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# Study on *N*-(4-Chlorobenzoyl) Fenamic Acid Crystal-Density Functional Theory Approach

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The *N*-(4-Cholorobenzoyl)Fenamic acid crystal have been grown, the structural and the lattice parameters are found through XRD analysis. The chemical bonding and their nature analysis was performed from the FTIR and FT-Raman spectra's. The molecular structure optimized through DFT (Density Functional Theory) computations and correlated through experimental one. From the optimized geometry from the computations provide to the structural, frequencies and other parameters are match with experiments. From hyper-conjugative interactions, charge delocalization used to study the stabile nature of molecules through NBO analysis. The thermodynamic properties are linearly deepened with temperature. And susceptibility of the crystal can be performed is found to decrease at different temperatures is calculated. The spectral analysis agreed well with experiments.

**Keywords:** NCF, XRD, NBO, MEP, DFT.

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## 1. INTRODUCTION

The Fenamic acid is used as the precursor to the amino acid and constituents of several alkaloids. The derivatives of fenamic acid and screens them for their potential biological activities. The formation of amides has attracted considerable interest owing to their importance in bioorganic, organic chemistry, as intermediates in organic synthesis and etc., in the chemical industry [1], its play a main role in biological activity [2]. The needs of amide bonds attract the chemists, biologists, in living systems; they determine the interactions of biologically active structures like peptides [3]. In this present work, we presented the formation of *N*-(4-cholorobenzoyl) Fenamic acid (NCF) crystal and characterized using appropriate spectroscopic methods. Several reports involved in an first principle, HF and DFT procedure the vibrational analysis of NCF and they have been presented and discussed. This investigation dealt the study of vibrational spectral analysis leads to the possible modes and their accurate wavenumber. Frist principle, HF and DFT computations are useful to assign their frequencies. The distribution of ED for many bonding/antibonding orbital and energies have been computed by NBO analysis through DFT method to give the exactness and the confirmation is starting from the hyperconjugation of appropriate interactions in molecules [3–5]. The charge transfer values were found through the HOMO and LUMO analysis. All the thermodynamic parameters were calculated and discussed. The molecular electrostatic potential surfaces of molecules, ED surfaces was computed through 6–311++G(d, p) basis set. The Structures obtained from ED surface versus ES potential surface depicts all information about the molecule [6–9].

Further this work deals with the mullikan charges and its populations to describe the charge, magnetic behavior of molecules changes with thermodynamical effects, Raman

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active, functional groups and the stretching analysis by FTIR are dealt.

## 2. EXPERIMENTAL AND COMPUTATIONAL

All Analar grade chemicals with an purity >99%., was used as purchased. The functional group with stretching and structural measurement of instrumental details is available in literatures and the data obtained through SAINT program with absorption corrections [4–7], the values of parameters are presented in Table I.

Synthesis of N-(4-Cholorobenzoyl)-Fenamic acid: The formation of N-(4-Chlorobenzoyl) Fenamic acid through the mixture of Fenamic acid (10 mmol) + THF (50 ml) + 4-choloro benzoyl chloride (10 mmol) + triethylamine (10 mmol) at 30 °C. The mixture is allowed to stirred around 15 h with 100 ml of water. Finally slow cooling method from 30 °C at rate of 0.1 °C per day.

Molecular modeling: The 3D molecular modeling of the compound was studied by Gaussian 09W [8] software package. The stereochemistry was assured through low energy molecular geometrics. The calculation ware made through basis set of 6–311++G(d, p) [9]. These sets of HF/6-311++G(d, p), and DFT/B3LYP/6-311++G(d,p) are used to find the structural information. Then, the NCF were used for the measurements for vibrational frequencies, IR and Raman Spectral studies used DFT [10], B3 [11] LYP [12]. The computed values give thermal behavior with aid of statistics. Combining the obtained result of the GAUSSVIEW program [13], symmetry assumption, vib. frequency assignments are formed. The NBO measurements [14] were made through NBO 3.1 program, from the main Gaussian 09W [8] package at B3LYP/6-31++G(d, p) sets, leads to know possible interactions in the filled orbitals. The Raman activities ($S_i$) computed through the package of GAUSSIAN 09W and convert to relative Raman intensities ($I_i$) using the relation [15–17].

$$I_i = \frac{f(\nu_0 - \nu_i)^4 \mathrm{Si}}{\nu_i [1 - \exp((-hc\nu_i)/kT)]}$$

Where the notations having the usual meanings.

**Table I.** Crystal data and structure refinement for N-(4- Chlorobenzoyl)Fenamic acid.

| Empirical formula | C14H10ClNO3 |
|---|---|
| Formula weight ($g \cdot mol^{-1}$) | 275.68 |
| T (K) | 100 (2) |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | |
| a (Å) | 6.6989 (5) |
| b (Å) | 7.2140 (6) |
| c (Å) | 25.1489 (18) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 92.624 (4) |
| $\gamma$ (°) | 90 |
| V (Å$^3$) | 1214.07 (16) |
| Z | 4 |
| $\mu$ ($mm^{-1}$) | 0.32 |
| $T\min \cdot T\max$ | 0.666, 0.746 |
| Reflections collected | 2991 |
| Independent reflections (Rint) | 0.024 |

**Table II.** Nonlinear optical properties of N-(4-Chlorobenzoyl)Fenamic acid at HF/6-311++G (d, p) and B3LYP/6-311++G(d, p) methods and basis set calculations.

| NLO behaviour | HF/6-311++G(d, p) | B3LYP/6-311++G(d, p) |
|---|---|---|
| | Energy (Hartrees) | |
| Optimized global minimum energy | −1274.167 | −1280.215 |
| | Moment(Debye) | |
| Dipole moment ($\mu$) | 1.8731 | 1.2915 |
| | Polarizability ($10^{-30}$ esu) | |
| Mean polarizability ($\alpha$) | 2.9650 | 1.7970 |
| Anisotropy of the polarizabilty ($\Delta_\alpha$) | 5.7324 | 4.1374 |
| First hyperpolarizability ($\beta$) | 4.9230 | 5.5190 |
| Vector-first hyperpolarizability ($\beta_{vec}$) | 2.3302 | 3.3114 |

## 3. NLO PROPERTY

The organic compounds exhibiting large hyperpolarizabilities [18–20] are stable and possess optical behavior. The nonlinear optical materials having the structural, electronic behavior of donor-acceptor with substitution of $\pi$-conjugation and NLO response is confirmed through $\beta$-first-order hyperpolarizability [21].

Molecular hyperpolarizability requires both diffusion and polarization. So, our crystal completely optimized at B3LYP/6-311++G(d, p), Gaussian 09W program. The tensor component $\beta$, $\beta^{vec}$ of the compounds calculated through the well known symmetry relation by Kleinman and Cartesian [21]. The requirements of the large value of hyperpolarizibility, $\beta$—is a measurement of the NLO

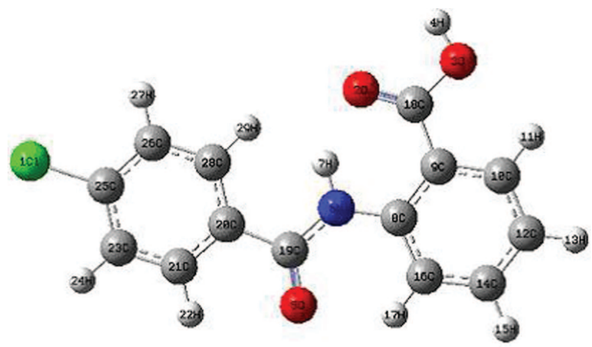

**Fig. 1.** Molecular structure of *N*-(4-Cholorobenzoyl)Fenamic acid.

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**Table III.** Optimized geometrical parameters of N-(4-Chlorobenzoyl)Fenamic acid by HF/6-311++G(d, p) and B3LYP/6-311++G(d, p) calculations.

| | Value (A°) | | | | Value (°) | | | | Value (°) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bond length | HF/6-311 ++G (d, p) | B3LYP/6-311++G (d, p) | Exp. | Bond angle | HF/6-311 ++G (d, p) | B3LYP/6-311++G (d, p) | Exp. | Dihedral angle | HF/6-311 ++G (d, p) | B3LYP/6-311++ (d, p) | Exp. |
| N6–H7 | 0.99 | 1.01 | 0.84 | H4–O3–C18 | 108.3 | 106.5 | 109.4 | H4–O3–C18–O2 | 0.2 | 0.3 | −4.3 |
| N6–C19 | 1.36 | 1.38 | 1.37 | O3–C18–O2 | 120.1 | 119.8 | 122.2 | O3–C18–C9–C10 | −0.6 | 0.5 | 5.8 |
| N6–C8 | 1.39 | 1.39 | 1.40 | C9–C8–N6 | 119.2 | 118.9 | 118.8 | H4–O3–C18–C9 | 179.9 | 180.0 | 175.5 |
| O3–H4 | 0.95 | 0.97 | 0.84 | C8–N6–H7 | 113.9 | 112.8 | 114.0 | C8–N6–C19–O5 | 3.8 | 2.9 | −2.0 |
| C19–O5 | 1.20 | 1.22 | 1.22 | C8–N6–C19 | 128.9 | 129.0 | 129.1 | H7–N6–C19–O5 | −180.0 | −179.9 | 176.0 |
| C19–C20 | 1.50 | 1.50 | 1.51 | H7–N6–C19 | 117.4 | 118.3 | 116.0 | O5–C19–C20–C28 | 180.0 | −179.9 | 176.0 |
| C25–C23 | 1.38 | 1.39 | 1.39 | N6–C19–O5 | 124.4 | 123.6 | 124.7 | Cl1–C25–C23–H24 | 0.8 | 0.7 | −0.2 |
| C18–O2 | 1.20 | 1.23 | 1.23 | O5–C19–C20 | 120.4 | 120.7 | 121.0 | Cl1–C25–C23–C21 | −180.0 | 180.0 | 179.8 |
| Cl1–C25 | 1.72 | 1.73 | 1.74 | H29–C28–C26 | 117.9 | 117.3 | 119.7 | Cl1–C25–C26–C28 | 180.0 | −180.0 | −0.5 |
| Cl1–O2 | 1.7418 | 1.7556 | 1.42 | Cl1–C25–C23 | 119.5 | 119.5 | 119.3 | C20–C19–N6–C28 | 180, 0 | −179, 9 | 177.2 |
| O2–O3 | 1.3806 | 1.3911 | 1.53 | Cl1–O2–O3 | 119.4057 | 119.3931 | 123.6 | Cl1–O2–O3–H4 | −179.7711 | −179.8714 | |
| O2–H7 | 1.3831 | 1.3925 | | Cl1–O2–H7 | 119.4234 | 119.4678 | 120.7 | Cl1–O2–H7–N6 | −179.7807 | −179.8672 | 178.4 |
| O3–H4 | 1.3846 | 1.3919 | 0.85 | O3–H4–O5 | 120.6348 | 120.7201 | 116.3 | O2–O3–H4–O5 | −0.2058 | −0.0653 | −176.5 |
| O3–C8 | 1.0731 | 1.0823 | | O3–H4–C9 | 17.8304 | 117.6575 | 118.5 | O2–O3–H4–C9 | −179.2518 | −179.2295 | 174.4 |
| H4–O5 | 1.3893 | 1.4007 | | H13–C12–C1 | 115.0855 | 4123.9514 | | H13–C12–C14–C25 | 174.4246 | 175.9823 | −174.5 |
| H4–C9 | 1.0741 | 1.0836 | 1.22 | C12–C14–H15 | 128.9167 | 128.9882 | | C12–C14–H15–C16 | −179.5643 | −179.9669 | 179.4 |
| O5–N6 | 1.3901 | 1.4 | 1.53 | C12–C14–C25 | 117.1009 | 117.9541 | | H13–C12–C14–C25 | 174.4346 | 175.9823 | |
| O5–C12 | 1.5058 | 1.5054 | 1.28 | C14–H15–C20 | 122.2628 | 122.3926 | | C25–C14–H15–C20 | −177.5602 | −178.8716 | |
| N6–C10 | 1.0728 | 1.0826 | 1.20 | H17–C16–C26 | 118.3867 | 119.0693 | | H17–C16–C26–H27 | −179.1265 | −179.3931 | |
| H7–H11 | 1.0733 | 1.0824 | 1.53 | C16–H17–C18 | 121.5012 | 121.3318 | | C16–H17–C18–H22 | −179.9907 | −179.9907 | |
| C12–H13 | 1.1946 | 1.221 | 1.10 | C16–H17–C21 | 119.8565 | 118.4534 | 119.3 | H15–C16–H17–C21 | −179.5552 | 179.9864 | |
| C12–C14 | 1.3652 | 1.3806 | | H17–C18–C19 | 118.5303 | 118.9655 | 121.6 | C26–H17–C18–C19 | 178.5942 | 179.5942 | |
| H13– H24 | 2.154 | 2.1421 | | H17–C18–H22 | 120.5065 | 120.294 | 120.7 | C21–H17–C18–H22 | −0.0763 | −0.0971 | |
| C14–H15 | 1.3948 | 1.3956 | | C19–C1–H22 | 120.9631 | 120.7405 | 115.3 | C19–C18–H22–C20 | −179.9204 | −179.9204 | |
| C14–C25 | 0.9933 | 1.0156 | | C18–C19–C20 | 121.5876 | 121.332 | | C18–C19–C20–H24 | 179.7162 | 179.7709 | |
| H15–C16 | 1.4122 | 1.4264 | | C18–C19–C23 | 119.8897 | 119.9431 | | C16–C26–H27H29 | −179.1265 | −179.9771 | |
| H15–C20 | 1.3963 | 1.4057 | | C20–C19–C23 | 118.5227 | 118.7249 | | C16–C26–C28–C23 | 179.5888 | 179.9888 | |
| C16–H17 | 1.3964 | 1.4053 | | H15–C20–C24 | 119.4354 | 118.6987 | | | | | |
| C26–H27 | 1.1362 | 1.8556 | | C19–C20–H24 | 120.184 | 120.8683 | | | | | |
| C28–H29 | 1.6418 | 1.5911 | | C16–C26–H27 | 125.8799 | 126.0719 | | | | | |
| C26–H27 | 1.3806 | 1.2234 | | C16–C26–C28 | 113.8559 | 113.9177 | | | | | |

*Note*: [a]For numbering of atoms refer Figure 1.

