# Theoretical investigation of the non-linear optical characteristics of 2 - (4-fluorophenyl) – 1 - phenyl - 1H - benzimidazole and 1- phenyl - 2- p- tolyl - 1H - benzimidazole

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## ABSTRACT

***Two benzimidazole derivatives, 2- (4-fluorophenyl)-1-phenyl-1H-benzimidazole (C19H13FN2) (FPBENZ) and 1- phenyl - 2- p-tolyl-1H-benzimidazole (C20H16N2) (TPBENZ), were the subject of a theoretical investigation. Data from the study were recorded and processed using the Gaussian03 programme. 6-31G basis sets have been used in DFT/B3LYP computations to examine the vibrational frequencies and geometrical characteristics. In the current work, the first order hyperpolarisability and dipole moment values of the title compounds are reported using $^{1}$HNMR, FTIR, and the topologies from HOMO-LUMO analyses. First order hyperpolarisability, dipole moment values, and topologies from HOMO-LUMO analyses all suggest that the aforementioned compounds might function as effective NLO materials.***

**Key words: IR, Raman, DFT, Hyperpolarizbility, NLO activity,Benzimidazoles**

## INTRODUCTION

Due to their characteristic linear and non-linear optical properties and also due to their thermal stability in guest-host systems, chromophores based on benzoimidazoles have drawn more and more interest. The covalent insertion of the NLO chromophores into polyamides, which results in NLO side chain polymers, is made possible by the imidazole ring's simple ability to be modified to accommodate functional groups. The majority of - conjugated systems have a significant impact on the second-order NLO response. The NLO is active in benzimidazoles[1]. We chose two benzimidazoles, 2- (4-fluorophenyl)- 1- phenyl- 1H- benzimidazole ($C_{19}H_{13}FN_2$) (FPBENZ) and 1- phenyl - 2- p- tolyl- 1H- benzimidazole ($C_{20}H_{16}N_2$), all of which include electron-donating groups (TPBENZ) For the aforementioned compounds, computational studies were done to explore the potential for application as NLO active components. As far as we know, there is no literature on the examination of chemical structures using FTIR, FTNMR, and quantum mechanical techniques such dipole moment, first order hyperpolarisability, highest occupied molecular orbital (LUMO), and natural bond analysis. Quantum mechanical computational techniques can be used to perform spectral activities. The wavenumbers of the title compound's FT-IR, FT-Raman, and theoretical calculations are provided in the current work.

## COMPUTATIONAL DETAILS

The chemical structure and vibrational frequencies of the molecule in the title were calculated using the Gaussian03 software programme utilising the B3LYP/6-31G basis sets. Scaling factors must be utilised to achieve a significantly better agreement with experimental data because the DFT hybrid B3LYP functional technique has a tendency to overestimate the basic modes. The Gaussview program's animation option, which provides a visual representation of the vibrational modes, aids with the assignment of the calculated wavenumbers.

## RESULTS AND DISCUSSION

Optimized geometry of FPBENZ (Figure - 1) and TPBENZ (Figure - 2 ) is given below :

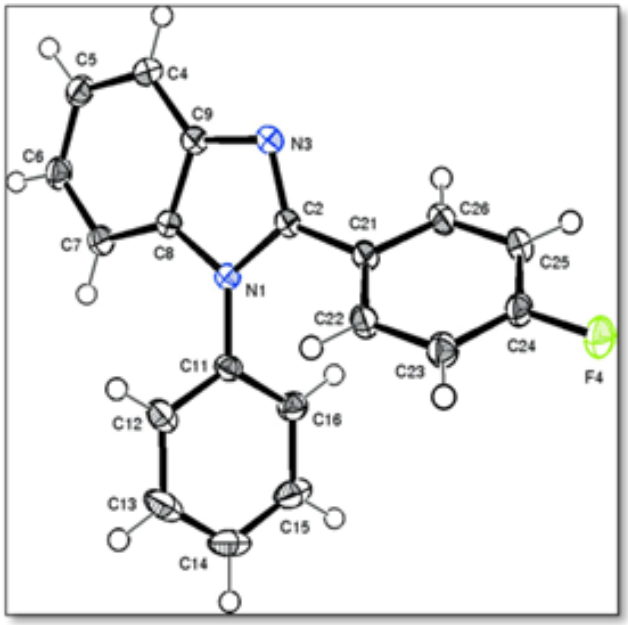



**Figure - 1**

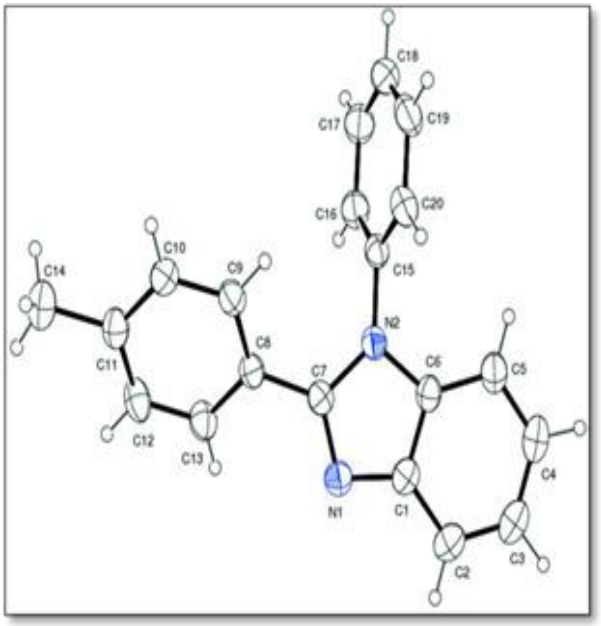



**Figure - 2**

**The experimental[2] and optimized bond length (A$^o$) and bond angles of 2- (4- fluorophenyl)- 1- phenyl- 1H- benzimidazole (Table - 1)**

