

**FT-IR, FT-Raman and UV-Visible Analysis of (2E, 6E)-2, 6-Dibenzylidene-4-(4-Hydroxyphenyl) Cyclohexanone-DFT Method****A. Sumathi*¹, D. Rajaraman¹, S. Bharanidharan², S. Kabilan¹ and K. Krishnasamy¹**1. Department of Chemistry, Annamalai University, Annamalainagar-608002, Tamilnadu, **INDIA**2. Department of Physics, Annamalai University, Annamalainagar-608002, Tamilnadu, **INDIA**Email: krishnasamybala56@gmail.comAccepted on 17th February 2016**ABSTRACT**

FT-IR, FT-Raman and UV-Visible spectra of (2E,6E)-2,6-dibenzylidene-4-(4-hydroxy phenyl) cyclohexanone (DHC) was recorded in the regions of 4000-400 cm⁻¹, 3500-50 cm⁻¹ and 200-800 nm, respectively. The geometrical parameters and harmonic wavenumbers were calculated using DFT/B3LYP/6-31G (d,p) level of basis set. The NLO behavior of the title molecule was measured using first order hyperpolarizability calculation. Hyperconjugative interaction and charge delocalization have been analyzed. The calculated HOMO-LUMO energy gap shows the stability of the molecule. Molecular electrostatic potential (MEP) was studied for predicting the reactive sites. Mulliken charges were also calculated. The theoretical IR, Raman and UV-Visible spectra of DHC have also been constructed and correlated with the experimental results.

Keywords: Cyclohexanone, synthesis, FT-IR, DFT, NLO, NBO, UV, NMR analysis.**INTRODUCTION**

The cytotoxic, anticancer, chemopreventative and mutagenic properties of chalcones has been discussed [1]. Numerous chalcone derivatives are used as agrochemicals [2] and drugs [3] due to their structurally important multipronged activities by the presence of carbonyl, vinyl and polar substituents in their structure. Heterocyclic analogs of chalcone are acts as anti-inflammatory, anti-tumour [4-6], antifungal, antibacterial [7], anti-tubercular, anti-protozal, anti-viral and gastro protective activities. Chalcones are important intermediates in the synthesis of many pharmaceuticals [8-10]. In addition substituted chalcones are used as better nonlinear optical materials [11-20]. In modern years, chalcones have been used in the field of material science as optical limiting [21], electrochemical sensing [22] and Langmuir film [23]. Some derivatives of the chalcone have been explained in literature as inhibitors of ovarian cancer cell proliferation [24] and pulmonary carcinogenesis [25]. The precise molecular recognition between chalcones and their guest provides a good opportunity for studying key aspects of supramolecular chemistry, which are also significant in a variety of disciplines including chemistry, biology, physics, medicine and related science and technology [26]. Bis (arylidine) ketones have been reported to be clinically useful drugs and they exhibit considerable Cytotoxicity To P388 Leukaemia Cells [27, 28].

MATERIALS AND METHODS

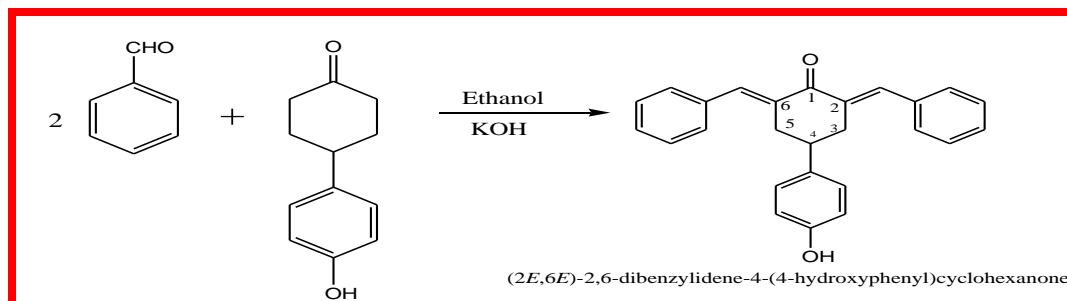
Theoretical Calculation: The entire calculation was performed at DFT levels on a Pentium 1V/ 3.02 GHz personal computer using Gaussian 03W [29] program package, invoking gradient geometry optimization [29, 30]. In the present study, the DFT/B3LYP/6-31G (d,p) basis set level was used to calculate the optimized parameters and vibrational wave numbers of the title molecule. The vibrational modes were assigned on the basis of TED analysis using the VEDA4 program [31]. The vibrational frequency assignments were made with a high degree of accuracy. The Natural Bond Orbital (NBO) calculation were performed using NBO 3.1 program as implemented in the Gaussian 03W package at the DFT/B3LYP level.

Gaussian 03W package is able to calculate the Raman activity. The Raman activities were transformed into Raman intensities using Raint program [32] by the expression:

$$I_i = 10^{-12} \times (v_0 - v_i)^4 \times \frac{1}{v_i} \times RA_i \quad (1)$$

Where I_i is the Raman intensity, RA_i is the Raman scattering activities, v_i is the wavenumber of the normal modes and v_0 denotes the wavenumber of the excitation laser [33].

Synthesis of (2E,6E)-2,6-dibenzylidene-4-(4-hydroxyphenyl)cyclohexanone: (2E,6E)-2,6-dibenzylidene-4-(4-hydroxyphenyl)cyclohexanone was prepared by dissolving 1 equivalent of 4-(4-hydroxyphenyl)cyclohexanone and 2 equivalents of benzaldehyde in absolute ethanol (20 mL). The Potassium hydroxide in water was added drop wise to the mixture. The mixture was refluxed for 3 h at 40 °C. The reaction is monitored by TLC, after the completion of reaction it was dried and washed with pet ether solvent. The separated solid was recrystallized with ethanol.



Characterization studies: All the solvents and chemicals were of purchased as analytical grade and used as such without further purification. The FT-IR spectrum of DHC was recorded using AVATAR – 330 FT-IR spectrophotometer. The sample was grained with KBr and Pellet technique was used to record the spectrum in cm^{-1} . The NMR spectrum of DHC was recorded on a BRUKER Avance III 400MHz, for ^1H , 100MHz for ^{13}C NMR spectra. The two dimensional NMR spectrum was recorded using standard pulse sequences. The chemical shifts are noted in (δ) units PPM relative to the internal standard Tetra methyl silane (TMS) for ^1H and ^{13}C spectra. SHIMADZU UV-1650 PC digital spectrophotometer was used for the UV-Visible studies.

RESULTS AND DISCUSSION

Geometrical analysis: The optimized molecular structure of the title molecule is shown in fig. 1. The geometrical parameters of DHC are calculated using B3LYP with 6-31G (d, p) level of theory. In this study title molecule consist of two phenyl, phenol and cyclohexanone moieties. The central cyclohexanone ring may exist as stable chair or boat conformation. But in the present study, the cyclohexanone ring conformation is observed as twisted form. In this study, the C2-C3/C5-C6 bond lengths (1.5 Å) are positively (~ 0.003 Å) deviated from C3-C4/C4-C5 (1.047 Å) bonds in the cyclohexanone ring, which

shows the deformation in the same. The dihedral angle of central cyclohexanone ring shows one side (C2-C3-C4-C5/C6-C5-C4-C3) is flattened with dihedral angle ($-2.6322/2.7021^\circ$) and the other side (C2-C1-C6-C5/C6-C1-C2-C3) exhibits the chair conformer with dihedral angle ($-57.786/57.857^\circ$), respectively. This represents the existence of chair conformation in the title molecule. The bond parameters values are listed in table. 1. The bond lengths, bond angles and dihedral angle values are nearly coincides with literature [34].

Table 1: Geometrical parameters of DHC

| Bond Parameters | | |
|-------------------------|-------------------------|-------------------|
| Bond Lengths (Å) | B3LYP/6-31G(d,p) | XRD Value* |
| C1-C2 | 1.5467 | 1.519 |
| C1-C6 | 1.5467 | 1.519 |
| C1-C11 | 1.5216 | |
| C1-H48 | 1.0995 | 0.97 |
| C2-C3 | 1.5144 | 1.5 |
| C2-H7 | 1.1023 | 0.97 |
| C2-H9 | 1.0954 | |
| C3-C4 | 1.4975 | 1.497 |
| C3-C35 | 1.3601 | |
| C4-C5 | 1.4975 | 1.497 |
| C4-O21 | 1.2605 | 1.209 |
| C5-C6 | 1.5145 | 1.5 |
| C5-C22 | 1.36 | 1.346 |
| C6-H8 | 1.1022 | 0.97 |
| C6-H10 | 1.0955 | 0.97 |
| Bond Angles (°) | | |
| C2-C1-C6 | 109.0726 | 109.3 |
| C2-C1-C11 | 112.3736 | |
| C2-C1-H48 | 107.5542 | 109.8 |
| C6-C1-C11 | 112.3793 | |
| C6-C1-H48 | 107.5582 | 109.8 |
| C11-C1-H48 | 107.6672 | |
| C1-C2-C3 | 112.2251 | |
| C1-C2-H7 | 108.2442 | 109.3 |
| C1-C2-H9 | 109.3437 | 109.3 |
| C3-C2-H7 | 110.6244 | 109.3 |
| C3-C2-H9 | 109.9579 | |
| H7-C2-H9 | 106.2512 | |
| C2-C3-C4 | 118.9736 | 118.8 |
| C2-C3-C35 | 124.9784 | |
| C4-C3-C35 | 116.0068 | |
| C3-C4-C5 | 119.4444 | |
| C3-C4-O21 | 120.2777 | 120.73 |

| | | |
|----------------------------|-----------|--------|
| C5-C4-O21 | 120.2746 | 120.73 |
| C4-C5-C6 | 118.9924 | 118.8 |
| C4-C5-C22 | 116.0082 | |
| C6-C5-C22 | 124.9573 | |
| C1-C6-C5 | 112.2341 | |
| C1-C6-H8 | 108.2399 | 107.9 |
| C1-C6-H10 | 109.3311 | |
| C5-C6-H8 | 110.6285 | |
| C5-C6-H10 | 109.9507 | |
| H8-C6-H10 | 106.2621 | 107.9 |
| C2-H9-H37 | 100.0063 | |
| Dihedral Angles (°) | | |
| C6-C1-C2-C3 | 57.8577 | |
| C6-C1-C2-H7 | -64.5094 | |
| C6-C1-C2-H9 | -179.8509 | |
| C2-C1-C6-C5 | -57.786 | -59.6 |
| C1-C2-C3-C4 | -28.1409 | 27 |
| C1-C2-C3-C35 | 149.4248 | -153.2 |
| C2-C3-C4-C5 | -2.6322 | |
| C3-C4-C5-C6 | 2.7021 | 5.7 |
| C3-C4-C5-C22 | -179.5397 | |
| O21-C4-C5-C6 | -177.9616 | -176 |
| O21-C4-C5-C22 | -0.2034 | 4.1 |
| C4-C5-C6-C1 | 28.0071 | 27 |

*The values compared from reference [34]

