Structure, Vibrational Analysis and Chemical Reactivity Descriptors of 4-Bromo-3-(Methoxymethoxy) Benzoic Acid: A DFT Study

S. Yadav¹, A. Khare¹, K. K. Yadav¹, P. C. Maurya¹, A. K. Singh², A. Kumar¹*

¹Department of Physics, University of Lucknow, Lucknow-226007, India
²Department of Chemistry, University of Lucknow, Lucknow-226007, India

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Abstract
In this study, the structure and various molecular parameters of 4-bromo-3-(methoxymethoxy) benzoic acid are determined at the B3LYP/6-311++G(d,p) level of theory. Present study provides comparison and discussion of calculated and experimental optimized parameters. The values of descriptors such as ionization energy, hardness, electrophilicity, condensed Fukui function and energy were determined to predict the reactivity of 4-bromo-3-(methoxymethoxy) benzoic acid. The influence of the solvent on reactivity parameters has been studied adopting the PCM model. The analysis shows that solvation alters the values of reactivity descriptors. A vibrational assessment of the molecule has also been performed. To gain a better understanding of the properties of the title molecule, parameters such as the molecular electrostatic potential surface and the HOMO-LUMO band gap have been computed. The dipole moment, polarizability and hyperpolarizability were also estimated to probe into non-linear optical properties of the chemical.

Keywords: Vibrational analysis; Reactivity; Fukui functions.

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1. Introduction
In this study the compound 4-bromo-3-(methoxymethoxy) benzoic acid (MBMMA) which is a derivative of bromo–hydroxy–benzoic acids is considered. A diverse range of biological properties such as antitumor, antiviral, antifungal, and antimitotic effects have been reported for ester derivatives [1,2]. These compounds have also been tested to act as antiproliferative agent [3]. Azo-ester bridged compounds were studied for enantiotropic liquid crystalline mesophase character and optical activity [4]. Molecular modelling studies revealed that many derivatives were well tolerated at the interface between ARF1 and its guanine nucleotide exchange factor ARNO. Fluorescence imaging assays confirmed the Golgi-disruptive properties of the ester derivatives [5]. Murthy et al. [6] recently described synthesis and crystal structure of the title compound. Keeping the above mentioned important properties and applications of ester derivatives in mind, the

* Corresponding author: akgkp25@yahoo.co.in
outcomes from DFT/B3LYP analyses of various properties of MBMMBA are presented here. This study on the MBMMBA included the optimization of equilibrium geometry as well as the estimation of ground state characteristics at the DFT/6-311++G (d, p) level. Theoretical infrared spectra are generated, and normal mode analysis of the identified compound is also completed. The vibrational evaluation carries comprehensive data about the intermolecular vibrations. The quantitative structure - activity association based on an analysis of the frontier orbital gap, dipole moment data, and the MBMMBA molecule's molecular electrostatic potential map were used to observe the active sites of the chemical compound. The efficacy of bioactivity of drug in pharmaceutical applications is strongly correlated with solvation phases [7,8]. So, local reactivity parameters have also been calculated for the title compound and effect of solvation on these parameters has been studied. The non linear optical parameters such as polarizability and first static hyperpolarizability of title compound have also been discussed elaborately. To the best of our knowledge, this type of study on the title compound has been done first time.

2. Materials and Methods

The DFT calculations [9] have been executed with the G09 software [10], Becke’s three parameter hybrid exchange functionals [11] and Lee–Yang–Parr correlation functionals (B3LYP) in the current communication [12,13]. The basis set 6-311++G(d, p) was used in particular because of its advantage in performing faster calculations with comparatively high precision [14,15]. The measured frequencies are scaled down by the necessary factor [16,17] to incorporate anharmonicity. MEPS was generated and displayed using Gaussview-5 [18] at the above mentioned theory. The wavenumber assessment was analyzed combinedly with the results of the Gaussview-5 and VEDA-4 software observations and symmetry considerations [19].

3.1. Molecular geometry

The chemical properties of MBMMBA were obtained using DFT at the above mentioned theory. Since the measured vibrational spectra do not contain any imaginary wavenumber, the optimized structure of the molecule MBMMBA (Fig. 1) is confirmed to be located at the local true minima on the potential energy surface.