## a. Bond length

| No | Bond length | Experimental value (A$^o$) | Optimized value B3LYP/6-31G |
|---|---|---|---|
| 1 | F4—C24 | 1.3633 | 1.35000 |
| 2 | N1—C2 | 1.3890 | 1.40717 |
| 3 | N1—C8 | 1.3877 | 1.45766 |
| 4 | N1—C11 | 1.4298 | 1.54000 |
| 5 | N3—C2 | 1.3186 | 1.40768 |
| 6 | N3—C9 | 1.3908 | 1.45750 |
| 7 | C2—C21 | 1.4735 | 1.54000 |
| 8 | C4—C5 | 1.3897 | 1.40491 |
| 9 | C4—C9 | 1.3976 | 1.38996 |
| 10 | C5—C6 | 1.4050 | 1.38996 |
| 11 | C6—C7 | 1.3864 | 1.40492 |
| 12 | C7—C8 | 1.3961 | 1.38028 |
| 13 | C8—C9 | 1.4052 | 1.44578 |
| 14 | C21—C22 | 1.3952 | 1.39516 |
| 15 | C21—C26 | 1.4005 | 1.39483 |
| 16 | C22—C23 | 1.3867 | 1.39471 |
| 17 | C23—C24 | 1.3825 | 1.39543 |
| 18 | C24—C25 | 1.3787 | 1.39482 |

| | | | |
|---|---|---|---|
| 19 | C25—C26 | 1.3893 | 1.39514 |
| 20 | C4—H4 | 0.9300 | 1.09891 |
| 21 | C5—H5 | 0.9300 | 1.10026 |
| 22 | C6—H6 | 0.9300 | 1.10025 |
| 23 | C7—H7 | 0.9300 | 1.09889 |
| 24 | C12—H12 | 0.9300 | 1.09965 |
| 25 | C13—H13 | 0.9300 | 1.09968 |
| 26 | C14—H14 | 0.9300 | 1.09968 |
| 27 | C11—C12 | 1.3939 | 1.39516 |
| 28 | C11—C16 | 1.3883 | 1.39483 |
| 29 | C12—C13 | 1.3919 | 1.39471 |
| 30 | C13—C14 | 1.384 | 1.39543 |
| 31 | C14—C15 | 1.3891 | 1.39483 |
| 32 | C15—C16 | 1.3920 | 1.38514 |
| 33 | C15—H15 | 0.9300 | 1.09976 |
| 34 | C16—H16 | 0.9300 | 1.09960 |
| 35 | C22—H22 | 0.9300 | 1.09960 |
| 36 | C23—H23 | 0.9300 | 1.09976 |
| 37 | C25—H25 | 0.9300 | 1.09968 |
| 38 | C26—H26 | 0.9300 | 1.09966 |

**b) Bond angles (Table – 2 )**

| No | Bond angles | Optimized value B3LYP/6-31G | Experimental value |
|---|---|---|---|
| 1 | C2—N1—C8 | 106.15 | 108.18308 |
| 2 | C2—N1—C11 | 128.03 | 127.09446 |
| 3 | C8—N1—C11 | 125.75 | 124.72246 |
| 4 | C2—N3—C9 | 104.91 | 108.17556 |
| 5 | N1—C2—N3 | 113.10 | 109.57281 |
| 6 | N1—C2—C21 | 123.13 | 125.22226 |
| 7 | N3—C2—C21 | 123.76 | 125.20494 |
| 8 | C5—C4—C9 | 117.69 | 118.45159 |
| 9 | C4—C5—C6 | 121.32 | 121.13865 |
| 10 | C5—C6—C7 | 121.80 | 121.14115 |
| 11 | C6—C7—C8 | 116.45 | 118.45527 |
| 12 | N1—C8—C7 | 131.97 | 132.56253 |
| 13 | N1—C8—C9 | 105.45 | 107.03388 |
| 14 | C7—C8—C9 | 122.51 | 120.40359 |
| 15 | N3—C9—C4 | 129.50 | 132.55593 |
| 16 | N3—C9—C8 | 110.38 | 107.03468 |
| 17 | C4—C9—C8 | 120.12 | 120.48939 |
| 18 | N1—C11—C12 | 119.29 | 119.99719 |
| 19 | N1—C11—C16 | 119.75 | 120.00431 |
| 20 | C12—C11—C16 | 120.96 | 119.9849 |
| 21 | C11—C12—C13 | 118.90 | 130.00859 |
| 22 | C12—C13—C14 | 120.69 | 119.00420 |
| 23 | C13—C14—C15 | 119.87 | 119.99398 |
| 24 | C14—C15—C16 | 120.29 | 120.00469 |

| | | | |
|---|---|---|---|
| 25 | C11—C16—C15 | 119.30 | 120.00003 |
| 26 | C2—C21—C22 | 121.34 | 119.99722 |
| 27 | C2—C21—C26 | 118.84 | 120.00430 |
| 28 | C22—C21—C26 | 119.75 | 119.98848 |
| 29 | C21—C22—C23 | 120.23 | 120.00862 |
| 30 | C22—C23—C24 | 118.14 | 119.99413 |
| 31 | F4—C24—C23 | 118.21 | 119.98107 |
| 32 | F4—C24—C25 | 118.13 | 120.02489 |
| 33 | C23—C24—C25 | 123.67 | 119.99403 |
| 34 | C24—C25—C26 | 117.52 | 120.00474 |
| 35 | C21—C26—C25 | 120.69 | 119.99997 |
| 36 | C5—C4—H4 | 121.00 | 120.27663 |
| 37 | C9—C4—H4 | 121.00 | 121.27141 |
| 38 | C4—C5—H5 | 119.00 | 119.11130 |
| 39 | C6—C5—H5 | 119.00 | 119.75004 |
| 40 | C5—C6—H6 | 119.00 | 119.75260 |
| 41 | C7—C6—H6 | 119.00 | 119.10625 |
| 42 | C6—C7—H7 | 122.00 | 120.27026 |
| 43 | C8—C7—H7 | 122.00 | 121.27447 |
| 44 | C11—C12—H12 | 121.00 | 119.98080 |
| 45 | C13—C12—H12 | 121.00 | 120.01057 |
| 46 | C12—C13—H13 | 120.00 | 120.01280 |
| 47 | C14—C13—H13 | 120.00 | 119.99300 |
| 48 | C13—C14—H14 | 120.00 | 119.98115 |
| 49 | C15—C14—H14 | 120.0 | 120.02486 |
| 50 | C14—C15—H15 | 120.00 | 120.01134 |
| 51 | C16—C15—H15 | 120.00 | 119.98397 |
| 52 | C11—C16—H16 | 120.00 | 120.00802 |

| | | | |
|---|---|---|---|
| 53 | C15—C16—H16 | 120.00 | 119.99194 |
| 54 | C21—C22—H22 | 120.00 | 120.00802 |
| 55 | C23—C22—H22 | 120.00 | 119.99201 |
| 56 | C22—C23—H23 | 121.00 | 119.98388 |
| 57 | C24—C23—H23 | 121.00 | 120.01139 |
| 58 | C24—C25—H25 | 121.00 | 119.99312 |
| 59 | C26—C25—H25 | 121.00 | 120.01275 |
| 60 | C21—C26—H26 | 120.00 | 119.98077 |
| 61 | C25—C26—H26 | 120.00 | 120.01056 |