**Table IV.** Definition of internal coordinates of N-(4-Chlorobenzoyl)Fenamic acid.

| No. | Symbol | Type | Definition |
|---|---|---|---|
| 1–8 | Pi | CH | C10–H11, C12–H13, C14–H15, C16–H17, C28–H29, C21–H22, C23–H24, C23–H27 |
| 9–11 | Si | CO | C19–O5, C18–O3, C18–O2 |
| 12 | Zi | OH | O3–H4 |
| 13 | Xi | CCl | C25–Cl1 |
| 14 | Yi | NH | N6–H7 |
| 15-28 | Qi | CC | C8–C9, C9–C10, C10–C12, C12–C14, C14–C16, C16–C8, C9–C18, C19–C20, C20–C21, C21–C23, C23–C25, C25–C26, C26–C28, C28–C20 |
| | | | In-plane bending |
| 29–40 | $\beta$ | Ring | C8–C9–C10, C9–C10–C12, C10–C12–C14, C12–C14–C16, C14–C16–C8, C16–C8–C9, C21–C20–C28, C20–C28–C26, C28–C26–C25, C26–C25–C23, C25–C23–C21, C23–C21–C20 |
| 41-56 | M | CH | H11–C10–C12, H11–C10–C9, H13–C12–C14, H13–C12–C10, H15–C14–C16, H15–C14–C12, H17–C16–C14, H17–C16–C8, H29–C28–C20,, H29–C28–C26, H27–C26–C28, H27–C26–C25, H22–C21–C23, H22–C21–C20, H24–C23–C21, H24–C23–C25 |
| 57–62 | R | OC | O5–C19–N6, O5–C19–C22, O3–H4–C18, O3–C18–C9, O2–C18–C9, O2–C18–O3 |
| 63–64 | $\alpha$ | Cl C | Cl1–C25–C26, Cl1–C25–C23 |
| 65 | N | HO | H4–O3–C18 |
| 66-67 | T | NH | H7–N6–C8, H7–N6–C19 |
| 68-71 | U | NC | N6–C8–C9, N6–C8–C16, N6–C19–H7, N6–C19–O5 |
| 72-75 | Φ | CC | C20–C19–O5, C20–C19–N6, C18–C9–C10, C18–C9–C8 |

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**Table IV.** Continued.

| No. | Symbol | Type | Definition |
|---|---|---|---|
| | | | Out-of-plane bending |
| 76–87 | $\alpha$ | Ring | C8–C9–C10–C12, C9–C10–C12–C14, C10–C12–C14–C16, C12–C14–C10–C8, C14–C16–C8–C9, C16–C8–C9–C10, C20–C21–C23–C25, C21–C23–C25–C26, C23–C25–C26–C28, C25–C26–C28–C20, C26–C28–C20–C21, C28–C20–C21–C23 |
| 88–95 | $\Delta$ | CH | H11–C10–C9–C12, H13–C12–C14–C10, H15–C14–C12–C16, H17–C16–C8–C14, H22–C21–C20–C23, H29–C28–C20–C26, H24–C23–C21–C25, H27–C26–C28–C25 |
| 96–98 | $\tau$ | OC | O3–C18–C9–O2, O2–C18–O3–C9, O5–C19–N6–C20 |
| 99–100 | $\tau$ | CC | C9–C18–O3–O2, C20–C19–N6–O5 |
| 101 | $\tau$ | Cl C | Cl1–C25–C23–C26 |
| 102 | $\tau$ | OH | H4–O3–C18–O2 |
| 103 | $\tau$ | NH | H7–N6–C19–C8 |
| 104–105 | $\tau$ | CN | N6–C8–C9–C16, N6–C19–O5–C20 |
| 106–109 | | Butterfly | H17–C10–C8–C9, N6–C8–C10–H17, H29–C28–C20–C2, C19–C20–C28–C26 |

active, possess intermolecular charge transfer nature from the movement of electron by '$\pi$ conjugation with donating/accepting compounds (Table II).

## 4. RESULTS AND DISCUSSION

### 4.1. Structural Aspects

The lengths, bonds of atoms and their coordinate are dependent with hybridization scheme. The energy −1280.4292 kJ/mol and the structure are shown in Figure 1, through DFT. The compound having C1 point group symmetry and the above values are presented in Table III. The full set of 109 internal coordinates of NCF was presented in Table IV and the local symmetry coordinates in Table V [22]. The energy calculations were shown in Figure 2. The minimum energy computations for 16 various conformers are given in Table VI. The TED is used to find the contribution maximum potential energy of molecule. The bond length of C19–O5 and C18–O2 is 1.22 Å and 1.23 Å are well suited with the C═O double bond. The calculated bond lengths of C19–O5 and C18–O2 thorugh HF/6-31++G(d, p), B3LYP/6-31++G(d, p) are 1.20 Å, 1.22 Å, and 1.20 Å, 1.23 Å correspondingly. The bond length of C19–N6 is 1.37 Å and C8–N6 is 1.40 Å similar normal C–N bond distance. The difference in bond length calculated for C–N is 0.01 Å. This is occur the repulsion of electrons lone pair of oxygen and nitrogen. The calculated C25–Cl1 bond length is nearly equal to experimental value. The bond angle O5–C19–N6 is 124.7°. The bond angle O5–C19–N6 calculated by basis sets are 124.4°, 123.6° respectively. The bond angles from HF methods are marginally higher obtained from B3LYP methods. The selected dihedral angles are summarized in Table SIV. The chlorine connected phenyl ring is planar with carbonyl connected dihedral angle of C20–C19–N6–C28 177.2°. The torsion angles determined from B3LYP methods are higher rather than HF methods.

### 4.2. Vibrational Assignments

The compound has 29 atoms having three Cartesian movements gives 80 internal modes, among these vibrations 54 are in-plane and 26 are out of plane. The respective

**Table V.** Definition of local symmetry coordinates of N-(4-Chlorobenzoyl)Fenamic acid.

| No. | Type | Definition[b] |
|---|---|---|
| 1–8 | CH | $P_1$, $P_2$, $P_3$, $P_4$, $P_5$, $P_6$, $P_7$, $P_8$ |
| 9–11 | CO | $S_9$, $S_{10}$, $S_{11}$ |
| 12 | OH | $Z_{12}$ |
| 13 | CCl | $X_{13}$ |
| 14 | NH | $Y_{14}$ |
| 15–28 | CCl | $Q_{15}$, $Q_{16}$, $Q_{17}$, $Q_{18}$, $Q_{19}$, $Q_{20}$, $Q_{21}$, $Q_{22}$, $Q_{23}$, $Q_{24}$, $Q_{25}$, $Q_{26}$, $Q_{27}$, $Q_{28}$ |
| 29 | $R_1$ trigd | $(\beta_{29}-\beta_{30}+\beta_{31}\text{-}\beta_{32}+\beta_{33}-\beta_{34})/\sqrt{6}$ |
| 30 | $R_1$ symd | $(-\beta_{29}-\beta_{30}+2\beta_{31}-\beta_{32}-\beta_{33}+2\beta_{34})/\sqrt{12}$ |
| 31 | $R_1$ asymd | $(\beta_{29}-\beta_{30}+\beta_{32}-\beta_{33})/2$ |
| 32 | $R_2$ trigd | $(\beta_{35}-\beta_{36}+\beta_{37}-\beta_{38}+\beta_{39}-\beta_{40})/\sqrt{6}$ |
| 33 | $R_2$ symd | $(\text{-}\beta_{35}-\beta_{36}+2\beta_{37}-\beta_{38}-\beta_{39}+2\beta_{40})/\sqrt{12}$ |
| 34 | $R_2$ asymd | $(\beta_{35}-\beta_{36}+\beta_{38}-\beta_{39})/2$ |
| 35–42 | bCH | $(M_{41}\text{-}M_{42})/\sqrt{2}$, $(M_{43}-M_{44})/\sqrt{2}$, $(M_{45}\text{-}M_{46})/\sqrt{2}$, $(M_{47}\text{-}M_{48})/\sqrt{2}$, $(M_{49}\text{-}M_{50})/\sqrt{2}$, $(M_{51}\text{-}M_{52})/\sqrt{2}$, $(M_{53}\text{-}M_{54})/\sqrt{2}$, $(M_{55}\text{-}M_{56})/\sqrt{2}$, |
| 43–45 | bOC | $(R_{57}\text{-}R_{58})/\sqrt{2}$,$(R_{59}\text{-}R_{60})/\sqrt{2}$, $(R_{61}\text{-}R_{62})/\sqrt{2}$, |
| 46 | bCCl | $(\alpha_{63}\text{-}\alpha_{64})/\sqrt{2}$, |
| 47 | bHO | $(N_{65})/\sqrt{2}$, |
| 48 | bNH | $(T_{66}\text{-}T_{67})/\sqrt{2}$, |
| 49–50 | bNC | $(U_{68}\text{-}U_{69})/\sqrt{2}$, $(U_{70}\text{-}U_{71})/\sqrt{2}$ |
| 51–52 | bCC | $(\Phi_{72}\text{-}\Phi_{73})/\sqrt{2}$, $(\Phi_{74}\text{-}\Phi_{75})/\sqrt{2}$ |
| 53 | t $R_1$ trigd | $(\tau_{76}-\tau_{77}+\tau_{78}-\tau_{79}+\tau_{80}-\tau_{81})/\sqrt{6}$ |
| 54 | t $R_1$Symd | $(\tau_{76}-\tau_{78}+\tau_{80}-\tau_{81})/\sqrt{2}$ |
| 55 | t $R_1$ asymd | $(-\tau_{76}+2\tau_{77}-\tau_{78}-\tau_{79}+2\tau_{80}-\tau_{81})/\sqrt{6}$ |
| 56 | t $R_2$ trigd | $(\tau_{82}-\tau_{83}+\tau_{84}-\tau_{85}+\tau_{86}-\tau_{87})/\sqrt{6}$ |
| 57 | t $R_2$ symd | $(\tau_{82}-\tau_{84}+\tau_{86}-\tau_{87})/\sqrt{2}$ |
| 58 | t $R_2$ asymd | $(-\tau_{82}+2\tau_{83}-\tau_{84}-\tau_{85}+2\tau_{86}-\tau_{87})/\sqrt{6}$ |
| 59–66 | $\omega$CH | $\Delta_{88}$, $\Delta_{89}$, $\Delta_{90}$, $\Delta_{91}$, $\Delta_{92}$, $\Delta_{93}$, $\Delta_{94}$, $\Delta_{95}$ |
| 67–69 | $\omega$OC | $\tau_{96}$, $\tau_{97}$, $\tau_{98}$ |
| 70–71 | $\omega$CC | $\tau_{99}$, $\tau_{100}$ |
| 72 | $\omega$CCl | $\tau_{101}$ |
| 73 | $\omega$OH | $\tau_{102}$ |
| 74 | $\omega$NH | $\tau_{103}$ |
| 75–76 | $\omega$CN | $\tau_{104}$, $\tau_{105}$ |
| 77–80 | Butterfly | $\tau_{106}$, $\tau_{107}$, $\tau_{108}$, $\tau_{109}$ |

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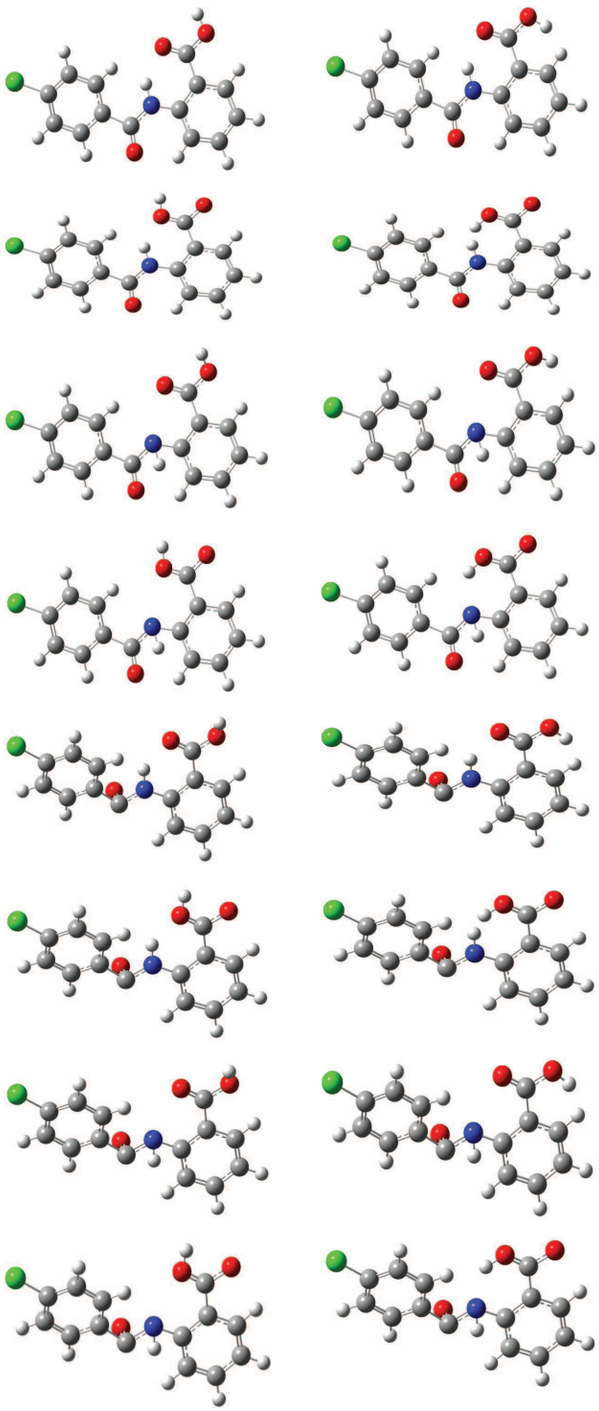

**Fig. 2.** Various conformers of *N*-(4-Cholorobenzoyl)Fenamic acid.

experimental quantities are mainly due to the combination of effects electron correlation and deficiencies in basis set are shown in Table VII. The Raman wave numbers of NCF with their corresponding IR values are shown in Figures 3 and 4.

