

ANALYSIS OF STRUCTURE - ACTIVITY RELATIONS OF THE NLO MATERIAL OF (3Z)- 1,1,1-TRIFLUORO-4-HYDROXY-4- (NAPHTHALEN-2-YL)BUT-3-EN-2-ONE BY EXPERIMENTAL AND THEORETICAL SPECTROSCOPIC TECHNIQUES

D.Jaya Reshmi¹ and D. Arul Dhas²,

¹Research Scholar, ²Assistant Professor,

^{1,2}Department of Physics, Physics Research Centre,

^{1,2}Nesamony Memorial Christian College, Marthandam, India

rajreshmidev@gmail.com¹, aruldhas_2k4@gmail.com²

Abstract

The experimental and theoretical study on the structure and vibrations of (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one were carried out. Introduction (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one compound are used in electro-optic switching elements for telecommunication, optical information processing, optical parametric oscillator, degenerate four wave mixing, optical disk data storage, laser remote sensing, laser driven fusion, colour display and medical diagnostic because of its NLO activity, structural and spectroscopic analysis has been performed using computation and experimental methods. The first order hyperpolarizability (β) and related properties (β , α and $\Delta\alpha$) of (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one were calculated. Stability of the molecule arising from hyper conjugative interactions, charge delocalization have been analysed using natural bond orbital (NBO) analysis. The results show that change in electron density (ED) in the charge σ^* and π^* antibonding orbitals and second order delocalization energies (E^2) confirms the occurrence of intramolecular charge transfer (ICT) within the molecule.

Key words: DFT, FTIR, FT-RAMAN, NBO analysis, NLO activity.

I. Introduction

π -Conjugated push pull molecules most largely recurrent architecture for the construction of efficient organic molecules for non-linear optics [1]. Naphthalene, a benzenoid polycyclic aromatic hydrocarbon (PAH) has the structure of fused pair of benzene rings. PAHs can be produced from both natural and human activities proved the clear evidence of the presence of PAHs in many astronomical objects [2-4]. Non linear optical materials have attracted the attention of researchers due to their great potential applications in various fields like laser technology, optical communication, optical data storage and optical signal processing [5-7]. There has been growing interest in using organic materials for nonlinear optical (NLO) devices, functioning as second harmonic generators, frequency converters and electro-optical modulators because of the large second order electric susceptibilities of organic materials. Vibrational spectral analysis of the molecules can provide deeper knowledge about the relationships between molecular architecture, non-linear response and hyperpolarizability, and promote the discovery of new efficient materials for technological applications. However, for a new synthesized molecule, it is difficult to describe its original and intricate vibrational spectral property. The detailed vibrational spectral studies are aided by DFT calculations to elucidate the assignment of the vibrational spectra and correlation between the molecular structure and NLO property by investigating the intramolecular charge transfer (ICT) interaction, the highest occupied molecular orbital (HOMO), lower unoccupied molecular orbital (LUMO) and the first order hyperpolarizability of the compound.

II. Experimental Details

The Infrared spectrum of the compound 4,4,4-Trifluoro-1-(2-naphthyl)-1,3-butanedione was recorded on a 1FS 66V spectrometer using KBr pellet technique from $4000\text{-}450\text{cm}^{-1}$. The FT-Raman spectrum of same compound is also recorded in the range of $3500\text{-}50\text{cm}^{-1}$. The ultra violet absorption spectra of the title compound were examined in the range $200\text{-}700\text{nm}$ using, UV-Vis recorded on a Cary (Varian) 50 Bio UV-Vis spectrophotometer using acetone and DMF solvents. The second harmonic generation behavior of the powdered material was tested using the Kurtz and Perry method.

III. Computational details

The structural characteristics and the fundamental vibrational modes of (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one, the DFT-B3LYP correlation functional calculations have been carried out. All the theoretical calculations of geometrical parameters in the ground state were performed using the Gaussian 09W program. The title molecule was optimized, after then the optimized structural parameters were used in the vibrational frequency, isotropic chemical shift and calculations of electronic properties. The vibrational frequencies, Infrared and Raman intensities of the title molecule were calculated.