**The experimental[3] and optimized bond length (A$^o$) and bond angles of 1- phenyl - 2- p- tolyl- 1H- benzimidazole**

**a) Bond length (Table – 3 )**

| No | Bond lengths | Experimental value(A$^o$) | Optimized value B3LYP/6-31G |
|---|---|---|---|
| 1 | N1—C1 | 1.387 | 1.45750 |
| 2 | N1—C7 | 1.318 | 1.40768 |
| 3 | N2—C6 | 1.383 | 1.45766 |
| 4 | N2—C7 | 1.383 | 1.40717 |
| 5 | N2—C15 | 1.431 | 1.54000 |
| 6 | C1—C2 | 1.393 | 1.38033 |
| 7 | C1—C6 | 1.389 | 1.44578 |
| 8 | C2—C3 | 1.370 | 1.40491 |
| 9 | C16—C17 | 1.373 | 1.39514 |
| 10 | C17—C18 | 1.352 | 1.39483 |

| | | | |
|---|---|---|---|
| 11 | C18—C19 | 1.378 | 1.39543 |
| 12 | C19—C20 | 1.388 | 1.39471 |
| 13 | C2—H2 | 0.9300 | 1.09891 |
| 14 | C3—H3 | 0.9300 | 1.10026 |
| 15 | C4—H4 | 0.9300 | 1.10025 |
| 16 | C5—H5 | 0.9300 | 1.09889 |
| 17 | C3—C4 | 1.387 | 1.38996 |
| 18 | C4—C5 | 1.372 | 1.40492 |
| 19 | C5—C6 | 1.381 | 1.38028 |
| 20 | C7—C8 | 1.468 | 1.5400 |
| 21 | C8—C9 | 1.386 | 1.39483 |
| 22 | C8—C13 | 1.386 | 1.39516 |
| 23 | C9—C10 | 1.377 | 1.39514 |
| 24 | C10—C11 | 1.381 | 1.39483 |
| 25 | C11—C12 | 1.382 | 1.39543 |
| 26 | C11—C14 | 1.506 | 1.5400 |
| 27 | C12—C13 | 1.379 | 1.39471 |
| 28 | C15—C16 | 1.371 | 1.39483 |
| 29 | C15—C20 | 1.373 | 1.39516 |
| 30 | C9—H9 | 0.9300 | 1.09960 |
| 31 | C10—H10 | 0.9300 | 1.09976 |
| 32 | C12—H12 | 0.9300 | 1.09968 |
| 33 | C13—H13 | 0.9300 | 1.09966 |
| 34 | C14—H14A | 0.9600 | 1.07000 |

| | | | |
|---|---|---|---|
| 35 | C14—H14B | 0.9600 | 1.07000 |
| 36 | C14—H14C | 0.9600 | 1.0700 |
| 37 | C16—H16 | 0.9300 | 1.09960 |
| 38 | C17—H17 | 0.9300 | 1.09976 |
| 39 | C18—H18 | 0.9300 | 1.09968 |
| 40 | C19—H19 | 0.9300 | 1.09968 |
| 41 | C20—H20 | 0,9300 | 1.09966 |

**b) Bond angle ( Table – 4 )**

| No | Bond angles | Experimental value | Optimized value B3LYP/6-31G |
|---|---|---|---|
| 1 | C1—N1—C7 | 105.41 | 103.78253 |
| 2 | C6—N2—C7 | 106.49 | 112.38875 |
| 3 | C6—N2—C15 | 122.81 | 120.93870 |
| 4 | C7—N2—C15 | 130.43 | 126.67162 |
| 5 | N1—C1—C2 | 130.20 | 130.33872 |
| 6 | N1—C1—C6 | 110.19 | 114.36519 |
| 7 | C2—C1—C6 | 119.61 | 115.29608 |
| 8 | C1—C2—C3 | 117.71 | 119.18779 |
| 9 | C2—C3—C4 | 121.64 | 122.68557 |
| 10 | C3—C4—C5 | 121.73 | 120.64021 |
| 11 | C4—C5—C6 | 116.43 | 116.76538 |
| 12 | N2—C6—C1 | 105.72 | 99.12817 |
| 13 | N2—C6—C5 | 131.41 | 133.44687 |
| 14 | C1—C6—C5 | 122.88 | 127.42493 |
| 15 | N1—C7—N2 | 112.19 | 110.33533 |
| 16 | N1—C7—C8 | 123.20 | 1210.69353 |

| | | | |
|---|---|---|---|
| 17 | N2—C7—C8 | 124.60 | 128.97104 |
| 18 | C7—C8—C9 | 123.12 | 122.14373 |
| 19 | C7—C8—C13 | 118.97 | 121.20764 |
| 20 | C9—C8—C13 | 117.81 | 116.64863 |
| 21 | C8—C9—C10 | 120.76 | 121.57575 |
| 22 | C9—C10—C11 | 121.86 | 121.83689 |
| 23 | C10—C11—C12 | 117.08 | 116.54345 |
| 24 | C10—C11—C14 | 120.82 | 121.78519 |
| 25 | C12—C11—C14 | 122.09 | 121.66909 |
| 26 | C11—C12—C13 | 121.77 | 121.83166 |
| 27 | C8—C13—C12 | 120.72 | 121.55593 |
| 28 | N2—C15—C16 | 119.43 | 119.45192 |
| 29 | N2—C15—C20 | 119.29 | 119.47555 |
| 30 | C16—C15—C20 | 121.25 | 121.07004 |
| 31 | C15—C16—C17 | 119.32 | 119.22475 |
| 32 | C16—C17—C18 | 120.5 | 119.61386 |
| 33 | C17—C18—C19 | 120.47 | 121.24334 |
| 34 | C18—C19—C20 | 119.9 | 119.65601 |
| 35 | C15—C20—C19 | 118.57 | 119.19114 |
| 36 | C1—C2—H2 | 121.00 | 120.32669 |
| 37 | C3—C2—H2 | 121.00 | 120.48250 |
| 38 | C2—C3—H3 | 119.00 | 117.82988 |
| 39 | C4—C3—H3 | 119.00 | 119.48455 |
| 40 | C3—C4—H4 | 119.00 | 121.61201 |
| 41 | C5—C4—H4 | 119.00 | 117.74777 |
| 42 | C4—C5—H5 | 122.00 | 119.57687 |
| 43 | C6—C5—H5 | 122.00 | 125.65775 |