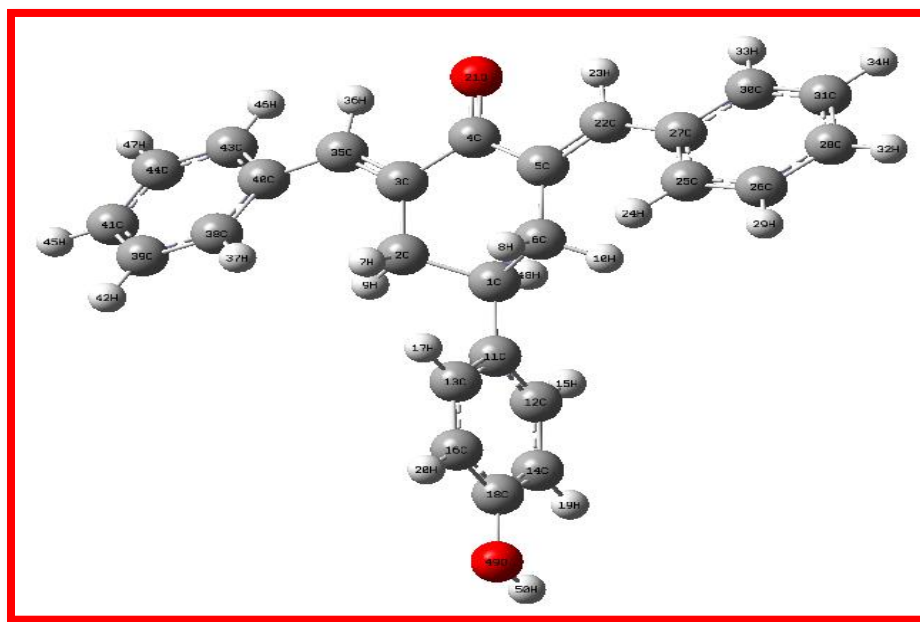


Fig 1: Optimized molecular structure of DHC

Vibrational Assignments: The title molecule consists of 50 atoms which undergoes 144 fundamental modes of vibrations. All the 144 vibrations are distributed as 97 in-plane and 47 out-of-plane bending vibrations. Vibrational spectral assignments have been carried on the recorded FT-IR and FT-Raman spectra based on the theoretically predicated wave number by B3LYP/6-31G (d, p) basis set and are presented in figs. 2, 3 and table 2.

C-H Vibrations: The aromatic structure shows the presence of C–H stretching vibrations in the region 2900–3150 cm^{-1} [35, 36], which is the characteristic region for the identification of the C–H stretching vibrations. In this region, the bands are not affected appreciably by the nature of the substituents. In this study, the C-H stretching bands observed at 3059 cm^{-1} in infrared spectrum and 3059 cm^{-1} in Raman spectrum and their corresponding harmonic value lies at 3046 cm^{-1} (mode no: 17) with the help of TED assignments $\geq 90\%$.

The C-H in-plane blending vibrations are calculated at 1493 cm^{-1} , 1446 cm^{-1} , 1386 cm^{-1} , 1176 cm^{-1} and 1088 cm^{-1} (mode nos: 34, 38, 40, 62 and 67). The bands observed at 1491 cm^{-1} , 1389 cm^{-1} , 1092 cm^{-1} in FT-IR spectrum and 1491 cm^{-1} , 1446 cm^{-1} , 1170 cm^{-1} in Raman counterpart with the TED assignments of $\geq 25\%$. The mixed modes of in-plane blending and out-of-plane bending vibrations are observed at 1290 (w) cm^{-1} in IR spectrum. The corresponding harmonic value lies at 1284 cm^{-1} (mode no: 51) with the help of TED assignments 39%. The C-H torsion mode observed at 985 cm^{-1} , 774 cm^{-1} in infrared spectrum and 999 cm^{-1} , 911 cm^{-1} in Raman spectrum. The calculated value lies at 996 cm^{-1} , 979 cm^{-1} , 914 cm^{-1} , 774 cm^{-1} (mode nos: 75, 78, 87 and 97).

C=O vibrations: A carbonyl group is an organic functional group composed of a carbon atom double-bonded to an oxygen atom. In cyclic ketones, the characteristic IR absorption frequencies of C=O group have been studied [37, 38]. The lone pair of electrons on oxygen also determines the nature of the carbonyl group. Normally carbonyl group vibrations occur in the region 1850–1600 cm^{-1} [39]. In our present study, the carbonyl stretching vibration is observed as a medium band in FT-IR at 1660 cm^{-1} and in the Raman counterpart it is observed at 1650 cm^{-1} as a weak band. The corresponding harmonic value lies at 1636 cm^{-1} with pure mode of vibrations (TED=86%). The C=O in plane bending vibrations are observed at 524 cm^{-1} (m) in infrared spectrum and 523 cm^{-1} (W) in Raman spectrum. The calculated value appeared at 527 cm^{-1} (mode no: 113).

CH₂ vibrations: The atoms in a CH₂ group, commonly found in organic compounds, can vibrate in six different ways: symmetric and asymmetric stretching, scissoring, rocking, wagging and twisting. In aromatic organic compound, the C–H stretching vibrations are usually observed below 3000 cm^{-1} [40, 41]. As revealed by TED ($\geq 86\%$) the peaks identified at 2923 and 2849 cm^{-1} in FT-IR are assigned to asymmetric and symmetric stretching modes of CH₂ vibration of the title molecule. ν_{asym} CH₂ mode is further supported by Raman band at 2865 cm^{-1} (mode nos: 20-22).

In DHC, the observed FT-Raman band 1294 cm^{-1} /FT-IR band 1290 cm^{-1} are assigned to CH₂ wagging and CH₂ twisting modes of C₆H₉, C₆H₁₀, C₃H₉ units respectively, which shows good correlation with scaled harmonic frequencies at 1284 cm^{-1} (mode no: 51). According to TED results, these modes are mixed with β_{HCC} mode. It is notable that both CH₂ scissoring and CH₂ rocking are sensitive to the molecular conformation. The CH₂ rocking mode was assigned at 1028 cm^{-1} (FT-IR) and 1030 cm^{-1} (Raman) and the calculated values at 1029 cm^{-1} (mode no: 70). These assignments are also supported by the literature Padmaja et al., [42] in addition to TED output.

C-C Vibrations: Socrates [43] mentioned that the presence of conjugate substituent such as C=C causes heavy doublet formation around the region 1625-1575 cm^{-1} . The very strong band is appeared at 1598 cm^{-1} in infrared spectrum and 1597 cm^{-1} , 1211 cm^{-1} , 70 cm^{-1} in Raman spectrum due to α , β unsaturated C=C stretching vibrations in the carbonyl position [44]. In the present study, the C=C stretching vibration observed at

1598 cm^{-1} in IR/1597 cm^{-1} in FT-Raman spectrum and its corresponding harmonic values lies at 1598 cm^{-1} (mode nos: 25) with the help of TED assignments $\geq 23\%$. The C=C stretching modes of the cyclohexanone portions are appeared in the range 1235 cm^{-1} , 1192 cm^{-1} , 1028 cm^{-1} , 748 cm^{-1} in the IR spectrum and 1030 cm^{-1} , 618 cm^{-1} in the Raman spectrum. The computed bands are present at 1241 cm^{-1} , 1195 cm^{-1} , 1029 cm^{-1} , 741 cm^{-1} , 612 cm^{-1} (mode nos: 54, 58, 70, 99, 108) with a TED contribution of $\geq 10\%$.

In the benzylic OH ring C-C the stretching modes are appeared in the range of 1270 cm^{-1} in Raman with related harmonic value appeared in 1249 cm^{-1} (mode no: 52) with TED ≥ 45 . In the same position stretching and in-plane bending modes are observed at 1149 cm^{-1} in IR spectrum and its calculated value appeared at 1147 cm^{-1} (mode no: 64). Carbon-carbon out-of-plane bending and torsion modes are appeared 936 cm^{-1} in IR spectrum and 938 cm^{-1} in Raman spectrum. The corresponding value lies at 930 cm^{-1} (mode no: 84) as a pure mode of vibrations (92%). In the same ring out of plane bending is appeared at 833 cm^{-1} in IR spectrum and 809 cm^{-1} in Raman spectrum. The related calculated values present in 836 cm^{-1} and 803 cm^{-1} (mode no: 105).

The aromatic benzene ring C-C stretching appeared in 1570 cm^{-1} in IR and the related harmonic value lies at 1565 cm^{-1} (mode no: 29) with TED assignments $\geq 57\%$. The good agreement allows us to perform the assignments of IR and Raman bands in the whole studied spectral regions.

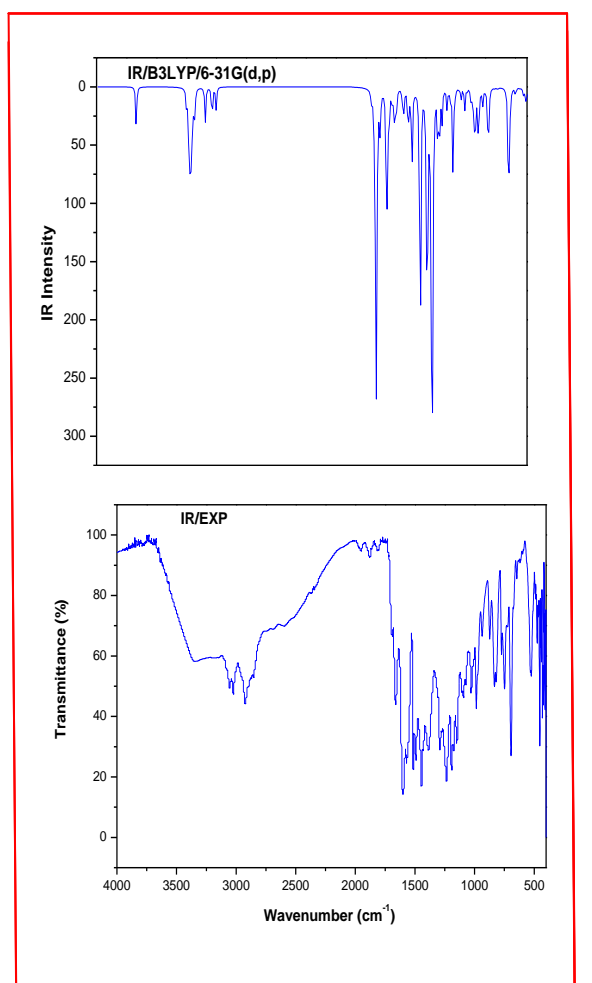


Fig 2: The Experimental and Theoretical FT-IR spectra of DHC

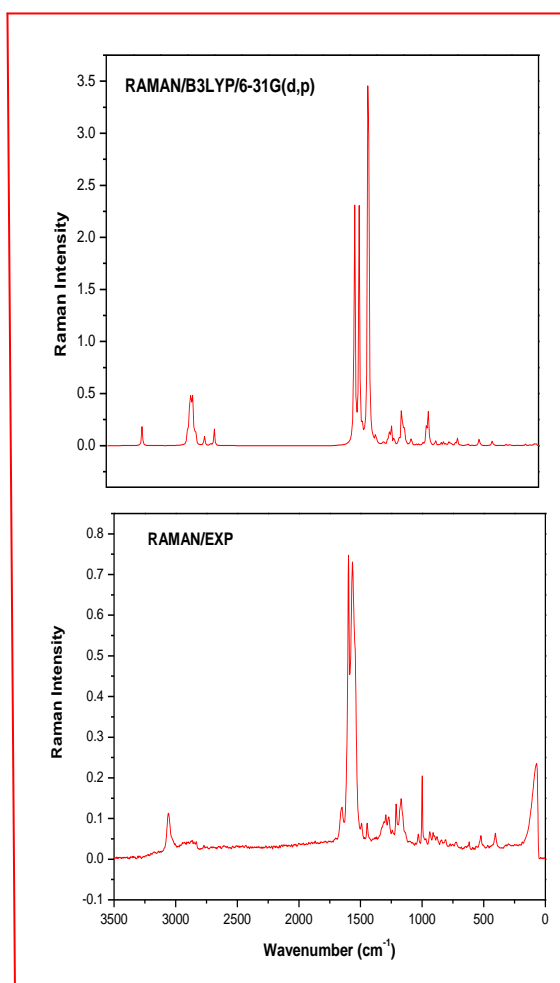


Fig 3: The Experimental and Theoretical FT-RAMAN spectra of DHC

Table 2: Comparison of the experimental and calculated vibrational wavenumber and proposed assignments of DHC

