Theoretical Investigations on the Structural, Vibrational and Optical Properties of 3-Bromo-4-Methyl Benzonitrile

N.Y. Sugirtha Suni, R. Ganapathi Raman, L. Guru Prasad

Abstract---The optimized geometry, Mulliken population analysis, highest occupied molecular orbital energy, lowest unoccupied molecular orbital energy, dipole moment, polarizability and first order hyperpolarizability of 3-bromo-4-methyl benzonitrile have been predicted with the aid of density functional theory (DFT) calculations with B3LYP using 6-311++G(d,p) basis set. Fourier Transform InfraRed (FTIR) and Fourier Transform - Raman (FT-Raman) spectrum were investigated and compared with the experimental data. The first order hyperpolarizability calculated by quantum chemical calculations shows that the title compound is an efficient molecule for future applications in non-linear optics. Natural bond orbital (NBO) analysis and several thermodynamic properties have been studied by DFT.

Keywords---3-bromo-4-methyl benzonitrile, density functional theory (DFT), FTIR, FT-Raman, Natural bond orbital (NBO).

I. INTRODUCTION

Nitrile group is one of the common groups occurring in nature which is a versatile precursor and intermediate for amines, aldehydes, drugs, agrochemicals, electronic materials and herbicides [R. C. Larock, 1989; S. Patai et al., 1983; Anna Berteotti et al., 2014]. Recently drugs manufactured from nitriles are used for a variety of pathological conditions [F. F. Fleming, et al., 2010]. The recent importance of nitriles in the field of medicine is due to its versatility which is due to the presence of polarized triple bond which allows it to undergo a variety of interactions [J. Y. Le Questel et al., 2000].

Dyes having nitrile group are very common because they have good mechanical property and thermal stability. Hence, they produce fructuous outputs in the field of solar technology. Since nitriles have a peak temperature of 350 °C at the end of its life period, the derivatives of nitriles find application in spacecrafts, marine engineering, electronic and integrated circuit package systems [P. Govindasamy et al., 2014].

Non-linear optics is related to the interaction of applied electromagnetic in several materials to generate new electromagnetic fields which is altered in wave number, phase, and other physical properties [Saxena et al., 2015]. Quantum chemical calculations are helpful in the description of the relationship between the electronic structure of the systems and in NLO response. The computational approach allows the calculation of molecular NLO properties inexpensively by determining higher order polarizability tensors of the molecule [Samsonowicz et al., 2014].

Benzonitrile, a phenyl cyanide compound was derived by heating benzoic acid with lead thiocyanate. When it reacts with strong acid, it produces toxic hydrogen cyanide buton heating it decomposes and produces very toxic vapours of hydrogen cyanide and nitrous oxide [V. Krishnakumar et al., 2004; M. Murugan et al., 2012]. Benzonitrile and most of its derivatives are used in industrial and medical field for manufacturing dyes, rubber chemicals, polymers, anhydrous metal salts, food preservatives, drugs and as intermediates for pharmaceuticals, organic chemicals, antiseptics, natural products, herbicides, epoxy curing agent, agrochemicals [Mahendra Kumar Trivedi et al., 2015].

Benzonitrile compounds are well known solvents in physical science laboratories. The substitution benzonitrile compounds possess strong and weak inhibitory effects based on their positions [A. Ajaypraveenkumar et al., 2017]. The para or meta position of benzonitrile is an example for weak catalytic effect in nitriase enzyme. But the substitution in the orthoposition of benzonitrile is a consequence of strong effect because of steric hindrance [M. Murugan et al., 2012; M. J. Frisch, et al., 2009].

Recently Dye-Sensitized Solar Cells (DSSCs) are found to be the most systematic and cheapest third-generation solar technology, which has the magnificent interest, as green and renewable energy converting device [Sanghoon Yoon et al., 2011; N. Robertson, 2006]. In DSSC, the dye sensitizers plays a supercilious and significant part which enhances future researches [Arokiiasamy Ajaypraveenkumar et al., 2017]. Properties like physical, electronic and the thermal properties of dye sensitizers has to be taken into account for DSSC synthesis. Hence computational and experimental investigations of these dye sensitizers has become an essential technique for identifying innovatory dye sensitizers with enhanced properties [David Pegu et al., 2013].