| | | | |
|---|---|---|---|
| 44 | C8—C9—H9 | 120.00 | 119.04160 |
| 45 | C10—C9—H9 | 120.00 | 119.38179 |
| 46 | C9—C10—H10 | 119.00 | 118.56429 |
| 47 | C11—C10—H10 | 119.00 | 119.59875 |
| 48 | C11—C12—H12 | 119.00 | 119.57197 |
| 49 | C13—C12—H12 | 119.00 | 118.59610 |
| 50 | C8—C13—H13 | 120.00 | 118.76396 |
| 51 | C12—C13—H13 | 120.00 | 119.67882 |
| 52 | C11—C14—H14A | 109.00 | 113.84058 |
| 53 | C11—C14—H14B | 109.00 | 113.82269 |
| 54 | C11—C14—H14C | 109.00 | 111.59477 |
| 55 | H14A—C14—H14B | 109.00 | 106.04195 |
| 56 | H14A—C14—H14C | 110.00 | 105.41103 |
| 57 | H14B—C14—H14C | 109.00 | 105.39224 |
| 58 | C15—C16—H16 | 120.00 | 119.55107 |
| 59 | C17—C16—H16 | 120.00 | 121.22409 |
| 60 | C16—C17—H17 | 120.00 | 118.86247 |
| 61 | C18—C17—H17 | 120.00 | 121.52306 |
| 62 | C17—C18—H18 | 120.00 | 119.38696 |
| 63 | C19—C18—H18 | 120.00 | 119.36956 |
| 64 | C18—C19—H19 | 120.00 | 121.46658 |
| 65 | C20—C19—H19 | 120.00 | 118.87724 |
| 66 | C15—C20—H20 | 121.00 | 119.53761 |
| 67 | C19—C20—H20 | 121.00 | 121.27125 |