The bond lengths, bond angles and dihedral angles of MBMMBA acquire after optimization have been compared with those reported in X-Ray crystal structure information [6] as provided in Table 1. “The geometric differences between the optimised molecule and the molecule in solid state result from the fact that the chemical conformation in the gas phase differs from that in the solid state, where intermolecular interactions play an important role in crystal structure stabilisation” [20]. The C-O bond lengths lie in the range 1.208-1.411Å which match well with the experimental values 1.275-1.428Å [6] and found nearly to the usual ester C-O lengths [21,22]. The length of
C-C bond in the phenyl ring is between 1.389 and 1.407 Å, and the C-C bond angles are between 118.559° and 120.843°.

A clear agreement is seen in these calculated bond length, bond angles with experimental value and also those with standard bond lengths and bond angles.

Fig. 1. Optimized structure of MBMMBA.

Table 1. The computationally optimized parameters of MBMMA and its Comparison with available experimental results [6].

| Parameter | Cal. Bond length (Å) | Exp. Bond length (Å) | Bond angle (in degree) | Cal. Bond angle (in degree) | Exp. Bond angle (in degree) | Cal. Dihedral Angle (in degree) | Exp. Dihedral Angle (in degree) |
|-----------|----------------------|----------------------|------------------------|-----------------------------|-----------------------------|--------------------------------|--------------------------------|
| C1-C2     | 1.389                | 1.380                | C4-C5-C11              | 121.448                     | 119.4                       | C2-C1-C6-H17                 | 180.0                          |
| C2-C3     | 1.407                | 1.400                | C6-C5-C11              | 118.223                     | 119.9                       | H15-C1-C6-C5                | -180.0                         |
| C3-C4     | 1.395                | 1.385                | C1-C5-C6              | 119.559                     | 119.3                       | H15-C1-C6-H17               | 0.0                            |
| C4-C5     | 1.400                | 1.402                | C1-C6-H17              | 120.945                     | 120.4                       | C1-C2-C3-C4                | 0.0                            |
| C5-C6     | 1.394                | 1.394                | C5-C6-H17              | 119.495                     | 120.4                       | C1-C2-C3-O7                | -180.0                         |
| C6-C1     | 1.390                | 1.373                | C3-O7-C8               | 118.774                     | 117.7                       | Br14-C2-C3-C4              | 180.0                          |
| C5-C11    | 1.485                | 1.476                | O7-C8-O9               | 104.736                     | 113.0                       | Br14-C2-C3-O7              | -0.0                          |
| C11-O12   | 1.208                | 1.275                | O7-C8-H18              | 111.107                     | 109.0                       | C2-C3-C4-C5               | 0.0                            |
| C11-O13   | 1.359                | 1.271                | O7-C8-H19              | 110.106                     | 109.0                       | C2-C3-C4-H16              | 180.0                          |
| C3-O7     | 1.354                | 1.371                | O9-C8-H18              | 111.163                     | 109.0                       | O7-C3-C4-C5               | 180.0                          |
| C8-O7     | 1.411                | 1.428                | O9-C8-H19              | 111.163                     | 109.0                       | O7-C3-C4-H16              | -178.8                         |
| C8-O9     | 1.389                | 1.390                | H18-C8-H19             | 109.483                     | 107.8                       | C2-C3-O7-C8              | 180.0                          |
| C10-O9    | 1.418                | 1.426                | C8-O9-C10              | 112.486                     | 113.7                       | C4-C3-O7-C8              | 180.0                          |
| C10-H20   | 1.088                | 0.980                | O9-C10-H20             | 106.565                     | 109.5                       | C5-C4-C5-C6               | 0.0                            |
| C10-H21   | 1.098                | 0.980                | O9-C10-H21             | 111.505                     | 109.5                       | C3-C4-C5-C11              | -180.0                         |
| C10-H22   | 1.098                | 0.980                | O9-C10-H22             | 111.504                     | 109.5                       | H16-C4-C5-C6              | -180.0                         |
| C8-H18    | 1.103                | 0.990                | H20-C10-H21            | 109.089                     | 109.5                       | H16-C4-C5-C11              | -0.0                           |
| C8-H19    | 1.103                | 0.990                | H20-C10-H22            | 109.091                     | 109.5                       | C4-C5-C6-C1               | -180.0                         |
| C4-H16    | 1.079                | 0.950                | H21-C10-H22            | 109.011                     | 109.5                       | C11-C5-C6-C1              | 179.996                        |
| C6-H17    | 1.082                | 0.950                | C5-C11-O12             | 125.037                     | 117.5                       | C11-C5-C6-H17              | 0.0                            |
| C1-H15    | 1.082                | 0.950                | C5-C11-O13             | 113.062                     | 117.5                       | C4-C5-C11-O12              | 180.0                          |
| C2-Br14   | 1.903                | 1.913                | O12-C11-O13            | 121.899                     | 123.3                       | C4-C5-C11-O13              | 0.0                            |
| O13-H23   | 0.968                | 0.823                | C11-O13-H23            | 106.632                     | 124.0                       | C6-C5-C11-O12              | 0.0                            |
| Bond angle (Å) | C3-C4-H16 | 118.788 | 120.1 | C6-C5-C11-O13 | 180.0 | -8.5 | - |
| C2-C1-C6   | 120.26               | 120.4                | C4-C5-C6               | 120.327                     | 120.6                       | C3-O7-C8-O9               | -180.0                         |
The Frontier Molecular Orbitals are vital parameters for determining the unique features of any compound. The LUMO presents the electron acceptability property of the compound and also susceptibility for the nucleophilic attack. Frontier orbital energy gap delivers the idea about molecular kinetic stability and chemical reactivity. By employing Gaussian view program, the energy of LUMO and HOMO have been estimated, which provides the detail about energy gap between these two as 4.46 eV. The frontier orbitals 3D plots and energy gap of MBMMBA are depicted in Fig. 2. This Fig. reveals that the HOMO is spread heavily over the phenyl ring region. The high charge density is localised mainly on carboxyl group due to HOMO-LUMO transition of reflection [21]. The expansion of LUMO is almost over the whole molecule. All the HOMO and LUMO have nodes, which placed symmetrically [23,24].

