | 0.8195 | 30.2431 | 31.0074 | 0.874 | 30.1334 |
| 17H           | 32.2216 | 1.6605 | 28.5611 | 32.2216 | 1.6605 | 28.5611 | 30.1511 | 1.731 | 28.4201 |
| 18H           | 29.2452 | 2.6369 | 26.8083 | 29.2452 | 2.6369 | 26.8083 | 29.191 | 2.6911 | 26.4999 |
| 19H           | 31.0626 | 0.8219 | 30.2407 | 31.0626 | 0.8219 | 30.2407 | 31.064 | 0.8181 | 30.2459 |
| 20H           | 32.0056 | -0.1235 | 32.1291 | 32.0056 | -0.1235 | 32.1291 | 31.9903 | -0.1082 | 32.0985 |
| 21H           | 31.1101 | 0.772 | 30.3381 | 31.1101 | 0.772 | 30.3381 | 31.0941 | 0.788 | 30.3061 |

| Table 4: Experimental and calculated 1H and 13C NMR chemical shifts (ppm) of propylbenzene. |

| Table 5: Theoretical electronic absorption spectra of propylbenzene (absorption wavelength \( \lambda \) (nm), excitation energies \( E \) (eV) and oscillator strengths (f)) obtained using the TD-DFT/B3LYP/6-311++G(d,p) method. |
Figure 4: ¹H and ¹³C NMR spectra of Propylbenzene in Gas and Solvant phase.

Figure 5: UV Visible spectra of Propylbenzene in Gas and Solvant Phase.
stability. Similarly, the electronegativity is increased from 3.45 up to 3.36, from Gas to solvent, if the value is greater than 1.7; the property of bond is changed from covalent to ionic. Accordingly, the bonds in the compound converted from covalent to ionic and are independent of solvent. Electropicity index is the measure of energy lowering due to maximal electron flow between donor [HOMO] and acceptor [LUMO]. From the Table 7, it is found that the Electropicity index of Propylbenzene is 3.45 in gas and 3.36 in solvent, which is moderate and this value ensure that the strong energy transformation between HOMO and LUMO. The dipole moment in a molecule is another important electronic property. Whenever the molecule has larger the dipole moment, the intermolecular interactions are very strong. The calculated dipole moment value for the title compound is 12.24 Debye in gas and 15.75 in solvent. It is too high which shows that; the Propylbenzene molecule has strong intermolecular interactions.

**Global softness and local region-selectivity**

Molecular charge distribution, molecular orbital surfaces and HOMO and LUMO energies have been used as reactivity descriptors in DFT study. The energy gap between the HOMO and LUMO orbital have been found to be adequate to study the stability and chemical reactivity of great variety of molecular system and is an important stability index. Besides the traditional reactivity descriptors there are a set of chemical reactivity descriptors which can be derived from DFT, such as global hardness (η), global softness, local softness (S), Fukui function (f) and global and local electropicity indexes (ω) [29-39]. These quantities are often defined by the Koopman’s theorem [40,41].

Electronegativity (χ) is the measure of the power of an electron or group of atoms to attract electrons towards itself [42] and according to Koopman’s theorem; it can be estimated by using the following equation:

\[ \chi = - \frac{1}{2} \left( E_{\text{HOMO}} + E_{\text{LUMO}} \right) \]  

(1)

Where \( E_{\text{HOMO}} \) is the energies of the highest occupied molecular orbital (HOMO) and \( E_{\text{LUMO}} \) is the energy of the lowest unoccupied molecular orbital (LUMO). Global hardness (η) measures the resistance of an atom to a charge transfer [41] and it is estimated using the equation:

\[ \eta = - \frac{1}{2} \left( E_{\text{HOMO}} + E_{\text{LUMO}} \right) \]  

(2)

Global softness (S) describes the capacity of an atom or group of atoms to receive electrons [43] and it is estimated by using the equation:

\[ S = \frac{1}{\eta} = -2 \left( E_{\text{HOMO}} - E_{\text{LUMO}} \right) \]  

(3)

Where, η is the global hardness values. Global electropicity index (ω) is estimated by using the electronegativity and chemical hardness parameters through the equation:

\[ \omega = \frac{\chi}{2\eta} \]  

(4)

A high value of electropicity describes a good electrophile while a small value of electropicity describes a good nucleophile.