Results obtained from theoretical methods for large molecules are applied for finding their applications in various fields in addition to their physico-chemical properties. Theoretical calculations are powerful tools for determining specific answers which can be authenticated with experimental values.
II. METHODOLOGY

The compound 3-bromo-4-methylbenzonitriilewas procured from Sigma Aldrich Chemical Company, USA with purity more than 99% were used without further purification for experimental studies. FT Raman spectrum was recorded within 3500 to 50 cm$^{-1}$ using EZR Raman, Enwaveoptronics, USA IFS66 V Spectrometer. FTIR spectra was recorded in the region 4000 to 400cm$^{-1}$ using 8400S Bruker, Alpha T, infrared spectrophotometer with KBr pellet technique. Both spectra are inscribed at normal temperature using a scan speed 30 cm$^{-1}$ min$^{-1}$.

III. COMPUTATIONAL DETAILS

All predictions were made using Gaussian 09 program package [M.J. Frisch et al, 2009] with aid of DFT with B3LYP using 6-31+G(d,p) basis set and viewed using GAUSS VIEW program. HOMO - LUMO energy was calculated by time dependent density functional theory (TDDFT). NBO analysis had been carried out to study interaction between filled and vacant orbitals and to elucidate the stability of the molecule. Electrostatic Potential map was marked by MOLKEL. Polarizability and hyperpolarizability were calculated for studying the NLO activity of the molecule. Different modes of vibration were found out through TED and predicted by VEDA.4.0. Software [M. Silverstein et al, 1981]. Sharma Kumar et al, 2015]. Polarizability, hyperpolarizability, dipole moment, Mulliken atomic charges and various thermodynamic parameters like entropy, enthalpy and Gibb’s free energy were also calculated and studied.

IV. RESULTS AND DISCUSSION

Optimized Parameters

Optimized structure of 3B4MBN is illustrated in fig. 3. All optimized parameters are tabulated in table 1. Most of the C-H bond length is 1.07 Å, but C2 – H11 and C2 – H12 bond lengths are slightly increased (1.2703 Å) due to methyl group substitution. Most of the C-C bond lengths are 1.54 Å, but C2 – C3, C4 – C5 and C6 – C7 are slightly decreased (1.3552 Å) due to substitution groups. These variation in bond lengths are due to variation in hybridization resulting in the substitution of different groups attached to the concerned carbon atoms. The C – Br bond length is longer (1.91 Å) than that of C – C interactions which is the common basis for intra molecular interactions confirming the stability of the molecule.

Fig.1: Optimized structure of 3B4MBN

Table 1: Optimized parameters of 3B4MBN

<table>
<thead>
<tr>
<th>Parameter</th>
<th>B3LYP</th>
<th>Parameter</th>
<th>B3LYP</th>
<th>Parameter</th>
<th>B3LYP</th>
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<td>BondLength Å</td>
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<td>Bond Angle(°)</td>
<td>6-311G+(d,p)</td>
<td>DihedralAngle(°)</td>
<td>6-311G+(d,p)</td>
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<tr>
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</tr>
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<td>C9 – C5 – C6 – C7</td>
<td>180.0</td>
<td></td>
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</table>
V. VIBRATIONAL ASSIGNMENTS

The investigated compound has 16 atoms and so it possess 42 normal vibrational modes. Out of 42 normal modes, 15 are stretching modes, 14 bending modes and 13 torsional modes. Vibrational frequencies calculated and observed are shown in table 2. Experimental and theoretical spectra obtained are shown in Fig-2 and Fig-3 respectively.

CH vibrations

C-H stretching vibrational peaks in aromatic compounds are found in the range 3100-3000 cm$^{-1}$[E.F.Monney, 1963]. The worked out stretching vibrations of the investigated compound was found to lie within 3212-3034 cm$^{-1}$. Observed frequencies are accomplished at 2978 and 3422 cm$^{-1}$. For substituted benzenes, three in-plane C-H vibrational peaks are found within 1300-1000 cm$^{-1}$ and three out-of-plane bending vibrational peaks appear within 1000-750 cm$^{-1}$[E.F.Monney, 1964]. Worked out in-plane bending vibrational peaks are found to lie within 1411-1016 cm$^{-1}$ which was in accordance with the experimental values 1040, 1146, 1190 and 1263 cm$^{-1}$ of FTIR and 1216 and 1232 cm$^{-1}$ of FT-Raman spectra. Calculated out-of-plane bending vibrations are found to lie within 838-975 cm$^{-1}$ which was in accordance with 883, 822 cm$^{-1}$ of FTIR and 866 cm$^{-1}$ of FT-Raman spectra respectively.