IV. Result and discussion

4.1. Optimized geometry

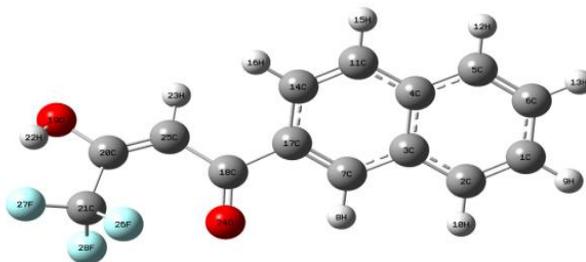


Fig: 1 (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one

The optimized molecular structure of title molecule is obtained from Gaussian 09W and Gaussview 05 program and they are shown in Fig. 1. The molecule contains CF_3 and $\text{C}=\text{O}$ (trifluoro butane dione group) connected with naphthalene ring. The comparative optimized structural parameters such as bond lengths bond angles and dihedral angle are presented in Table 1 along with available experimental data. Unlike benzene, the carbon-carbon bonds in naphthalene are not of the same length. The bonds, $\text{C}_1\text{-C}_2$, $\text{C}_{11}\text{-C}_{14}$, $\text{C}_5\text{-C}_6$, $\text{C}_7\text{-C}_{17}$ are ca. 1.37\AA , where as the other carbon bands are like $\text{C}_2\text{-C}_3$, $\text{C}_3\text{-C}_4$, $\text{C}_4\text{-C}_5$, $\text{C}_3\text{-C}_7$, $\text{C}_4\text{-C}_{11}$, $\text{C}_{11}\text{-C}_{14}$ ca. 1.41\AA in B3LYP/6-311G(d,p) basis set the bonds $\text{C}_1\text{-C}_2$, $\text{C}_{11}\text{-C}_{14}$, $\text{C}_5\text{-C}_6$ and $\text{C}_7\text{-C}_{17}$ are double bond character. The corresponding experimental values 1.36\AA . The increasing bond length $\text{C}_7\text{-C}_{17}$ value is 1.37\AA due to the attaching carbonyl group in the place of C_{17} . All C-H bond length are 1.083\AA B3LYP this shows that C-H bond lengths computed with B3LYP/6-311G(d,p) basis set are deviated to the experimental data (0.950\AA). Other C-C bonds $\text{C}_{17}\text{-C}_{18}$, $\text{C}_{18}\text{-C}_{19}$, $\text{C}_{20}\text{-C}_{25}$ and $\text{C}_{20}\text{-C}_{23}$ bond length values are 1.520 , 1.477 , 1.344 and 1.533\AA due to the butanedione group attached. The hydroxyl group attached in C_{20} atom very low value occurs in bond length $\text{C}_{20}\text{-C}_{25}$. Exactly at the substitution place the bond angle ($\text{C}_7\text{-C}_{14}\text{-C}_{17}$) 119° , ($\text{C}_7\text{-C}_{17}\text{-C}_{18}$) is 117° lower than the hexagonal angle 120° and $\text{C}_3\text{-C}_7\text{-C}_{17}$ (121.6), $\text{C}_{11}\text{-C}_{14}\text{-C}_{17}$ (120.7) bigger than the hexagonal angle 120° . This clearly shows that the substitution of trifluorobutane dione group in place of hydrogen appreciably affects the $\text{C}_7\text{-C}_{14}\text{-C}_{17}$ bond angle and the title molecule is non planar. The comparative graph of bond length, bond angle and dihedral angle are presented in respectively.

