Molecular Investigation and Nonlinear Optical Response of Dihydropyrimidinone: A Comparative Spectroscopic and Quantum Computational Studies

Abstract

Organic molecule ethyl-4-(4-chloro-3-nitrophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate has been synthesized. The molecular structure has been characterized using FT-IR, FT-Raman, $^1$H and $^{13}$C- NMR spectral studies. The structure of the title molecule was theoretically investigated by DFT method using B3LYP/6-31G(d,p) basis set. The firm assignments of vibrational bands are allowed using experimental and computations. The nonlinear optical property of the title molecule has been calculated using first hyperpolarizability components. The intra-molecular charge transfer occurring in the molecule have been analyzed by NBO analysis. The electronic and charge transfer properties have been studied using frontier molecular orbitals. $^1$H and $^{13}$C-NMR spectra were recorded and calculated using the gauge independent atomic orbital (GIAO) method.

Keywords: CNPC; PES; NBO; NLO; HOMO-LUMO

Introduction

Organic materials are attractive due to their optical properties, electronics, and integrated photonics [1-3]. Organic molecules with electron deficient pyrimidine ring tend to act as electron acceptor and are very effectively used in Organic light emitting diodes (OLEDs) [4]. The higher light harvesting efficiency achieved by pyrimidine adopted porphyrin sensitizers show more advantage in oxidized dyes. New organic dyes with pyrimidine-2-carboxylic acid forms coordination bond with TiO$_2$, improves the interaction between the anchor and semiconductor [5]. Pyrimidine show considerable efforts in the development of bipolar materials to overcome the unipolar character of the organic materials [6]. Recent work from Lin et al., reported that pyrimidine used as $\pi$-conjugated spacer in organic photosensitizers in dye sensitized solar cells (DSSCs) [7]. The electron withdrawing character of pyrimidone chromophore exhibits the white photoluminescence in both liquid and solid state [8]. Moreover, pyrimidine based iridium complex exhibit external quantum efficiency up to 28.6% due to high photoluminescence quantum yield determines the excellent device performance and high efficiency [9].

In this paper, we report the synthesis, spectral and nonlinear optical investigation of ethyl-4-(4-chloro-3-nitrophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (CNPC). Here the molecular structure and electronic structural properties of the title molecule were studied using experimental and also with theoretical approach. For unambiguous vibrational spectral assignments precisely potential energy distribution have been performed and related with recorded FT-IR and FT-Raman spectra, respectively. This work also covers the molecular electrostatic potential mapped surface and energy gap analysis along with global reactivity descriptors. The charge transfer interactions occur in the CNPC molecule and stabilization arising from the donor-acceptors interactions are examined using Natural bond orbital analysis. The first hyperpolarizability ($\beta$) components examining the nonlinear response of the title molecule. The NMR chemical shifts calculated using Gauge-independent atomic orbitals and experimental chemical shifts were also analyzed in the present work.

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Experimental

Synthesis of ethyl 4-(4-chloro-3-nitrophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro pyrimidine-5-carboxylate

4-Chloro-3-nitrobenzaldehyde (1.84 ml, 0.01 mmol) and urea (1.8 g, 0.03 mmol) was added to an ethanolic solution of ethyl acetocetate (1.34 ml, 0.01 mmol). To the mixture CeCl₃.7H₂O (0.465 g, 25%) was added and stirred well. Then, the reaction mixture was refluxed at 90°C for 2-3 hours and the completion of the reaction was monitored by thin layer chromatography. After completion, the reaction mixture was poured onto crushed ice and stirred up to 5-10 minutes. The solid product was separated, filtered under suction, washed with ice-cold water and then recrystallized from absolute ethanol. The synthesis of CNPC molecule is shown in Scheme 1. Melting point=185˚C; Yield=87%.

Computational Details

The quantum chemical calculations of CNPC was performed using the B3LYP level of theory supplemented with 6-31G(d,p) basis set, using Gaussian 03 program package invoking geometry optimization [10]. Initial geometry generated from geometrical parameters was minimized without any constraint in the potential energy surface at DFT level. The optimized minimum structure parameters were used in the vibrational wavenumber calculations at the DFT level to characterize all stationary points as minima. The harmonic vibrational wavenumber calculations resulting in IR and Raman intensities and Raman depolarization ratios. The vibrational modes were assigned based on potential energy surface at DFT level. The optimized minimum (0˚) was minimized without any constraint in the potential energy surface scan curve and optimized structure of CNPC is shown in Table 1. From the results, there are three maximum energy conformers (0˚, 170˚ and 360˚) and two minimum conformers (100˚ and 270˚) were identified. The most stable conformer was identified at 270˚ rotation with the relative energy -1542.44631 Hartree. Hence this structure is the global minimum conformer and is used for the further investigations. The various possible conformers of CNPC during PES scan were shown in Table 1.