**Table VI.** Optimized global minimum energies of different conformers of N-(4-Chlorobenzoyl) Fenamic acid calculated at HF/6-311+G(d, p) and B3LYP/6-311++G(d, p) level of theory.

| | Optimized global minimum energies (in Hartrees) | |
|---|---|---|
| Conformer | HF/6-311++G(d,p) | B3LYP/6-311++G(d,p) |
| A | 1280.5170 a.u. | 1281.437 a.u. |
| B | 1283.4035 a.u. | 1280.5670 a.u. |
| C | 1285.4071a.u. | 1280.0872 a.u. |
| D | 1289.4907 a.u. | 1280.4370 a.u. |
| E | 1281.4037 a.u. | 1280.4337 a.u. |
| F | 1282.9217 a.u. | 1283.0837 a.u. |
| G | 1280.5741 a.u. | 1280.3379 a.u. |
| H | 1281.6088 a.u. | 1280.4370 a.u. |
| I | 1280.4370 a.u. | 1280.4292* a.u. |
| J | 1284.437 a.u. | 1283.0371 a.u. |
| K | 1282.4007 a.u. | 1281.9001 a.u. |
| L | 1282.0437 a.u. | 1283.0537 a.u. |
| M | 1281.94370 a.u. | 1282.9037 a.u. |
| N | 1287.0065 a.u. | 1286.0675 a.u. |
| O | 1284.0245 a.u. | 1285.0178 a.u. |
| P | 1283.4307 a.u. | 1285.4456 a.u. |

*Note*: *Global minimum energy.

#### *4.2.1. C–H vibrations*

From the FTIR spectra the C–H (characteristic region) stretching is available in the range of wavelength 3100–3000 $cm^{-1}$ [31] are identified, and the bands observed for various wavelengths 3100, 3050, 3005, 2990, 2981, 2972, 29512912 $cm^{-1}$. The C–H in-plane and out of- plane vibrations occurs due to the intensity from strong in the regions of 1300–1000 and 1000–750 $cm^{-1}$ [31]. The bands for C–H in plane vibrations are occurred at 1412, 1407, 1394, 1386, 1372, 1360, 1353, 1345 $cm^{-1}$, and the C–H out-of-plane vibrations observed at 844, 836, 822, 818, 810, 800 and 798, 781 $cm^{-1}$. The computed frequencies are well suited with recorded spectra.

#### *4.2.2. C–C Vibrations*

This type of stretching is observed in the range of 1400–1625 $cm^{-1}$ [31], and its observed at 1752, 1738, 1724, 1715, 1702, 1691, 1653, 1630, 1622, 1609, 1591, 1580, 1573, 1561 $cm^{-1}$ in FT-IR spectra, respectively. This observation leads the affect the ring mode of vibrations. This theoretical comparison is agreed well with the basis sets (Table VII).

#### *4.2.3. N–H Vibrations*

This type of vibrations occurred in the range 3500–3220 $cm^{-1}$, and the locality of sucking up hydrogen bonding, physical state with the polarity of the solvent were used. The N–H stretching makes sharper and $NH_2$ stretching makes weaker vibrations [31]. The band 3201 $cm^{-1}$ is confirmed the N–H stretching vibration the corresponding values is shown in Table VII.

C═O vibrations: The C═O group vibrations happening in the region 1850–1600 $cm^{-1}$ [31]. The C–O

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**Table VII.** The observed (FTIR and FT-Raman) and calculated (unscaled and scaled) fundamental harmonic frequencies ($cm^{-1}$), force constant (mdyn $A^{-1}$), infrared-intensity (km/mol), Raman activity (Å $amu^{-1}$) and probable assignments of N-(4-Chlorobenzoyl)Fenamic acid are analysed based on SQM force field calculation using B3LYP/6-311+G(d, p) and B3LYP/6-311++G(d, p) method and basis set calculations.

| | | | HF/6-311++G(d, p) | | | | | B3LYP/6-311++G(d, p) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Observed frequencies | | Calculated frequency | | | | | Calculated frequency | | | | | |
| Mode no's | FTIR | FT-Raman | Unscaled | Scaled | Force const | IR intensity | Raman activity | Unscaled | Scaled | Force const | IR intensity | Raman activity | Assignments (TED %) |
| 1 | | 3341 (s) | 4122 | 3970 | 10.667 | 179.51 | 85.05 | 3771 | 3343 | 8.920 | 116.90 | 126.47 | νOH (99) |
| 2 | 3201 (s) | – | 3842 | 3775 | 9.3823 | 135.73 | 86.59 | 3477 | 3204 | 7.683 | 154.79 | 194.86 | νNH (98) |
| 3 | 3100 (w) | – | 3437 | 3424 | 7.6131 | 8.58 | 48.68 | 3249 | 3103 | 6.795 | 11.37 | 56.00 | νCH (97) |
| 4 | 3050 (w) | – | 3389 | 3321 | 7.4050 | 2.93 | 104.74 | 3217 | 3049 | 6.668 | 2.66 | 136.89 | νCH (96) |
| 5 | 3005 (w) | – | 3379 | 3320 | 7.3736 | 1.51 | 102.77 | 3209 | 3007 | 6.642 | 3.09 | 158.34 | νCH (95) |
| 6 | 2990 (w) | – | 3369 | 3352 | 7.3332 | 1.31 | 85.25 | 3204 | 2992 | 6.617 | 0.96 | 74.98 | νCH (94) |
| 7 | 2981 (w) | – | 3360 | 3344 | 7.2591 | 0.99 | 67.77 | 3196 | 2984 | 6.551 | 0.38 | 63.53 | νCH (91) |
| 8 | 2972 (w) | – | 3353 | 3323 | 7.2553 | 14.60 | 165.60 | 3192 | 2975 | 6.561 | 11.56 | 206.61 | νCH (89) |
| 9 | 2951 (w) | – | 3350 | 3312 | 7.2089 | 2.42 | 40.62 | 3183 | 2951 | 6.500 | 0.87 | 47.81 | νCH (88) |
| 10 | 2912 (w) | – | 3331 | 3301 | 7.1249 | 7.05 | 75.96 | 3173 | 2914 | 6.456 | 5.50 | 91.84 | νCH (87) |
| 11 | 1810 (s) | – | 2926 | 1798 | 14.007 | 207.43 | 126.74 | 1738 | 1813 | 9.515 | 132.74 | 265.37 | νC═O (76), νCH (24) |
| 12 | 1791 (s) | – | 2921 | 1784 | 22.418 | 710.34 | 43.92 | 1724 | 1790 | 18.16 | 400.67 | 138.15 | νC═O (75), νCH (23) |
| 13 | 1775 (s) | – | 2798 | 1747 | 6.0624 | 280.83 | 39.38 | 1647 | 1774 | 6.896 | 111.64 | 51.52 | νC–O (74), νCH (22) |
| 14 | 1752 (vs) | – | 2785 | 1731 | 9.7989 | 93.51 | 196.49 | 1631 | 1754 | 7.644 | 197.46 | 604.77 | νCC (73), νCH (21) |
| 15 | 1738 (vs) | – | 2774 | 1726 | 6.2577 | 360.03 | 65.35 | 1626 | 1737 | 5.332 | 295.57 | 24.91 | νCC (72), νCH (20) |
| 16 | 1724(vs) | – | 2749 | 1706 | 11.472 | 8.49 | 4.05 | 1606 | 1723 | 10.15 | 7.43 | 32.68 | νCC (71), νCH (29) |
| 17 | 1715 (s) | – | 2712 | 1668 | 4.8311 | 351.95 | 13.86 | 1568 | 1717 | 3.812 | 409.76 | 57.73 | νCC (70), νCH (28) |
| 18 | 1702 (s) | – | 2655 | 1621 | 3.6695 | 100.67 | 0.44 | 1521 | 1704 | 3.095 | 104.07 | 2.41 | νCC (69), νCH (30) |
| 19 | 1691 (s) | – | 2621 | 1590 | 3.6532 | 24.48 | 20.55 | 1490 | 1694 | 3.243 | 19.93 | 67.88 | νCC (68), νCH (31) |
| 20 | 1653 (s) | – | 2597 | 1579 | 3.3727 | 113.18 | 14.49 | 1479 | 1652 | 3.003 | 120.67 | 53.14 | νCC (67), νCH (32) |
| 21 | 1630 (s) | – | 2537 | 1527 | 3.6147 | 11.94 | 2.75 | 1427 | 1631 | 3.369 | 4.52 | 7.01 | νCC (66), νCH (28) |
| 22 | 1622 (s) | – | 2497 | 1481 | 3.6502 | 207.27 | 7.74 | 1381 | 1623 | 3.993 | 123.23 | 9.57 | νCC (65), νCH (33) |
| 23 | 1609 (s) | – | 2444 | 1438 | 1.6912 | 61.38 | 14.91 | 1338 | 1608 | 1.663 | 25.99 | 74.46 | νCC (64), νCH (35) |
| 24 | 1591 (vs) | – | 2429 | 1433 | 2.1955 | 260.93 | 61.73 | 1333 | 1595 | 2.678 | 69.75 | 15.74 | νCC63 (), νC═O (29) |
| 25 | 1580 (vs) | – | 2397 | 1425 | 2.6432 | 294.13 | 75.05 | 1325 | 1583 | 8.500 | 8.00 | 16.02 | νCC (62), νC═O (28) |
| 26 | 1573 (s) | – | 2359 | 1418 | 3.0539 | 30.82 | 6.38 | 1318 | 1576 | 2.251 | 321.10 | 293.51 | νCC (61), νC═O (27) |
| 27 | 1561 (s) | – | 2337 | 1399 | 2.0056 | 153.67 | 46.68 | 1268 | 1563 | 1.918 | 104.01 | 439.48 | νCC (59), bOH (25) |
| 28 | 1481 (vs) | – | 2307 | 1378 | 1.4908 | 186.11 | 2.22 | 1263 | 1484 | 3.075 | 94.87 | 49.83 | bOH (58), bNH (29) |
| 29 | 1462 (s) | – | 2301 | 1356 | 1.2750 | 36.62 | 2.63 | 1212 | 1465 | 1.027 | 11.19 | 7.56 | bNH (57), νCN (37) |
| 30 | 1451 (vs) | – | 1974 | 1802 | 2.6042 | 22.57 | 11.18 | 1202 | 1452 | 1.329 | 221.87 | 34.31 | νCN (56), bCH (43) |
| 31 | 1428 (w) | – | 1958 | 1886 | 1.7084 | 6.84 | 12.47 | 1186 | 1427 | 1.067 | 216.50 | 76.93 | ν CN (55), bCH (40) |
| 32 | 1412(ms) | – | 1915 | 1864 | 2.2472 | 45.21 | 17.00 | 1164 | 1415 | 1.404 | 81.51 | 3.88 | bCH (54), νCN (39) |
| 33 | 1407 (s) | – | 1812 | 1736 | 2.7658 | 352.97 | 17.89 | 1136 | 1409 | 1.048 | 12.70 | 23.08 | bCH (53), $R_1$ symd (35) |
| 34 | 1394 (ms) | – | 1892 | 1721 | 3.1263 | 42.50 | 47.56 | 1121 | 1390 | 2.409 | 140.65 | 0.65 | bCH (52), $R_2$ symd (34) |
| 35 | 1386 (vs) | – | 1883 | 1701 | 1.7831 | 1.54 | 0.63 | 1101 | 1385 | 2.565 | 58.38 | 96.54 | bCH (51), $R_1$ asymd (37) |
| 36 | 1372 (s) | – | 1866 | 1682 | 3.7775 | 0.38 | 11.92 | 1082 | 1376 | 3.528 | 65.60 | 5.36 | bCH (50), $R_2$ asymd (38) |
| 37 | 1360 (ms) | – | 1841 | 1669 | 2.0979 | 19.61 | 51.51 | 1069 | 1364 | 1.674 | 8.77 | 55.53 | bCH (49), $R_1$ trigd (44) |
| 38 | 1353 (w) | – | 1825 | 1629 | 0.9935 | 1.59 | 0.27 | 1029 | 1355 | 2.333 | 48.90 | 7.53 | bCH (47), $R_2$ trigd (43) |
| 39 | 1345 (w) | – | 1809 | 1618 | 0.9907 | 1.59 | 0.05 | 1018 | 1347 | 0.804 | 1.22 | 0.21 | bCH (48) |
| 40 | 1101 (s) | – | 1704 | 1590 | 2.5371 | 38.05 | 1.35 | 999 | 1104 | 0.795 | 1.07 | 0.32 | νCCl (67) |
| 41 | 1095 (s) | – | 1700 | 1567 | 0.9748 | 0.93 | 0.19 | 987 | 1097 | 0.782 | 1.18 | 0.17 | $R_1$ symd (44), bCH (39) |
| 42 | 1086 (w) | – | 1683 | 1456 | 0.9669 | 0.14 | 1.33 | 972 | 1089 | 0.753 | 0.32 | 1.17 | $R_2$ symd (45), bCH (42) |
| 43 | 1071 (w) | – | 1005 | 999 | 0.8428 | 9.46 | 0.28 | 907 | 1074 | 3.307 | 41.14 | 24.37 | $R_1$ asymd (43), bCH (41) |
| 44 | 1066 (s) | – | 990 | 984 | 3.6466 | 35.37 | 25.26 | 904 | 1069 | 0.689 | 4.03 | 0.15 | $R_2$ asymd (50), bCH (44) |
| 45 | 1052 (ms) | – | 987 | 964 | 0.9781 | 26.08 | 0.99 | 864 | 1053 | 1.013 | 18.54 | 3.84 | $R_1$ trigd (51), bCH (29) |
| 46 | 1044 (w) | – | 975 | 950 | 0.6685 | 1.40 | 0.54 | 856 | 1047 | 1.269 | 11.72 | 0.80 | $R_2$ trigd (42), bCH (32) |
| 47 | 996 (w) | – | 961 | 943 | 2.4708 | 7.40 | 1.48 | 839 | 994 | 0.548 | 8.10 | 0.50 | bC═O (44), ωCH (35) |
| 48 | 981 (w) | – | 956 | 899 | 1.9770 | 9.02 | 1.17 | 816 | 980 | 1.293 | 1.69 | 0.66 | bC═O (46), ωCH (39) |
| 49 | 940 (w) | – | 945 | 865 | 1.0341 | 145.39 | 3.08 | 774 | 943 | 0.586 | 119.94 | 2.32 | ωOH (47), ωCH (44) |
| 50 | 893 (w) | – | 935 | 845 | 0.7643 | 21.79 | 0.60 | 773 | 895 | 1.734 | 19.73 | 6.74 | bC–O (52), ωCH (43) |
| 51 | 876 (w) | – | 931 | 834 | 1.9905 | 32.96 | 2.82 | 766 | 878 | 0.656 | 4.40 | 0.58 | bCC (59), ωCH (41) |
| 52 | 862 (w) | – | 892 | 823 | 1.6782 | 15.80 | 27.63 | 762 | 864 | 0.564 | 17.90 | 4.59 | bCC (60), ωCH (40) |
| 53 | 844 (w) | – | 890 | 813 | 1.5653 | 22.85 | 6.74 | 732 | 847 | 1.659 | 4.38 | 33.08 | ωCH (58), bC═O (33) |
| 54 | 836 (w) | – | 867 | 809 | 1.0457 | 0.61 | 1.79 | 721 | 839 | 1.203 | 28.37 | 0.65 | ωCH (69), bC═O (32) |
| 55 | 822 (w) | – | 847 | 789 | 0.4294 | 51.26 | 0.91 | 696 | 825 | 1.164 | 15.84 | 0.55 | ωCH (57), bC═O (31) |