| Mode No | Calculated Frequencies (cm ⁻¹) | | Observed Frequencies (cm ⁻¹) | | IR Intensity | Raman Intensity | Reduced Masses | Force Consts | Vibrational Assignments ≥ 10% (TED) |
|---------|--|--------|--|----------|--------------|-----------------|----------------|--------------|---|
| | Un Scaled | Scaled | FT-IR | FT-Raman | Rel. | Rel. | | | |
| 1 | 3668 | 3525 | | | 12.80 | 0.41 | 1.066 | 8.452 | vO ₄₉ H ₅₀ (100) |
| 2 | 3248 | 3121 | | | 3.36 | 0.21 | 1.093 | 6.793 | vC ₃₈ H ₃₇ (92) |
| 3 | 3247 | 3120 | | | 2.79 | 0.18 | 1.093 | 6.790 | vC ₂₅ H ₂₄ (91) |
| 4 | 3235 | 3108 | | | 2.24 | 0.44 | 1.094 | 6.746 | vC ₁₆ H ₂₀ (93) |
| 5 | 3224 | 3098 | | | 3.19 | 1.96 | 1.098 | 6.725 | vC ₂₈ H ₃₂ (15)+vC ₃₁ H ₃₄ (13)+vC ₄₁ H ₄₅ (26)+vC ₄₄ H ₄₇ (23) |
| 6 | 3224 | 3098 | | | 32.22 | 0.06 | 1.098 | 6.724 | vC ₂₈ H ₃₂ (26)+vC ₃₁ H ₃₄ (23)+vC ₄₁ H ₄₅ (15)+vC ₄₄ H ₄₇ (13) |
| 7 | 3210 | 3085 | | | 13.61 | 0.32 | 1.093 | 6.638 | vC ₃₉ H ₄₂ (27)+vC ₄₁ H ₄₅ (16)+vC ₄₃ H ₄₆ (26)+vC ₄₄ H ₄₇ (22) |
| 8 | 3210 | 3085 | | | 6.41 | 0.49 | 1.093 | 6.638 | vC ₂₆ H ₂₉ (27)+vC ₂₈ H ₃₂ (16)+vC ₃₀ H ₃₃ (26)+vC ₃₁ H ₃₄ (22) |
| 9 | 3202 | 3076 | | | 4.87 | 0.37 | 1.095 | 6.612 | vC ₁₂ H ₁₅ (70)+vC ₁₄ H ₁₉ (26) |
| 10 | 3199 | 3074 | | | 0.44 | 0.48 | 1.088 | 6.563 | vC ₃₉ H ₄₂ (41)+vC ₄₁ H ₄₅ (15)+vC ₄₃ H ₄₆ (34) |
| 11 | 3199 | 3074 | | | 0.46 | 0.38 | 1.088 | 6.563 | vC ₂₆ H ₂₉ (41)+vC ₂₈ H ₃₂ (15)+vC ₃₀ H ₃₃ (34) |
| 12 | 3196 | 3071 | | | 7.65 | 0.12 | 1.089 | 6.553 | vC ₁₃ H ₁₇ (91) |
| 13 | 3192 | 3067 | | | 0.57 | 0.05 | 1.086 | 6.516 | vC ₃₉ H ₄₂ (12)+vC ₄₁ H ₄₅ (21)+vC ₄₃ H ₄₆ (23)+vC ₄₄ H ₄₇ (29) |
| 14 | 3192 | 3067 | | | 1.57 | 0.10 | 1.086 | 6.516 | vC ₂₆ H ₂₉ (13)+vC ₂₈ H ₃₂ (21)+vC ₃₀ H ₃₃ (23)+vC ₃₁ H ₃₄ (29) |
| 15 | 3180 | 3055 | | | 7.89 | 0.24 | 1.088 | 6.480 | vC ₁₂ H ₁₅ (27)+vC ₁₄ H ₁₉ (72) |
| 16 | 3171 | 3046 | | | 0.09 | 0.30 | 1.086 | 6.435 | vC ₂₂ H ₂₃ (52)+vC ₃₅ H ₃₆ (47) |
| 17 | 3170 | 3046 | 3059 | 3059 | 0.63 | 0.00 | 1.086 | 6.431 | vC ₂₂ H ₂₃ (47)+vC ₃₅ H ₃₆ (52) |
| 18 | 3092 | 2971 | | | 4.69 | 0.32 | 1.091 | 6.149 | vC ₂ H ₉ (55)+vC ₆ H ₁₀ (36) |
| 19 | 3090 | 2969 | | | 7.14 | 0.04 | 1.089 | 6.127 | vC ₂ H ₉ (37)+vC ₆ H ₁₀ (57) |
| 20 | 3034 | 2916 | 2923 | | 11.81 | 0.08 | 1.081 | 5.864 | vC ₁ H ₄₈ (86) |
| 21 | 3001 | 2883 | | 2865 | 6.01 | 0.56 | 1.070 | 5.673 | vC ₁ H ₄₈ (12)+vC ₂ H ₇ (26)+vC ₆ H ₈ (58) |

| | | | | | | | | | |
|----|------|------|------|------|--------|--------|-------|--------|---|
| 22 | 3000 | 2882 | 2849 | | 1.13 | 0.07 | 1.069 | 5.668 | $\nu\text{C}_2\text{H}_7$ (63)+ $\nu\text{C}_6\text{H}_8$ (31) |
| 23 | 1703 | 1636 | 1660 | 1650 | 3.74 | 41.67 | 8.395 | 14.338 | $\nu\text{O}_2\text{C}_4$ (86) |
| 24 | 1676 | 1610 | | | 10.27 | 1.14 | 5.939 | 9.829 | $\nu\text{C}_{13}\text{C}_{16}$ (35)+ $\nu\text{C}_{11}\text{C}_{12}$ (18) |
| 25 | 1664 | 1598 | 1598 | 1597 | 100.00 | 0.07 | 6.358 | 10.367 | $\nu\text{C}_5\text{C}_{22}$ (23)+ $\nu\text{C}_3\text{C}_{35}$ (22) |
| 26 | 1659 | 1594 | | | 0.21 | 35.68 | 5.388 | 8.736 | $\nu\text{C}_{30}\text{C}_{31}$ (11)+ $\nu\text{C}_{43}\text{C}_{44}$ (11)+ $\nu\text{C}_{25}\text{C}_{26}$ (10)+ $\nu\text{C}_{38}\text{C}_{39}$ (10) |
| 27 | 1657 | 1592 | | | 39.02 | 0.10 | 5.697 | 9.219 | $\nu\text{C}_{25}\text{C}_{26}$ (20) |
| 28 | 1647 | 1583 | | | 3.66 | 0.20 | 5.800 | 9.271 | $\beta\text{C}_{11}\text{C}_{12}\text{C}_{14}$ (13)+ $\nu\text{C}_{14}\text{C}_{18}$ (35) |
| 29 | 1629 | 1565 | 1570 | | 1.06 | 1.53 | 4.882 | 7.633 | $\nu\text{C}_{28}\text{C}_{31}$ (15)+ $\nu\text{C}_{27}\text{C}_{30}$ (12) |
| 30 | 1628 | 1564 | | | 12.75 | 0.07 | 4.958 | 7.740 | $\nu\text{C}_{28}\text{C}_{31}$ (14)+ $\nu\text{C}_{27}\text{C}_{30}$ (10) |
| 31 | 1576 | 1514 | 1514 | | 34.72 | 100.00 | 8.538 | 12.489 | $\nu\text{O}_2\text{C}_4$ (62) |
| 32 | 1570 | 1509 | | | 21.07 | 5.32 | 2.535 | 3.682 | $\beta\text{H}_{15}\text{C}_{12}\text{C}_{14}$ (17)+ $\beta\text{H}_{17}\text{C}_{13}\text{C}_{16}$ (16)+ $\beta\text{H}_{19}\text{C}_{14}\text{C}_{12}$ (18)+ $\beta\text{H}_{20}\text{C}_{16}\text{C}_{13}$ (10) |
| 33 | 1555 | 1494 | | | 14.44 | 0.02 | 2.051 | 2.920 | $\beta\text{H}_{42}\text{C}_{39}\text{C}_{38}$ (12)+ $\beta\text{H}_{46}\text{C}_{43}\text{C}_{40}$ (12)+ $\beta\text{H}_{47}\text{C}_{44}\text{C}_{43}$ (10) |
| 34 | 1554 | 1493 | 1491 | 1491 | 0.36 | 0.00 | 2.072 | 2.948 | $\beta\text{H}_{29}\text{C}_{26}\text{C}_{28}$ (12)+ $\beta\text{H}_{33}\text{C}_{30}\text{C}_{27}$ (11)+ $\beta\text{H}_{34}\text{C}_{31}\text{C}_{30}$ (10) |
| 35 | 1535 | 1475 | | | 0.63 | 0.36 | 1.090 | 1.514 | $\beta\text{H}_7\text{C}_2\text{H}_9$ (47)+ $\beta\text{H}_8\text{C}_6\text{H}_{10}$ (39) |
| 36 | 1525 | 1465 | | | 5.73 | 0.03 | 1.083 | 1.485 | $\beta\text{H}_7\text{C}_2\text{H}_9$ (42)+ $\beta\text{H}_8\text{C}_6\text{H}_{10}$ (49) |
| 37 | 1506 | 1447 | | | 6.94 | 1.56 | 2.061 | 2.755 | $\beta\text{H}_{32}\text{C}_{28}\text{C}_{31}$ (11)+ $\beta\text{H}_{45}\text{C}_{41}\text{C}_{44}$ (13) |
| 38 | 1505 | 1446 | | 1446 | 9.56 | 0.29 | 2.075 | 2.771 | $\beta\text{H}_{32}\text{C}_{28}\text{C}_{31}$ (13)+ $\beta\text{H}_{45}\text{C}_{41}\text{H}_{44}$ (11) |
| 39 | 1490 | 1432 | | | 5.66 | 0.07 | 2.380 | 3.115 | $\beta\text{C}_{11}\text{C}_{12}\text{C}_{14}$ (15)+ $\beta\text{H}_{20}\text{C}_{16}\text{C}_{13}$ (13)+ $\beta\text{H}_{48}\text{C}_1\text{C}_{11}$ (19) |
| 40 | 1443 | 1386 | 1389 | | 4.37 | 0.42 | 1.573 | 1.928 | $\beta\text{H}_{23}\text{C}_{22}\text{C}_5$ (27)+ $\beta\text{H}_{36}\text{C}_{35}\text{C}_3$ (29) |
| 41 | 1432 | 1376 | | | 7.48 | 0.39 | 1.482 | 1.790 | $\beta\text{H}_{23}\text{C}_{22}\text{C}_5$ (30)+ $\beta\text{H}_{36}\text{C}_{35}\text{C}_3$ (28) |
| 42 | 1424 | 1368 | | | 1.17 | 0.19 | 1.510 | 1.803 | $\beta\text{H}_{48}\text{C}_1\text{C}_{11}$ (30) |
| 43 | 1397 | 1342 | | | 2.05 | 0.28 | 1.529 | 1.758 | $\beta\text{H}_{37}\text{C}_{38}\text{C}_{40}$ (30)+ $\beta\text{H}_{46}\text{C}_{43}\text{C}_{40}$ (22) |
| 44 | 1397 | 1342 | | | 4.65 | 0.65 | 1.566 | 1.800 | $\beta\text{H}_{24}\text{C}_{25}\text{C}_{27}$ (25)+ $\beta\text{H}_{33}\text{C}_{30}\text{C}_{27}$ (22) |
| 45 | 1393 | 1338 | | | 8.45 | 0.04 | 2.260 | 2.583 | $\nu\text{C}_{11}\text{C}_{12}$ (16)+ $\nu\text{C}_{16}\text{C}_{18}$ |