![Fig. 2. Graphical presentation of band gap between FMO of MBMMBA.](image)

The MESP surface, which is used to represent electrostatic potential and in addition to molecular shape, size is a precious mean for the exploration of connection between structure and the characteristics of substances, including biomolecules [23]. The MESP representation through color grading with mode of alignment for electrostatic potential dissipated in Fig. 3. The MESP graphic provides information about electrostatic potential of the molecule [24] and hence one can predict the sites in the molecule for electrophilic and nucleophilic attack. The MESP of the MBMMBA shows a clear variation in potential between carboxylic oxygen (dark red region in MESP, which is electronegative) and hydrogen atoms which bear most of the positive charge (green). The negative potential region surrounding the oxygen has been exhibited by the MESP plot. There are many...
active electrophilic sites in the molecule whereas region near carboxylic group is more prone to active for nucleophillic attack.

Fig. 3. MESP surface of MBMMBA.

3.3. Vibrational analysis

The 4-bromo-3-(methoxymethoxy) benzoic acid compound containing n (=23) atoms have (3n-6 = 63) possible fundamental vibrational modes. These modes have been elaborated and categorized as stretching (symmetric and asymmetric), scissoring, rocking, out of plane torsion modes and given in the Table 2. The vibrational frequencies have been scaled down with a factor of 0.9682 to encarporate the anharmonicity [25,26].

Table 2. Vibrational assignment of numerous modes modes of MBMMBA.

| Scaled Frequency | Assignment                                                                 | Scaled Frequency | Assignment                                                                 |
|------------------|---------------------------------------------------------------------------|------------------|---------------------------------------------------------------------------|
| 3647             | \(\nu\)\{(O13-H23)(100)\]                                               | 1196            | \(\nu\)\{(O9-C8)(18)\] + \(\tau\)\{(H21-C10-O9-C8)(23)\] +\{(H22-C10-O9-C8)(23)\] |
| 3123             | \(\nu\)\{(C4-H16)(99)\]                                               | 1153            | \(\beta\)\{[H23-O13-C11](29)\]                                           |
| 3107             | \(\nu\)\{[C1-H15](30)+[C6-H17](69)\]                                   | 1139            | \(\tau\)\{[H20-C10-O9-C8](22)+[H21-C10-O9-C8](20)+ [H22-C10-O9-C8](20)\] |
| 3093             | \(\nu\)\{[(C1-H15)(69)+(C6-H17)(30)]\]                                | 1118            | \(\nu\)\{[C1-C6](19)\]+ \(\beta\)\{[H17-C6-C1](47)\]                  |
| 3030             | \(\nu\)\{[C10-H22](94)\]                                              | 1109            | \(\nu\)\{[O9-C8](30)+[O9-C10](34)\]                                    |
| 2929             | \(\nu\)\{[(C10-H21)(50)+(C10-H22)(50)]\]                            | 1105            | \(\beta\)\{[H18-C8-O9](24)\] + \(\tau\)\{[H20-C10-O9-C8](18)+ [H18-C8-O9-C10](31)\] |
| 2883             | \(\nu\)\{[(C10-H21)(47)+(C10-H22)(47)]\]                            | 1064            | \(\nu\)\{[O13-C11](39)\]                                              |
C-H vibrations