CBr vibrations

C-Br vibrations has two stretching and three in-plane bending vibrational modes. A frequency range of 1129-480 cm$^{-1}$ is assigned for interaction of Carbon atom with heavy atoms like Cl, Br, I. [N Sundaraganesan et al, 2005, J Senthilkumar et al, 2015]. Calculate values for C-Br vibrations was found to lie in 908-124 cm$^{-1}$, 956 cm$^{-1}$ of FTIR spectra was ascribed to C-Br vibrations. Bending vibration occur within 531 cm$^{-1}$[V. Arjunan et al, 2013]. Calculated frequency at 580 cm$^{-1}$ corresponds to C-Br bending vibration.

C≡N vibrations

In the benzonitrile molecule, since cyano group (C≡N) is attached together with the phenyl ring there is no change in the vibrational wave number of such group. In aromatic compounds with C≡N group attached together with phenyl ring, a vibrational peak has been observed within 2240-2221 cm$^{-1}$[N B Colthup et al, 1990, Sundaraganesan N et al, 2009]. Br and OH are the electron acceptors group, because it decreases the intensity of IR band and hence the wave number increases to the upper limit of the respective spectral band region. CH$_3$ is the electron donor group, since it increases the intensity of IR band and wave number valued creases[Rastogi V K et al, 2010]. Thus, electron acceptor groups play an important part in shifting vibrational wave number for C≡N bond. Calculated frequency for C≡N vibrations is 2333 cm$^{-1}$ which is in accordance with 2318 cm$^{-1}$ and 2338 cm$^{-1}$ of FTIR and FT-Raman spectrum.

CC vibrations

Ringed C-C stretching vibration appears within 1650-1400 cm$^{-1}$[Popov A A et al, 2004]. Worked out values for CC vibrations lies within 1636-1232 cm$^{-1}$. Observed values are 1649, 1545, 1381, 1263 cm$^{-1}$ and 1664, 1238 cm$^{-1}$ of FTIR and FT-Raman spectra which are well matching with calculated values.

CCCC torsional vibrations

Ringed torsions are observed below 800 cm$^{-1}$[Mulliken R S, 1985]. The calculated peaks at 686, 609, 434, 291, 264, 215 and 146 cm$^{-1}$ are ascribed to C-C-C-C torsional vibrations that are mixed with C-C-C-H and C-C-C-N torsions. Observed values are 691 cm$^{-1}$ and 672, 280, 256 cm$^{-1}$ of FTIR and FT-Raman spectra.

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**Fig. 2: FTIR Spectra of 3B4MBN**
### Table 2: Vibrational assignments with TED (%) for the investigated compound