Vibrational Assignments

The stretching and bending vibrations of C-Cl normally occur in the low wavenumber region 760-505 cm⁻¹ [14]. Vibrational couplings are possible due to lowering of the molecular symmetry and the presence of heavy atom. The C-Cl stretching vibration of CNPC is observed as strong band at 688 cm⁻¹ in FT-IR spectrum along with the β_CCC bending vibration. The calculated wavenumber corresponds to the C-Cl stretching mode is 693 cm⁻¹ with 68% of PED contribution. The chloro substituted aromatic compounds have a band of strong to medium intensity in the region 385-265 cm⁻¹ due to C-Cl in-plane deformation [15]. The in-plane β_CCC is observed at 338 cm⁻¹ in FT-Raman spectrum with medium intensity. The calculated in-plane and out-of-plane bending vibrations.

Results and Discussion

Molecular conformational analysis

In order to investigate the stable conformer, potential energy surface scan was performed to CNPC molecule. In this PES scan process, the internal redundant coordinate of the dihedral angle D(C11–C13–C16–C20) chosen for the conformational flexibility within the molecule. During this scan the geometrical parameters was relaxed, while the D(C11–C13–C16–C20) torsional angle raised from 0˚ to 360˚ rotation by a step of 10˚ interval. The potential energy surface scan curve and optimized structure of CNPC is shown in Figure 1. From the results, there are three maximum energy conformers (0˚, 170˚ and 360˚) and two minimum conformers (100˚ and 270˚) were identified. The most stable conformer was identified at 270˚ rotation with the relative energy -1542.44631 Hartree. Hence this structure is the global minimum conformer and is used for the further investigations. The various possible conformers of CNPC during PES scan were shown in Table 1.
Figure 1  The potential energy surface scans curve and optimized structure of CNPC.

Figure 2  The experimental and theoretical FT-IR spectra of CNPC.
bending vibrations are computed at 297, 337 and 376 cm$^{-1}$, respectively.

**NO$_2$ vibrations**

The nitro stretching vibrations are the most characteristic bands in the spectra of nitro compounds, not only because of their spectral positions but also for their strong intensities. The nitro substituted aromatic compounds show asymmetric stretching mode in the region of 1600-1500 cm$^{-1}$ and symmetric stretching mode in the region of 1385-1325 cm$^{-1}$ [16]. In the present case, the asymmetric stretching vibrations of NO$_2$ are observed at 1500 cm$^{-1}$/FT-IR with medium intensity (27.45) and at 1502 cm$^{-1}$/FT-Raman spectrum. The calculated wavenumber at 1538 cm$^{-1}$ is assigned for the asymmetric NO$_2$ vibrations. The in-plane deformation of NO$_2$ is observed at 563 cm$^{-1}$ in FT-IR and well agreed with the computed wavenumber at 562 cm$^{-1}$.

**N–H and C–N vibrations**

In heterocyclic molecules, the N–H stretching vibrations are usually appearing in the region of 3500-3300 cm$^{-1}$ [17]. The band observed at 3354 cm$^{-1}$ in FT-IR spectrum is assigned for the N-H stretching vibration. The N$_3$–H$_4$ and N$_5$–H$_6$ stretching modes of dihydropyrimidinone have been calculated at 3501 and 3509 cm$^{-1}$. The C–N stretching vibrations are normally occurring in the region 1400-1200 cm$^{-1}$ [18]. The strong bands observed at 1229, 1205

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Table 2 The selected fundamental vibrational assignments of CNPC.