Fukui indices are a measurement of the chemical reactivity, as well as an indicator of the reactive regions and the nucleophilic and electrophilic behaviors of the molecule. The regions of a molecule where the Fukui function is large are chemically softer than the regions where the Fukui function is small, and by invoking HSAB principle in a local sense, one may establish the behavior of different sites with respect to hard or soft reagents. Condensed to atom Fukui function is reactive descriptor to identify nucleophilic and electrophilic attack site in candidate molecules, perhaps it is also used to recognize the electron acceptor center and donor centers. \( f_+ \) for any given site is positive then it is a preferred site for nucleophilic attack, on the contrary negative value implies electrophilic attack.

The Fukui function is defined as [44,45]:

\[ f(r) = \int \frac{\partial \rho(r)}{\partial N} dr \]  

(5)

Where \( \rho(r) \) is the electron density and \( N \) is the number of electrons and \( r \) is the external potential exerted by the nucleus.

Phenyl ring gets activated at ortho and para positions as there are electron releasing substituent such as –OH, –NH2, –OR, R, etc. Propyl substituent in fact is an electron releasing substituent, consequently promotes the ortho and para positions for electrophilic attack a common reactivity trend observed in phenyl compounds. Local reactivity descriptors such as \( f_k+, f_k-, \Delta f, \Delta \omega \) for the different sites of phenyl ring are in conformity with the observed reactivity trend of the candidate molecule.

\( f_k+, f_k-, \Delta f, \Delta \omega \) unambiguously reveal the nucleophilic attack to be in the decreasing sequence as C6>C4>C2 and that of electrophilic attack is to be found in the order C1>C3>C5 in the phenyl ring. This trend for attack of electrophile is in conformity with that of AS and \( \Delta \omega \). The ortho and para positions show the tendency for attack of electrophile which is indeed a common trend observed in alkyl substituted phenyl ring compounds.

**Molecular electrostatic potential (MEP) maps**

The molecular electrical potential surfaces illustrate the charge distributions of molecules three dimensionally. This map allows us to visualize variably charged regions of a molecule. Knowledge of the charge distributions can be used to determine how molecules interact with one another and it is also be used to determine the nature of the chemical bond. Molecular electrostatic potential is calculated at the B3LYP/6-311+G(d,p) optimized geometry [46,47]. There is a great deal of intermediary potential energy, the non red or blue regions indicate that the electro negativity difference is not very great. In a molecule with a great electro negativity difference, charge is very polarized, and there are significant differences in electron density in different regions of the molecule. This great electro negativity difference leads to regions that are almost entirely red and almost entirely blue [48]. Greater regions of intermediary potential, yellow and green, and smaller or no regions of extreme potential, red and blue, are key indicators of a smaller electronegativity.

The color code of these maps is in the range between -6.15 a.u. (Deep red) to 6.15 a.u. (deepest blue) in compound. The positive (blue) regions of MEP are related to electrophilic reactivity and the negative (green) regions to nucleophilic reactivity shown in Figure 6. From the MEP map of the candidate molecule the red regions of the molecule found to be ready for electrophilic attack, and especially in the phenyl ring the atoms are clouded with red colour. From the findings of the Fukui local reactivity descriptor the atoms C1, C3 and C5 are nucleophile ready for electrophilic attack and atoms C2, C4 and C6 are the regions for nucleophilic attack. Molecular electrostatic potential map can be confirmed with the finding of the Fukui descriptors.
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 Propylbenzene compound was calculated using DFT-B3LYP method and 6-311+G(d,p) basis set, based on the finite-field approach.

The Polarizability and hyperpolarizability tensors (Table 8) \((\alpha_{xx}, \alpha_{yy}, \alpha_{zz} \alpha_{xy}, \alpha_{yz}, \alpha_{xz})\) and \((\beta_{xx}, \beta_{yy}, \beta_{zz}, \beta_{xy}, \beta_{yz}, \beta_{xz})\) can be obtained by a frequency job output file of Gaussian. However, \(\alpha\) and \(\beta\) values of Gaussian output are in atomic units (a.u.). So they have been converted into electronic units (esu) \((1\text{ a.u.}=0.1482\times10^{-24}\text{esu}, 1\text{ a.u.}=8.6393\times10^{-33}\text{ esu})\). The calculations of the total molecular dipole moment \((\mu)\) and first order hyperpolarizability \((\beta)\) from the Gaussian output have been explained in detail previously \([49,50]\). DFT has been extensively used as an effective method to investigate the organic NLO materials \([51-55]\).

