International Journal of Technical Research and Applications e-ISSN: 2320-8163,
www.ijtra.com Special Issue 37 (February, 2016), PP. 1-5

EXPERIMENTAL FT-IR, FT-RAMAN AND THEORETICAL QUANTUM CHEMICAL COMPUTATIONS ON THE MOLECULAR STRUCTURE P-BROMOBENZOTRIFLUORIDE

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Abstract— **In the present study, the vibrational normal modes of p-bromobenzotrifluoride have been analyzed. The FT-IR and FT-Raman spectra have been recorded using NEXUS - 670 spectrophotometer. The matching of theoretical and experimental frequencies and their vibrational assignments have been done with the help of potential energy distribution obtained from GAR2PED program package. The energy gap between highest occupied and lowest unoccupied molecular orbitals of the title molecule has been predicted. The maximum absorption wavelengths obtained from theoretical UV-Vis spectra for various solvents have been compared with HOMO-LUMO energy gap results. To test the non-linear optical response of molecule, the properties such as; dipole moment, polarizability and hyperpolarizability have been predicted. The details about the presence of inter- and intramolecular charge transfer probabilities have been predicted theoretically using NBO analysis. Certain thermodynamic parameters have been predicted to understand the thermal stability of a molecule at room temperature.**

Index terms- **p-bromobenzotrifluoride; FT-IR; FT-Raman; HOMO-LUMO; Natural bond orbitals; NLO properties.**

I. INTRODUCTION

Benzotrifluoride often known as trifluorotoluene is used as a solvent in organic synthesis and is acts as an intermediate in the production of pesticides and pharmaceuticals [1]. Due to its intense usage in pharmaceutical industry, benzotrifluoride and its derivatives have been investigated [2-5]. Vibrational spectra of benzene derivatives such as; Benzotrifluoride and mono-substituted derivatives have been investigated by Green et.al [2]. Vibrational spectra and normal coordinate analysis of substituted trifluoromethyl benzenes have been investigated by Yadav et.al [3,4]. Vibrational spectroscopic studies, NLO, HOMO-LUMO and electronic structure calculations of α,α,α-trichlorotoluene along with quantum chemical studies have been performed by Govindarajan et.al [5]. In the present study, the detailed vibrational spectroscopic characterization, normal coordinate analysis, HOMO-LUMO energy gap analysis, Natural bond orbital (NBO) analysis, and thermo chemical analysis have been proposed. The inadequacy observed in the literature as well as its pharmaceutical importance impressed us to do both experimental and theoretical studies on p-BBTF.

II. EXPERIMENTAL DETAILS

The p-BBTF with a stated purity of 98% was purchased from Sigma Aldrich Company, India. The infrared spectrum of the sample was recorded on a BRUKER FT-IR instrument with a spectral resolution of 1.0 cm^{-1} in the region of 400 to 4000 cm^{-1}. A KBr pellet of solid sample was prepared from the mixture of KBr and the sample in 200:1 ratio using hydraulic press. Multi-tasking OPUS software was used for signal averaging, signal enhancement, base line correction and other spectral manipulations.

The FT-Raman spectrum was recorded using BRUKER RFS 27 stand alone FT-Raman spectrometer as powder sealed in a capillary tube in the region 0–4000 cm^{-1}. The line 1064 nm of Nd:YAG laser was used as an exciting source with an output power of about 100 mW at the sample position. Spectrum was accumulated for 100 scans with a resolution of 2 cm^{-1}.

III. COMPUTATIONAL DETAILS

The implementation of quantum chemical theoretical computations usually gives us supportive evidence to the experimental results. In this work, theoretical Hartree-Fock (HF) and density functional methods (DFT) have been approached to find the single point energy, geometry optimization, vibrational frequencies and second order perturbation energies of the title molecule. The entire calculations have been carried out using Gaussian 09W software package with the internally stored DFT/B3LYP/6-31+G(d,p) basis set [6–8]. For spectrum simulations and isodensity plots, visualization interface Gauss View 5.0 has been used [9]. The vibrational frequency assignments of this molecule were carried out using Gar2ped program package [10].