| Mode No. | Calculated wavenumber | Observed wavenumber | Intensity | PED ≥ 10% |
|----------|-----------------------|---------------------|-----------|-----------|
|          | Unscaled              | Scaled              | FT-IR     | FT-Raman  |
| 1        | 3620                  | 3501                | 3354      | 6.84      | 1.96      |
| 2        | 3210                  | 3104                | 3109      | 0.18      | 2.14      |
| 3        | 3194                  | 3089                | 3070      | 0.04      | 1.59      |
| 4        | 3078                  | 2976                | 2966      | 0.67      | 2.48      |
| 5        | 3036                  | 2936                | 2933      | 2.24      | 8.36      |
| 6        | 1789                  | 1730                | 1699      | 1679      | 100.00    | 6.75      |
| 7        | 1715                  | 1659                | 1639      | 1635      | 56.86     | 12.96     |
| 8        | 1663                  | 1608                | 1593      | 1613      | 28.76     | 13.15     |
| 9        | 1639                  | 1585                | 1593      | 1613      | 28.76     | 13.15     |
| 10       | 1607                  | 1554                | 1500      | 1503      | 27.45     | 5.59      |
| 11       | 1591                  | 1538                | 1500      | 1503      | 27.45     | 5.59      |
| 12       | 1505                  | 1455                | 1452      | 5.23      | 0.28      |
| 13       | 1462                  | 1414                | 1416      | 15.14     | 4.10      |
| 14       | 1422                  | 1375                | 1377      | 1375      | 3.70      | 1.97      |
| 15       | 1358                  | 1313                | 1323      | 6.66      | 1.25      |
| 16       | 1339                  | 1295                | 1280      | 1275      | 19.93     | 3.45      |
| 17       | 1277                  | 1235                | 1229      | 4.48      | 1.18      |
| 18       | 1259                  | 1217                | 1219      | 1205      | 67.71     | 4.59      |
| 19       | 1214                  | 1173                | 1165      | 1168      | 1.12      | 13.48     |
| 20       | 1176                  | 1137                | 1157      | 1157      | 0.44      | 0.25      |
| 21       | 1145                  | 1107                | 1108      | 1108      | 0.83      | 1.03      |
| 22       | 1123                  | 1086                | 1089      | 1089      | 6.16      | 1.77      |
| 23       | 1061                  | 1026                | 1023      | 9.27      | 7.51      |
| 24       | 1054                  | 1019                | 1016      | 1016      | 0.72      | 0.42      |
| 25       | 1035                  | 1001                | 1003      | 1003      | 0.54      | 2.40      |
| 26       | 985                   | 953                 | 956       | 963       | 0.03      | 0.10      |
| 27       | 802                   | 776                 | 777       | 777       | 0.83      | 2.13      |
| 28       | 785                   | 759                 | 759       | 759       | 1.36      | 2.19      |
| 29       | 758                   | 733                 | 723       | 723       | 5.65      | 2.34      |
| 30       | 653                   | 631                 | 638       | 638       | 2.16      | 3.56      |
| 31       | 626                   | 605                 | 595       | 595       | 6.11      | 1.55      |
| 32       | 581                   | 562                 | 563       | 563       | 8.64      | 1.92      |
| 33       | 517                   | 499                 | 499       | 499       | 0.10      | 3.66      |
| 34       | 349                   | 337                 | 338       | 338       | 1.28      | 1.10      |
| 35       | 339                   | 328                 | 316       | 316       | 0.48      | 3.63      |
| 36       | 247                   | 239                 | 238       | 238       | 0.63      | 1.81      |
FT-Raman shows wavenumber at 1446 and 1416 cm\(^{-1}\) with bending vibrations of β-CNH and 1217 cm\(^{-1}\) are in good agreement with the calculated wavenumber at 1235 cm\(^{-1}\) in FT-IR [19]. In the title molecule, the strong band observed at 1699 cm\(^{-1}\) is attributed to C=O stretching vibrations of dihydropyrimidine ring. The results of computation give the wavenumber of the corresponding mode at 1730 cm\(^{-1}\) has a contribution of 79% from C=O and minor contribution of 14% from C-N vibration. The C=O stretching vibration of ester group is observed at 1639 cm\(^{-1}\) in FT-IR and 1635 cm\(^{-1}\)/FT-Raman. The corresponding computed wavenumber for C=O is 1659 cm\(^{-1}\) and the deviation is attributed to intermolecular C=O dipole-dipole interaction in the molecule. The bands responses to the ester C=O stretching vibrations are in the region of 2950-2900 cm\(^{-1}\) [20]. These vibrations are intense and partly due to an interaction with C=C vibration. The strong band observed at 1089 cm\(^{-1}\) in FT-IR and 1089 cm\(^{-1}\) in FT-Raman assigned to ester C=O stretching vibrations. It is well agreed with calculated wavenumber at 1086 cm\(^{-1}\).