**Comparative study of vibrational spectra of FPBENZ ( Figure - 3 ) and TPBENZ ( Figure - 4 )**

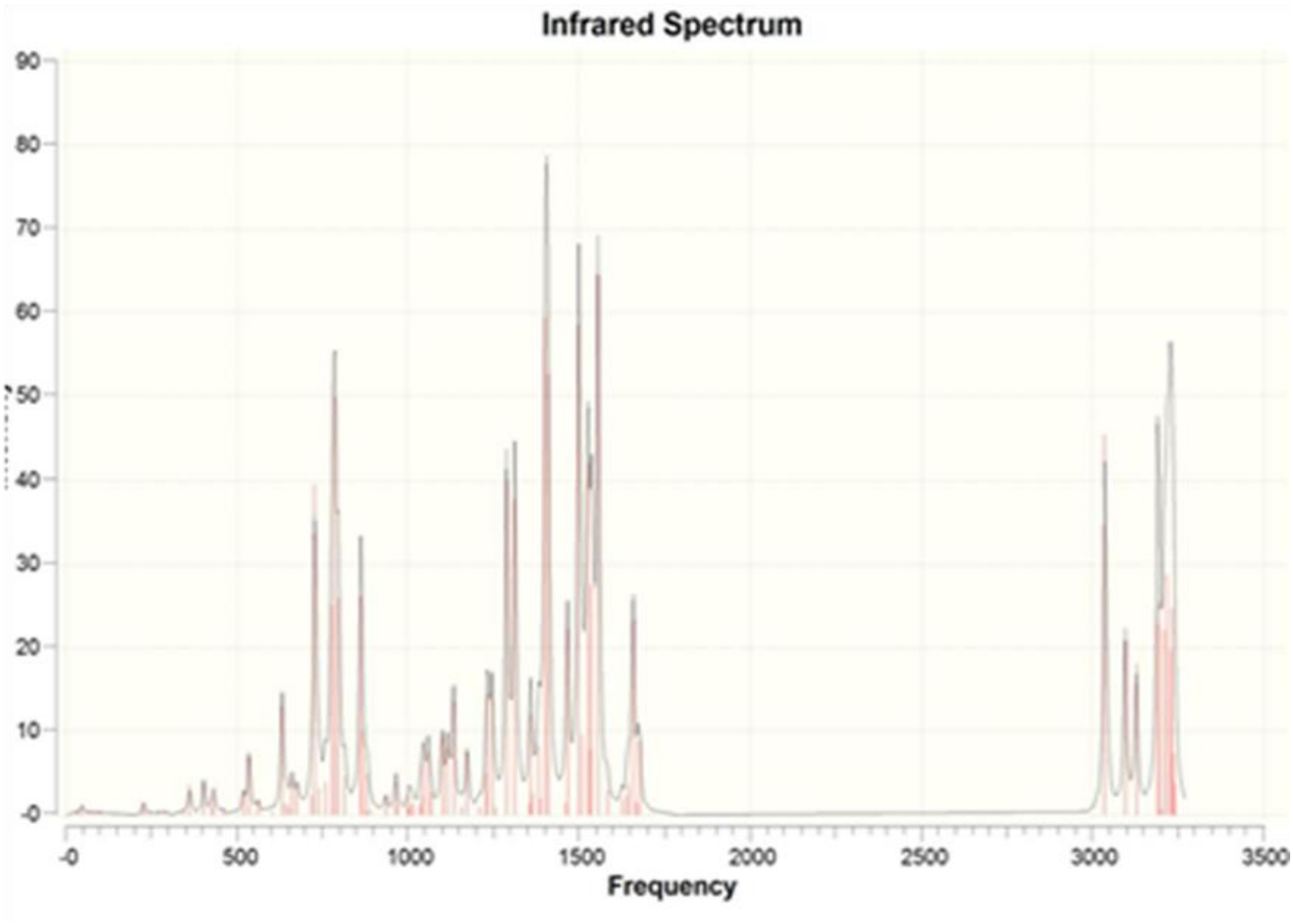



**Figure – 3 IR spectrum of FPBENZ**

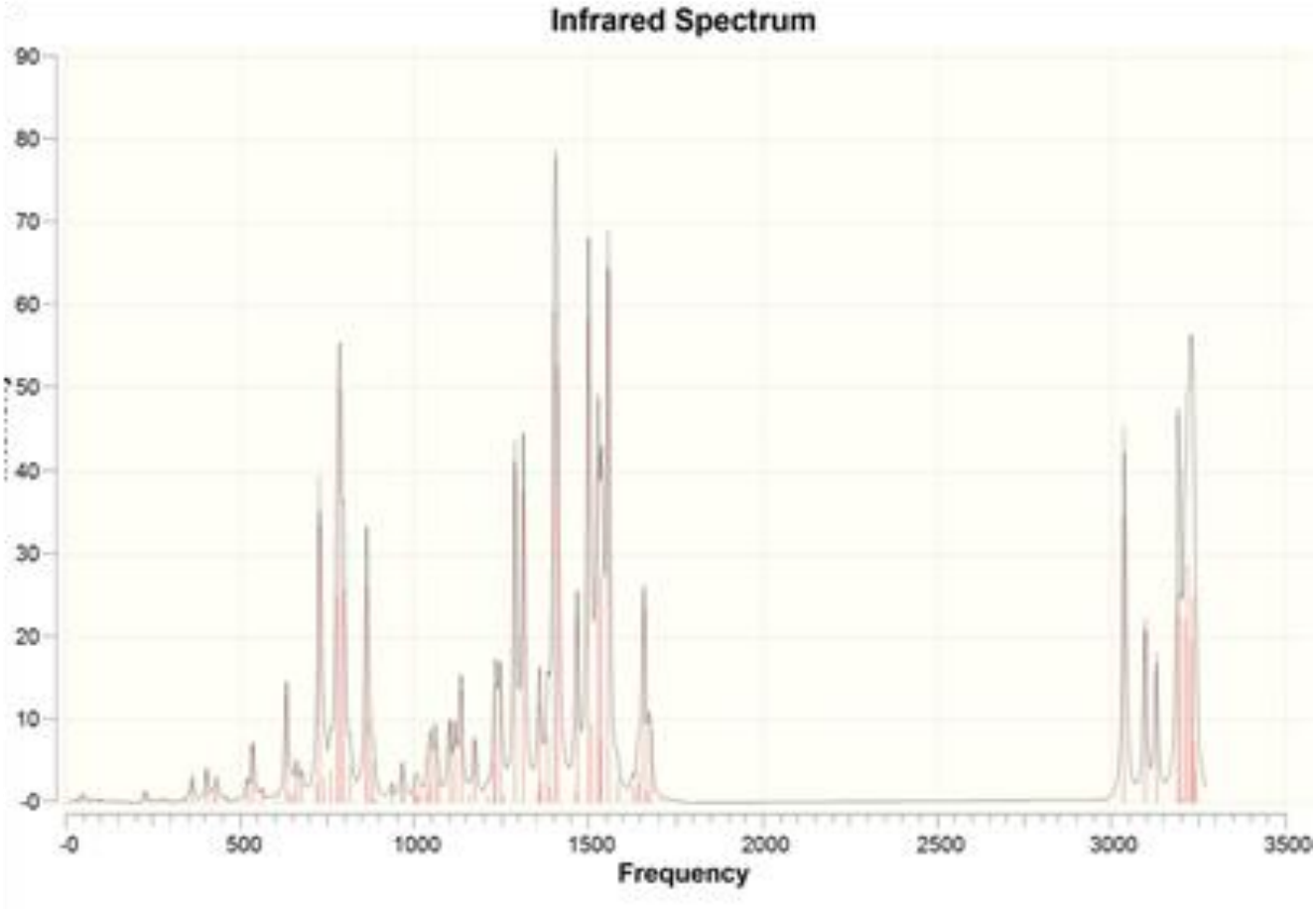



**Figure - 4 IR spectrum of TPBENZ**

The band obtained in the vibrational spectra gives important information regarding the structure and chemical properties of molecules. The characteristic vibrational frequency of Benzimidazole, phenyl, C-F [from FPBENZ] and methyl [from TPBENZ] groups was analyzed.

**1) Aromatic C-H vibration**

The nitrogen heterocyclic aromatic compounds commonly exhibit stretching vibration in the region 3100-3000 $cm^{-1}$. According to the present investigation the C-H stretching vibration bands due to 4-fluro phenyl group is 3237.75 $cm^{-1}$ and phenyl group attached to imidazole and 1-phenyl groups has value 3220.59 $cm^{-1}$. C-H stretching frequency obtained from 4-methyl phenyl group is 3228.75 $cm^{-1}$ and phenyl group of attached to imidazole and 1-phenyl group has C-H stretching frequency is 3218.9 $cm^{-1}$.Also the C-H in plane deformation vibration band of variable intensity appear in the region 1300-1180[1224.61 for FPBENZ & 1221.98 for TPBENZ]. Aromatic C-H bending vibration for FPBENZ is observed at 1555.55 $cm^{-1}$ and for TPBENZ it is 1538.41 $cm^{-1}$.

**2) C=C and C-C vibrations**

The C=C stretching vibrations are observed in the region 1670-1430 $cm^{-1}$.The C=C frequency is increases as alkyl group attached to the double bond. But the presence of electronegative group decreases the value. In FPBENZ the C=C

stretching vibration observed at 1407.4 $cm^{-1}$. In TPBENZ the value is 1399.2 $cm^{-1}$.