IV. RESULT AND DISCUSSION

A. Molecular structure

The optimized molecular structure of p-BBTF shown in Fig. 1 consists of electron withdrawing Bromine and CF_3 groups at the para and meta positions, respectively on the benzene ring, respectively. The optimized geometrical parameters such as bond length, bond angle and dihedral angle of the title molecules are presented in Table 1. In the present study, the p-BBTF is considered as substituted benzene. Hence its optimized geometrical parameters are compared with that of benzene.

In general, C–C bond lengths of the pure benzene ring appear in the range 1.40 Å. It shows that the intermediate distance is consistent with electron delocalization *i.e* the electrons for C–C bonding are distributed equally between each of the six carbon atoms. In the p-BBTF is concerned, the C–C bond lengths of the ring varying from 1.3916 Å to 1.3949 Å. The C–H bond length of the ring usually appears in the range 1.09 Å. In p-BBTF molecule, the average C–H bond length calculated at B3LYP/6-311++(d,p) is found to be 1.0823 Å. On the other hand, due to the symmetry of pure benzene, the C–C–C and C–C–H bond angles are almost equal to 120° [11]. In the case of p-BBTF, the C–C–C and C–C–H bond angles are slightly varied. Especially, the deviation of 1.3° is observed at C2–C1–C6. The optimized geometrical results showed that the electron withdrawing substituents may cause a change in bond lengths and bond angles of the ring. In contrast, the dihedral angles are not affected significantly by the addition of substituents.

B. Normal Coordinate Analysis

In order to investigate the vibrational characteristics of p-BBTF, the percentage of potential energy distribution has been done. For this purpose, the possible sets of redundant internal coordinates and sets of non-redundant symmetry coordinates have been constructed by following the recommendations of Fogarasi and Pulay [12–14]. In the case of p-BBTF, the possible sets of 52 internal coordinates including redundancy are given in Table 2 and the redundant free sets of symmetry coordinates followed by the recommendations [12–14] are given in Table 3. From Table 3, 19 pure vibrational modes and 20 mixed vibrations are observed.

C. Vibrational Frequency Assignments

In the present study, the vibrational frequency assignments are predicted on the basis of potential energy distribution (PED) results obtained from the Gar2ped [10] output. Table 4 reports the complete vibrational assignments of fundamental normal modes associated with the title molecule along with the calculated reduced mass, force constants, IR intensity, and Raman intensity. Here, Raman scattering activities (S_i) obtained from the Gaussian 09W program are subsequently converted into the relative Raman intensities (I_i) using the following relationship derived from the intensity theory of Raman scattering [15,16].

$$I_i = \frac{f(\upsilon_0 - \upsilon_i)^4 S_i}{\upsilon_i\left[1 - exp\left(\frac{hc\upsilon_i}{K_T T}\right)\right]} \qquad (1)$$

where υ_0 is the exciting frequency (cm^{-1}), υ_i is the vibrational wavenumber of the i^{th} normal mode, h, c and k_b are universal constants, and f is the suitable chosen common scaling factor for all the peak intensities.

Due to the neglect of anharmonicity effect, certain theoretically computed frequencies are found to be in disagreement with that of the experimental frequencies. To overcome the discrepancies between observed and calculated wavenumbers, linear scaling procedure is employed. The scaling factors of 0.9059 is used for HF/6-311++G(d,p) and 0.9668 is used for DFT/6-311++G(d,p) methods [17,18]. The scaled values at DFT/6-311++G(d,p) level of theory yield good results when compared to experimental IR and Raman frequencies. The vibrational assignments of vibrational normal modes are discussed below.