C–H vibrations

The C–H stretching vibrations of aromatic ring absorb in its characteristic region 3100-3000 cm\(^{-1}\) [21]. The strong bands observed at 3109 cm\(^{-1}\) in FT-IR and 3070 cm\(^{-1}\) in FT-Raman confirms the C-H stretching vibrations of title molecule. The wavenumber computed at 3104, 3101 and 3089 cm\(^{-1}\) are well agreed with the experimental observations of C–H wavenumber. In the region below 3000 cm\(^{-1}\) are found aliphatic C–H stretching vibrations. The wavenumber corresponds to \(v_{\text{C-H}}\) is observed as strong band at 2966 cm\(^{-1}\) in IR spectrum and its calculated wavenumber shows 2976 cm\(^{-1}\) with 99% of PED contribution. In substituted phenyl rings, the C–H in-plane bending vibrational modes can be expected in the region 1300-1000 cm\(^{-1}\) [22]. In our study, the \(v_{\text{C-H}}\) in-plane bending vibrations are computed at 1452, 1246, 1134 and 1113 cm\(^{-1}\). The strong band observed at 1452 cm\(^{-1}\) in FT-IR represents the C–H in-plane bending vibration of the phenyl ring. The C–H out of plane bending vibrations is expected to occur in the region 1000-675 cm\(^{-1}\) [23]. The C–H out of plane bending vibration is observed as strong bands in both FT-IR and FT-Raman spectra at 956, 879, 817 and 963, 869 cm\(^{-1}\), respectively. These spectral wavenumber agreed with the calculated wavenumber at 953, 892, 827 and 819 cm\(^{-1}\).

Ring vibrations

The ring C–C stretching vibrations occur in the region 1625-1430 cm\(^{-1}\). In the phenyl ring, the six carbon atoms undergo coupled vibrations called skeletal vibration [24,25]. In present investigation, the ring C–C stretching vibrations are observed as a strong band at 1593, 1503 cm\(^{-1}\) in FT-Raman and medium band at 1500 cm\(^{-1}\) in FT-IR are assigned for the ring vibrations. The theoretical wavenumber in the range 1585-1538 cm\(^{-1}\) represents the ring C–C vibrations. The strong bands at 1168 and 1023 cm\(^{-1}\) in FT-Raman and weak band at 1165 cm\(^{-1}\) in FT-IR outcomes the phenyl ring breathing and trigonal bending vibration of the title molecule. These fundamental wavenumber computed at 1173 and 1026 cm\(^{-1}\) represents the ring breathing and trigonal bending vibrations of aromatic ring system.

CH\(_3\) and CH\(_2\) group vibrations

In methyl groups, the symmetric stretching vibrations are observed lower wavenumber when compared to the asymmetric stretching vibrations of C-H bonds. The CH\(_3\) symmetric vibrations are expected to occur in the range of 2950-2900 cm\(^{-1}\) and CH\(_2\) asymmetric stretching vibrations are expected in the range 3050-2950 cm\(^{-1}\) [26,27]. The weak band observed at 2933 cm\(^{-1}\)/FT-IR and strong band at 2934 cm\(^{-1}\)/FT-Raman spectrum assigned for the symmetric stretching vibrations of the methyl group present in the carbonylate side chain. This mode has been calculated at 2936 cm\(^{-1}\). The symmetric C–H vibrations of methyl and methylene group of CNPC calculated at 2955 and 2950 cm\(^{-1}\). The asymmetric vibrations of the methyl and methylene groups of title molecule computed in the region 3039-2987 cm\(^{-1}\). In many molecules, the symmetric deformations CH\(_3\) appears with an
hyperconjugative interaction of π(C−C)→π*(C−C) bonds of the phenyl ring increases ED at the six conjugated π-bonds. From the NBO analysis, the π-electron delocalization in phenyl ring revealed by the ED at the three conjugated π-bond (≈1.63-1.67e) and π*(≈0.30-0.45e) resulting to the stabilization energies of ≈69.54-96.99 kJ/mol, respectively. The π-electron cloud movement can make the molecule highly polarized and causes internal charge transfer, which is responsible for the activity of the title molecule. The orbital overlap between n(Cl)→π*(C−C) bond orbital, which increases ED(0.4526) that weakens the respective anti-bonds (C7−C8=1.398Å) when compared to other C−C bonds of the phenyl ring leading to the stabilization of 62.38 kJ/mol. The most important interactions are n(LP2)O2→σ*(C−C), n(LP2)O1→π*(C−C) bond orbital, which provides stabilization energy of ≈69.54-96.99 kJ/mol, respectively. The orbital occupancies of donor, acceptor and donor-acceptor interactions are visualized with the help of Chemcraft 1.8 software. The donor-acceptor interaction orbitals of CNPC were shown in Figure 4. These types of interactions are responsible for the pharmaceutical and biological activity of the title molecule.