**Table VII.** Continued.

| | | | HF/6-311++G(d, p) | | | | | B3LYP/6-311++G(d, p) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Observed frequencies | | Calculated frequency | | | | | Calculated frequency | | | | | |
| Mode no's | FTIR | FT-raman | Unscaled | Scaled | Force const | IR intensity | Raman activity | Unscaled | Scaled | Force const | IR intensity | Raman activity | Assignments (TED %) |
| 56 | 818 (w) | – | 805 | 767 | 1.6070 | 66.44 | 0.30 | 652 | 819 | 1.348 | 49.47 | 0.64 | $\omega$CH (76), $\omega$OH (24) |
| 57 | 810(w) | – | 788 | 745 | 1.8961 | 5.58 | 6.95 | 643 | 815 | 1.704 | 6.30 | 7.14 | $\omega$CH (65), $\omega$NH (36) |
| 58 | 800 (w) | – | 748 | 734 | 1.6570 | 1.98 | 10.49 | 606 | 803 | 1.483 | 2.87 | 12.11 | $\omega$CH (54), bCCN (37) |
| 59 | – | 798 (ms) | 708 | 703 | 0.2703 | 102.28 | 1.39 | 566 | 797 | 0.226 | 82.20 | 1.84 | $\omega$CH (33), bCCN (39) |
| 60 | – | 781 (w) | 690 | 667 | 0.6768 | 7.07 | 0.09 | 544 | 785 | 1.108 | 11.30 | 0.05 | $\omega$CH (54), $\omega$C═O (48) |
| 61 | 776 (w) | – | 687 | 656 | 0.9671 | 9.61 | 0.17 | 540 | 777 | 0.567 | 6.77 | 0.16 | $\omega$NH (55), $\omega$C═O (33) |
| 62 | 758 (w) | – | 662 | 645 | 1.1272 | 16.66 | 0.13 | 521 | 759 | 1.108 | 23.65 | 0.55 | bCCN (50), $\omega$C–O (32) |
| 63 | 749 (w) | – | 631 | 623 | 0.6610 | 19.41 | 0.28 | 485 | 745 | 0.491 | 11.36 | 0.36 | bCCN (59) $\omega$C–C (21) |
| 64 | 739(w) | – | 570 | 534 | 0.9198 | 6.65 | 1.82 | 442 | 737 | 0.857 | 7.23 | 2.98 | t$R_1$ symd (68), bCCN (20) |
| 65 | – | 721 (w) | 567 | 522 | 0.3914 | 11.60 | 0.29 | 427 | 726 | 0.323 | 10.40 | 0.38 | t$R_2$ symd (67), bCCN (28) |
| 66 | 714 (w) | – | 545 | 512 | 0.3573 | 0.27 | 0.15 | 417 | 718 | 0.301 | 0.24 | 0.19 | t$R_1$ symd (61), $\omega$C–C (22) |
| 67 | 703 (w) | – | 517 | 509 | 0.9086 | 3.08 | 4.30 | 393 | 705 | 0.791 | 5.12 | 4.41 | t$R_2$ symd (55), $\omega$C–C (42) |
| 68 | 694 (w) | – | 466 | 454 | 0.7356 | 3.87 | 0.87 | 341 | 697 | 0.685 | 1.56 | 0.62 | t$R_1$ trigd (54), $\omega$CCN (39) |
| 69 | 681 (w) | – | 446 | 423 | 0.4642 | 0.28 | 2.03 | 322 | 683 | 0.395 | 1.43 | 4.34 | t$R_2$ trigd (63), bCCl (20) |
| 70 | 474 (w) | – | 421 | 409 | 0.4048 | 0.92 | 1.02 | 295 | 472 | 0.332 | 0.43 | 0.63 | $\omega$C═O (53), t$R_1$ symd (32) |
| 71 | 460 (w) | – | 390 | 382 | 0.3632 | 0.58 | 0.30 | 272 | 464 | 0.323 | 0.12 | 0.37 | $\omega$C═O (41), t$R_2$ symd (31) |
| 72 | 452 (w) | – | 368 | 356 | 0.2452 | 3.28 | 2.44 | 245 | 453 | 0.205 | 2.64 | 2.43 | $\omega$C–O (42), t$R_1$ asymd (30) |
| 73 | 432 (w) | – | 315 | 309 | 0.2205 | 1.45 | 2.01 | 202 | 430 | 0.194 | 1.18 | 1.12 | $\omega$C–C (60), t$R_2$ asymd (29) |
| 74 | 425 (vw) | – | 294 | 278 | 0.1894 | 8.36 | 0.62 | 181 | 426 | 0.165 | 9.22 | 0.48 | $\omega$C–C (50), $\omega$CCN (39) |
| 75 | – | 258 (w) | 253 | 245 | 0.0726 | 0.58 | 1.70 | 140 | 259 | 0.064 | 0.33 | 1.64 | bCCl (65) |
| 76 | 238 (w) | – | 208 | 154 | 0.0523 | 2.40 | 1.90 | 97 | 236 | 0.043 | 2.99 | 0.37 | $\omega$CCN (45), $\omega$CCl (40) |
| 77 | 221 (w) | – | 105 | 99 | 0.0411 | 3.70 | 0.33 | 97 | 224 | 0.040 | 1.65 | 2.02 | $\omega$CCN (55) |
| 78 | 176 (vw) | 177 (vw) | 88 | 83 | 0.0224 | 0.25 | 0.40 | 63 | 177 | 0.021 | 0.39 | 0.39 | $\omega$CCl (68) |
| 79 | 163 (vw) | 164 (vw) | 75 | 72 | 0.0047 | 0.55 | 0.65 | 30 | 165 | 0.034 | 0.57 | 0.76 | Butterfly (65) |
| 80 | 114 (w) | – | 67 | 60 | 0.0013 | 0.24 | 1.84 | 15 | 113 | 0.012 | 0.06 | 2.72 | Butterfly (70) |

*Abbreviations:* $\nu$—Stretching; b—In-plane bending; $\omega$—Out-of-plane bending; asymd—Asymmetric; symd—Symmetric; t—Torsion; trig—Trigonal; w—Weak; vw—Very week; vs—Very strong; s—Strong; ms—Medium strong.

stretching of NCF are occurred at 1810, 1791, 1775 $cm^{-1}$ are confirmed by their TED values (Table VII).

#### *4.2.4. C–N Vibrations*

This type of stretching is generally occurred in the range of wavelength 1400–1200 $cm^{-1}$. These types of vibrations in NCF are found at 1451, 1428 $cm^{-1}$, and the bending vibrations and the changes are well match with standard values [31].

#### *4.2.5. HOMO–LUMO*

The HOMO–LUMO analysis has been carried out and the values are presented in Table VIII, corresponding energy and the used electric field ($\pm$0.02, $\pm$0.04 V$Å^{-1}$) are shown in Figure 5. The most relevant parameters $I_P$, $E_A$, $\mu$, $\chi$, $\eta$, S, $\omega$ and $\alpha$ were computed [32]. The energy values of HOMO and LUMO through Koopmans' theorem with DFT [33–35] with B3LYP functions used to calculate the above said parameters.

#### *4.2.6. Natural Bond Orbital Analysis*

This NBO method is extracted from HF and DFT methods. The values of NCF computed through NBO analysis by the application of basis sets B3LYP/6-31++G(d, p) are given in Table IX. The both carbon C10 and C19 for NCF possess same negative charges at the same time N6 has highly negative charge because of resonance for NCF. In Table X, the natural atomic orbitals with its positions with respective energy of NCF are given and interpreted. The molecular nature of NABOs gives the chemical nature, of electronic interactions, with changes in shape/size. The NAOs energies are computed through Kohn-Sham operator ($F$) from the following expression.

$$\varepsilon_i^{(A)} = \langle \theta_i^{(A)} | F | \theta_i^{(A)*} \rangle$$

The NAOs gives fingerprint information about the molecules by inter atomic and intra-atomic interactions benefactions. The bonding, bond orbitals with positions of NBO are given in Table XI of NCF molecule determined basis set B3LYP/6-31++G(d, p) are depicted in Figure 6. The positions of NBOs in NCF give chemical environment, spatial symmetry and etc., The Lewis and optimized structure parameters shown in Table XI.

For NCF, there is no availability of anti-bonding orbitals, the bonding orbital for N6–C8 with 0.98945 (61.35%) N6 character in a *sp* 2.27hybrid (38.65%) C8—in a *sp* 2.89 hybrid orbital of NCF. The orbital O3–C8

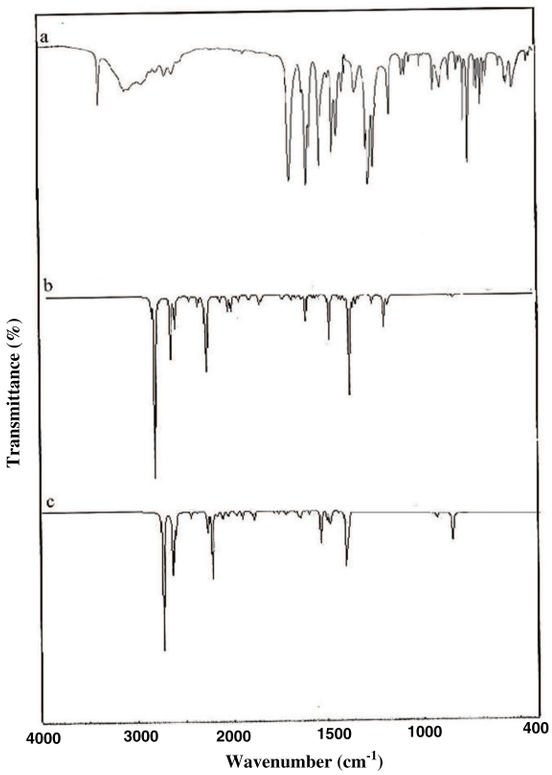


**Fig. 3.** Comparison of observed and calculated IR spectra of *N*-(4-Cholorobenzoyl)Fenamic acid (a) observed in solid phase (b) calculated with HF/6-311+G(d, p) and (c) calculated with B3LYP/6-311++G(d, p).

with 0.99453 (67.80%) O3 character in a *sp* 7.88 hybrid (32.20%) for NCF.

### *4.2.7. Donor Acceptor Interactions*

The interactions either can be strengthen/weaken bonds. The donor and acceptor interaction is responsible for the formation of Lewis structure by delocalization electron (Table XII). The computation from donor (filled) and the acceptor (empty) with help of perturbation of second order.