C-H mode of vibrations in the form of symmetric stretching appear at frequencies 3123 cm\(^{-1}\), 3107 cm\(^{-1}\) and 2865 cm\(^{-1}\) in this study which is in consonance with earlier reported data [27]. The bending modes involving C-H group are observed at 1464 and 1260 cm\(^{-1}\) with high intensity. The mixed modes involving C-H vibrations with variable intensities are seen at low frequencies. These modes contribute significantly in potential energy distribution (PED).

C-C vibrations

Different modes of C-C vibrations with important contribution in PED are observed in the normal mode analysis. The asymmetric stretching is found at 1568 cm\(^{-1}\) with moderate intensity. The high intensity symmetric mode is observed at 1379 cm\(^{-1}\) for C4-C3 stretching. The molecule exhibits bending of C2-C1-C6 at 1010 cm\(^{-1}\) with moderate intensity. The plane torsion modes are observed at 946, 684 and 600 cm\(^{-1}\) having low intensity.

O-C and O-H vibrations

The O-C stretching mode is recorded at 1729 cm\(^{-1}\) with very high intensity for (O12-C11) in consonance with value reported in literature [28]. The asymmetric stretching mode is recorded at 1110 and 1066 cm\(^{-1}\) with high intensity. Torsional mode appears at the frequency 749 cm\(^{-1}\) in the title compound. Bending modes were calculated at 641 and 569 cm\(^{-1}\) at low intensities. O-C stretching contribute in mix mode of vibrations also. These modes are recorded at frequencies 1245 and 1196 cm\(^{-1}\) in present case. The symmetric stretching
mode for O13-H23 is observed at 3647 cm\(^{-1}\) with prominent contribution in potential energy distribution.

C-Br vibrations
C-Br stretching vibrations are seen in the low frequency range at 433 and 429 cm\(^{-1}\) with good contribution in PED. The mode at the frequency 433 cm\(^{-1}\) is recognised as stretching vibration of Br14-C2 with moderate intensity. Another vibration which is the torsion vibration accounted for the scaled frequency 429 cm\(^{-1}\).

3.4. Thermodynamic parameters

In this section some electronic and thermodynamic parameters have been calculated through theoretical methods and represented through some specific symbols.

Table 3. Various thermodynamic parameters derived at [B3LYP/6-311++G(d,p)] level of theory.

| Thermodynamic Parameter | MBMMBA  |
|-------------------------|---------|
| ZPE (kcal/mol)          | 106.05  |
| E (kcal/mol)            | 115.13  |
| \(C_v\) (cal/mol-K)     | 49.19   |
| S (cal/mol-K)           | 123.67  |

ZPE (Zero point energy), thermal energy (E), entropy (S), heat capacity (\(C_v\)) for molecule MBMMBA calculated at same level. Reaction path could be facilitated through these parameters.

3.5. Reactivity descriptors

Local reactivity descriptors
The atomic energy has been calculated by employing the application of Gauss View software and the reactivity parameters such as Fukui function (\(f_k^\pm\)) has been calculated for the description. These data extract the information about reactive sites of MBMMBA. These sites are defined as neutral, electrophilic and nucleophilic sites [29]. These parameters have been calculated by following derivations[30,31]:

\[
\begin{align*}
  f_k^+ &= q_k(N+1) - q_k(N) \\
  f_k^- &= q_k(N) - q_k(N-1) \\
  f_k^0 &= (q_k(N+1)-q_k(N-1))/2
\end{align*}
\]

Where \(f_k^+\), \(f_k^-\) and \(f_k^0\) are Fukui function nucleophilic attack, electrophilic attack and radical attack respectively, and \(q_k\), \(q_{k(N+1)}\), \(q_{k(N-1)}\) is electronic population of atom \(k\) in neutral, anion and cation form of compound.
Table 4. Values of condensed Fukui function in MBMMBA from NBO charges in gas and aqueous phase.