**NLO Optics**

Nonlinear optical studies is at the forefront of current research

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**Table 3** The donor-acceptor interactions in NBO basis for CNPC.

| Type | Donor | ED/e | Acceptor | ED/e | *E(0)kJ/mol | *E(j)-E(i) a.u | ²F(i,j) a.u |
|------|-------|------|----------|------|-------------|---------------|------------|
| n-π* | C7-C8 | 1.6767 | C9-C11 | 0.3025 | 69.54 | 0.32 | 0.065 |
| π-π* | C11-C14 | 0.3247 | C7-C8 | 0.3266 | 97.66 | 0.32 | 0.069 |
| π-π* | N34-O36 | 0.5941 | C7-C8 | 0.3266 | 58.16 | 0.18 | 0.047 |
| π-π* | C7-C11 | 1.6405 | C7-C8 | 0.4526 | 91.09 | 0.25 | 0.07 |
| π-π* | C13-C14 | 1.6381 | C7-C8 | 0.4526 | 84.24 | 0.29 | 0.067 |
| π-σ* | C7-C11 | 0.0285 | C7-C8 | 0.4526 | 84.24 | 0.29 | 0.067 |
| π-π* | C9-C11 | 0.0285 | C7-C8 | 0.4526 | 84.24 | 0.29 | 0.067 |
| π-π* | C9-C11 | 0.0285 | C7-C8 | 0.4526 | 84.24 | 0.29 | 0.067 |
| π-π* | C13-C14 | 1.6381 | C7-C8 | 0.4526 | 84.24 | 0.29 | 0.067 |
| π-π* | C19-C20 | 1.8423 | O1-C25 | 0.3047 | 97.31 | 0.29 | 0.076 |
| π-σ* | LP(2) O1 | 1.8548 | O2-C25 | 0.0958 | 130.46 | 0.62 | 0.126 |
| π-σ* | LP(2) O2 | 1.8548 | O2-C25 | 0.0958 | 130.46 | 0.62 | 0.126 |
| π-σ* | LP(1) O2 | 1.9637 | O1-C25 | 0.0183 | 29.04 | 1.16 | 0.081 |
| π-σ* | LP(2) O2 | 1.8048 | O1-C25 | 0.0307 | 185.94 | 0.33 | 0.112 |
| π-σ* | LP(1) N3 | 1.7345 | C13-C16 | 0.0456 | 30.17 | 0.65 | 0.065 |
| n-σ* | C16-H17 | 0.0232 | C13-C16 | 0.0456 | 30.17 | 0.65 | 0.065 |
| n-σ* | C18-O33 | 0.0439 | C13-C16 | 0.0456 | 30.17 | 0.65 | 0.065 |
| n-σ* | C18-O33 | 0.3284 | C16-H17 | 0.0232 | 12.76 | 0.67 | 0.043 |
| n-σ* | LP(1) N5 | 1.6803 | C18-O33 | 0.3284 | 160.92 | 0.34 | 0.103 |
| n-σ* | LP(2) O33 | 1.8465 | C19-C20 | 0.2326 | 169.83 | 0.34 | 0.103 |
| n-σ* | LP(2) O33 | 1.8465 | C19-C20 | 0.2326 | 169.83 | 0.34 | 0.103 |
| n-σ* | LP(2) O35 | 1.4357 | N34-O35 | 0.0683 | 25.52 | 0.71 | 0.106 |
| n-σ* | LP(2) O35 | 1.4357 | N34-O35 | 0.0683 | 25.52 | 0.71 | 0.106 |

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The stability of the title molecule is evaluated with the help of Chemcraft 1.8 software. These types of interactions are responsible for the pharmaceutical and biological activity of the title molecule.
because of its prominence in providing the key functions of optical switching, optical modulation, optical logic and optical memory for the emerging technologies in areas such as signal processing, telecommunications and optical interconnections [29,30]. The molecular polarizability and hyperpolarizability are calculated about $4.71 \times 10^{-30}$ esu and $2.61 \times 10^{-30}$ esu, respectively.