D. C–H Vibrations

Aromatic compounds commonly produce multiple week bands in the region of 3100–3000 cm^{-1} due to aromatic C–H stretching vibrations which is the characteristic region for direct identification of the molecular structure [19–23]. In this region, the bands are not much affected by the nature of the substituents. In the case of p-BBTF, the four hydrogen atoms attached to the benzene ring give rise to four stretching vibrations, four in-plane bending and four out-of-plane bending vibrations. The C–H stretching vibrations of p-BBTF are identified at 3104, 3080 cm^{-1} in FT-IR and 3081 cm^{-1} in FT-Raman spectrum. The theoretically predicted scaled values of 3103, 3101, 3090 and 3088 cm^{-1} at DFT/6-311++G(d,p) show good agreement with experimental observations. The percentage of PED for these modes is almost 100%. It clearly indicates C–H stretching vibrations are very pure modes.

In FT-Raman and FT-IR spectra the bands due to the C–H in-plane deformation vibrations occur in the region 1290–900 cm^{-1} [24]. In the present study, the peaks at 1466, 1287 and 1171 cm^{-1} in FT-IR spectrum are assigned to C–H in-plane bending deformations. The strongest absorptions for aromatic compounds occur in the region 1000–650 cm^{-1} due to C–H out-of-plane bending of aromatic ring [19–24]. The peaks identified at 950 and 830 cm^{-1} in FT-IR spectrum are ascribed to C–H out-of-plane bending vibrations. But the peaks for both in-plane and out-of-plane bending vibrations in FT-Raman spectrum are absent. Hence the theoretically calculated values are compared with experimental IR and both the experimental and theoretical values are seen coinciding with each other.

E. Ring Vibrations

The ring stretching vibrations are prominent because double bonds are in conjugation with the ring produced variable intensity bands at various positions. The actual position of these modes is not determined by the nature of the substituents but also by the form of substitution around the ring. Usually, these bands are observed at 1625–1590, 1590–1575, 1540–1470, 1465–1430 and 1380–1280 cm^{-1} as reported by Varsanyi [25]. In the present study, the peaks found at 1582, 1553, 1383 cm^{-1} in FT-IR are assigned to C–C stretching vibrations of the benzene ring. The scaled theoretical values of 1581, 1560, 1380, 1278, 1050 and 1034 cm^{-1} at DFT/6-311++G(d,p) shows good agreement with experimental observations. The ring in-plane vibrations are identified at 692 and 629 cm^{-1} in FT-IR and 692 and 631 cm^{-1} in FT-Raman and ring out-of-plane vibrations are observed at 721 cm^{-1} in FT-IR spectrum. The theoretically predicted values at DFT/6-311++G(d,p) scaled down by 0.9668 coincides well with the experimental observations as well as the assignments proposed by the literature [25].

F. C–Br vibrations

The heavier mass of bromine obviously makes C–Br stretching to appear at longer wavelength regions (200–480 cm^{-1}) as reported by Varsanyi [25]. As expected, the peak for C–Br stretching is observed at 437 cm^{-1}. The in-plane and out-of-plane bending modes of C–Br bond does not exists in both FT-IR and FT-Raman spectra. Hence the theoretically scaled values of 260 and 66 cm^{-1} by DFT/6-311++G(d,p) method are assigned to in-plane and out-of-plane bending vibrations of C–Br bond.

G. Trifluoromethyl group vibrations

The CF_3 group vibrations of the title molecule play a prominent contribution to vibrational spectra. In the case of CF_3 group, the stretching vibrations are usually observed between 1340 and 1110 [25]. The C–F symmetric stretching of the title molecule is 1123, 1074 and 1063 cm^{-1} and it is assigned to stretching vibrations of C–F bond. The bending deformations corresponding to CF_3 group are not active in both the recorded FT-IR and FT-Raman spectra. Hence the theoretically predicted values of 551, 477, 364, 217 and 192 cm^{-1} are assigned to CF_3 bending deformations based on PED result. These vibrations were also confirmed from the molecular visualization by using Gauss View 5.0 [9].