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|----|------|------|------|------|-------|-------|-------|-------|---|
| | | | | | | | | | (23)+ β H ₅₀ O ₄₉ C ₁₈ (13)+ β H ₁₅ C ₁₂ C ₁₄ (12)+ β H ₁₇ C ₁₃ C ₁₆ (20) |
| 46 | 1386 | 1331 | | | 0.91 | 1.01 | 1.253 | 1.417 | Γ C ₁ C ₆ C ₁₁ H ₄₈ (68) |
| 47 | 1378 | 1324 | | | 1.47 | 1.94 | 1.545 | 1.729 | β H ₉ C ₂ C ₃ (14) |
| 48 | 1363 | 1309 | | | 21.05 | 0.15 | 1.567 | 1.715 | ν C ₃ C ₄ (10)+ β H ₉ C ₂ C ₃ (22)+ τ H ₈ C ₆ C ₅ C ₄ (10)+ τ H ₁₀ C ₆ C ₅ C ₂₂ (10) |
| 49 | 1363 | 1309 | | | 1.09 | 4.55 | 6.186 | 6.769 | ν C ₂₆ C ₂₈ (12)+ ν C ₂₇ C ₃₀ (13)+ ν C ₃₈ C ₄₀ (11) |
| 50 | 1360 | 1307 | | | 5.55 | 0.17 | 5.668 | 6.179 | ν C ₂₆ C ₂₈ (35)+ ν C ₂₇ C ₃₀ (41)+ ν C ₃₈ C ₄₀ (10) |
| 51 | 1336 | 1284 | 1290 | 1294 | 0.79 | 1.94 | 1.339 | 1.408 | β H ₉ C ₂ C ₃ (12)+ β H ₁₀ C ₆ C ₅ (17)+ Γ C ₂ C ₁ C ₃ H ₉ (10) |
| 52 | 1300 | 1249 | | 1270 | 17.32 | 0.11 | 2.605 | 2.594 | ν C ₁₃ C ₁₆ (13)+ ν O ₄₉ C ₁₈ (33) |
| 53 | 1293 | 1242 | | | 2.12 | 1.07 | 1.651 | 1.625 | β H ₄₈ C ₁ C ₁₁ (13)+ τ H ₈ C ₆ C ₅ C ₄ (15) |
| 54 | 1291 | 1241 | 1235 | | 67.51 | 0.34 | 3.090 | 3.037 | ν C ₃ C ₄ (18) |
| 55 | 1266 | 1217 | | 1211 | 0.00 | 12.38 | 2.685 | 2.536 | ν C ₄₀ C ₄₃ (10)+ ν C ₂₂ C ₂₇ (15)+ ν C ₃₅ C ₄₀ (15) |
| 56 | 1246 | 1197 | | | 4.91 | 0.21 | 1.255 | 1.148 | β H ₃₇ C ₃₈ C ₄₀ (10)+ β H ₄₂ C ₃₉ C ₃₈ (13) |
| 57 | 1245 | 1196 | | | 0.30 | 4.79 | 1.332 | 1.217 | β H ₄₂ C ₃₉ C ₃₈ (25) |
| 58 | 1243 | 1195 | 1192 | | 0.29 | 1.47 | 1.872 | 1.705 | ν C ₁ C ₁₁ (22) |
| 59 | 1235 | 1187 | | | 94.33 | 0.45 | 1.889 | 1.699 | ν C ₃ C ₄ (12) |
| 60 | 1230 | 1181 | | | 2.23 | 0.15 | 1.128 | 1.005 | β H ₁₅ C ₁₂ C ₁₄ (19)+ β H ₁₇ C ₁₃ C ₁₆ (12)+ β H ₁₉ C ₁₄ C ₁₂ (26)+ β H ₂₀ C ₁₆ C ₁₃ (18) |
| 61 | 1224 | 1176 | | | 0.01 | 0.13 | 1.083 | 0.956 | β H ₃₂ C ₂₈ C ₃₁ (18)+ β H ₃₄ C ₃₁ C ₃₀ (12)+ β H ₄₅ C ₄₁ C ₄₄ (18)+ β H ₄₇ C ₄₄ C ₄₃ (13) |
| 62 | 1224 | 1176 | | 1170 | 5.57 | 0.37 | 1.114 | 0.982 | β H ₃₂ C ₂₈ C ₃₁ (19)+ β H ₃₄ C ₃₁ C ₃₀ (12)+ β H ₄₅ C ₄₁ C ₄₄ (18)+ β H ₄₇ C ₄₄ C ₄₃ (11) |
| 63 | 1201 | 1154 | | | 74.18 | 0.13 | 1.246 | 1.060 | β H ₉ C ₂ C ₃ (11)+ β H ₁₀ C ₆ C ₅ (22)+ Γ C ₁ C ₆ C ₁₁ H ₄₈ (11)+ τ H ₇ C ₂ C ₁ C ₆ (12) |
| 64 | 1189 | 1142 | 1147 | | 92.08 | 0.39 | 1.432 | 1.193 | ν C ₁₆ C ₁₈ (18)+ β H ₅₀ O ₄₉ C ₁₈ (44)+ β H ₂₀ C ₁₆ C ₁₃ (13) |
| 65 | 1177 | 1130 | | | 0.13 | 2.29 | 2.928 | 2.388 | ν C ₂ C ₃ (11)+ ν C ₅ C ₆ (10) |
| 66 | 1146 | 1101 | | | 20.59 | 0.02 | 1.466 | 1.134 | β H ₅₀ O ₄₉ C ₁₈ (14)+ β H ₁₅ C ₁₂ C ₁₄ |

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|----|------|------|------|------|-------|-------|-------|-------|--|
| | | | | | | | | | (10)+ β H ₁₇ C ₁₃ C ₁₆ (14)+ β H ₁₉ C ₁₄ C ₁₂ (11)+ β H ₂₀ C ₁₆ C ₁₃ (12) |
| 67 | 1132 | 1088 | 1092 | | 11.11 | 0.24 | 1.875 | 1.415 | β H ₁₉ C ₁₄ C ₁₂ (25) |
| 68 | 1129 | 1085 | | | 1.89 | 0.06 | 1.764 | 1.325 | ν C ₃₀ C ₃₁ (10) |
| 69 | 1112 | 1068 | | | 11.46 | 0.37 | 3.540 | 2.578 | ν C ₁ C ₆ (34)+ ν C ₁ C ₂ (24) |
| 70 | 1071 | 1029 | 1028 | 1030 | 0.34 | 0.63 | 2.205 | 1.491 | ν C ₁ C ₂ (15) |
| 71 | 1069 | 1027 | | | 5.95 | 0.00 | 2.182 | 1.469 | ν C ₃₉ C ₄₁ (14)+ ν C ₄₁ C ₄₄ (15) |
| 72 | 1065 | 1024 | | | 0.52 | 0.11 | 2.479 | 1.658 | β C ₁₂ C ₁₄ C ₁₈ (20) |
| 73 | 1049 | 1008 | | | 0.29 | 0.01 | 2.774 | 1.800 | β C ₁₃ C ₁₆ C ₁₈ (30)+ β C ₁₂ C ₁₄ C ₁₈ (34)+ β C ₁₄ C ₁₈ C ₁₆ (17) |
| 74 | 1042 | 1001 | | | 2.26 | 0.03 | 5.326 | 3.405 | β C ₄₁ C ₄₄ C ₄₃ (11)+ β C ₃₈ C ₃₉ C ₄₁ (11)+ β C ₃₉ C ₄₁ C ₄₄ (11) |
| 75 | 1037 | 996 | | 999 | 0.98 | 6.68 | 1.859 | 1.177 | τ H ₂₉ C ₂₆ C ₂₈ H ₃₂ (12)+ τ H ₃₃ C ₃₀ C ₃₁ H ₃₄ (10)+ τ H ₄₂ C ₃₉ C ₄₁ H ₄₅ (14) + τ H ₄₆ C ₄₃ C ₄₄ H ₄₇ (11) |
| 76 | 1035 | 995 | | | 0.22 | 0.27 | 1.344 | 0.849 | τ H ₂₉ C ₂₆ C ₂₈ H ₃₂ (21)+ τ H ₃₃ C ₃₀ C ₃₁ H ₃₄ (18)+ τ H ₄₂ C ₃₉ C ₄₁ H ₄₅ (20) + τ H ₄₆ C ₄₃ C ₄₄ H ₄₇ (17) |
| 77 | 1034 | 994 | | | 0.65 | 2.23 | 2.679 | 1.689 | τ H ₃₃ C ₃₀ C ₃₁ H ₃₄ (28) |
| 78 | 1019 | 979 | 985 | | 7.36 | 10.42 | 1.527 | 0.934 | Γ C ₂₂ C ₅ C ₂₇ H ₂₃ (31)+ Γ C ₃₅ C ₃ C ₄₀ H ₃₆ (35) |
| 79 | 1019 | 979 | | | 20.46 | 0.12 | 3.638 | 2.224 | τ H ₃₇ C ₃₈ C ₃₉ H ₄₂ (22) |
| 80 | 1007 | 967 | | | 0.01 | 0.39 | 1.475 | 0.881 | Γ C ₂₂ C ₅ C ₂₇ H ₂₃ (14)+ τ H ₃₃ C ₃₀ C ₃₁ H ₃₄ (10)+ Γ C ₃₅ C ₃ C ₄₀ H ₃₆ (13) + τ H ₃₇ C ₃₈ C ₃₉ H ₄₂ (11) |
| 81 | 1004 | 964 | | | 0.53 | 0.11 | 1.392 | 0.826 | τ H ₂₉ C ₂₆ C ₂₈ C ₃₁ (10)+ τ H ₃₃ C ₃₀ C ₃₁ H ₃₄ (22)+ τ H ₃₇ C ₃₈ C ₃₉ H ₄₂ (21) + τ H ₄₆ C ₄₃ C ₄₄ H ₄₇ (22) |
| 82 | 1001 | 962 | | | 1.13 | 0.42 | 1.471 | 0.868 | Γ C ₂₂ C ₅ C ₂₇ H ₂₃ (18)+ τ H ₃₃ C ₃₀ C ₃₁ H ₃₄ (12)+ Γ C ₃₅ C ₃ C ₄₀ H ₃₆ (17) + τ H ₃₇ C ₃₈ C ₃₉ H ₄₂ (11) |
| 83 | 990 | 952 | | | 0.09 | 0.01 | 1.358 | 0.785 | τ H ₁₇ C ₁₃ C ₁₆ H ₂₀ (84) |
| 84 | 968 | 930 | 936 | 938 | 0.41 | 0.01 | 1.381 | 0.763 | τ H ₁₅ C ₁₂ C ₁₄ H ₁₉ (80)+ τ H ₁₉ C ₁₄ C ₁₈ O ₄₉ (12) |
| 85 | 961 | 923 | | | 0.03 | 0.18 | 2.141 | 1.164 | ν C ₁ C ₆ (15)+ ν C ₁ C ₂ (17) |
| 86 | 953 | 915 | | | 1.38 | 2.02 | 1.690 | 0.903 | τ H ₃₇ C ₃₈ C ₃₉ H ₄₂ (12) |
| 87 | 951 | 914 | | 911 | 2.56 | 0.00 | 1.350 | 0.720 | τ H ₂₄ C ₂₅ C ₂₆ C ₂₈ |