<table>
<thead>
<tr>
<th>Normal Modes</th>
<th>Mode Label</th>
<th>Experimental (cm(^{-1}))</th>
<th>FT-IR</th>
<th>FT-Raman</th>
<th>IR Intensity(Km/mol)</th>
<th>assignments with TED (%)</th>
<th>Raman Activity</th>
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<tr>
<td>1 A</td>
<td>A</td>
<td>100 1.0617</td>
<td>0.1773</td>
<td>rCCCBr (44) + rCCCC (23)</td>
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<tr>
<td>2 A</td>
<td>A</td>
<td>124 4.3168</td>
<td>5.2611</td>
<td>rCCC(42)+rCCCN(30)+rCCCBr(17)</td>
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<tr>
<td>3 A</td>
<td>A</td>
<td>130 0.6043</td>
<td>1.7295</td>
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<td>4 A</td>
<td>A</td>
<td>146 0.2664</td>
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<td>5 A</td>
<td>A</td>
<td>215 0.079</td>
<td>0.566</td>
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<td>A</td>
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<td>8 A</td>
<td>A</td>
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<td>9 A</td>
<td>A</td>
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<td>1420 2.3195</td>
<td>21.6692</td>
<td>vCC(39)+vHCC(13)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>31 A</td>
<td>A</td>
<td>1479 11.1233</td>
<td>9.0024</td>
<td>δCH(65)+vHCC(32)</td>
<td></td>
<td></td>
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<tr>
<td>32 A</td>
<td>A</td>
<td>1487 9.9904</td>
<td>8.9552</td>
<td>vHCC(41)+vHCC(23)+6vCH(23)</td>
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<tr>
<td>33 A</td>
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<td>2.7083</td>
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<tr>
<td>34 A</td>
<td>A</td>
<td>1578 21.3915</td>
<td>5.8967</td>
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<tr>
<td>35 A</td>
<td>A</td>
<td>1649 1664 1636</td>
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<tr>
<td>36 A</td>
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<td>2318 2338 2333</td>
<td>44.6019</td>
<td>598.2007</td>
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<tr>
<td>37 A</td>
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<td>2978 3034</td>
<td>10.519</td>
<td>251.8793</td>
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<td></td>
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<tr>
<td>38 A</td>
<td>A</td>
<td>3086 6.7118</td>
<td>72.5802</td>
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<td></td>
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</tr>
<tr>
<td>39 A</td>
<td>A</td>
<td>3116 15.4586</td>
<td>62.2122</td>
<td>vCH(92)</td>
<td></td>
<td></td>
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<tr>
<td>40 A</td>
<td>A</td>
<td>3175 6.6118</td>
<td>90.9568</td>
<td>vCH(91)</td>
<td></td>
<td></td>
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<tr>
<td>41 A</td>
<td>A</td>
<td>3202 6.6803</td>
<td>126.4837</td>
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<td></td>
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<tr>
<td>42 A</td>
<td>A</td>
<td>3422 5.085</td>
<td>54.4065</td>
<td>vCH(100)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Charge Distribution Analysis**

The bonding capacity of molecules depend on its number of unpaired electrons in the atoms and hence the atomic charge distribution has been calculated by Mulliken population analysis[GunaseKaran S et al, 2008]. It plays an efficient role in applying quantum chemistry calculation to molecular systems since atomic charge has influence on parameters like dipole moment, polarizability, electronic structure and other properties of molecular systems [Prabhaaran M et al, 2014]. Calculated Mulliken charges is shown in Table.3.3.In the present compound carbon atom possess both signed charge distribution.

![Raman Spectra](image-url)
Hydrogen atoms having positive charge distribution acts as the acceptor atoms, bromine and nitrogen atoms possessing negative charge distribution acts as the donor atoms. Hence transfer of charges takes place between the donor and acceptor atoms resulting in charge interactions accountable for the stability of a molecule.

Table 3: Mulliken Charges

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<tr>
<th>Sl.No</th>
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<tr>
<td>3</td>
<td>C</td>
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<tr>
<td>4</td>
<td>C</td>
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<tr>
<td>5</td>
<td>C</td>
<td>2.163608</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
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</tr>
<tr>
<td>7</td>
<td>C</td>
<td>0.990713</td>
</tr>
<tr>
<td>8</td>
<td>Br</td>
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<tr>
<td>9</td>
<td>C</td>
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<tr>
<td>10</td>
<td>N</td>
<td>-0.16466</td>
</tr>
<tr>
<td>11</td>
<td>H</td>
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</tr>
<tr>
<td>12</td>
<td>H</td>
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<td>13</td>
<td>H</td>
<td>0.218825</td>
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<tr>
<td>14</td>
<td>H</td>
<td>0.222052</td>
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<tr>
<td>15</td>
<td>H</td>
<td>0.185441</td>
</tr>
<tr>
<td>16</td>
<td>H</td>
<td>0.240767</td>
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</table>