H. Charge Transfer properties of p-BBTF

In the molecular system, the investigation of structural insights such as; hyperconjugative interactions, hydrogen bonding interactions, occupancies of molecular orbitals and the distribution of electrons in various subshell are important. NBO analysis is found to be the perfect tool for identification of all the above said parameters [26]. The distribution of atomic electrons in various subshells, the occupancies of lone pair, antibonding orbitals and the second order perturbation energies of most interacting NBO's are summarized as follows;

I. Natural Population Analysis (NPA) of p-BBTF

The NPA [27] of p-BBTF enables us to know about charge distributions over the subshells of atomic orbitals. Table 5 depicts the accumulation of natural charges on atoms of the title molecule. In the present study, fluorine atoms F11 (–0.3498 e), F12 (–0.3532 e), F13 (–0.3535 e) in the trifluoromethyl substitution are found to be the most electronegative atoms in the molecule and the hydrogens attached to the ring carbon atoms are found to be the most electropositive atoms in the title molecule. Moreover, the natural population analysis showed that the 108 electrons in the title molecule are distributed on the sub-shells as follows

Core: 47.99171 (99.9827% of 48)
Valence: 59.78727 (99.6455% of 60)
Rydberg: 0.22102 (0.2046% of 108)

4.4.2 Natural atomic orbital (NAO) analysis of p-BBTF

The occupancies and energies of lone pair atomic orbitals and antibonding molecular orbitals of p-BBTF are given in Table 6. In general, the no of electrons in the lone pair atomic orbitals are equal to 2.0 e and that for anti-bonding atomic orbitals are equal to zero. The deficiency of partial charges in the lone pair and the excess charges in the anti-bonding atomic orbitals in the Table 6 clearly depicts the charge delocalization between loan pair to anti-bonding atomic orbitals. It is worth mentioning that the significant changes in occupancies are observed in the substituent positions.

J. NBO analysis of p-BBTF

In the present study, the NBO analysis of p-BBTF is being performed to estimate the delocalization electron density from the occupied molecular orbitals to unoccupied anti-bonding molecular orbitals. The second order perturbation energies of lone pair and anti-bonding molecular orbitals of most interacting NBO's which is responsible for the dominant stability of the molecule are listed in Table 7. For each donor (i) and acceptor (j), the stabilization energy E_2 associated with the delocalization $i \rightarrow j$ is estimated as

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

where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements and *F(i,j)* is the off diagonal NBO Fock matrix element. The higher second order perturbation energies reported for the interactions LP(3)F12 → BD*(1)C10–F13, LP(3)F13 → BD*(1)C10–F12, and LP(3)Br9 → BD*(2)C1–C6 shows their significant contributions towards stability of the molecule. Also the interactions LP(3)F12 → BD*(1)C10–F11, LP(3)F13 → BD*(1)C10–F11 contributed significantly to the stability of the molecule.

K. HOMO-LUMO energy gap and UV-Vis Spectra

In order to explain electron transitions, the energy gap between highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of p-BBTF is predicted and the electron density isosurface for both the orbitals are given in Fig. 4 along with UV-Vis spectra of the title molecule in gaseous phase and different solvent media. In the present study, the energy of the HOMO orbital is found to be –0.27376 a.u**.** and that for LUMO orbital is found to be –0.06064 a.u. The energy gap between HOMO and LUMO orbital is reported as – 0.21312 a.u. The energy gap calculated by B3LYP/6-311++G(d,p) is well coincide with the relation $E = \frac{hc}{\lambda}$. Here λ is the maximum absorption wavelength for the one electrons transition from HOMO to LUMO which was confirmed from the UV-Vis spectrum of molecule in gaseous phase as shown in Fig. 4b. In order to find the salvation effect of the molecule, UV-Vis spectra of p-BBTF in different solvent has been drawn theoretically by employing polarizable continuum model TD-DFT method [28] in Gaussian 09W software package. It is clearly seen that absorption wavelength does not change with respect to the solvent instead the oscillator strength or intensity of the peak change considerably.