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|-----|-----|-----|-----|-----|-------|------|-------|-------|--|
| | | | | | | | | | (12)+ τ H ₂₉ C ₂₆ C ₂₈ H ₃₂ (15)+ τ H ₃₇ C ₃₈ C ₃₉ H ₄₂ (14) + τ H ₄₂ C ₃₉ C ₄₁ H ₄₅ (16) |
| 88 | 922 | 886 | | | 7.80 | 0.19 | 1.492 | 0.747 | Γ C ₂ C ₁ C ₃ H ₉ (35)+ τ H ₁₀ C ₆ C ₅ C ₂₂ (16) |
| 89 | 901 | 866 | 873 | | 0.97 | 1.17 | 4.397 | 2.105 | β C ₁₄ C ₁₈ C ₁₆ (15) |
| 90 | 878 | 844 | | | 0.11 | 1.53 | 1.257 | 0.571 | τ H ₂₄ C ₂₅ C ₂₆ C ₂₈ (14)+ τ H ₂₉ C ₂₆ C ₂₈ C ₃₁ (11)+ Γ C ₃₀ C ₂₇ C ₃₁ H ₃₃ (21) + Γ C ₄₃ C ₄₀ C ₄₄ H ₄₆ (23) |
| 91 | 878 | 843 | | | 0.02 | 0.02 | 1.254 | 0.569 | τ H ₂₄ C ₂₅ C ₂₆ C ₂₈ (14)+ τ H ₂₉ C ₂₆ C ₂₈ C ₃₁ (11)+ Γ C ₃₀ C ₂₇ C ₃₁ H ₃₃ (21) + Γ C ₃₈ C ₃₉ C ₄₀ H ₃₇ (25) |
| 92 | 870 | 836 | 833 | | 3.51 | 0.02 | 1.786 | 0.797 | τ H ₂₀ C ₁₆ C ₁₈ O ₄₉ (60) |
| 93 | 857 | 823 | | | 3.15 | 0.79 | 5.363 | 2.319 | β C ₂₆ C ₂₈ C ₃₁ (11) |
| 94 | 847 | 813 | | | 5.52 | 0.10 | 2.028 | 0.857 | τ H ₁₉ C ₁₄ C ₁₈ O ₄₉ (16)+ τ H ₂₀ C ₁₆ C ₁₈ O ₄₉ (24) |
| 95 | 835 | 803 | | 809 | 19.54 | 0.15 | 1.750 | 0.720 | τ H ₁₉ C ₁₄ C ₁₈ O ₄₉ (60) |
| 96 | 826 | 794 | | | 4.80 | 2.37 | 5.202 | 2.092 | β C ₁₁ C ₁₂ C ₁₄ (12)+ ν C ₁₆ C ₁₈ (10)+ ν O ₄₉ C ₁₈ (18) |
| 97 | 806 | 774 | 774 | | 21.15 | 1.23 | 2.518 | 0.964 | τ H ₂₉ C ₂₆ C ₂₈ C ₃₁ (10) |
| 98 | 788 | 757 | | | 0.62 | 0.08 | 1.860 | 0.681 | τ H ₂₉ C ₂₆ C ₂₈ C ₃₁ (16)+ Γ C ₃₈ C ₃₉ C ₄₀ H ₃₇ (12) |
| 99 | 771 | 741 | 748 | | 5.56 | 1.28 | 4.195 | 1.470 | ν C ₂ C ₃ (11)+ ν C ₅ C ₆ (10) |
| 100 | 755 | 725 | | | 0.42 | 0.00 | 3.923 | 1.317 | τ C ₁₁ C ₁₃ C ₁₈ C ₁₆ (31)+ τ C ₁₄ C ₁₂ C ₁₈ C ₁₆ (23)+ τ C ₁₃ C ₁₆ C ₁₄ C ₁₈ (13) |
| 101 | 752 | 722 | | | 0.37 | 3.99 | 2.801 | 0.932 | Γ O ₂₁ C ₃ C ₅ C ₄ (40) |
| 102 | 725 | 697 | | | 0.39 | 0.27 | 1.738 | 0.539 | τ C ₂₇ C ₃₀ C ₂₈ C ₃₁ (13)+ τ C ₄₀ C ₄₃ C ₄₁ C ₄₄ (24)+ τ C ₃₉ C ₃₈ C ₄₁ C ₄₄ (16) + τ C ₄₁ C ₃₉ C ₄₄ C ₄₃ (13) |
| 103 | 725 | 696 | 694 | | 26.42 | 0.03 | 1.820 | 0.563 | τ C ₂₇ C ₃₀ C ₂₈ C ₃₁ (20)+ τ C ₂₆ C ₂₅ C ₂₈ C ₃₁ (10)+ τ C ₃₉ C ₃₈ C ₄₁ C ₄₄ (16) + τ C ₄₁ C ₃₉ C ₄₄ C ₄₃ (13) |
| 104 | 712 | 684 | | | 1.03 | 0.01 | 4.867 | 1.453 | β C ₁₃ C ₁₆ C ₁₈ (20) |
| 105 | 673 | 647 | 644 | | 0.39 | 0.38 | 6.858 | 1.831 | β C ₁₁ C ₁₃ C ₁₆ (22)+ β C ₁₃ C ₁₆ C ₁₈ (11)+ β C ₁₂ C ₁₄ C ₁₈ (23) |
| 106 | 654 | 629 | | | 0.05 | 0.42 | 6.383 | 1.610 | β C ₂₈ C ₃₁ C ₃₀ (18)+ β C ₄₁ C ₄₄ C ₄₃ (10)+ β C ₃₈ C ₃₉ C ₄₁ (15) |
| 107 | 651 | 626 | | | 0.31 | 0.75 | 6.358 | 1.589 | β C ₂₈ C ₃₁ C ₃₀ (23)+ β C ₄₁ C ₄₄ C ₄₃ (17)+ β C ₂₅ C ₂₆ C ₂₈ (10) |

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|-----|-----|-----|-----|-----|-------|------|-------|-------|---|
| | | | | | | | | | $+\beta C_{38}C_{39}C_{41}(20)$ |
| 108 | 637 | 612 | | 618 | 0.37 | 0.06 | 5.776 | 1.380 | $\beta C_3C_4C_5(22)$ |
| 109 | 615 | 591 | | | 0.01 | 0.24 | 6.547 | 1.460 | $\beta C_{25}C_{27}C_{30}(17)+\beta C_{39}C_{41}C_{44}(25)$ |
| 110 | 578 | 555 | | | 0.18 | 0.03 | 3.996 | 0.787 | $\nu C_2C_3(10)+\beta C_3C_4O_{21}(28)$ |
| 111 | 558 | 536 | | | 21.43 | 0.40 | 3.887 | 0.713 | $\Gamma C_{35}C_2C_4C_3(16)+\Gamma C_{22}C_4C_6C_5(13)$ |
| 112 | 552 | 530 | | | 6.74 | 4.17 | 2.977 | 0.534 | $\Gamma C_{35}C_{40}C_{43}C_{38}(11)+\Gamma C_{22}C_{27}C_{30}C_{25}(11)+\Gamma C_{11}C_2C_6C_1(10)$ |
| 113 | 548 | 527 | 524 | 523 | 14.10 | 0.10 | 3.141 | 0.557 | $\beta C_3C_4O_{21}(16)+\tau C_{13}C_{16}C_{14}C_{18}(13)+\tau C_{13}C_{16}C_{18}O_{49}(11)$ |
| 114 | 544 | 523 | | | 5.79 | 1.90 | 4.885 | 0.852 | $\beta C_3C_4C_5(12)$ |
| 115 | 531 | 510 | | | 0.06 | 0.16 | 3.189 | 0.529 | $\Gamma C_{35}C_{40}C_{43}C_{38}(15)+\Gamma C_{22}C_{27}C_{30}C_{25}(15)$ |
| 116 | 496 | 477 | | | 2.62 | 0.02 | 3.000 | 0.435 | $\beta C_2C_1C_6(19)$ |
| 117 | 457 | 439 | | | 0.28 | 0.39 | 3.593 | 0.442 | $\Gamma C_{22}C_{27}C_{30}C_{25}(18)+\Gamma C_{35}C_2C_4C_3(17)$ |
| 118 | 435 | 418 | | | 0.43 | 0.02 | 3.034 | 0.338 | $\tau C_{11}C_{13}C_{18}C_{16}(22)+\tau C_{14}C_{12}C_{18}C_{16}(39)+\tau C_{13}C_{16}C_{14}C_{18}(23)$ |
| 119 | 432 | 415 | | | 0.25 | 1.36 | 2.914 | 0.320 | $\tau C_{28}C_{26}C_{31}C_{30}(11)+\tau C_{41}C_{39}C_{44}C_{43}(10)+\Gamma C_{35}C_2C_4C_3(10)$ |
| 120 | 429 | 412 | | | 1.70 | 0.03 | 3.014 | 0.327 | $\tau C_{11}C_{13}C_{18}C_{16}(10)+\tau C_{26}C_{25}C_{28}C_{31}(13)+\tau C_{28}C_{26}C_{31}C_{30}(15)+\tau C_{41}C_{39}C_{44}C_{43}(10)$ |
| 121 | 427 | 410 | | 405 | 0.01 | 4.28 | 2.950 | 0.317 | $\tau C_{27}C_{30}C_{28}C_{31}(14)+\tau C_{40}C_{43}C_{41}C_{44}(12)+\tau C_{26}C_{25}C_{28}C_{31}(16)+\tau C_{39}C_{38}C_{41}C_{44}(15)$ |
| 122 | 414 | 398 | | | 2.04 | 0.38 | 4.717 | 0.476 | $\tau C_{11}C_{13}C_{18}C_{16}(21)+\tau C_{13}C_{16}C_{18}O_{49}(22)$ |
| 123 | 406 | 390 | | | 4.39 | 0.24 | 3.780 | 0.367 | $\beta C_{16}C_{18}O_{49}(64)$ |
| 124 | 362 | 347 | | | 54.22 | 0.52 | 1.105 | 0.085 | $\tau H_{50}O_{49}C_{18}C_{14}(96)$ |
| 125 | 329 | 316 | | | 1.02 | 0.19 | 4.703 | 0.300 | $\beta C_{22}C_{27}C_{30}(11)+\beta C_{35}C_{40}C_{43}(11)$ |
| 126 | 299 | 287 | | | 0.33 | 1.93 | 3.580 | 0.189 | $\beta C_{22}C_{27}C_{30}(13)+\beta C_{35}C_{40}C_{43}(13)+\beta C_2C_1C_6(12)$ |
| 127 | 298 | 286 | | | 0.48 | 0.05 | 7.802 | 0.407 | $\beta C_3C_4O_{21}(12)+\beta C_4C_3C_{35}(13)+\beta C_4C_5C_6(17)$ |
| 128 | 269 | 258 | | | 0.15 | 0.60 | 4.620 | 0.197 | $\tau C_{13}C_{16}C_{18}O_{49}(11)$ |