Table 1: Selected optimized parameters of (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one

parameter	Bond length	XRD(e)	parameter	Bond Angle	XRD(e)
C ₁ -C ₂	1.364	1.372	C ₃ -C ₄ -C ₁₇	121.7	121.6
C ₃ -C ₇	1.415	1.412	C ₇ -C ₁₇ -C ₁₄	119.0	118.7
C ₁₇ -C ₁₈	1.498	1.520	C ₁₄ -C ₁₇ -C ₁₈	123.6	117.6
C ₂₀ -C ₂₁	1.525	1.533	C ₇ -C ₁₇ -C ₁₈	117.3	121.5
C ₂₀ -O ₁₉	1.268	1.349	C ₁₁ -C ₁₄ -C ₁₇	121.3	120.7

4.2. Vibrational assignments

4.2.1. C-H vibrations

The substituted naphthalene gives rise to C-H stretching, C-H in-plane and C-H out-of-plane bending vibrations. The (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one molecule gives rise to seven C-H stretching, seven C-H in-plane bending vibration and seven C-H out-of-plane bending vibration. Since (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one is monosubstituted naphthalene ring system it has seven adjacent C-H moieties. The expected seven C-H stretching vibrations corresponds to mode nos. 1-7. Calculated frequencies and the corresponding experimental frequencies are observed respectively to stretching modes of C₅-H₁₂, C₆-H₁₃, C₁-H₉, C₇-H₈, C₂-H₁₀, C₁₄-H₁₆, C₁₁-H₁₅ unit. The vibrations of 1-7 assigned to aromatic C-H stretching in the region 3090-2970 cm⁻¹ are in agreement with literature value [8, 9]. The C-H stretching vibrations are calculated 3163-3265 cm⁻¹ which are in agreement with observed ones. These vibrations are not found to be affected due to the nature and position of the substituent, most of aromatic compounds have nearly four infrared peaks in the region 3080-3010 cm⁻¹ due to ring C-H stretching bonds [10,11]. The C-H in-plane-bending vibrations usually occur in the region 1390-990 cm⁻¹ and are very useful for characterization purposes [12]. It is noted from literature [13] that strong band around 1200 cm⁻¹ appears due to valence oscillations in naphthalene. The C-H in plane bending vibrations assigned in the region 1190-1041 cm⁻¹ which is agreement with literatures [8-13]. The strong peaks below 960 cm⁻¹, clearly indicate its aromaticity. Substitution patterns on the ring can be judged from the out-of-plane bending of the ring C-H bonds in the region 960-675 cm⁻¹ and these bands are highly informative [14].

4.2.2. C=C vibrations

Naphthalene ring vibrations are found to make a major contribution in IR and Raman. Naphthalene ring stretching vibrations usually occur in the region 1640-1400cm⁻¹ [15]. In this compound the C=C stretching mode is identified as very strong band at 1600cm⁻¹ and strong band at 1427cm⁻¹ in IR and at 1600cm⁻¹ and 1428cm⁻¹ in Raman respectively. The ring stretching vibrations are very much important in the spectrum of naphthalene and its derivatives are highly characteristic of the aromatic ring itself. The C=C aromatic stretching, known as semicircle stretching, predicted 1610 agreement with experimental observation of FT-IR spectra values at 1600 cm⁻¹. Many ring vibrations are affected by the substitution to the aromatic ring of naphthalene. The six ring carbon atoms undergo coupled vibrations, called skeletal vibration and give a maximum of four bands in the region 1660-1420 cm⁻¹. The naphthalene derivatives, the C-H out of plane bending vibrations occur at 810-785cm⁻¹ due to three adjacent hydrogen atoms on the ring, and at 780-760cm⁻¹ for four adjacent hydrogen atoms. IR bands at 970,850, and 711cm⁻¹ and the Raman bands at 1018cm⁻¹ shows the possibility of C-H out of plane bending modes. The IR bands at 1456, 1380, 1310, 1280 and 1166cm⁻¹ and the Raman bands at 1274 and 1166cm⁻¹ correspond to the naphthalene C-H in-plane bending modes, which are mixed with other vibrational modes.

4.2.3. C=O vibrations

The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy. This multiply bonded group is highly polar and therefore gives rise to an intense infrared absorption band. The lone pair of electrons on oxygen also determines the nature of the carbonyl group. The C=O stretching of ketones are expected in the region 1715 cm⁻¹[16]. The characteristic ketonic frequency C=O in the present study appears at 1760vw cm⁻¹ in FT-IR spectrum which is calculated at 1630 cm⁻¹. The carbon oxygen double bond is formed by π-π bonding. Carbon and Oxygen atoms are electronegative, hence the bonding of electrons between them are not equally distributed.