Fig. 4: Mulliken Charges Plot of 3B4MBN

Fig. 5: Molecular electrostatic potential plot and Counter map of 3B4MBN

Molecular electrostatic potential (MEP) at a point is the space surrounding a molecule where its electrostatic effect due to total charge distribution can be felt at that point, which correlates with partial charges, electro negativity, dipole moment and the active reactivity property of the molecule[A Ajaypraveenkumar et al. 2017,Murray J S et al.1996]. MEP is used to speculate the reactivity sites for electrophilic and nucleophilic attacks which is employed in investigating hydrogen bonding interactions, crystalline behaviour, molecular cluster and a broad range of macroscopic properties [Mauricio AlcoleaPalafox, 2000, KerassaAicha et al. 2015, Y R Shen, 1984, ArockiasamyAjaypraveenkumar et al. 2017, Mehmet Cinar et al, 2015, Y X Sun et al. 2009, C Andraud et al. 1994]. Fig 3.5 gives the electrostatic potential map and counter map of the molecule under investigation. Electrostatic potential regions are presented by different colours at the surface. The red coloured area denotesthe region of negative electrostatic potential, blue coloured area denotes the region of positive electrostatic potential and green coloured portion denotes zero electrostatic potential region. The red coloured area of negative electrostatic potential corresponds to electrophilic activity and blue coloured area of positive electrostatic potential corresponds to nucleophilic activity sites.

Molecular Orbital Analysis

Frontier molecular orbitals (HOMO and LUMO) are the valuable tools to describe the reactivity of a molecule[Neda et al, 2017]. In HOMO-LUMO plot red colour represents positive phase, green colour represents negative phase [K.Rajalakshmi et al, 2017]. HOMO-LUMO plot is shown in fig6.

The HOMO-LUMO obtained for the molecule is 5.83eV. Energy gap is an effective tool that predicts the kinetic stability of a molecule [K.Rajalekshmi et al, 2014]. Larger the energy gap more stable will be the molecule but its chemical reactivity is low, smaller the energy gap the molecule will be less stable but its chemical reactivity is high. As the softness of the molecule increases, its chemical reactivity also increases. Also increase in hardness decreases the chemical reactivity of a molecule.
In general molecules possessing large energy gap are less polarized and are called as hard molecules which are highly stable with low chemical reactivity. As the softness increases, higher will be its chemical reactivity. Calculated energy parameters are listed in Table 3.4. The density of state (DOS) spectrum of the title molecule is shown in Fig. 3.7.

Table 4: Energy parameters of 3B4MBN

<table>
<thead>
<tr>
<th>Basic set</th>
<th>6-311++G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF energy (a.u)</td>
<td>-2937.44</td>
</tr>
<tr>
<td>Dipole moment(Debye)</td>
<td>2.340Debye</td>
</tr>
<tr>
<td>LUMO(eV)</td>
<td>-1.76</td>
</tr>
<tr>
<td>HOMO(eV)</td>
<td>-7.59</td>
</tr>
<tr>
<td>ENERGY GAP(eV)</td>
<td>5.83</td>
</tr>
<tr>
<td>Electronegativity (χ)</td>
<td>-4.625</td>
</tr>
<tr>
<td>Chemical Potential (µ)</td>
<td>4.625</td>
</tr>
<tr>
<td>Global Hardness (η)</td>
<td>2.675</td>
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<tr>
<td>Global softness (s)</td>
<td>0.373831776</td>
</tr>
<tr>
<td>Electrophilicity Index (ω)</td>
<td>6.1859375</td>
</tr>
<tr>
<td>EHOMO-1(eV)</td>
<td>-7.69</td>
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<tr>
<td>ELUMO+1(eV)</td>
<td>-1.38</td>
</tr>
<tr>
<td>EHOMO-1 - ELUMO+1(eV)</td>
<td>-6.31</td>
</tr>
</tbody>
</table>

Natural Bond Orbitals (NBO) Analysis

Highest amount of electron density orbital details and most precise ‘natural Lewis structure’ are determined through the NBO analysis. These analyses have been enhancing the interactions between the intra and intermolecular interactions during the interactions of filled and virtual orbitals which information are got from NBO analysis. NBO analysis was investigated for charge transfer among bonds as well as molecular systems. The second order micro disturbance theory explained the results of the interacting stabilization energy are the more rigorous interaction between electron donor-acceptor orbital and the greater scope of conjugation of the whole system was reported [K Chaitanya, 2012].

Intramolecular charge transfer (ICT) is a main reason for stabilization of the system has been held at the intramolecular relations are facade by the orbital overlap between bonding C–C, C–Norbitals and C–Br antibonding orbital as shown in Table 3.4. The bonds are weakened in C–C, C–N and C–Br antibonding orbital in which communications are perceived as escalation in electron density (ED).