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|-----|-----|-----|----|--|------|-------|-------|-------|---|
| 129 | 267 | 257 | | | 0.49 | 0.78 | 6.177 | 0.260 | $\beta C_{11}C_{13}C_{16}(10)+\nu C_1C_{11}(13)+\beta C_2C_1C_6(13)$ |
| 130 | 256 | 246 | | | 0.20 | 1.35 | 4.283 | 0.165 | $\beta C_1C_{11}C_{13}(16)$ |
| 131 | 206 | 197 | | | 0.11 | 0.30 | 6.379 | 0.159 | $\beta C_6C_1C_{11}(22)$ |
| 132 | 189 | 181 | | | 0.24 | 0.76 | 4.147 | 0.087 | $\beta C_6C_1C_{11}(12)+\tau C_{13}C_{16}C_{18}O_4(13)$ |
| 133 | 163 | 156 | | | 0.10 | 0.36 | 6.002 | 0.094 | $\tau C_3C_{35}C_{40}C_{43}(26)$ |
| 134 | 136 | 131 | | | 0.04 | 1.42 | 3.480 | 0.038 | $\tau C_5C_{22}C_{27}C_{30}(16)+\tau C_3C_{35}C_{40}C_{43}(16)+\Gamma C_5C_1C_6C_4(16)$ |
| 135 | 120 | 115 | | | 0.03 | 6.15 | 4.984 | 0.042 | $\tau C_3C_{35}C_{40}C_{43}(18)+\tau C_3C_{35}C_{40}C_{43}(17)+\tau C_3C_2C_4C_5(10)$ |
| 136 | 109 | 105 | | | 0.02 | 0.05 | 4.000 | 0.028 | $\beta C_5C_{22}C_{27}(14)+\beta C_3C_{35}C_{40}(14)$ |
| 137 | 81 | 78 | | | 0.01 | 3.85 | 4.922 | 0.019 | $\tau C_4C_5C_{22}C_{27}(17)+\tau C_4C_3C_{35}C_{40}(23)+\Gamma C_{35}C_{40}C_{43}C_{38}(17)+\Gamma C_{22}C_{27}C_{30}C_{25}(13)$ |
| 138 | 81 | 77 | 70 | | 0.69 | 1.44 | 6.364 | 0.024 | $\tau C_4C_5C_{22}C_{27}(18)+\tau C_4C_3C_{35}C_{40}(12)+\Gamma C_{22}C_{27}C_{30}C_{25}(13)$ |
| 139 | 57 | 54 | | | 0.19 | 5.38 | 4.924 | 0.009 | $\beta C_6C_5C_{22}(11)+\beta C_4C_3C_{35}(10)+\tau C_1C_6C_2C_3(10)+\Gamma C_{11}C_2C_6C_1(16)$ |
| 140 | 39 | 37 | | | 0.04 | 8.72 | 5.081 | 0.005 | $\beta C_6C_1C_{11}(21)+\tau C_6C_1C_{11}C_{13}(13)+\Gamma C_1C_{11}C_{13}C_{12}(21)$ |
| 141 | 35 | 34 | | | 0.02 | 23.64 | 4.310 | 0.003 | $\beta C_5C_{22}C_{27}(11)+\beta C_3C_{35}C_{40}(10)+\tau C_5C_{22}C_{27}C_{30}(17)+\tau C_3C_{35}C_{40}C_{43}(15)$ |
| 142 | 34 | 32 | | | 0.24 | 4.27 | 3.684 | 0.003 | $\tau C_6C_1C_{11}C_{13}(46)+\tau C_5C_{22}C_{27}C_{30}(14)+\tau C_3C_{35}C_{40}C_{43}(15)$ |
| 143 | 22 | 21 | | | 0.15 | 39.05 | 4.273 | 0.001 | $\beta C_6C_1C_{11}(11)+\tau C_6C_1C_{11}C_{13}(30)+\Gamma C_1C_{11}C_{13}C_{12}(21)$ |
| 144 | 18 | 17 | | | 0.43 | 2.41 | 6.708 | 0.001 | $\tau C_3C_2C_4C_5(53)$ |

Nonlinear optical effects: NLO is the important role of current research because it provides the key functions of frequency shifting, optical logic, optical modulation, optical switching and optical memory for the technologies in areas such as telecommunications, signal processing and optical interconnection [45, 46].

The first hyperpolarizabilities (β_0 , α_0 and $\Delta\alpha$) of FMCH is calculated using B3LYP/6-31G (d, p) basis set, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a 3x3x3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to Kleinman

symmetry [47]. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

$$E = E^0 - \mu_\alpha F_\alpha - 1/2\alpha_{\alpha\beta} F_\alpha F_\beta - 1/6\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma \quad (2)$$

Where E^0 is the energy of the unperturbed molecules, F_α is the field at the origin, and $\mu_\alpha, \alpha_{\alpha\beta}, \beta_{\alpha\beta\gamma}$ is the components of the dipole moment, polarizability and the first hyperpolarizabilities, respectively. The total static dipole moment μ , the mean polarizability α_0 , the anisotropy of polarizability $\Delta\alpha$ and the mean first hyperpolarizability β_0 , using the x, y, z components are defined as [48]

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (3)$$

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (4)$$

$$\Delta\alpha = 2^{-1/2} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{xz}^2) \right]^{1/2} \quad (5)$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (6)$$

In this study, the calculated total molecular dipole moment (μ) polarizability (α_0), and hyperpolarizability (β_0) of the specimen are 1.27586 Debye, 0.67737×10^{-30} esu, 10.7839×10^{-30} esu, respectively and the calculated components are listed in the table3. The above functions of the molecular system is calculated using B3LYP/6-31G (d, p) method, based on the finite field approach. Urea is one of the prototype molecules used in the study of the NLO properties of molecular systems and used as a threshold value for comparative purposes. The computed hyperpolarizability β_0 is 10.7839×10^{-30} esu and is twenty eight times greater than urea (β of urea is 0.3728×10^{-30} esu). Thus this molecule must acts as a prospective building block for nonlinear optical materials.

Table 3: The non-linear measurements of DHC

| Parameters | B3LYP/6-31G(d,p) |
|---|--------------------------------|
| Dipole moment (μ) | |
| μ_x | -0.92282 |
| μ_y | 0.58190 |
| μ_z | -0.66151 |
| μ | 1.27586 Debye |
| Polarizability (α_0) | |
| | $\times 10^{-30}$ esu |
| α_{xx} | 315.67430 |
| α_{xy} | -26.51635 |
| α_{yy} | 237.66648 |
| α_{xz} | -32.27150 |
| α_{yz} | 133.99943 |
| α_{zz} | 372.11508 |
| α_0 | 0.67737×10^{-30} esu |
| Hyperpolarizability (β_0) | |
| | $\times 10^{-30}$ esu |
| β_{xxx} | 428.13646 |
| β_{xxy} | -291.17456 |
| β_{xyy} | 206.79926 |
| β_{yyy} | 64.07525 |
| β_{xxz} | -336.37040 |
| β_{xvz} | 390.51476 |
| β_{vvz} | 92.92484 |
| β_{xzz} | 563.68058 |
| β_{vzz} | 306.01220 |
| β_{zzz} | 582.86403 |
| β_0 | 10.78395×10^{-30} esu |

Standard value for urea ($\mu=1.3732$ Debye, $\beta_0=0.3728 \times 10^{-30}$ esu): esu-electrostatic unit

Natural bond orbital (NBO) analysis: The NBO analysis carried out for FMCH in order to understand various second-order interactions between the filled orbital of one subsystem and vacant orbital of another subsystem, which is a measure of the inter-molecular delocalization or hyper-conjugation. NBO analysis provides the most accurate possible ‘natural Lewis structure’ picture of ‘j’ because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. A useful aspect of the NBO method is that it gives information about interactions of both filled and virtual orbital spaces that could enhance the analysis of intra- and inter- molecular interactions. The second-order Fock-matrix was carried out to evaluate the donor–acceptor interactions in the NBO basis. The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j) the stabilization energy ($E^{(2)}$) [49–52] associated with the delocalization $i \rightarrow j$ is determined as,

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\epsilon_j - \epsilon_i} \quad (7)$$

Where, q_i is the donor orbital occupancy, ϵ_i and ϵ_j are diagonal elements (orbital energies) and $F(i, j)$ is off diagonal NBO Fock matrix elements. In NBO analysis large $E^{(2)}$ value shows the intensive interaction between electron donors and electron-acceptors and greater the extent of conjugation of the whole system, the possible intensive interactions are given in table 4. The second-order perturbation theory analysis [53] of Fock matrix in NBO basis shows strong intra-molecular hyper-conjugative interactions of π electrons.