| ATOM | Gas Phase | Aqueous Phase |
|------|-----------|---------------|
|      | \(f_k^0\) | \(f_k^-\) | \(f_k^+\) | \(\overline{f_k^+}\) | \(\overline{f_k^-}\) | \(\overline{f_k^c}\) |
| 1C   | -0.04467 | -0.04877 | -0.05286 | -0.042 | -0.01668 | -0.04841 |
| 2C   | -0.10738 | -0.14393 | -0.18047 | -0.10987 | -0.07955 | -0.17915 |
| 3C   | -0.02671 | -0.01396 | -0.00121 | -0.02154 | -0.08316 | 0.00234 |
| 4C   | -0.07276 | -0.10475 | -0.13674 | -0.08666 | -0.06304 | -0.12392 |
| 5C   | -0.07738 | -0.11742 | -0.15745 | -0.08367 | -0.07519 | -0.15653 |
| 6C   | -0.04266 | -0.15124 | -0.25982 | -0.06338 | -0.10576 | -0.26993 |
| 7O   | -0.02265 | -0.22239 | -0.42212 | -0.01941 | -0.07783 | -0.44412 |
| 8C   | 0.00213 | 0.081605 | 0.16108 | 0.00218 | 0.004445 | 0.16159 |
| 9O   | -0.00926 | -0.14928 | -0.2893 | -0.00459 | -0.00866 | -0.31917 |
| 10C  | 0.00029 | -0.04926 | -0.1008 | -0.00146 | -0.0007 | -0.09653 |
| 11C  | -0.11916 | 0.14456 | 0.40828 | -0.14236 | -0.06851 | 0.42611 |
| 12O  | -0.14963 | -0.24911 | -0.34859 | -0.16451 | -0.10577 | -0.3908 |
| 13O  | -0.0656 | -0.21081 | -0.35601 | -0.0708 | -0.04471 | -0.35111 |
| 14Br | -0.11734 | -0.1286 | -0.13985 | -0.0783 | -0.13837 | -0.16537 |
| 15H  | -0.02831 | 0.03402 | 0.09635 | -0.02093 | -0.02322 | 0.1027 |
| 16H  | -0.02122 | 0.041245 | 0.10371 | -0.02143 | -0.02235 | 0.11042 |
| 17H  | -0.02451 | 0.0414 | 0.10731 | -0.02371 | -0.02135 | 0.10593 |
| 18H  | -0.00762 | 0.02184 | 0.0513 | -0.00823 | -0.01896 | 0.064 |
| 19H  | -0.00761 | 0.02185 | 0.05131 | -0.00823 | -0.01896 | 0.064 |
| 20H  | -0.01633 | 0.03557 | 0.08747 | -0.00242 | -0.00462 | 0.08628 |
| 21H  | -0.00887 | 0.03211 | 0.07309 | -0.00292 | -0.00506 | 0.08235 |
| 22H  | -0.00888 | 0.03211 | 0.0731 | -0.00292 | -0.00506 | 0.08235 |

In the above table, \(f_k^0, f_k^+, f_k^-\), used to represent neutral, nucleophilic an electrophilic sites. The value of Fukui functions considering NBO charges for the respective atom of the molecule in gas and aqueous phase are tabulated in Table 4. Regarding this observation the maximum value of local reactivity descriptor \(f_k^+\) matches to C10 atom of the molecule, it means C10 is the favorable electrophilic site and C11 is recognized as nucleophilic site according to our study. There are plenty of nucleophilic and electrophilic sites present in the molecule as revealed by the calculated data. The solvation modify the local reactivity sites and values for the molecule as also evident from the Table 4.