The NBO method demonstrates the bonding concepts parameters. The orbital interaction is similar trend with the energy difference. So, the strong interactions happens only effective donors with effective acceptors. The interaction between the bonding and anti-bonding explained through NBO represented with 2nd order perturbation energy [36].

$$E^{(2)} = DE_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

where, all the notations having the usual meaning. In the donor orbital, $\sigma$CC $\rightarrow$ $\sigma^*$CC interaction of C8–C16, antiperiplanar C8–C9 orbital give 12.71 kJ mol$^{-1}$ for NCF. The donor orbital, $\pi$CC $\rightarrow$ $\pi^*$CC interaction of C20–C2, antiperiplanar C26–C28 orbital gives 20.22 kJ mol$^{-1}$ for NCF. The 252 donor orbital, $n$Cl $\rightarrow$ $\pi^*$CC interaction of Cl1 carbon lone pair and the antiperiplanar C23–C25, orbital give 16.50 kJ mol$^{-1}$ for NCF. The

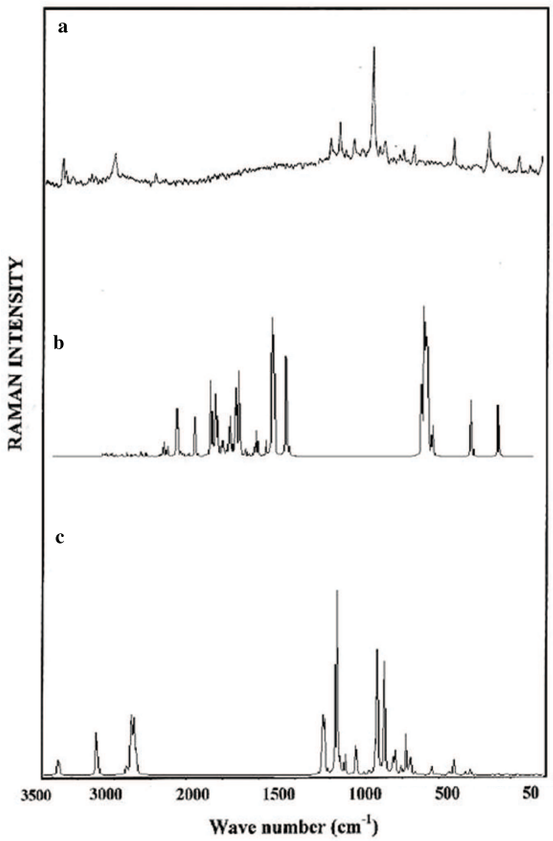


**Fig. 4.** Comparison of observed and calculated Raman spectra of *N*-(4-Cholorobenzoyl)Fenamic acid observed in solid phase (b) calculated with HF/6-311+G(d, p) and (c) calculated with B3LYP/6-311++G(d, p).

donor orbital, $n$N $\rightarrow$ $\sigma^*$OC interaction of N6, antiperiplanar O5–C19 orbital gives 13.04 kJ mol$^{-1}$ for NCF (Figs. 6 and 7).

### *4.2.8. Molecular Electrostatic Potentials (MEPS)*

The nucleophilic and electrophilic interaction is identified through Molecular electrostatic potentials with hydrogen bonding [37]. $V(r)$—the interaction energy between electron charge and the proton at position $r$. So, this physical quantity $V(r)$ found through experiment and compu-

**Table VIII.** HOMO–LUMO energy gap and related molecular properties of N-(4-Chlorobenzoyl)Fenamic acid.

| Molecular properties | HF/6-311++G (d, p) | B3LYP/6-311++G (d, p) |
|---|---|---|
| HOMO | −0.3204 a.u | −0.2626 a.u |
| LUMO | −0.0743 a.u. | −0.0942 a.u. |
| Energy gap | 0.2461 a.u. | 0.1683 a.u. |
| Ionisation Potential (I) | 0.3204 a.u. | 0.26261 a.u. |
| Electron affinity (A) | 0.0743 a.u. | 0.9425 a.u. |
| Global softness (s) | 8.1267 a.u. | 11.8793 a.u. |
| Global Hardness ($\eta$) | 0.1230 a.u. | 0.0841 a.u. |
| Electro negativity ($\chi$) | 0.1973 a.u. | 0.1784 a.u. |
| Global Electrophilicity ($\omega$) | 1.5821 a.u. | 1.0598 a.u. |



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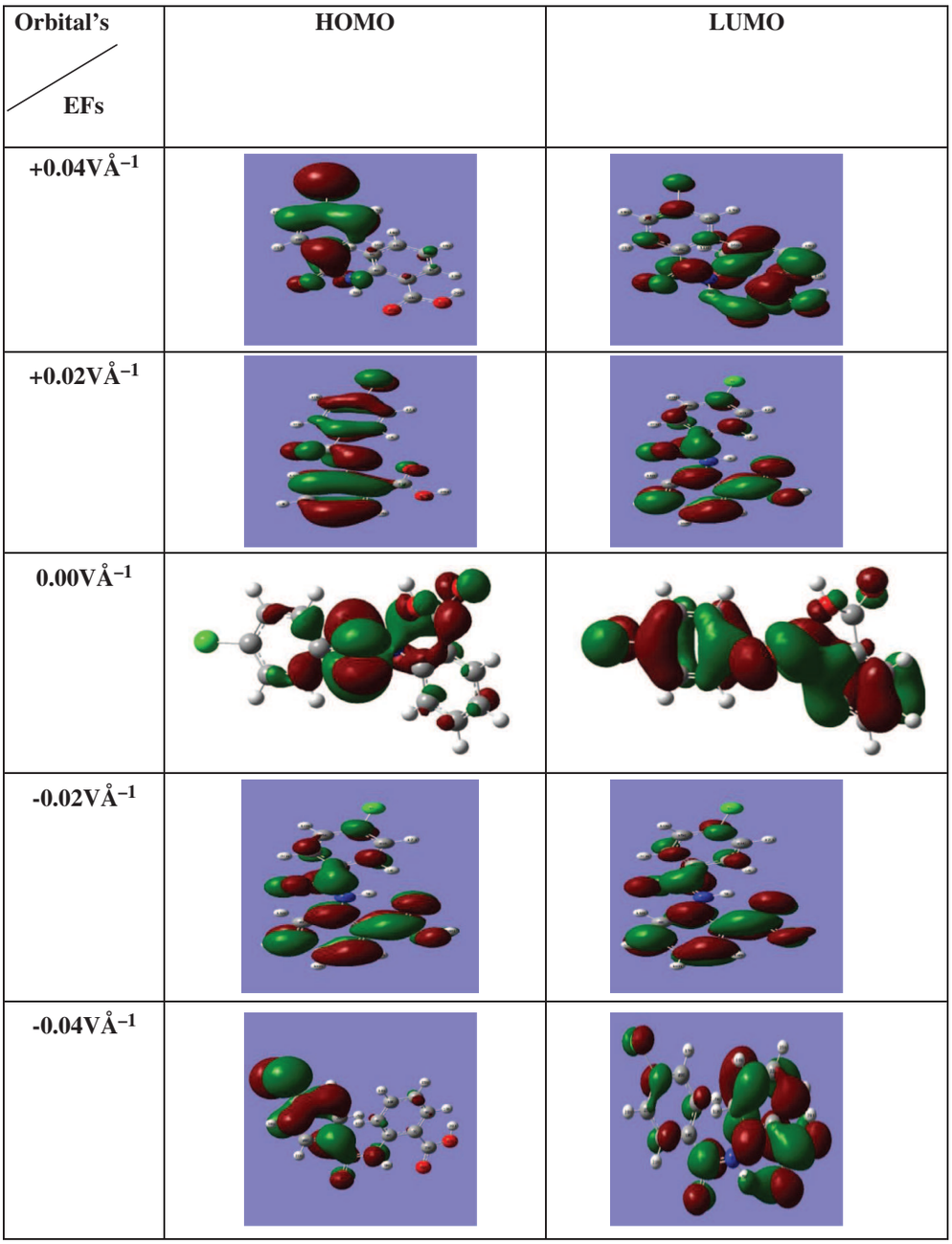


**Fig. 5.** Frontier orbital energy of *N*-(4-Cholorobenzoyl)Fenamic acid.

tations (MEP).

$$V(r) = \sum Z_A / \mid R_A - r \mid - \int \rho(r') / \mid r' - r \mid dr'$$

Where, the notations having the usual meaning.

In order to found nucleophilic and electophilic attack through MEP was computed through the basis sets B3LYP/6-31++G(d, p), and the electron rich, medium and poor regions are depicted in the Figure 8. The electron density in the isosurface is 0.002 a.u. The $V(r)$ values are negative refer nucleophilic and it is connected with chlorine and oxygen atoms of NCF, very high negative value indicate the existence of carbon atoms in the ring of NCF, rather than positive indicates the electrophilic nature. So, there is a chance for many reactions of several $V(r)$ values is shown in Figures 9 and 10.

The thermodynamic properties such as Cp, Cv, S, U, G and H for the compounds NCF were obtained through sets B3LYP/6-311++G(d, p) method and were presented in Table XIII. And the Figure 11 shows the association of Cp,

**Table IX.** Calculated atomic charges of N-(4-Chlorobenzoyl)Fenamic acid by natural bond orbital (NBO) analysis by B3LYP/6-311++G(d, p) method.

| Atom No. | Charge | Core | Valence | Rydberg | Total |
|---|---|---|---|---|---|
| Cl1 | 0.00190 | 4.99985 | 3.49429 | 0.00397 | 8.49810 |
| O2 | −0.33975 | 0.99988 | 3.33729 | 0.00258 | 4.33975 |
| O3 | −0.28273 | 0.99995 | 3.28139 | 0.00139 | 4.28273 |
| H4 | 0.24354 | 0.00000 | 0.25526 | 0.00120 | 0.25646 |
| O5 | −0.28949 | 0.99995 | 3.28826 | 0.00128 | 4.28949 |
| N6 | −0.30895 | 0.99965 | 2.80447 | 0.00483 | 3.80895 |
| H7 | 0.19027 | 0.00000 | 0.30845 | 0.00128 | 0.30973 |
| C8 | 0.08159 | 0.99940 | 1.91143 | 0.00759 | 2.91841 |
| C9 | −0.07196 | 0.99938 | 2.06461 | 0.00796 | 3.07196 |
| C10 | −0.08570 | 0.99953 | 2.08002 | 0.00615 | 3.08570 |
| H11 | 0.10860 | 0.00000 | 0.39044 | 0.00096 | 0.39140 |
| C12 | −0.09046 | 0.99959 | 2.08474 | 0.00614 | 3.09046 |
| H13 | 0.10429 | 0.00000 | 0.39510 | 0.00061 | 0.39571 |
| C14 | −0.09011 | 0.99958 | 2.08437 | 0.00615 | 3.09011 |
| H15 | 0.10445 | 0.00000 | 0.39463 | 0.00091 | 0.39555 |
| C16 | −0.09118 | 0.99953 | 2.08553 | 0.00612 | 3.09118 |
| H17 | 0.11351 | 0.00000 | 0.38520 | 0.00129 | 0.38649 |
| C18 | 0.38867 | 0.99967 | 1.59567 | 0.01599 | 2.61133 |
| C19 | 0.32665 | 0.99962 | 1.65845 | 0.01528 | 2.67335 |
| C20 | −0.06620 | 0.99944 | 2.05947 | 0.00729 | 3.06620 |
| C21 | −0.08766 | 0.99952 | 2.08215 | 0.00599 | 3.08766 |
| H22 | 0.10676 | 0.00000 | 0.39218 | 0.00107 | 0.39324 |
| C23 | −0.10537 | 0.99950 | 2.09829 | 0.00759 | 3.10537 |
| H24 | 0.11145 | 0.00000 | 0.38738 | 0.00117 | 0.38855 |
| C25 | −0.01240 | 0.99931 | 2.00421 | 0.00888 | 3.01240 |
| C26 | −0.10428 | 0.99950 | 2.09731 | 0.00748 | 3.10428 |
| H27 | 0.11194 | 0.00000 | 0.38690 | 0.00116 | 0.38806 |
| C28 | −0.07940 | 0.99952 | 2.07377 | 0.00610 | 3.07940 |
| H29 | 0.11202 | 0.00000 | 0.38704 | 0.00093 | 0.38798 |