### 3) C=N and C-N vibrations

The C=N and C-N stretching vibration observed at the region 1680-1200 $cm^{-1}$. In FPBENZ the C=N and C-N stretching vibrations are observed at 1672.07 $cm^{-1}$ and 1289.38 $cm^{-1}$. The TPBENZ are observed at 1643.46 $cm^{-1}$ and 1248.46 $cm^{-1}$. The electron donating group in TPBENZ result the lengthening of C=N bond hence bond order reduced. Nitrogen atom a H bond acceptor resulting inter molecular H bonding. In the case of FPBENZ the F atom accept electron from neighboring group hence N atom does not take part in H bonding.

### 4) Methyl C-H vibration

The methyl group is an less electronegative group hence its vibrational value in TPBENZ is 3045.6 $cm^{-1}$. C-H deformation value is obtained at the region 1420.3 $cm^{-1}$.

**Comparative study of 1H NMR spectra of FPBENZ ( Figure – 5 ) and TPBENZ ( Figure – 6 )**

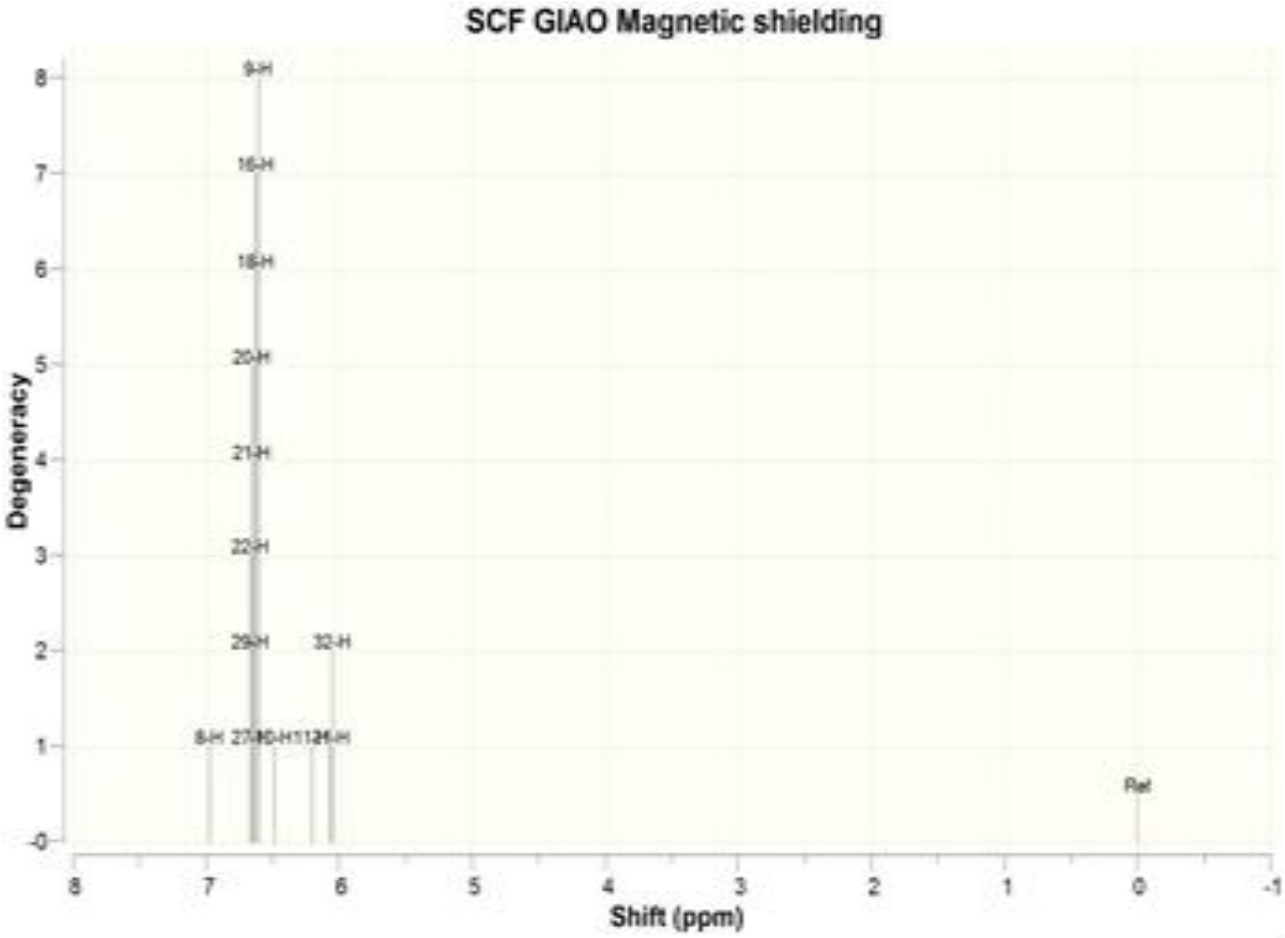



**Figure - 5 $^{1}$H NMR spectra of FPBENZ**

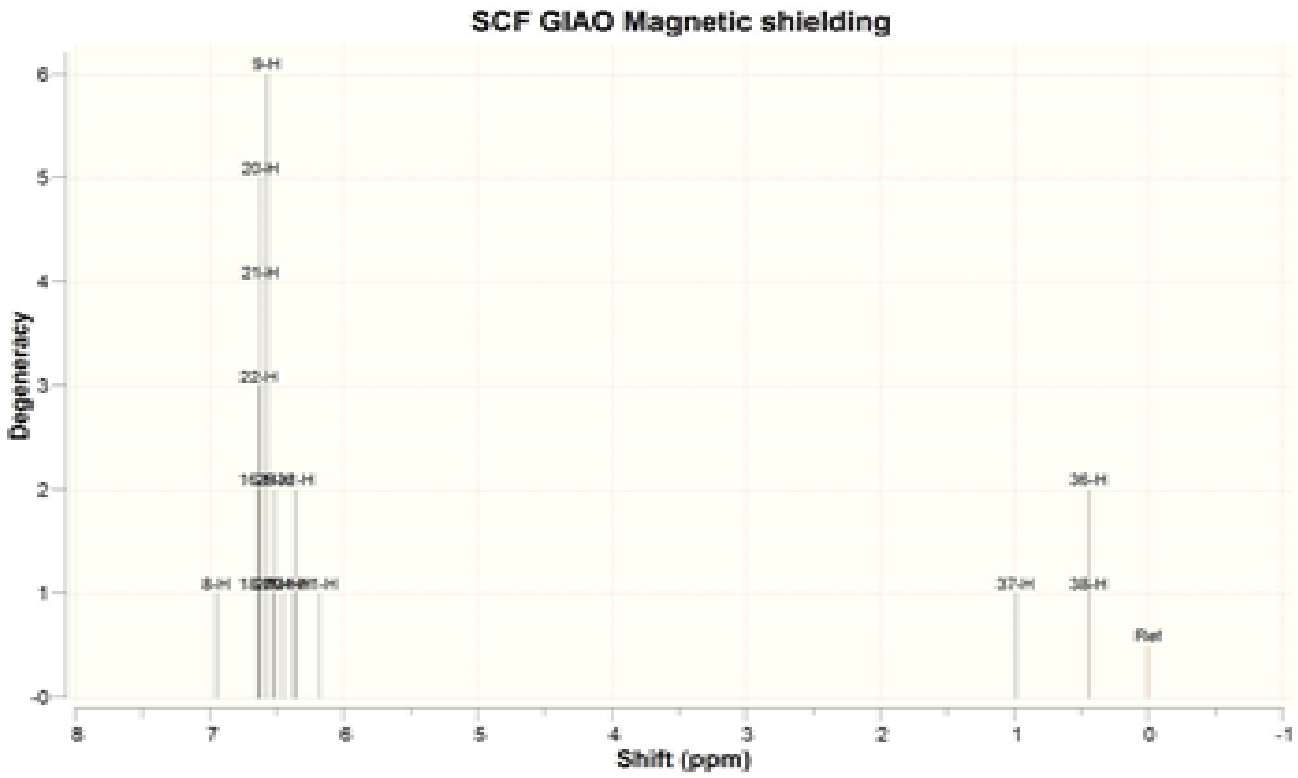


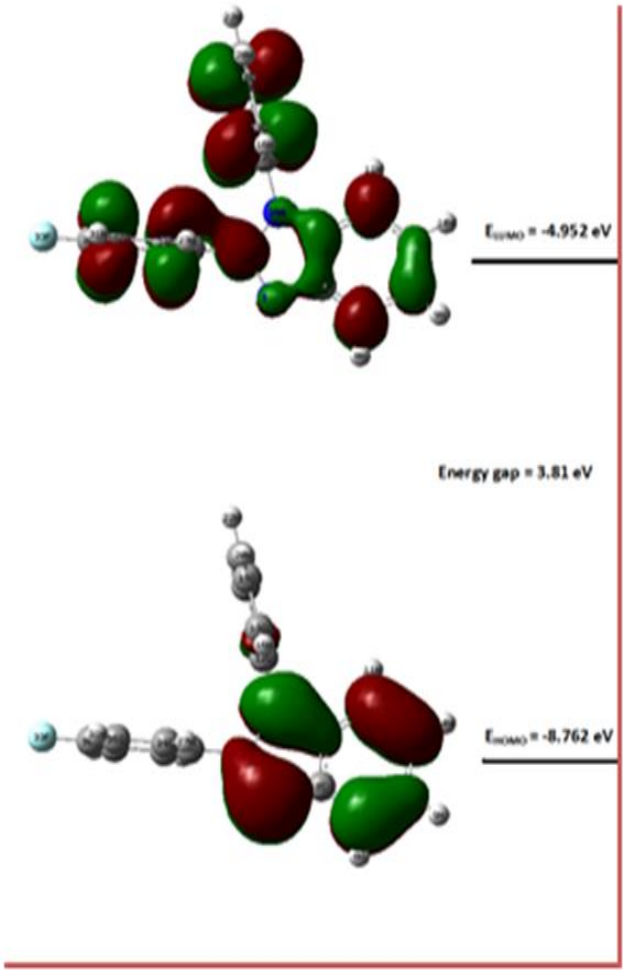

**Figure - 6 $^{1}$H NMR spectra of TPBENZ**

The FPBENZ and TPBENZ was characterized by $^{1}$H NMR using GIAO method using 6-31G basis set. Aromatic proton in the FPBENZ and TPBENZ was observed in the region 6-7 ppm. But in TPBENZ the methyl group is present in the Para position of phenyl group attached to the second portion of Benzimidazole. It gives 3H singlet 4-1 ppm. In this compound the presence of electron donating group resulting in up field shift [low δ value]. But in FPBENZ high electronegative group result high δ value [down field shift].

## Frontier Molecular Orbital Analysis

Multi aryl compounds are characterized by HOMO and LUMO separation, which arises due to significant degree of inter-molecular charge transfer (ICT) from the electron-donor to the efficient electron acceptor group. The frontier molecular orbital determine the way in which molecules interact with each other.The HOMO is the orbital that primarily act as an electron donor and the LUMO is the orbital that largely act as the electron acceptors. The gap between HOMO and LUMO characterizes the molecular stability and activity.The more conjugation (free movement of electrons) there is in a molecule, the less of an energy gap will exist between HOMO and LUMO and also the molecular orbital energy gap decreased with a decrease in electro negativity functional group.The HOMO-LUMO energy gap of FPBENZ and TPBENZ has been calculated at DFT/6-31G levels. The molecular topology of

HOMO-LUMO orbitals of FPBENZ and TPBENZ are shown in following (Figure 7 &8).