4.2.4 CF₃Group vibrations

In the vibration spectra of the bands found over a wide frequency range 1360–1000 cm⁻¹ may be due to C–F stretching vibrations [17]. C–F stretching vibrations observed at 1145cm⁻¹ in FT-IR and 1344cm⁻¹ in FT-Raman. The corresponding calculated value is 1139 and 1339cm⁻¹. For the distribution of CF₃ group frequencies, nine fundamental vibrations can be associated to each CF₃ group. Three stretching, three bending, two rocking modes and a one out of plane bending describe the motion of the CF₃ group. The CF₃ asymmetric stretching frequencies are established at 1145 cm⁻¹ in FTIR and 1125 cm⁻¹ in FT-Raman spectrum. The corresponding calculated value is 1146 and 1111cm⁻¹.The F-C-F bending occur in the region 650cm⁻¹ [16].The observed spectrum shows the CF₃ in plane bending mode as intense at 595 cm⁻¹(FTIR) and weak one at 556 cm⁻¹ (Raman).The CF₃ deformation modes mainly coupled with in-plane bending vibrations. The bands obtained at 280 cm⁻¹ in Raman corresponds to CF₃ out-of-plane modes.

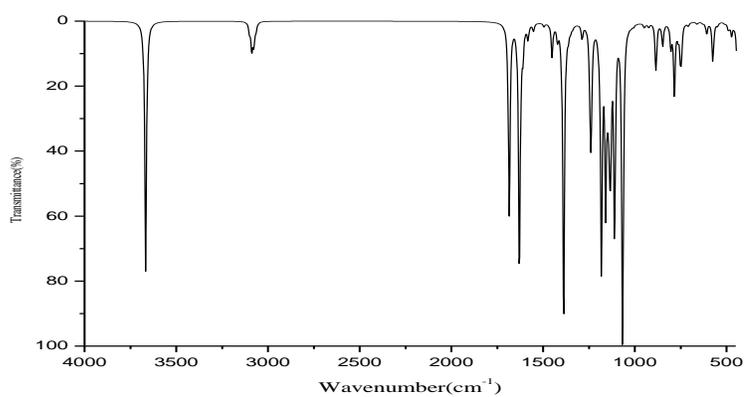


Fig. 2 FT-IR Spectrum for (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one

4.3 NBO analysis

The larger the E⁽²⁾ value shows the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. The possible intensive interactions are given in Table 2. Delocalization of electron density between occupied Lewis Type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor–acceptor interaction. NBO analysis has been performed on the molecule at the B3LYP/6-311G (d,p) level in order to elucidate the conjugation, hyper-conjugation and delocalization of electron density within the molecule. The intra molecular interaction is formed by the orbital overlap between bonding (σ and π (C–C, C–H, and C–F) and antibonding σ^* and π^* (C–C, C–H and C–F) bond orbital which results intra molecular charge transfer (ICT) causing stabilization of the system. The stabilization energy contributions from the σ (C₃-C₄) \rightarrow σ^* (C₃-C₇) interaction is 78.952, σ (C₁₇-C₁₈) \rightarrow σ^* (C₃-C₇) interaction is 10.711KJ/mol. The σ (C₁₈-O₂₄) \rightarrow σ^* (C₇-C₁₇) interaction is 21.756KJ/mol and σ (C₁-C₂) \rightarrow σ^* (C₅-C₆) having 75.060 KJ/mol. The title compound occur the highest stabilization energy. The oxygen has larger percentage of NBO and gives the larger polarization coefficient because it has higher electro negativity. The anti-bonding orbital for both σ^* (C₁-C₂) and σ^* (C₁-C₆) with 0.014 and 0.017 electrons has 50% character for the title compound. The maximum occupancy is 1.979 obtained for σ (C₁-C₂), σ (C₁-C₆), σ (C₂-C₃) and σ (C₃-C₄). The important interaction energy is 364.97KJ/mol. This value is identified at donor C₁₈-O₂₄ NBOs and their corresponding NBOs are BD* (C₇-C₁₇), BD* (C₂₀-C₂₅) respectively.