**Table X.** The atomic orbital occupancies of N-(4-Chlorobenzoyl)Fenamic acid.

| Atom No. | Atomic orbital | Type | Occupancy | Energy |
|---|---|---|---|---|
| Cl1 | 1*s* | Core | 1.00000 | 100.26798 |
| | 2S | Core | 0.99989 | 10.44957 |
| | 3*s* | Valence | 0.92229 | 1.04466 |
| | $2p_x$ | Core | 0.99996 | 7.24887 |
| | $3p_x$ | Valence | 0.64292 | 0.29877 |
| | $2p_y$ | Core | 1.00000 | 7.23946 |
| | $3p_y$ | Valence | 0.97007 | 0.33718 |
| | $2p_z$ | Core | 1.00000 | 7.23976 |
| | $3p_z$ | Valence | 0.95901 | 0.33589 |
| O2 | 1*s* | Core | 0.99988 | 18.99391 |
| | 2*s* | Valence | 0.85486 | 0.98207 |
| | $2p_x$ | | 0.88258 | 0.35474 |
| | $2p_y$ | | 0.77033 | 0.34801 |
| | $2p_z$ | | 0.82951 | 0.37481 |
| O3 | 1*s* | Core | 0.99925 | −10.14082 |
| | 2*s* | Valence | 0.47942 | −0.26739 |
| | $2p_x$ | | 0.50015 | −0.17565 |
| | $2p_y$ | | 0.53112 | −0.13400 |
| | $2p_z$ | | 0.54289 | −0.17418 |
| H4 | 1*s* | 0.25526 | 0.05942 | |
| O5 | 1*s* | Core | 0.99995 | 18.91139 |
| | 2*s* | Valence | 0.90872 | 0.93627 |
| | $2p_x$ | | 0.59125 | −0.10523 |
| | $2p_y$ | | 0.54782 | −0.09490 |
| | $2p_z$ | | 0.50081 | −0.14384 |
| N6 | 1*s* | Core | 0.99930 | −10.15001 |
| | 2*s* | Valence | 0.47024 | −0.26109 |
| | $2p_x$ | | 0.54358 | −0.10588 |
| | $2p_y$ | | 0.46447 | −0.17872 |
| | $2p_z$ | | 0.53570 | −0.16876 |
| H7 | 1*s* | 0.30845 | 0.03874 | |
| C8 | 1*s* | Core | 0.99942 | −10.07650 |
| | 2*s* | Valence | 0.47989 | −0.21222 |
| | $2p_x$ | | 0.59253 | −0.10361 |
| | $2p_y$ | | 0.54662 | −0.09270 |
| | $2p_z$ | | 0.49831 | −0.14200 |
| C9 | 1*s* | Core | 0.99925 | −10.13773 |
| | 2*s* | Valence | 0.47974 | −0.26322 |
| | $2p_x$ | | 0.50441 | −0.16927 |
| | $2p_y$ | | 0.52918 | −0.12804 |
| | $2p_z$ | | 0.53417 | −0.16828 |
| C10 | 1*s* | Core | 0.99981 | −14.19507 |
| | 2*s* | Valence | 0.70664 | −0.58062 |
| | $2p_x$ | | 0.85110 | −0.24053 |
| | $2p_y$ | | 0.63738 | −0.20406 |
| | $2p_z$ | | 0.74154 | −0.21898 |
| H8 | 1*s* | | 0.29190 | 0.13661 |
| H9 | 1*s* | | 0.29370 | 0.13965 |
| C10 | 1*s* | Core | 1.00000 | −476.35301 |
| | 2*s* | Valence | 0.99996 | −61.65895 |
| | $2p_x$ | | 0.99998 | −55.46011 |
| | $2p_x$ | | 0.99994 | −7.53218 |
| | $2p_y$ | | 0.66108 | 0.28076 |
| | $2p_z$ | | 0.99999 | −55.45820 |
| H11 | 1*s* | Valence | 0.39044 | 0.04317 |
| Cl12 | 1*s* | Core | 1.00000 | −100.17221 |
| | 2*s* | Valence | 0.99989 | −10.57899 |
| | $2p_x$ | | 0.99999 | −1.01104 |
| | $2p_y$ | | 0.99995 | −7.24518 |
| | $2p_z$ | | 1.00000 | −7.23720 |
| H13 | 1*s* | Valence | 0.39510 | 0.04377 |
| C14 | 1*s* | Core | 1.00000 | −476.34441 |
| | 2*s* | Valence | 0.99996 | −61.66163 |
| | $2p_x$ | | 0.99998 | −55.44435 |
| | $2p_y$ | | 0.99994 | −7.51947 |
| | $2p_z$ | | 0.65868 | −0.26512 |
| H15 | 1*s* | Valence | 0.39463 | 0.04346 |
| C16 | 1*s* | Core | 0.99953 | 10.05866 |
| | 2*s* | Valence | 0.47120 | 0.17896 |
| | $2p_x$ | | 0.58561 | 0.08237 |
| | $2p_y$ | | 0.54500 | 0.07649 |
| | $2p_z$ | | 0.48373 | 0.12866 |
| H17 | 1*s* | Valence | 0.38520 | 0.05077 |
| C18 | 1*s* | Core | 0.99967 | 10.27251 |
| | 2*s* | Valence | 0.44444 | 0.30013 |
| | $2p_x$ | | 0.37973 | 0.17836 |
| | $2p_y$ | | 0.43698 | 0.10897 |
| | $2p_z$ | | 0.33453 | 0.08808 |
| C19 | 1*s* | Core | 0.99962 | 10.23767 |
| | 2*s* | Valence | 0.44171 | 0.28016 |
| | $2p_x$ | | 0.45236 | 0.09293 |
| | $2p_y$ | | 0.38165 | 0.13140 |
| | $2p_z$ | | 0.38273 | 0.12986 |
| C20 | 1*s* | Core | 0.99944 | 10.09975 |
| | 2*s* | Valence | 0.44514 | 0.18738 |
| | $2p_x$ | | 0.54173 | −0.12776 |
| | $2p_y$ | | 0.53748 | −0.12715 |
| | $2p_z$ | | 0.53512 | −0.12917 |

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**Table X.** Continued.

| Atom No. | Atomic orbital | Type | Occupancy | Energy |
|---|---|---|---|---|
| C21 | 1*s* | Core | 0.99952 | 10.07895 |
| | 2*s* | Valence | 0.46828 | −0.19252 |
| | $2p_x$ | | 0.54507 | −0.09596 |
| | $2p_y$ | | 0.54172 | −0.11929 |
| | $2p_z$ | | 0.52708 | −0.12076 |
| H22 | 1*s* | Valence | 0.39218 | 0.02465 |
| C23 | 1*s* | Core | 0.99950 | 10.07511 |
| | 2*s* | Valence | 0.47196 | −0.19654 |
| | $2p_x$ | | 0.54230 | −0.09748 |
| | $2p_y$ | | 0.53847 | −0.12449 |
| | $2p_z$ | | 0.54556 | −0.12488 |
| H24 | 1*s* | Valence | 0.38738 | 0.03138 |
| C25 | 1*s* | Core | 0.99931 | −10.15040 |
| | 2*s* | Valence | 0.46449 | −0.25034 |
| | $2p_x$ | | 0.46131 | −0.19285 |
| | $2p_y$ | | 0.54067 | −0.14637 |
| | $2p_z$ | | 0.53774 | −0.15090 |
| C26 | 1*s* | Core | 0.99950 | −10.07376 |
| | 2*s* | Valence | 0.47271 | −0.19576 |
| | $2p_x$ | | 0.54861 | −0.09522 |
| | $2p_y$ | | 0.54600 | −0.12217 |
| | $2p_z$ | | 0.52999 | −0.12425 |
| H27 | 1*s* | Valence | 0.38690 | 0.03417 |
| C28 | 1*s* | Core | 0.99952 | −10.07546 |
| | 2*s* | Valence | 0.46941 | −0.18905 |
| | $2p_x$ | | 0.53622 | −0.08891 |
| | $2p_y$ | | 0.53064 | −0.11424 |
| | $2p_z$ | | 0.53751 | −0.11695 |
| H29 | 1*s* | Valence | 0.38704 | 0.03859 |

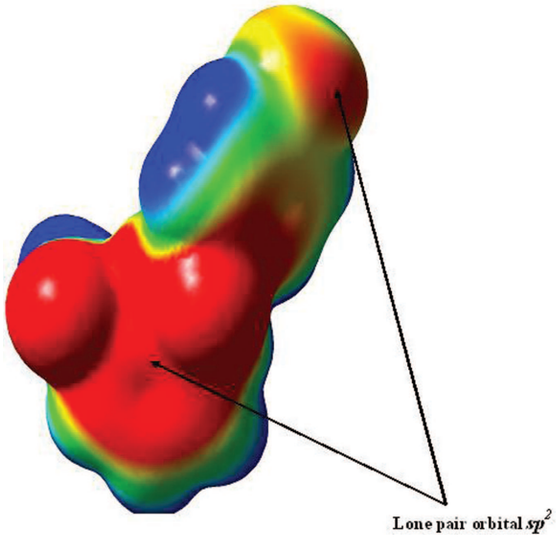


**Fig. 6.** The lone pair structure of ($sp^2$) for *N*-(4-Cholorobenzoyl)Fenamic acid.

G, S with temperature through B3LYP/6-311++G(d, p) sets. Table XIV shows that all the thermodynamical quantities are increasing trend with respect to temperature from 10 to 500 K, this due to the vibrational intensities increases with temperature [37]. The regression factors ($R_2$) versus

**Table XI.** Bond orbital analysis of *N*-(4-Cholorobenzoyl)Fenamic acid by B3LYP/6-311++G(d, p) method.

| Bond orbital | Occupancy | Atom | Contribution from parent NBO (%) | Coefficients | Atom hybrid contributions (%) |
|---|---|---|---|---|---|
| Cl1–C25 | 0.99299 | Cl1 | 54.93 | 0.7411 | s(16.78) + p4.96(83.22) |
| | | C25 | 45.07 | 0.6714 | s(22.55) + p3.44(77.45) |
| O3–C8 | 0.99453 | O3 | 67.80 | 0.8234 | s(1.13) + p7.88(98.87) |
| | | C8 | 32.20 | 0.5674 | s(1.60) + p6.69(98.40) |
| O5–C9 | 0.99135 | O5 | 68.41 | 0.8271 | s(1.52) + p64.95(98.48) |
| | | C9 | 31.59 | 0.5620 | s(1.85) + p53.16(98.15) |
| N6–C8 | 0.98945 | N6 | 61.35 | 0.7833 | s(30.57) + p2.27(69.43) |
| | | C8 | 38.65 | 0.6217 | s(25.69) + p2.89(74.31) |
| N6–C19 | 0.99254 | N6 | 62.31 | 0.7894 | s(29.00) + p2.45(71.00) |
| | | C19 | 37.69 | 0.6139 | s(30.89) + p2.24(69.11) |
| C8–C16 | 0.98684 | C8 | 50.96 | 0.7139 | s(37.51) + p1.67(62.49) |
| | | C16 | 49.04 | 0.7003 | s(34.99) + p1.86(65.01) |
| C9–C10 | 0.98316 | C9 | 51.67 | 0.7188 | s(36.27) + p1.76(63.73) |
| | | C10 | 48.33 | 0.6952 | s(35.29) + p1.83(64.71) |
| C9–C18 | 0.98896 | C9 | 51.56 | 0.7180 | s(27.21) + p2.68(72.79) |
| | | C18 | 48.44 | 0.6960 | s(41.85) + p1.39(58.15) |
| C10–C12 | 0.98831 | C10 | 50.48 | 0.7105 | s(35.85) + p1.79(64.15) |
| | | C12 | 49.52 | 0.7037 | s(35.48) + p1.82(64.52) |
| C12–C14 | 0.99023 | C12 | 49.98 | 0.7069 | s(35.67) + p1.80(64.33) |
| | | C14 | 50.02 | 0.7073 | s(35.54) + p1.81(64.46) |
| C14–C16 | 0.98767 | C14 | 49.46 | 0.7033 | s(35.66) + p1.80(64.34) |
| | | C16 | 50.54 | 0.7109 | s(35.85) + p1.79(64.15) |
| C19–C20 | 0.98749 | C19 | 48.55 | 0.6968 | s(38.47) + p1.60(61.53) |
| | | C20 | 51.45 | 0.7173 | s(28.65) + p2.49(71.35) |
| C20–C21 | 0.98473 | C20 | 50.96 | 0.7139 | s(35.65) + p1.81(64.35) |
| | | C21 | 49.04 | 0.7003 | s(35.63) + p1.81(64.37) |
| C20–C28 | 0.98456 | C20 | 51.14 | 0.7151 | s(35.69) + p1.80(64.31) |
| | | C28 | 48.86 | 0.6990 | s(35.60) + p1.81(64.40) |

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**Table XI.** Continued.

| Bond orbital | Occupancy | Atom | Contribution from parent NBO (%) | Coefficients | Atom hybrid contributions (%) |
|---|---|---|---|---|---|
| C21–C23 | 0.98388 | C21 | 49.94 | 0.7067 | s(35.58) + p1.81(64.42) |
| | | C23 | 50.06 | 0.7075 | s(35.82) + p1.79(64.18) |
| C23–C25 | 0.99056 | C23 | 49.66 | 0.7047 | s(35.66) + p1.80(64.34) |
| | | C25 | 50.34 | 0.7095 | s(38.66) + p1.59(61.34) |
| C25–C26 | 0.99064 | C25 | 50.42 | 0.7101 | s(38.72) + p1.58(61.28) |
| | | C26 | 49.58 | 0.7041 | s(35.58) + p1.81(64.42) |
| C26–C28 | 0.98401 | C26 | 50.19 | 0.7085 | s(35.85) + p1.79(64.15) |
| | | C28 | 49.81 | 0.7057 | s(35.38) + p1.83(64.62) |
| Cl1–C25 | 0.01722 | Cl1 | 45.07 | 0.6714 | s(16.78) + p4.96(83.22) |
| | | C25 | 54.93 | −0.7411 | s(22.55) + p3.44(77.45) |

**Table XII.** Second order perturbation theory analysis of Fock matrix of N(4-Chlorobenzoyl)Fenamic acid by NBO method.

| Donor (i) → Acceptor (j) | $E^{(2)a}$ (kJ mol$^{-1}$) | E(j)–E(i)$^b$ (a.u.) | F(I, j)$^c$ (a.u.) |
|---|---|---|---|
| $\pi$C8–C9 → $\pi^*$C10–C12 | 9.65 | 0.29 | 0.067 |
| $\pi$C8–C9 → $\pi^*$C14–C16 | 9.64 | 0.30 | 0.068 |
| $\sigma$C8–C16 → $\sigma^*$C8–C9 | 12.71 | 1.26 | 0.074 |
| $\pi$C10–C12 → $\pi^*$C8–C9 | 11.11 | 0.27 | 0.070 |
| $\pi$C10–C12 → $\pi^*$C14–C16 | 9.88 | 0.28 | 0.067 |
| $\pi$C14–C16 → $\pi^*$C8–C9 | 11.11 | 0.27 | 0.070 |
| $\pi$C14–C16 → $\pi^*$C10–C12 | 10.34 | 0.27 | 0.068 |
| $\pi$C20–C21 → $\pi^*$C23–C25 | 10.62 | 0.27 | 0.068 |
| $\pi$C20–C21 → $\pi^*$C26–C28 | 20.22 | 0.28 | 0.068 |
| $\pi$C23–C25 → $\pi^*$C20–C21 | 9.33 | 0.29 | 0.066 |
| $\pi$C23–C25 → $\pi^*$C26–C28 | 9.81 | 0.29 | 0.068 |
| $\pi$C26–C28 → $\pi^*$C20–C21 | 10.68 | 0.27 | 0.068 |
| $\pi$C26–C28 → $\pi^*$C23–C25 | 10.72 | 0.26 | 0.067 |
| $n_3$Cl1 → $\pi^*$C23–C25 | 16.50 | 0.31 | 0.062 |
| $n_2$O2 → $\pi^*$O3–C18 | 13.15 | 0.31 | 0.080 |
| $n_2$O2 → $\sigma^*$O2–C18 | 9.08 | 0.45 | 0.081 |
| $n_2$O3 → $\sigma^*$C9–C18 | 13.55 | 0.59 | 0.058 |
| $n_2$O5 → $\sigma^*$N6–C19 | 6.91 | 0.53 | 0.077 |
| $n_2$O5 → $\sigma^*$C19–C20 | 4.27 | 0.60 | 0.065 |
| $n_1$N6 → $\pi^*$O5–C19 | 13.04 | 0.30 | 0.079 |
| $n_1$N6 → $\sigma^*$C8–C16 | 12.56 | 0.89 | 0.064 |
| $\pi^*$C23–C25 → $\pi^*$C20–C21 | 120.99 | 0.01 | 0.083 |
| $\pi^*$C23–C25 → $\pi^*$C26–C28 | 81.27 | 0.02 | 0.078 |