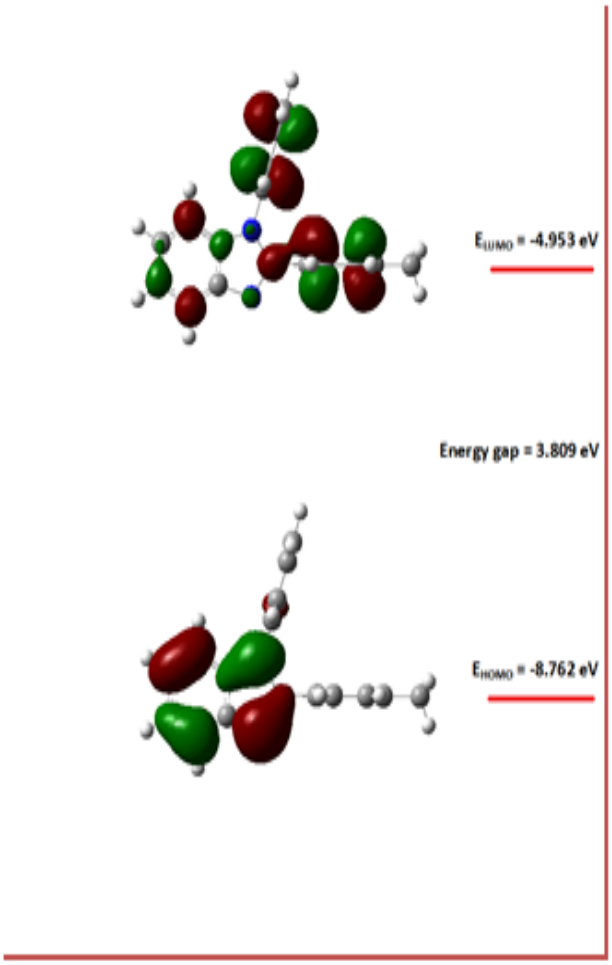




**Figure – 7 HOMO-LUMO plot of FPBENZ**

**Figure - 8 HOMO-LUMO plot of TPBENZ**

The Figure - 7 represents the molecular topology of FPBENZ. In this compound the more electronegative element such as F is attached to the para position of TPBENZ, which is high electron withdrawing group, also the HOMO is located over Benzimidazole and phenyl ring where as LUMO is localized over C-F bonds. The HOMO-LUMO energy of FPBENZ are found to be

HOMO = -8.762

LUMO = -4.952

Energy gap = 3.81 eV

The Figure – 8 represents the molecular topology of TPBENZ. In this compound the less electronegative group such as $CH_3$ is attached to the para position of TPBENZ, which is electron donating group. Also the HOMO is located over Benzimidazole and phenyl ring. Whereas LUMO is localized over entire molecule. The HOMO-LUMO energy of TPBENZ are found to be

HOMO = -8.762

LUMO = -4.952

Energy gap = 3.809 Ev

The energy gap difference between FPBENZ and TPBENZ is very small and the value is 0.001. Indicating that both the molecules can effectively be used electron transport materials.

A molecule with a small HOMO-LUMO energy gap is more polarizable and is generally associated with a high chemical reactivity and low kinetic stability [4;5]. Frontier molecular orbital consist of π – aromatic orbitals, so an electron transition from HOMO to LUMO is mainly derived from the electronic transitions of π-π*. Frontier molecular orbital analysis supports the fact that the FPBENZ and TPBENZ has approximately same energy band gap. So they could be a suitable NLO active and electron transport material.

## Nonlinear Optical Properties

The first hyperpolarisability ($\beta_o$) of thin novel molecular systems are calculated using the effective core potential basis set method (HF/6-31G). $E_o$ being the energy of an unperturbed molecule, the Taylor series expansion of the energy in an external electric field is

$$E = E_o - \sum \mu_i F_i - 1/2 \sum \alpha_{ij} F^i F^j - 1/6 \sum \beta_{ijk} F^i F^j F^k - 1/24 \sum F^i F^j F^k F^k + \ldots\ldots\ldots$$

$\beta_{ijk}$ gives the component of first hyperpolarisability. The first hyperpolarisability can be represented by a 3x3x3x matrix of third rank tensor and is given as

$$\beta_o = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

Where

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

The 27 component of the 3D matrix can be reduced to 10 components due to Kleinman symmetry [5] . The non- zero first order hyperpolarisability values are obtained by the numerical second order derivative of the electric dipole according to the applied field strength. There is a rather strong relationship between the calculated dipole moment and the first order hyperpolarisability values. Therefore in this study the dipole moment values may be responsible for enhancing or decreasing the first order hyperpolarisability values. The first order hyperpolarisability is more dominant in xyy direction [$\beta_{xyy}$] thus the charge transfer mechanism is more in particular direction assigned.

| The calculated first hyperpolarisability of the FPBENZ ( Table - 5) | | The calculated first hyperpolarisability of the FPBENZ ( Table - 5) | |
|---|---|---|---|
| βxxx | -39.354385 | βxxx | 1.26054 |
| βxxy | -2.4106683 | Bxxy | 6.599463 |
| βxyy | -31.1094101 | βxyy | -54.4215 |
| βyyy | 2.7758085 | βyyy | 10.27804 |
| βxxz | 1.7519203 | βxxz | -13.0814 |
| βxyz | 2.1912738 | βxyz | 94 |
| βyyz | 30.2317176 | βyyz | 1.240114 |
| βxzz | -125.6349063 | βxzz | -125.213 |
| βyzz | 24.1696052 | βyzz | 11.97998 |
| βzzz | 201.5675507 | βzzz | -240.902 |

The calculated first hyperpolarisability of the FPBENZ ( Table - 5) is 2.64 * $10^{-30}$ esu. And TPBENZ ( Table - 6) is 2.64* $10^{-30}$ esu. This is larger than that of standard NLO material urea (0.13x $10^{-30}$ esu) [6]. But experimental evaluation of this data is not readily available. We conclude that the FPBENZ and TPBENZ is an attractive object for future studies of nonlinear optical properties. The dipole moment value calculated for FPBENZ is 4.2347 D. and the TPBENZ is 3.9379 D.

## CONCLUSION

Multy aryl compounds widely used as electron transport material, NLO materials and drugs. The theoretical and experimental comparative studies of these compounds are important to understand the nature, property and applicability.

2-(4-fluorophenyl)-1-(phenyl)-1H- benzimidazole and 1-(phenyl)- 2- (p- tolyl)- 1-H-benzimidazole were theoretically studied using Gaussian03 software. The geometry optimization of the title compounds were carried out using DFT using B3LYP/6-31G basis set. The position of proton of FPBENZ and TPBENZ were analyzed by $^{1}$HNMR spectra. Also different vibrations were studied using FTIR spectroscopy. The topologies from HOMO-LUMO analysis, first order hyperpolarisability and dipole moment values indicate that the title compounds could be an efficient NLO material. The first hyperpolarisability of FPBENZ and TPBENZ were found to be about 20 times greater than urea. Also the comparative study of experimental values of geometric parameters is approximately good agreement with theoretically calculated values. These results suggest that the title compounds could be an effective NLO active and electron transport material. Also the presence of electronegative group has a negligible effect on HOMO- LUMO energy band gap. Hence both compounds can be used as electron transport and NLO active materials.

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