L. Non-linear Optical Properties

The increasing volume of information processing and communication is continuing to be a big challenge in the modern technology. In the past decades, most of the materials used for devices are minarals, i.e., metals or semiconductors. Now the usage of organic materials in opto-elecctronics has increased dramatically. To test the non-linear optical response of the p-BBTF, the finite-field approach has been implemented. Based on the finite-field approach, the non-linear optical parameters such as dipole moment, polarizability, anisotropy polarizability and first order hyperpolarizability of p-BBTF molecule are calculated using B3LYP/6-311++G(d,p) basis set level. The numerical values of above mentioned parameters are listed in Table 8. In the presence of an external electric field (E), the energy of the system is a function of the electric field. First hyperpolarizability is a third-rank tensor that can be described by a 3×3×3 matrix. The 27 components of the 3D matrix can be reduced to 10 components because of the Kleinman symmetry [29]. The components of β is defined as the coefficients in the Taylor series expansion of energy in an external electric field.

When an external electric field is weak and homogeneous, Taylor series expansion becomes

$$E = E^0 - \frac{\mu_i F_i}{1!} - \frac{\alpha_{ij} F_i F_j}{2!} - \frac{\beta_{ijk} F_i F_j F_k}{3!} - \frac{\gamma_{ijkl} F_i F_j F_k F_l}{4!} + \dots\dots$$

where E is the energy of the unperturbed molecules, F_i is the field at origin and μ_i , α_{ij}, β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, first hyperpolarizabilities and the second hyperpolarizabilities, respectively.

The total static dipole moment μ, mean polarizability α_0, anisotropy of the polarizability $\Delta\alpha$ and first hyperpolarizability β_{tot} using x, y and z components, are defined as

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha_0 = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})}{3}$$

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

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

here

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

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

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

Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore it was used frequently as a threshold value for comparative purposes. The calculated values of α_0 and β_{tot} for the title compound are –78.2786 Debye-Å. and 950.2235Debye-Å^2, respectively. For comparative purpose, the components of dipole moments, polarizability and hyperpolarizability of urea compound calculated at B3LYP/ 6-311++G(d,p) method are also given in the Table 8. While comparing, the hyperpolarizability of the title molecule is 51.32 times greater than that of urea. Hence the title molecule is suitable for non-linear optical device applications.

M. Thermodynamic parameters of p-BBTF at 298.15 K

In the present study, the thermodynamic parameters of p-BBTF have been predicted by DFT method with 6-311++G(d,p) basis set combinations. To understand the thermo dynamical system of the molecule at room temperature, the essential parameters such as; zero point vibrational energy, rotational constants, rotational temperatures, entropy, specific heat capacity, translational energy, rotational energy and vibrational energy have been reported to the greater extent. Here the entropy and specific heat capacity of a molecule are found to be 101.032 and 34.2490 cal/mol-Kelvin, respectively.

V. CONCLUSION

The detailed vibrational characteristics of p-BBTF have been proposed. The optimized geometrical parameters have been predicted by DFT/6-311++G(d,p) method. The presence of inter- and intramolecular charge transfer properties have been investigated using NPA, NAO and NBO analysis. The results clearly show the interactions which contributed significantly to the dominant stability of p-BBTF. The HOMO-LUMO energy gap has been predicted and it has been verified theoretically by UV-Vis spectrum of p-BBTF in gaseous phase. The NLO properties have also been predicted and found that the hyperpolarizability of the title molecule is 51.32 times greater than that of reference urea. Finally, certain thermodynamic parameters have been predicted to find the thermodynamical system of p-BBTF at room temperature.

VI. ACKNOWLEDGMENTS

The author T. Karthick sincerely acknowledged University Grant Commission, New Delhi for providing financial assistance under Dr.D.S.Kothari fellowship scheme. Prof. Poonam Tandon is thankful to UGC for financial support under UGC Research Award.

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