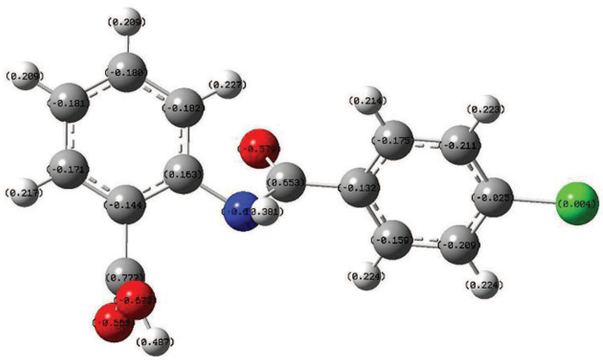

**Fig. 7.** NBO charge values of *N*-(4-Cholorobenzoyl)Fenamic acid.

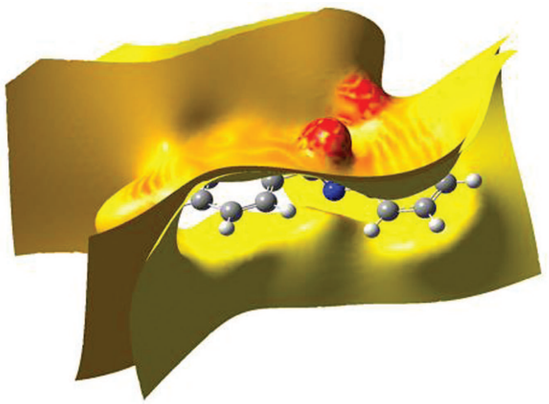

**Fig. 8.** The total electron density surface of *N*-(4-Cholorobenzoyl)Fenamic acid.

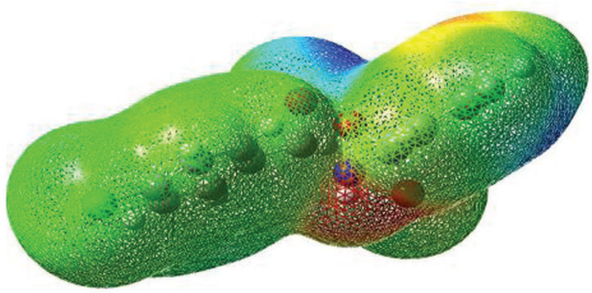

**Fig. 9.** The contour map of electrostatic potential surface of *N*-(4-Cholorobenzoyl)Fenamic acid.

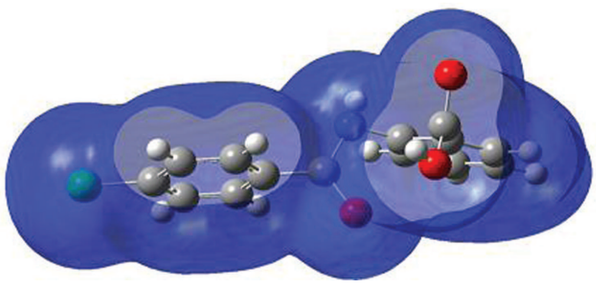

**Fig. 10.** The molecular electrostatic potential surface of *N*-(4-Cholorobenzoyl)Fenamic acid.

**Table XIII.** Thermodynamic functions of *N*-(4-Cholorobenzoyl)Fenamic acid determined at different temperatures with B3LYP/6-311++G(d, p) level.

| Temperature (*K*) | $C_V$ (J/K/mol) | $C_p$ (J/K/mol) | U (kJ/mol) | H (kJ/mol) | S (J/K/mol) | G (kJ/mol) | Q | ln(Q) |
|---|---|---|---|---|---|---|---|---|
| 10.000 | 23.503 | 31.052 | 59.505 | 60.038 | 164.033 | 51.056 | 4.30991E+06 | 14.2522 |
| 20.000 | 24.002 | 39.106 | 63.706 | 60.856 | 188.390 | 58.165 | 8.82568E+07 | 17.2950 |
| 30.000 | 26.028 | 34.342 | 61.961 | 61.126 | 197.097 | 54.023 | 3.79622E+08 | 18.5643 |
| 40.000 | 24.470 | 34.997 | 64.809 | 61.987 | 209.167 | 53.965 | 1.43618E+09 | 20.6321 |
| 50.000 | 28.105 | 37.007 | 64.431 | 62.798 | 213.666 | 53.061 | 3.58697E+09 | 21.7005 |
| 60.000 | 31.094 | 38.262 | 64.710 | 63.992 | 221.376 | 48.027 | 7.67820E+09 | 22.7888 |
| 80.000 | 33.477 | 44.071 | 62.675 | 63.998 | 235.180 | 44.267 | 2.94980E+10 | 22.9990 |
| 90.000 | 36.912 | 46.823 | 62.986 | 63.988 | 240.409 | 43.823 | 4.90732E+10 | 23.5200 |
| 100.000 | 41.234 | 47.745 | 63.232 | 64.069 | 245.480 | 41.448 | 7.89225E+10 | 24.0007 |
| 110.000 | 42.039 | 50.042 | 63.649 | 64.562 | 250.259 | 38.026 | 1.66498E+11 | 24.5050 |
| 120.000 | 44.059 | 52.439 | 64.222 | 65.099 | 254.811 | 36.903 | 1.69948E+11 | 25.9998 |
| 130.000 | 46.939 | 56.005 | 65.432 | 65.987 | 261.393 | 35.800 | 2.50060E+11 | 25.2713 |
| 140.000 | 51.966 | 57.455 | 66.997 | 66.945 | 263.868 | 34.231 | 3.59900E+11 | 26.9956 |
| 150.000 | 51.424 | 59.739 | 66.987 | 66.481 | 267.961 | 26.821 | 5.66665E+11 | 27.3423 |
| 160.000 | 53.002 | 61.231 | 66.103 | 67.441 | 273.889 | 25.785 | 7.96560E+11 | 27.6663 |
| 170.000 | 55.531 | 63.840 | 67.884 | 68.060 | 275.580 | 23.009 | 1.07893E+12 | 27.9288 |
| 180.000 | 57.587 | 65.988 | 68.906 | 68.533 | 279.220 | 18.286 | 1.99195E+12 | 28.8768 |
| 190.000 | 59 789 | 65.441 | 68.445 | 70.993 | 282.981 | 17.565 | 1.89008E+12 | 28.7773 |
| 200.000 | 61.127 | 69.449 | 69.990 | 70.094 | 285.408 | 14.600 | 2.60569E+12 | 28.6555 |
| 210.000 | 62.470 | 71.015 | 71.069 | 72.419 | 291.226 | 11.713 | 3.31947E+12 | 28.2341 |
| 220.000 | 64.691 | 72.768 | 71.342 | 72.992 | 293.487 | 8.790 | 4.86567E+12 | 29.9754 |
| 230.000 | 66.030 | 74.175 | 72.766 | 73.988 | 296.455 | 5.307 | 6.66798E+12 | 29.8851 |
| 240.000 | 67.973 | 76.110 | 72.954 | 74.888 | 305.926 | 3.878 | 8.45635E+12 | 29.7225 |
| 250.000 | 69.452 | 77.886 | 73.527 | 74.314 | 306.729 | 5.018 | 1.99223E+13 | 30.9851 |
| 260.000 | 70.879 | 81.194 | 73.763 | 75.009 | 308.869 | 5.044 | 1.66677E+13 | 30. 6466 |
| 270.000 | 72. 076 | 81. 223 | 74. 922 | 76.998 | 311. 945 | 8. 111 | 1.99113E+13 | 30.8805 |
| 280.000 | 73.219 | 82.996 | 74.009 | 77. 787 | 312. 331 | 9.438 | 2.88970E+13 | 30. 9033 |
| 290.000 | 75.095 | 83.404 | 75.283 | 78.941 | 315.178 | 12.595 | 2.72009E+13 | 31.8443 |
| 300.000 | 76.414 | 84.328 | 76.519 | 78.456 | 318.051 | 17.771 | 3.98535E+13 | 31.9921 |
| 310.000 | 77.701 | 88.015 | 77.314 | 79.805 | 321.879 | 19.906 | 4.77577E+13 | 31.6670 |
| 320.000 | 78.940 | 88.755 | 78.725 | 80.985 | 324.988 | 23.709 | 6.51450E+13 | 31.8177 |
| 330.000 | 80.384 | 89.520 | 78. 300 | 81. 455 | 327. 465 | 26.691 | 7.55882E+13 | 31.9775 |
| 340.000 | 81. 933 | 91.685 | 79. 756 | 82. 488 | 330. 111 | 29. 780 | 9.45640E+13 | 32.9177 |
| 350.000 | 82.085 | 91.225 | 80.769 | 83. 600 | 332. 422 | 33. 143 | 1.07499E+14 | 32.9723 |
| 360.000 | 83.828 | 92.967 | 81.157 | 84.080 | 335.546 | 35.411 | 1.80367E+14 | 32.3452 |
| 370.000 | 84. 623 | 93.999 | 82. 566 | 85. 209 | 337.190 | 39.578 | 1.87188E+14 | 32.9950 |
| 380.000 | 86.599 | 94.275 | 83. 599 | 86. 509 | 341.401 | 44.109 | 2.23399E+14 | 33. 5644 |
| 390.000 | 87.899 | 95.056 | 84.332 | 87.899 | 342.432 | 45. 086 | 2.39901E+14 | 33.9924 |
| 400.000 | 88.677 | 96.099 | 84.566 | 88.222 | 344.834 | 51.026 | 3.65043E+14 | 33.7885 |
| 410.000 | 88.282 | 97.977 | 85.600 | 89.721 | 346.799 | 53.492 | 4.09729E+14 | 33.4650 |
| 420.000 | 90. 677 | 99.514 | 86. 609 | 90.664 | 351.796 | 59.980 | 4.59400E+14 | 33. 4459 |
| 430.000 | 90.923 | 99. 729 | 88. 668 | 91. 415 | 352.405 | 60.493 | 6.07208E+14 | 34.0398 |
| 440.000 | 91.999 | 100.624 | 88.790 | 92.386 | 354.973 | 64.291 | 7.63189E+14 | 34.6444 |
| 450.000 | 92.734 | 100.522 | 89.401 | 93.427 | 356.540 | 67.876 | 8.06609E+14 | 34.2294 |
| 460.000 | 93.879 | 101.245 | 90.298 | 94.546 | 359.780 | 71.685 | 1.47006E+15 | 34.8234 |
| 470.000 | 93.977 | 102.549 | 91.655 | 95.736 | 361.694 | 74.715 | 1.93822E+15 | 34.9645 |
| 480.000 | 94.696 | 102.999 | 92.187 | 96.996 | 363.779 | 78.255 | 1.99459E+15 | 34.9881 |
| 490.000 | 95.665 | 103.800 | 93.768 | 97.320 | 365.824 | 82.418 | 1.46265E+15 | 35.5634 |
| 500.000 | 95.916 | 104.656 | 94.345 | 98.719 | 367.232 | 85.456 | 2.25678E+15 | 35. 9640 |

temperature is almost 0.999 (0.987 for thermal energy). The correlation equations for above parameters from the following expressions.

$$C^0_{p,m} = 1.201 + 0.401T - 0.94 \times 10^{-4}T^2$$

$$S^0_m = 23.67 + 0.194T + 0.7 \times 10^{-4}T^2$$

$$H^0_m = 33.58 + 0.0729T + 0.7 \times 10^{-4}T^2$$

#### *4.2.9. Mullliken Charges*

The charge distribution of atoms in molecules used to study the molecular system. These charges provide information of partical aomic charges. It is common, the population analysis of Mulliken and Natural are gives the atomic charges of atoms of molecules. The variation in MPA, of distribution of charges from applied fields ($\pm 0.02$, $\pm 0.04$ VÅ$^{-1}$) are shown in Table XIV.

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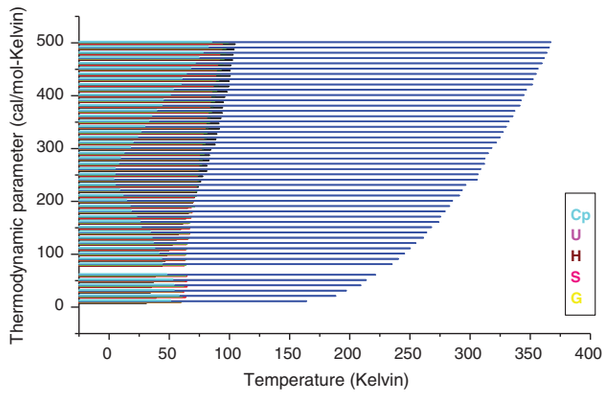


**Fig. 11.** Correlation graphic of thermodynamic parameters and Temperature for entropy (S). Heat capacity at constant pressure (Cp), Gibb's free energy(G) energy change of *N*-(4-Cholorobenzoyl)Fenamic acid.

#### *4.2.10. Mullikan Population Analysis*

The total number of electrons density $\rho(\vec{r})$ with chemical potential ($\mu$) the Fukui function, $f(\vec{r})$ is $f(\vec{r}) = \left(\delta\mu/\delta v(\vec{r})\right)_N = \left(\partial\rho(\vec{r})/\partial N\right)_{V(\vec{r})}$.