**Global reactivity descriptors**

Theoretically computed values of LUMO and HOMO serve as the foundation for estimating the compound's electron affinity and ionisation potential. According to Janak theorem and Perdew et. al. [32,33] ionization potential (I) and electron affinity (A) and other parameters have been derived as follows:

\[ I = -E_{\text{HOMO}} \quad \text{and} \quad A = -E_{\text{LUMO}} \]

\[ \eta = (I-A)/2 \; ; \text{where } \eta \text{ represents hardness of the compound,} \]

Chemical Potential \((\mu) = -(I+A)/2\)

\[ S=1/\eta \; ; S \text{ abbreviated as the softness of the molecules,} \]

\[ \chi = (I+A)/2 \; ; \chi \text{ as electro negativity,} \]

\[ \omega = \mu^2/2\eta \; ; \omega \text{ as electrophilicity index.} \]

The details of all global reactivity variables are listed in Table 5.
Table 5. Global reactivity descriptors for MBMMBA.

| Electronic Parameter | MBMMBA  |
|----------------------|---------|
| I (eV)               | 6.76    |
| A (eV)               | 2.03    |
| E_g (eV)             | 4.46    |
| χ (eV)               | 4.39    |
| η (eV)               | 2.36    |
| μ (au)               | 3.67    |

3.6. Electric moments

The values of dipole moment (μ_total), polarizability (α_o) and hyperpolarizability (β) have been calculated for the compound MBMMBA and tabulated in the Table 6. The dipole moment for 4-bromo-3-(methoxymethoxy) benzoic acid has been measured as 4.0955 Debye and the polarizability presented in the Table 6 is found to be 2.1880 x 10^{-23} esu, that supports the small frontier orbital gap for MBMMBA on the basis of the discussion for 2nd perturbation theory which says that the large participation to the polarizability will be obtained from small gap between unoccupied orbitals and occupied orbitals [34]. The value of β_{total} which is abbrevation of hyperpolarizability has been measured as 9.7419 x 10^{-30} esu (50 times larger than 0.1947 x 10^{-30} esu, the hyperpolarizability value of of urea). This very high value of total 1st order static hyperpolarizability β_{total} reveals that MBMMBA molecule has good non-linear optical properties.

Table 6. Calculated value of dipole moment, polarizability and hyperpolarizability for MBMMBA.

| Dipole Moment (μ_{total}) in Debye | First order static hyperpolarizability (β) |
|------------------------------------|---------------------------------------------|
| μ_x                                | β_{xxx}                                    |
| 0.1153                             | -851.4206911                                |
| μ_y                                | β_{xyy}                                    |
| 4.0883                             | 271.0771818                                 |
| μ_z                                | β_{yy}                                     |
| 0.2145                             | -249.4401503                                |
| μ_{tot}                            | β_{yy}                                     |
| 4.0955                             | 31.7071976                                  |
| Polarizability (α_o) in esu.       | β_{xxx}                                    |
| α_{xx}                             | -0.3304575                                  |
| 194.5268422                        | -0.1753489                                  |
| α_{xy}                             | β_{xy}                                     |
| -6.96532                           | -0.0542168                                  |
| α_{yy}                             | β_{yy}                                     |
| 163.8507996                        | -12.9384306                                 |
| α_{xz}                             | β_{zz}                                     |
| 0.0004749                          | 35.3735385                                  |
| α_{yz}                             | β_{zz}                                     |
| 0.0010543                          | 0.0525921                                   |
| α_{zz}                             | β_{zz}                                     |
| 84.5393417                         | 1164.0059 au                                |
| α_o                                | β_{total} (au)                              |
| 2.1880 x 10^{-23} esu              | 9.7419 x 10^{-30} esu                      |

5. Conclusion

The compound 4-bromo-3-(methoxymethoxy)benzoic acid (C_{9}H_{9}BrO_{4}), which belongs to the derivative of bromo–hydroxy–benzoic acids has been studied for molecular structure (bond length, bond angle), vibrational analysis, LUMO-HOMO, MESP, electronic and thermodynamic parameters and the resultant data is summerised in the form of schematic graphics and tables. The bond length and bond angle are in fair agreement with experimental values. The energy gap between HOMO and LUMO is 4.46 eV which
shows more reactive nature of the molecule. The MESP plot of molecule indicates active electrophilic site in the molecule is over the carbon atoms whereas region near carboxylic group is prone to active for nucleophillic attack. All the vibrational modes of molecules have been calculated along with potential energy distribution. The thermal paramters of the molecule have been also calculated. The local reactivity descriptors data indicates that the most desirable site for electrophilic attack is observed at C11 and that for nucleophilic and free redical attacks are found at C10 and C11 respectively; and solvation influences these sites. The hyperpolarizability has been measured as $9.7419 \times 10^{-30}$ esu (50 times larger than that of urea) making the compoud as a good non-linear optical agent.

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