Table 4: The NBO analysis of DHC

| Type | Donor NBO (i) | ED/e | Acceptor NBO (j) | ED/e | $E^{(2)}$ KJ/mol | $E(j)-E(i)$ a.u. | $F(i,j)$ a.u. |
|-----------------|---------------|------|------------------|-------|---------------------|---------------------|------------------|
| $\pi - \pi^*$ | C 4 - O 21 | 1.97 | C 3 - C 35 | 0.12 | 16.86 | 0.4 | 0.04 |
| | | | C 5 - C 22 | 0.12 | 16.86 | 0.4 | 0.04 |
| $\pi - \pi^*$ | C 5 - C 22 | 1.82 | C 4 - O 21 | 0.24 | 89.62 | 0.28 | 0.07 |
| | | | C 6 - H 8 | 0.019 | 13.81 | 0.69 | 0.04 |
| $\pi - \pi^*$ | C 13 - C 16 | 1.71 | C 25 - C 27 | 0.38 | 43.22 | 0.29 | 0.05 |
| | | | C 11 - C 12 | 0.35 | 74.27 | 0.29 | 0.07 |
| $\pi - \pi^*$ | C 14 - C 18 | 1.66 | C 14 - C 18 | 0.39 | 91.17 | 0.28 | 0.07 |
| | | | C 11 - C 12 | 0.35 | 88.91 | 0.3 | 0.07 |
| $\pi - \pi^*$ | C 14 - C 18 | 1.66 | C 13 - C 16 | 0.33 | 72.93 | 0.29 | 0.06 |
| | | | C 5 - C 22 | 0.12 | 50.33 | 0.3 | 0.06 |
| $\pi - \pi^*$ | C 25 - C 27 | 1.62 | C 26 - C 28 | 0.33 | 84.89 | 0.27 | 0.07 |
| | | | C 30 - C 31 | 0.30 | 78.74 | 0.28 | 0.07 |
| $\pi - \pi^*$ | C 26 - C 28 | 1.65 | C 25 - C 27 | 0.38 | 86.02 | 0.28 | 0.07 |
| | | | C 30 - C 31 | 0.30 | 79.87 | 0.28 | 0.07 |
| $\pi - \pi^*$ | C 30 - C 31 | 1.67 | C 25 - C 27 | 0.38 | 78.37 | 0.28 | 0.07 |
| | | | C 26 - C 28 | 0.33 | 85.1 | 0.28 | 0.07 |
| $\pi - \pi^*$ | C 38 - C 40 | 1.62 | C 3 - C 35 | 0.12 | 50.5 | 0.3 | 0.06 |
| | | | C 39 - C 41 | 0.33 | 84.89 | 0.27 | 0.07 |
| $\pi - \pi^*$ | C 39 - C 41 | 1.65 | C 43 - C 44 | 0.31 | 78.74 | 0.28 | 0.07 |
| | | | C 38 - C 40 | 0.38 | 86.06 | 0.28 | 0.07 |
| $\pi - \pi^*$ | C 43 - C 44 | 1.67 | C 43 - C 44 | 0.31 | 79.83 | 0.28 | 0.07 |
| | | | C 38 - C 40 | 0.38 | 78.32 | 0.28 | 0.07 |
| $n - \sigma^*$ | LP (1) O 21 | 1.98 | C 39 - C 41 | 0.33 | 85.14 | 0.28 | 0.07 |
| | | | C 3 - C 4 | 0.06 | 7.7 | 1.13 | 0.04 |
| $n - \sigma^*$ | LP (2) O 21 | 1.89 | C 4 - C 5 | 0.06 | 7.7 | 1.13 | 0.04 |
| | | | C 3 - C 4 | 0.06 | 70.71 | 0.69 | 0.1 |
| $n - \sigma^*$ | LP (1) O 49 | 1.98 | C 4 - C 5 | 0.06 | 70.71 | 0.69 | 0.1 |
| | | | C 22 - H 23 | 0.02 | 5.44 | 0.72 | 0.03 |
| $n - \sigma^*$ | LP (2) O 49 | 1.88 | C 35 - H 36 | 0.02 | 5.44 | 0.72 | 0.03 |
| | | | C 14 - C 18 | 0.02 | 25.31 | 1.15 | 0.08 |
| $\pi^* - \pi^*$ | C 4 - O 21 | 0.24 | C 14 - C 18 | 0.39 | 109.6 | 0.34 | 0.09 |
| $\pi^* - \pi^*$ | C 4 - O 21 | 0.24 | C 3 - C 35 | 0.12 | 125 | 0.04 | 0.07 |

| | | | | | | | |
|---------------|-------------|------|-------------|------|-------|------|------|
| | | | C 5 - C 22 | 0.12 | 124.9 | 0.04 | 0.07 |
| $\pi^*-\pi^*$ | C 14 - C 18 | 0.39 | C 11 - C 12 | 0.35 | 1045 | 0.01 | 0.08 |
| $\pi^*-\pi^*$ | C 25 - C 27 | 0.38 | C 5 - C 22 | 0.12 | 259.8 | 0.02 | 0.07 |

NBO analysis were calculated for DHC at the DFT/B3LYP/6-31G (d,p) level in order to elucidate the intra molecular hybridization and delocalization of electron density within the molecule. The importance of hyperconjugative interaction and electron density transfer (EDT) from lone pair electrons to the anti-bonding orbital has been analyzed and the results were tabulated in Table. 4. Several donor – acceptor interaction have been observed for the chalcone and among the strongly occupied NBOs the most importance delocalization sites are in the π system and in the lone pairs(n) of the oxygen. The intra-molecular interaction are formed by the orbital overlap between bonding n(LPO49) and anti-bonding $\pi^*(C14-C18)$ orbital which results in intra-molecular charge transfer (ICT) causing stabilization of the system. These interactions are observed as increase in electron density in C14-C18 anti-bonding orbital. The most important interaction energy of n (LPO49) \rightarrow $\pi^*(C14-C18)$ is 109.62 KJ mol⁻¹ respectively. This large energy provides the stabilization to the molecular structure.

UV-Visible Studies: The calculated results involving the vertical excitation energies, oscillator strength (f) and wavelength are carried out and compared with the measured experimental wavelength and are given in the table 5. The observed and simulated (experimental and gas phase) UV–Vis. spectra are shown in fig. 4. Typically, according to the Frank-Condon principle, the maximum absorption peak (λ_{max}) corresponds in a UV-Visible spectrum to vertical excitation. The TD-DFT/B3LYP/6-31G (d, p) calculation predicts one intense electronic transition at 344 nm with an oscillator strength $f = 0.6946$ is in agreement with the measured experimental data ($\lambda_{exp} = 335$ nm) and are assigned to $\pi \rightarrow \pi^*$ transition as shown in fig. 4.

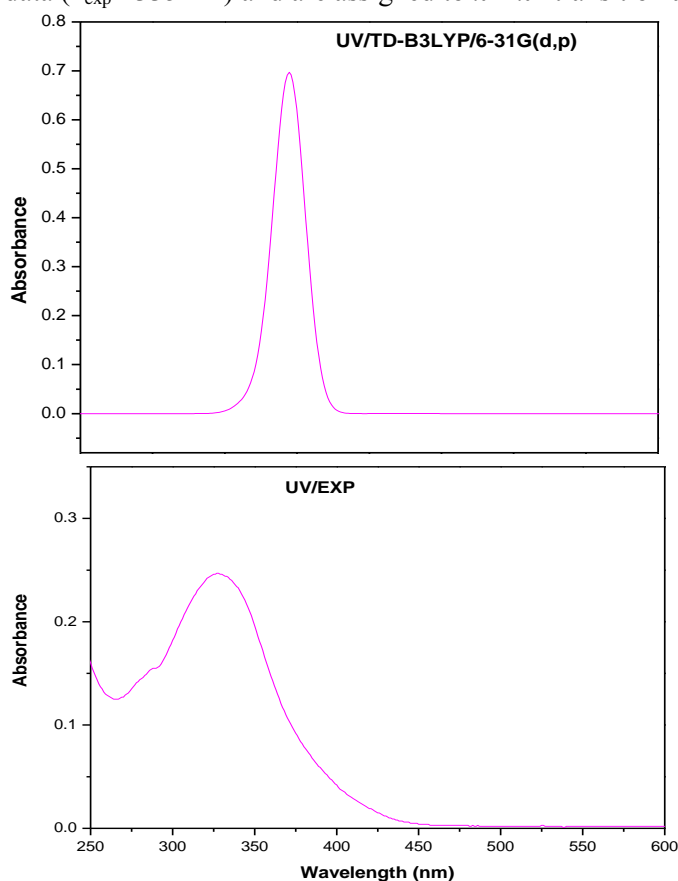
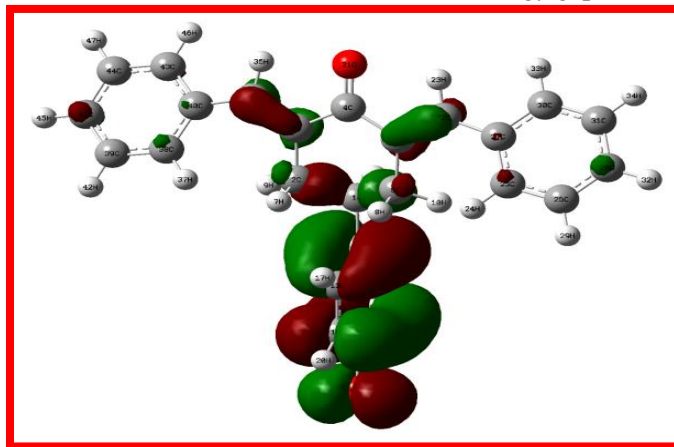


Fig 4: Experimental and Theoretical UV-Visible spectra of DHC

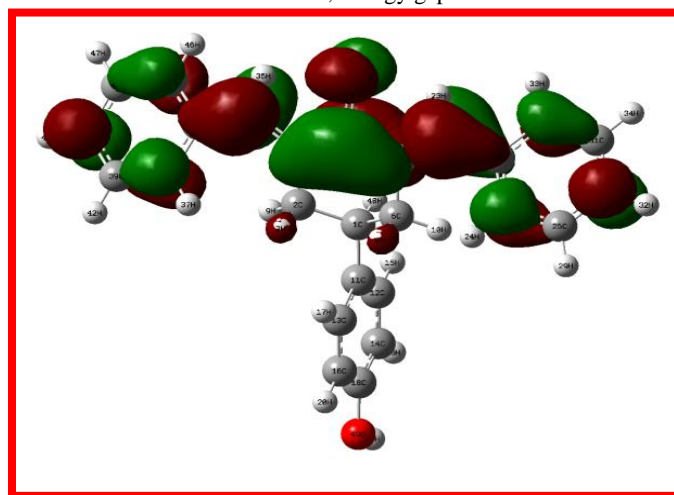
Table 5: Theoretical and Experimental UV-Vis spectral value of DHC

| States | Calculated | Calculated | Experimental | Oscillator | Assignment | Transitions |
|--------|-----------------|-----------------|-----------------|--------------|----------------|-------------------------|
| | Wavelength (nm) | Wavelength (eV) | Wavelength (nm) | Strength (f) | | |
| 1 | 423.9 | 2.92 | | 0.0003 | H-2->L+0(+85%) | $\pi \rightarrow \pi^*$ |
| 2 | 344.7 | 3.6 | 335 | 0.6946 | H-0->L+0(+87%) | $\pi \rightarrow \pi^*$ |
| 3 | 320.3 | 3.87 | | 0.0312 | H-3->L+0(+88%) | $\pi \rightarrow \pi^*$ |

HOMO - LUMO Energy: The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) plots of the title compound is shown in fig 5. The frontier molecular orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule [54]. The red color represents the negative charge and green color represents positive charge for the title molecule. The HOMO is orbital that acts as an electron donor and the LUMO is the orbital that acts as an electron acceptor. The HOMO is located over mainly on phenol and partially cyclohexanone rings except phenyl rings and the LUMO is located all over the molecule except the phenol ring. Their corresponding energy value is -5.9209 eV and -2.1221 eV respectively. The calculated HOMO and LUMO energies clearly show that charge transfer occurs within the molecule. The calculated HOMO-LUMO energy gap value is found to be 3.7988 eV.