The β₀ value of the title compound is seven times greater than that of reference urea. 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 [31]. The first hyperpolarizability values of similar pyrimidine derivatives are reported as, 1.19, 1.35 and $0.30 \times 10^{-30}$ esu, respectively [32-34]. The first hyperpolarizability components of CNPC were listed in Table 4.

### Molecular Electrostatic Potential

Molecular electrostatic potential is related to the electronic density of the molecule and is a very useful descriptor in understanding the charge sites as well as hydrogen bonding interactions [35,36]. The electrostatic potential $V(r)$ are also well suited for analyzing processes based on the “recognition” of one molecule by another, as in drug-receptor, and enzyme substrate interactions, because it is through their potentials that the two species first “see” each other [37,38]. Being a real physical property $V(r)$s can be determined experimentally by diffraction or by computational methods [39]. The MEP mapped surface and 2D contour map of CNPC were shown in Figure 5. In order to predict the possible electrophilic and nucleophilic charge sites for the investigated molecule, MEP mapped surfaces are

### Table 4 The first hyperpolarizability components of CNPC

| Parameters | B3LYP/6-31G(d,p) |
|------------|------------------|
| Dipole moment ($\mu$) | Debye |
| $\mu_1$ | 2.5812 |
| $\mu_2$ | -1.1982 |
| $\mu_3$ | -0.1884 |
| $\mu$ | 2.8519 Debye |
| Polarizability ($\alpha_0$) | $\times 10^{-30}$ esu |
| $\alpha_{xx}$ | 246.60 |
| $\alpha_{yy}$ | 8.27 |
| $\alpha_{zz}$ | 239.80 |
| $\alpha_{xy}$ | 1.66 |
| $\alpha_{xz}$ | 21.69 |
| $\alpha_{yz}$ | 177.97 |
| $\alpha$ | $4.7147 \times 10^{-30}$ esu |
| Hyperpolarizability ($\beta_0$) | $\times 10^{-30}$ esu |
| $\beta_{xxx}$ | -12.65 |
| $\beta_{xxy}$ | 11.97 |
| $\beta_{xyy}$ | 248.19 |
| $\beta_{yyy}$ | -372.31 |
| $\beta_{xxz}$ | -34.20 |
| $\beta_{xzy}$ | -12.66 |
| $\beta_{yyz}$ | 37.17 |
| $\beta_{xzx}$ | -97.30 |
| $\beta_{yxz}$ | 94.09 |
| $\beta_{yzz}$ | $2.6143 \times 10^{-30}$ esu |

*Reference urea ($\mu$=1.3732 Debye, $\beta_0$=0.3728 $\times 10^{-30}$ esu)
generated. The positive (blue) regions to nucleophilic reactivity and the negative (red and yellow) regions of MEP were related to electrophilic reactivity shown in Figure 5. The negative potentials are commonly observed in the region of electron-negative atoms with lone pair electrons. In our study, the negative regions are localized in the oxygen atoms present in the nitro group and also with the oxygen atoms present in the two carbonyl groups, which are electrophilic nature. The positive potentials are localized over the hydrogen atoms bonded with the nitrogen atoms of dihydroprymidine ring, which are nucleophilic in nature.

Energy Gap Analysis

Frontier molecular orbitals and their energies are very useful for the physicists and chemists. The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one-electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied orbital (LUMO). The eigen values of HOMO/LUMO and their energy gap reflect the chemical activity of the molecule. In order to gain insight into the electronic structure of CNPC, it’s theoretical molecular orbital distributions were calculated with the Gaussian program at B3LYP/6-31G(d,p) level using the density functional theory. As shown in the Figure 6 the highest occupied molecular orbitals of CNPC were mostly dispersed on the 4-chloro-3-nitrophenyl moiety. In contrast, the LUMO were localized on the electron deficient pyrimidine ring together with the carboxylate side chain. The clear separation of the HOMO and LUMO suggested that the HOMO-LUMO excitation would shift the electron density distributions from the donor di-substituted phenyl moiety to the acceptor pyrimidine moiety leading to a polarized excited state. The contour map of title molecule describes the electron density mapped surface of the CNPC. It is more important, such separation of HOMO-LUMO can provide holes and electron-transporting channel, respectively.