Table 2: NBO analysis for (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one

Donor NBO(i)	ED(i) (e)	Acceptor NBO(j)	ED(j) (e)	E ⁽²⁾ (kJ/mol)
$\sigma(C_3-C_4)$	1.963 -0.668	$\sigma^*(C_7-C_{17})$	0.020 0.589	78.952
$\sigma(C_3-C_7)$	1.972 -0.686	$\sigma^*(C_7-C_{17})$	0.020 0.589	15.773
$\sigma(C_{18}-O_{24})$	1.993 -0.064	$\sigma^*(C_{20}-O_{25})$	0.018 0.609	20.668
$\sigma(C_7-C_{17})$	1.971 -0.703	$\sigma^*(C_{11}-C_{14})$	0.014 0.604	76.818

4.4. Mulliken charge analysis

The charge distribution on a molecule has a significant influence on the vibrational spectra. C₂₁ atom exhibit more positive (0.715e) while the other carbon atoms exhibit negative charges except C₁₈ which suggests an extensive charge delocalization in the entire molecule through C₂₀-C₂₃. In carbon atoms C₁₇ more negative due to charge transfer to the ring from fluorine and oxygen. The Charge analysis shows that the presence of C₂₁ imposes highly positive charges on the fluorine atom of the butyl group. The negatively charged fluorine atom F₂₆, F₂₇ and F₂₈ conforms that charge is transferred from carbon to fluorine atom. The presence of negative charge on F and O atom and net positive charge on H atom may suggest the formation of intramolecular interaction in solid forms.

4.5. NLO behavior

It is an important and inexpensive way to evaluate the NLO properties of materials by theoretical calculations. Non- linear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields. The first hyperpolarizabilities (β) of the title molecule along with related properties (μ , α and α_s) are calculated using B3LYP/ 6-311G(d,p) method. The calculated value of the linear polarizability and first-order hyperpolarizability is 1.4774×10^{-1} . Based on these facts, it could be concluded that the present material has a reasonably good propensity for non- linear optical activity.

4.6. HOMO–LUMO analysis

The HOMO and the LUMO are very important parameters for chemical reaction. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor, and the gap between HOMO and LUMO characterizes the molecular chemical stability. The energy gap between the HOMO and the LUMO molecular orbitals is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. The energy value of HOMO is computed -0.34677eV and LUMO is -0.22969 eV , and the energy gap value is -0.11708eV in acetone for title molecule. The HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. The positive phase is red and the negative one is green.

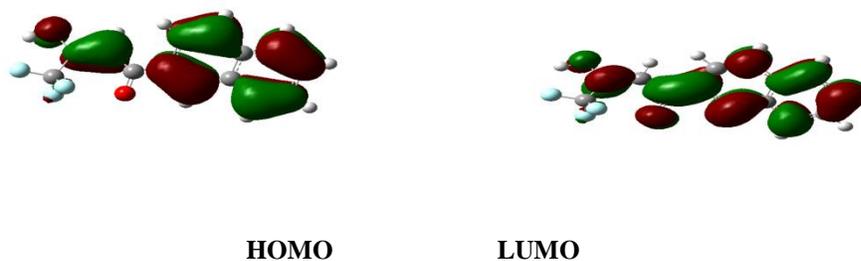


Fig. 3 HOMO and LUMO plots for (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one

V.Conclusion

Vibrational wavenumbers, infrared intensities calculated by B3LYP/6-311G (d, p) level agrees well with the experimental data. The bond length C₁₈-O₂₄ (1.256Å) is smaller when compared with C₂₀-O₁₉ (1.268Å) which indicates an extension of conjugation in the aromatic ring of naphthalene to oxygen. The calculated value of the linear polarizability and first-order hyperpolarizability shows more NLO activity (3Z)-1,1,1-trifluoro-4-hydroxy-4-(naphthalen-2-yl)but-3-en-2-one.

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