Homo= -5.92089 eV, Energy gap= 3.75879 eV



Lumo= -2.16210 eV

Fig 5: The HOMO-LUMO Energy diagram of DHC

Molecular Electrostatic Potential: Molecular electrostatic potential (MEP) generally allows to show variably charged regions of a molecule in terms of color grading. It was used to predict the electrophilic and nucleophilic attack of the molecule. The order of electrostatic potential exist as red < orange < yellow < green < blue. Red represent most negative electrostatic potential, blue represent regions of most positive electrostatic potential and green represents regions of zero potential. The electrophiles tend to the negative and the nucleophiles tend to the region of positive. We concluded that carbonyl group behaves as electrophiles region and it is denoted as red color. Likewise, the nucleophiles region was graphically shown as blue color. Molecular surfaces explained by B3LYP/6-31G (d, p) are shown in fig. 6.

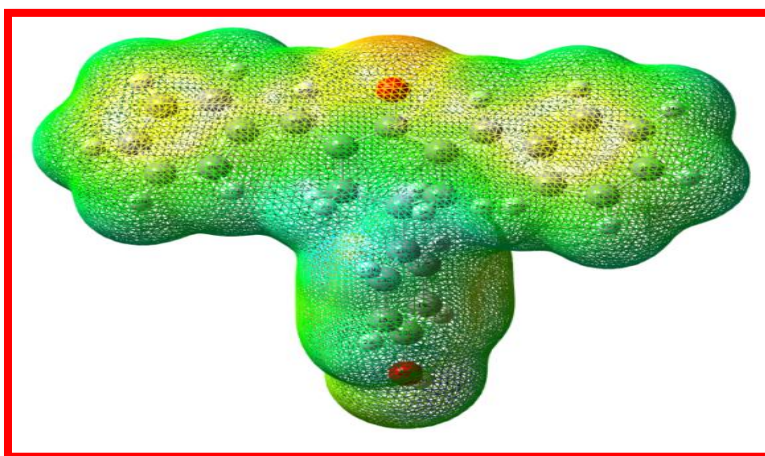


Fig 6: MEP diagram of DHC

Mulliken Atomic Charges: In the uses of quantum mechanical calculation to molecular system, the calculation of effective Mulliken atomic charge plays an important role of the system [55]. The charges are calculated by DFT/ B3LYP/6-31G (d, p) level of theory which is tabulated in table 7 and displayed in fig 7. The Mulliken charge is directly related to the vibrational properties of the molecule, and quantifies how the electronic structure changes under atomic displacement; it is therefore related directly to the chemical bonds present in the molecule. The maximum negative charge belongs to O49 atoms (-0.5738) high positive charge belongs to C4 atom (0.3695).

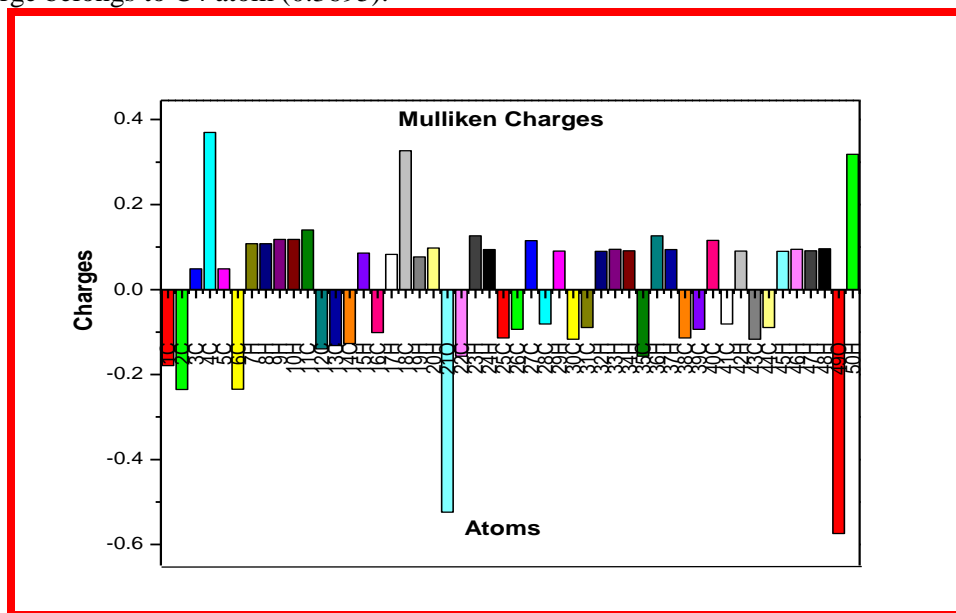


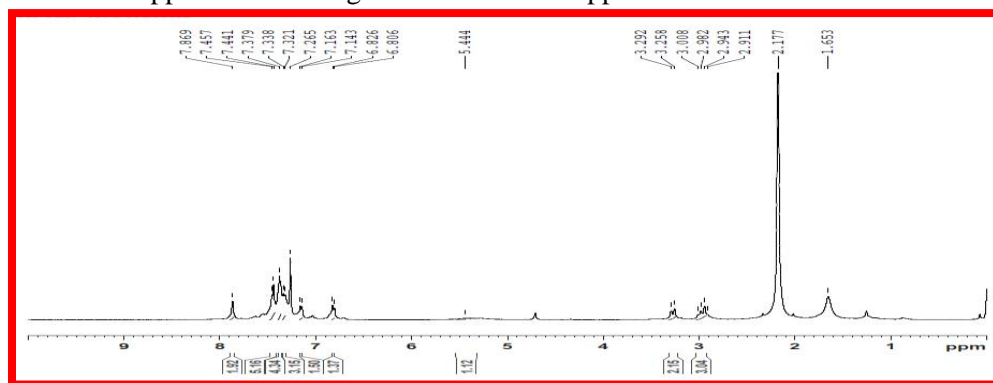
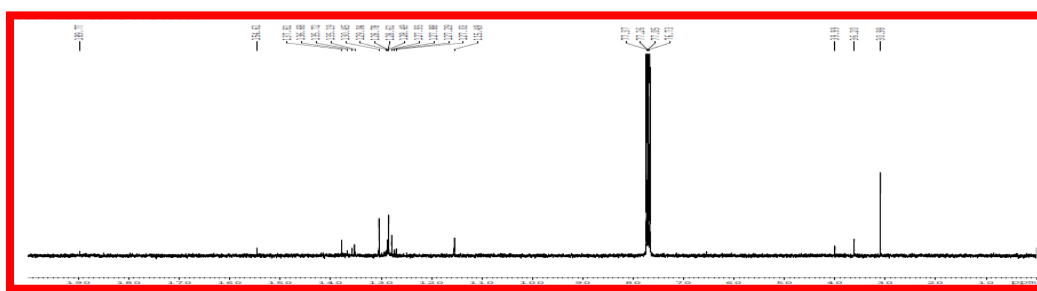
Fig 7: Mulliken Atomic Charges plot of DHC

Table 6. The Mulliken Atomic Charges of DHC

| Atoms | Charges | Atoms | Charges | Atoms | Charges |
|-------|-----------|-------|-----------|-------|-----------|
| 1C | -0.179222 | 18C | 0.326426 | 35C | -0.157135 |
| 2C | -0.234928 | 19H | 0.076854 | 36H | 0.126667 |
| 3C | 0.048936 | 20H | 0.097544 | 37H | 0.094425 |
| 4C | 0.369553 | 21O | -0.523749 | 38C | -0.113991 |
| 5C | 0.048857 | 22C | -0.157031 | 39C | -0.093543 |
| 6C | -0.234852 | 23H | 0.126741 | 40C | 0.115812 |
| 7H | 0.107913 | 24H | 0.094369 | 41C | -0.081243 |
| 8H | 0.10789 | 25C | -0.113831 | 42H | 0.090678 |
| 9H | 0.118203 | 26C | -0.093517 | 43C | -0.11666 |
| 10H | 0.118303 | 27C | 0.11538 | 44C | -0.089616 |
| 11C | 0.140403 | 28C | -0.081248 | 45H | 0.090116 |
| 12C | -0.139564 | 29H | 0.090664 | 46H | 0.094896 |
| 13C | -0.131954 | 30C | -0.116548 | 47H | 0.091102 |
| 14C | -0.126695 | 31C | -0.08961 | 48H | 0.095721 |
| 15H | 0.086073 | 32H | 0.090104 | 49O | -0.573897 |
| 16C | -0.101553 | 33H | 0.094867 | 50H | 0.318066 |
| 17H | 0.082731 | 34H | 0.091091 | | |

NMR Analysis: Fig. 8 shows the ^1H NMR of spectrum of the DHC. The doublets appeared at 3.27 ppm and 2.96 ppm is due to C-3 and C-5 methylene protons respectively. The methane proton H (4) merged with the methylene proton at 2.96 ppm. The olefinic protons appeared as a singlet at 7.87 ppm. The OH proton appears as a broad singlet at 5.44 ppm. The multiplets in the range of 6.81-7.46 ppm are due to aromatic protons.

Fig. 9 shows the ^{13}C NMR of spectrum of the DHC. Weak signal appeared at 189.7 ppm is assigned to the carbonyl carbon. The signal at 36.2 ppm corresponds to methylene carbons (C-3 and C-5). The methine carbon C-4 of cyclohexyl ring appears at 39.9 ppm. The olefinic carbon is appeared at 137.8 ppm. The aromatic carbons are appeared in the region of 115.4-136.6 ppm.

**Fig 8.** ^1H NMR of spectrum of the DHC**Fig 9.** ^{13}C NMR of spectrum of DHC

APPLICATIONS

The hyperpolarizability value of DHC (β_0) is twenty eight times (10.7839×10^{-30} esu) greater than urea. This indicates that the synthesized target molecule DHC is the better candidate for the NLO properties.

CONCLUSIONS

A complete vibrational analysis of DHC is performed using DFT method for the first time. The optimized geometries and harmonic vibrational wave numbers have been carried out using the B3LYP/6-31G (d, p) method. The theoretical results compared with the experimental observations. The differences between the observed and scaled frequencies of the most of the fundamentals are very small. The TED calculation regarding the normal modes of vibration provides a strong support for the frequency assignments. The magnitude of the molecular hyperpolarizability (β_0) shows that the molecule DHC has twenty eight times greater than that of the urea, hence this molecule has more NLO activity. The NBO analysis revealed that the most important interaction energy of $n(\text{LPO}49) \rightarrow \pi^*(\text{C}14\text{-C}18)$ is $109.62 \text{ KJ mol}^{-1}$. This transition gives the strongest stabilization to the molecular system. The HOMO-LUMO energy gap value has substantial influence on the intra-molecular charge transfer and bioactivity of the title molecule. Molecular electrostatic potential (MEP) was discussed from reactive sites of the title molecule. Mullikan atomic charge showed 049 atom is having maximum negative charge.

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