HOMO= -6.8682 eV
LUMO= -2.7783 eV
Energy gap ΔE= 4.0899 Ev

NMR Analysis

Gauge independent atomic orbital method is used as a default method to calculate the NMR chemical shifts of the CNPC molecule. The recorded 1H-NMR and 13C-NMR spectra of the CNPC molecule are shown in Figure 7. Table 5, contains the assignments of experimental and theoretical chemical shift values of the title compound. The GIAO-NMR calculations were performed by B3LYP/6-31G(d,p) level of theory. Chemical shift of any ‘x’ proton (6X) is equal to the difference between isotropic magnetic shielding (IMS) of TMS and proton (x). It is defined by the equation: \( \delta X = \text{IMS}_{TMS} - \text{IMS}_X \) [40]. The theoretical NMR chemical shifts repositioned using proper scale factors. The 1H-NMR chemical shifts of CNPC (with respect to TMS) appeared in the range of 0.838-2.373 ppm experimentally and 0.862-2.778 ppm theoretically. The triplet and singlet observed at 1.064 and 2.373 ppm, respectively. The confirmation of the compound formation is observed by the singlet at 5.110 ppm in 1H-NMR chemical shift shows good agreement with the peak computed at 4.820 ppm. The quartet observed at the range of 3.584-3.988 ppm corresponds to the methylene group protons of the title molecule. Theoretical chemical shift for methylene group is computed in the range of 3.584-3.667 ppm, respectively. The experimental aromatic protons show nice accordance with the theoretical values.

In 13C-NMR spectrum the fourteen signals confirms the fourteen carbons of the title molecule experimentally in the range of 13.95-165.10 ppm and theoretically at 12.04-169.06 ppm, respectively. The signal observed at 53.17 ppm confirms the ring formation chiral carbon of the title molecule; its theoretical prediction coincides well with 56.47 ppm. The two signals 165.10 and 156.67 ppm at downfield region confirms the two carbonyl carbons \( (C^{165}_{165}) \) and \( (C^{156}_{156}) \) of the CNPC molecule. These carbonyl carbon signals computed at 164.00 and 146.96 ppm. The peaks appeared at 13.95, 17.65 and 59.11 corresponds to the two methyl and one methylene carbon of the CNPC molecule. The calculated data of these carbons are 12.04, 21.14 and 60.95 ppm, respectively.

Table 5 The theoretical and experimental chemical shift values of CNPC.

| Atoms | DFT | Exp. | Atoms | DFT | Exp. |
|-------|-----|------|-------|-----|------|
| C29   | 12.04 | 13.95 | C_{29}H_{13} | 0.862-1.064 | 1.014-1.061 |
| C21   | 21.14 | 17.69 | C_{21}H_{13} | 0.838-2.373 | 2.225 |
| C16   | 56.47 | 53.17 | C_{16}H_{13} | 3.584-3.667 | 3.918-3.988 |
| C26   | 60.95 | 59.19 | H_{17} | 4.820 | 5.11 |
| C14   | 125.14 | 117.30 | ArC−H | 6.814-7.456 | 6.943-7.411 |
| C20   | 100.50 | 98.76 | N−H | 3.886 | 7.781 |
| C8    | 134.99 | 119.81 | N−H | 5.008 | 9.250 |
| C11   | 132.01 | 122.84 | |
| C9    | 129.50 | 130.19 | |
| C13   | 145.39 | 142.27 | |
| C7    | 150.94 | 148.77 | |
| C19   | 146.31 | 151.89 | |
| C18   | 146.96 | 156.64 | |
| C25   | 164.06 | 165.10 | |
\[ \Delta E = 4.0899 \text{ eV} \]

\[ \Delta E = 5.4912 \text{ eV} \]

LUMO = -2.778243 eV

LUMO+1 = -1.888443 eV

HOMO = -6.868056 eV

HOMO-1 = -7.379623 eV

Figure 6
The frontier molecular orbitals of CNPC.

Figure 7
The \(^1\text{H}\) and \(^13\text{C}\)-NMR spectra of CNPC.
seven times greater than that of reference urea and their similar NLO molecules. Thus our title molecule is good candidate for the nonlinear optical studies. The molecular charge sites are identified by the molecular electrostatic potential mapped surface. The structural confirmation by $^1$H and $^{13}$C-NMR reports with computed chemical shifts shown very good agreement.
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