\[
\Delta \alpha = \frac{1}{2} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{xz}^2) \right]^{1/2} \quad (7)
\]

\[
\langle \beta \rangle = \left[ (\beta_{xx} + \beta_{yy})^2 + (\beta_{yy} + \beta_{zz})^2 + (\beta_{zz} + \beta_{xx})^2 + (\beta_{xy} + \beta_{yz} + \beta_{xz})^2 \right]^{1/2} \quad (8)
\]

In Table 7, the calculated parameters described above and electronic dipole moment \(\mu(i=x, y, z)\) and total dipole moment \((\mu_{tot})\) for title compound are listed. The total dipole moment was calculated using the following equation \([56]\).

\[
\mu_{tot} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (9)
\]

It is well known that, molecule with high values of dipole moment, molecular Polarizability, and first hyperpolarizability having more active NLO properties. The first hyperpolarizability \((\beta)\) and the component of hyperpolarizability \(\beta_x, \beta_y, \beta_z\) of Propylbenzene along with related properties \((\mu, \alpha_{tot}, \Delta \alpha)\) are reported in Table 6. The calculated value of dipole moment is found to be 0.16111 Debye. The highest value of dipole moment is observed for component \(\mu_z\).

\[
\Delta \alpha = \frac{1}{3} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2 + 6\alpha_{xz}^2] \quad (7)
\]

\[
\langle \beta \rangle = \left[ (\beta_{xx} + \beta_{yy})^2 + (\beta_{yy} + \beta_{zz})^2 + (\beta_{zz} + \beta_{xx})^2 + (\beta_{xy} + \beta_{yz} + \beta_{xz})^2 \right]^{1/2} \quad (8)
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\]

\[
\langle \beta \rangle = \left[ (\beta_{xx} + \beta_{yy})^2 + (\beta_{yy} + \beta_{zz})^2 + (\beta_{zz} + \beta_{xx})^2 + (\beta_{xy} + \beta_{yz} + \beta_{xz})^2 \right]^{1/2} \quad (8)
\]

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\mu_{tot} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (9)
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\[
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\]

\[
\langle \beta \rangle = \left[ (\beta_{xx} + \beta_{yy})^2 + (\beta_{yy} + \beta_{zz})^2 + (\beta_{zz} + \beta_{xx})^2 + (\beta_{xy} + \beta_{yz} + \beta_{xz})^2 \right]^{1/2} \quad (8)
\]

It is well known that, molecule with high values of dipole moment, molecular Polarizability, and first hyperpolarizability having more active NLO properties. The first hyperpolarizability \((\beta)\) and the component of hyperpolarizability \(\beta_x, \beta_y, \beta_z\) of Propylbenzene along with related properties \((\mu, \alpha_{tot}, \Delta \alpha)\) are reported in Table 6. The calculated value of dipole moment is found to be 0.16111 Debye. The highest value of dipole moment is observed for component \(\mu_z\).
So that, the Propylbenzene can be used to prepare NLO crystals and those crystal is able to produce second order harmonic waves.

**Conclusion**

In the present investigation, FT-IR, FT-Raman and $^{13}$C NMR and $^{1}H$ NMR spectra of the Propylbenzene were recorded and the observed vibrational frequencies were assigned depending upon their expected region. The chronological change of fingerprint and group frequency region of the amino acid with respect to the functional group has also monitored. The change of geometrical parameters along with the substitutions was deeply analyzed. The simulated $^{13}$C NMR expected region. The chronological change of fingerprint and group vibrational frequencies were assigned depending upon their and 1H NMR were compared with the recorded spectrum and the chemical shifts related to TMS were studied. The change of chemical properties of the molecule by the substitutions has been analysed. The electrical and optical properties of the Propylbenzene were profoundly investigated using frontier molecular orbital (Figure 7). From the UV-Visible spectra, it was found that the present compound was optically active and posses NLO properties. The molecular electrostatic potential (MEP) map was performed and from which the change the chemical properties of the compound was also discussed. The possible sites of nucleophilic and electrophilic attacks in the molecule were determined through local reactivity and Fukui condensed softness indices.

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