If $\Delta f(\vec{r}) > 0$ at the point $\vec{r}$ implies the site is favor to nucleophilic attack (electron accepting region), while $\Delta f(\vec{r}) < 0$, it favor to electrophilic attack (electron donating region). MPA computation at $N_k(N+1)$, $N_k(N-1)$, $N_k(N)$ with dual descriptor ($\Delta f_k$) (Table XV and Fig. 12) are describing the mechanical properties of hardness, softness and Fukui function gives information of site and respective chemical system [37].

#### *4.2.11. Magnetic Susceptibility*

The magnetic behavior at various temperatures of the molecules measured through their susceptibility ($\chi_m$) [38],

**Table XIV.** Mulliken's Charges for the Zero, Various applied electric field (±0.02, 0.04 VÅ$^{-1}$) of *N*-(4-Cholorobenzoyl)Fenamic acid.

| | | 0.02 VÅ$^{-1}$ | | 0.04 VÅ$^{-1}$ | |
|---|---|---|---|---|---|
| Atom No. | 0.00 VÅ$^{-1}$ | Positive field | Negative field | Positive field | Negative field |
| Cl11 | −0.012057 | 0.040778 | 0.040778 | 0.419482 | 0.419482 |
| C2 | 0.558367 | 0.449797 | 0.449797 | 0.403721 | 0.403721 |
| O3 | −0.422950 | −0.475358 | −0.475358 | −0.709904 | −0.709904 |
| N4 | −0.868393 | −0.803006 | −0.803006 | −0.819284 | −0.819284 |
| H5 | 0.418683 | 0.418582 | 0.418582 | 0.259718 | 0.259718 |
| C6 | 0.372819 | 0.348057 | 0.348057 | 0.305902 | 0.305902 |
| C7 | −0.243496 | −0.231976 | −0.231976 | −0.174703 | −0.174703 |
| C8 | −0.110047 | −0.118798 | −0.118798 | −0.151775 | −0.151775 |
| C9 | −0.091688 | −0.090632 | −0.090632 | −0.145257 | −0.145257 |
| C10 | −0.126269 | −0.133951 | −0.133951 | −0.078745 | −0.078745 |
| H11 | 0.233371 | 0.210974 | 0.210974 | 0.205014 | 0.205014 |
| C12 | −0.142168 | −0.151481 | −0.151481 | −0.087734 | −0.087734 |
| H13 | 0.188810 | 0.213017 | 0.213017 | 0.211910 | 0.211910 |
| H14 | 0.160683 | 0.177326 | 0.177326 | 0.311043 | 0.311043 |
| H15 | 0.160428 | 0.195463 | 0.195463 | 0.339240 | 0.339240 |
| H16 | 0.196972 | 0.169155 | 0.169155 | 0.210775 | 0.210775 |
| H17 | 0.189937 | 0.187787 | 0.187787 | 0.329027 | 0.329027 |
| C18 | −0.190323 | −0.126797 | −0.126797 | −0.083811 | −0.083811 |
| H19 | 0.192215 | 0.234146 | 0.234146 | 0.165504 | 0.165504 |
| C20 | −0.065367 | −0.123809 | −0.123809 | −0.120760 | −0.120760 |
| H21 | 0.197997 | 0.203634 | 0.203634 | 0.005668 | 0.005668 |
| C22 | −0.272740 | −0.297794 | −0.297794 | −0.369611 | −0.369611 |
| C23 | −0.095121 | −0.082654 | −0.082654 | −0.007973 | −0.007973 |
| C24 | 0.552575 | 0.536893 | 0.536893 | 0.524651 | 0.524651 |
| C25 | −0.058080 | −0.057621 | −0.057621 | −0.043881 | −0.043881 |
| O26 | −0.445516 | −0.436059 | −0.436059 | −0.614102 | −0.614102 |
| O27 | −0.574130 | −0.583055 | −0.583055 | −0.600006 | −0.600006 |
| C28 | −0.102829 | −0.089537 | −0.089537 | −0.130894 | −0.130894 |
| H29 | 0.398318 | 0.416918 | 0.416918 | 0.446784 | 0.446784 |

**Table XV.** Mulliken population analysis calculated at $N_k(N+1)$, $N_k(N-1)$, $N_k(N)$ and condensed fukui function of *N*-(4-Cholorobenzoyl)Fenamic acid.

| Atom No. | $N_k(N+1)$ | $N_k(N-1)$ | $N_k(N)$ | $f_k^+$ | $f_k^-$ | $f_k^0$ | Δf(r) |
|---|---|---|---|---|---|---|---|
| Cl11 | −0.001036 | 0.041851 | −0.012057 | 0.011021 | −0.053908 | −0.021443 | 0.064929 |
| C2 | 0.119952 | −0.039104 | 0.558367 | −0.438415 | 0.597471 | 0.079528 | −1.035886 |
| O3 | 0.118266 | 0.014037 | −0.422950 | 0.541217 | −0.436987 | 0.052114 | −0.489101 |
| N4 | −0.066072 | 0.311347 | −0.868393 | 0.802321 | −1.17874 | −0.188709 | 1.981061 |
| H5 | 0.000991 | −0.012275 | 0.418683 | −0.417692 | 0.430958 | 0.006633 | −0.84865 |

**Table XV.** Continued.

| Atom No. | $N_k(N+1)$ | $N_k(N-1)$ | $N_k(N)$ | $f_k^+$ | $f_k^-$ | $f_k^0$ | Δf(r) |
|---|---|---|---|---|---|---|---|
| C6 | 0.175790 | 0.029643 | 0.372819 | −0.197029 | 0.343176 | 0.0730735 | −0.540205 |
| C7 | 0.014148 | 0.124775 | −0.243496 | 0.257644 | 0.368271 | −0.055313 | −0.110627 |
| C8 | −0.114387 | 0.252026 | −0.110047 | −0.00434 | −0.362073 | −0.183206 | 0.357733 |
| C9 | 0.113130 | −0.051263 | −0.091688 | 0.204818 | −0.040425 | 0.02718 | 0.245243 |
| C10 | 0.215074 | −0.155486 | −0.126269 | 0.341343 | 0.029217 | 0.18528 | 0.312126 |
| H11 | 0.003212 | −0.010537 | 0.233371 | −0.230159 | 0.243941 | 0.006829 | −0.4741 |
| C12 | −0.063396 | 0.357706 | −0.142168 | 0.078772 | −0.500474 | −0.210551 | 0.579246 |
| H13 | −0.005658 | 0.000929 | 0.188810 | −0.194468 | 0.187881 | −0.003293 | −0.382349 |
| H14 | −0.011365 | 0.004725 | 0.160683 | −0.172048 | 0.155958 | 0.008045 | −0.328006 |
| H15 | 0.001670 | −0.016127 | 0.160428 | −0.158758 | 0.176555 | 0.008898 | −0.335313 |
| H16 | −0.003986 | −0.000820 | 0.196972 | −0.200958 | 0.197792 | −0.001583 | −0.39875 |
| H17 | 0.001381 | 0.000073 | 0.189937 | −0.188556 | 0.189864 | 0.000654 | −0.37842 |
| C18 | 0.010171 | 0.071230 | −0.190323 | 0.200494 | −0.261553 | −0.030529 | 0.462047 |
| H19 | 0.001424 | −0.001221 | 0.192215 | −0.190791 | 0.193436 | 0.000132 | −0.384227 |
| C20 | 0.080460 | 0.014588 | −0.065367 | 0.145827 | −0.079955 | 0.032936 | 0.225782 |
| H21 | −0.004729 | −0.000038 | 0.197997 | −0.202726 | 0.198035 | 0.0023455 | −0.400761 |
| C22 | 0.135656 | 0.059215 | −0.272740 | 0.408396 | −0.331955 | 0.0382205 | 0.740351 |
| C23 | −0.046179 | −0.011319 | −0.095121 | 0.048942 | −0.083802 | −0.01743 | 0.132744 |
| C24 | 0.175329 | −0.014310 | 0.552575 | −0.377246 | 0.566885 | 0.094819 | −0.944131 |
| C25 | −0.047253 | 0.019954 | −0.058080 | 0.010827 | −0.078034 | −0.033603 | 0.088861 |
| O26 | 0.097485 | 0.018301 | −0.445516 | 0.543001 | 0.427215 | 0.039592 | 0.115786 |
| O27 | 0.016035 | 0.003106 | −0.574130 | 0.590165 | −0.577236 | 0.006487 | 0.115786 |
| C28 | 0.085582 | −0.010620 | −0.102829 | 0.188411 | −0.092209 | 0.048101 | 0.28062 |
| H29 | −0.001694 | −0.000388 | 0.398318 | −0.400012 | 0.398706 | 0.000653 | −0.798718 |

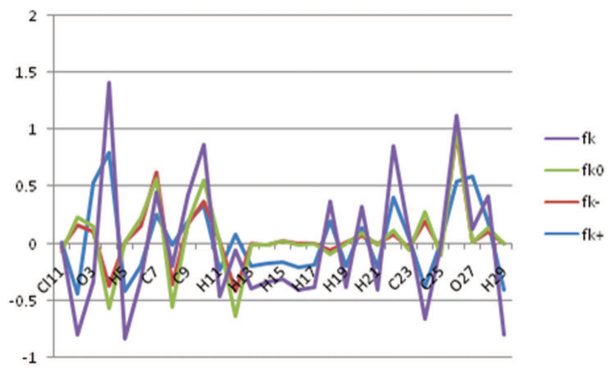


**Fig. 12.** Correlation graphic of condensed fukui function of N-(4-Cholorobenzoyl)Fenamic.

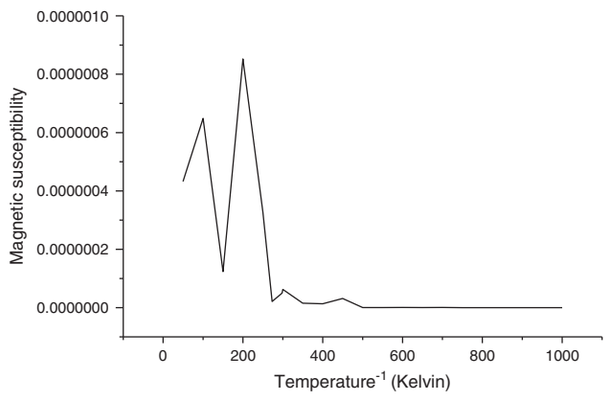


**Fig. 13.** Graphical representation of magnetic susceptibility with temperature$^{-1}$ of *N*-(4-Cholorobenzoyl)Fenamic acid.

**Table XVI.** Magnetic susceptibility of *N*-(4-Cholorobenzoyl)Fenamic acid by B3LYP/6-311++G(d, p).

| Temperature | Magnetic susceptibility | 1/Temperature |
|---|---|---|
| 50 | 4.32568E–07 | 0.02 |
| 100 | 6.48622E–07 | 0.01 |
| 150 | 1.23418E–07 | 0.006667 |
| 200 | 8.52368E–07 | 0.005 |
| 250 | 3.26792E–07 | 0.004 |
| 273 | 2.12564E–08 | 0.003663 |
| 298.15 | 4.98342E–08 | 0.003354 |
| 300 | 6.25825E–08 | 0.003333 |
| 350 | 1.54398E–08 | 0.002857 |
| 400 | 1.34567E–08 | 0.0025 |
| 450 | 3.15432E–08 | 0.002222 |
| 500 | 2.74450E–10 | 0.002 |
| 550 | 4.67545E–10 | 0.001818 |
| 600 | 7.67564E–10 | 0.001667 |
| 650 | 4.82568E–10 | 0.001538 |
| 700 | 8.48622E–10 | 0.001429 |
| 750 | 2.13498E–11 | 0.001333 |
| 800 | 3.72748E–11 | 0.00125 |
| 850 | 4.56927E–11 | 0.001176 |
| 900 | 2.74735E–11 | 0.001111 |
| 950 | 5.67859E–11 | 0.001053 |
| 1000 | 7.12567E–11 | 0.001 |

and this is due to presence of free electrons and its values given in Table XVI and in Figure 13. The effective magnetic moment is $1.9647 \times 10^{-5}$ (BM).

## 5. CONCLUSION

There is a well agreement between the computed and experimental results of synthesized crystals

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and their possible vibrational modes of NCF. The HOMO–LUMO energy gap computed through sets B3LYP/6-311++G(d, p) level revealed the chemical nature and molecular stability. The NBO investigation yields the interaction of intramolecular, charge transfer in orbitals like bonding and anti-bonding. The donor orbital, $\pi CC \rightarrow \pi^{*}CC$ interaction in C20–C21 and the C26–C28 anti-bonding gives 20.22 kJ $mol^{-1}$. NLO property observed through first hyperpolarizability values. The MEP analysis gives that the electrophilic attack in Cl of NCF. Thermodynamic parameters were obtained the paramagnetic behavior confirmed with magnetic study. The changes occur in MPA charges are very less and almost uniform throughout is confirmed through EFs.

## ABBREVIATIONS AND UNITS

$\nu_o$—exciting frequency (in $cm^{-1}$ units), $\nu_i$—vibrational wave number of the *i*th normal mode, $h$, $c$ and $k$ are universal constants, $f$—scaling factor, electronic potential ($I_P$), electron affinities ($E_A$), chemical potential ($\mu$) it is the negative of electro negativity ($\chi$), hardness ($\eta$), softness ($S$), electrophilic index ($\omega$) and the electric dipole polarizability ($\alpha$). Σ—runs over all the nuclei A in the compound and polarization and reorganization effects are neglected. $Z_A$—charge of the nucleus A, located at $R_A$ and $\rho(r')$—electron density function, specific heat capacity at constant pressure (Cp) and constant volume (Cv), entropy (S), internal heat energy (U), Gibb's free energy (G) and enthalpy change (H).

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### Conflict of Interest

The authors have no conflict of interest.

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