The natural bond orbital (NBO) analysis provides an efficient method to investigate the intra-and intermolecular bonding and interaction among bonds, charge transfer or conjugative interaction in molecular systems. It can also calculate the analysis of the delocalization of charge in the system. The stabilization energy E (2) is very small energy between the filled and vacant orbitals; this is predicted through the hyper conjugative electron transfer route. The highest value of the E (2) is represents it. This E (2) is mainly the reason for delocalization of electron density in between occupied Lewis-type NBO orbitals and formally unoccupied non-Lewis NBO orbitals [M Kurt et al, 2011, Arockiasamy Ajaypraveenkumar et al, 2017]. The stabilization capacity of the compound E (2) allied with the delocalization i-j is estimated as:

\[
E(2) = -n_\sigma \left( \frac{\langle \sigma | F | \sigma \rangle^2}{\epsilon_\sigma} - \epsilon_\sigma \right) = -n_\sigma \frac{F_\sigma^2}{\Delta E}
\]
Here, $\langle \sigma | F | \sigma \rangle$ or $E^2_{ij}$ is the Fock matrix element I and j orbital. $\varepsilon_r^d$ and $\varepsilon_d$ are the energies of $\sigma^*$ and $\sigma$ and $n_0$ is the population of the donor $\sigma$ orbital [E. GladisAnitha et al., 2015]. The system is stable because of the transfer of intramolecular charges that happens by the intramolecular interaction which is caused by the overlapping of orbitals between bonding $\pi$ (C1 – C6), $\pi$ (C4 – C5) and antibonding $\pi^*$ (C2 – C3), $\pi^*$ (C1 – C6) orbitals.

**Table 5: NBO Analysis of 3B4MBN**

<table>
<thead>
<tr>
<th>Donor (i)</th>
<th>Type</th>
<th>Acceptor (j)</th>
<th>Type</th>
<th>$E^{(2)}$</th>
<th>$E^{(3)}$</th>
<th>$E^{(4)}$</th>
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<tbody>
<tr>
<td>C1 - C2</td>
<td>$\sigma$</td>
<td>C1 - C6</td>
<td>$\sigma^*$</td>
<td>0.02388</td>
<td>3.5</td>
<td>1.29</td>
</tr>
<tr>
<td>C1 - C2</td>
<td>$\sigma$</td>
<td>C3 – H11</td>
<td>$\sigma^*$</td>
<td>0.03184</td>
<td>3.24</td>
<td>1.27</td>
</tr>
<tr>
<td>C1 - C6</td>
<td>$\sigma$</td>
<td>C1 - C2</td>
<td>$\sigma^*$</td>
<td>0.0242</td>
<td>4.03</td>
<td>1.25</td>
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<tr>
<td>C1 - C6</td>
<td>$\sigma$</td>
<td>C2 - Br8</td>
<td>$\sigma^*$</td>
<td>0.03096</td>
<td>5.27</td>
<td>0.79</td>
</tr>
<tr>
<td>C1 - C6</td>
<td>$\pi$</td>
<td>C2 - C3</td>
<td>$\pi^*$</td>
<td>0.44833</td>
<td>23.16</td>
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<tr>
<td>C1 - C6</td>
<td>$\pi$</td>
<td>C4 - C5</td>
<td>$\pi^*$</td>
<td>0.28292</td>
<td>16.55</td>
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</tr>
<tr>
<td>C1 - C7</td>
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<td>C5 - C6</td>
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<td>C3 - C4</td>
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<td>1.27</td>
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<tr>
<td>C2 - C3</td>
<td>$\sigma$</td>
<td>H 11 - N10</td>
<td>$\sigma^*$</td>
<td>0.01172</td>
<td>4.96</td>
<td>1.7</td>
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<tr>
<td>C2 - C3</td>
<td>$\pi$</td>
<td>C4 - C5</td>
<td>$\pi^*$</td>
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<td>18</td>
<td>0.31</td>
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<tr>
<td>C2 - Br8</td>
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<tr>
<td>C3 - C4</td>
<td>$\sigma$</td>
<td>C9 - H 15</td>
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<td>C3 - H11</td>
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<td>C4 - C5</td>
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<td>C1 - C6</td>
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**NLO property**

NLO activity is a quantitative approach for constructing new electromagnetic fields, to shift the wave numbers, phase and other properties of a material. Polarizability ($\alpha$) is used to evaluate the scatteringcross-sections of different scattering processes, the strength of molecular interactions and the collision processes taking place in the interaction of the material with the applied electromagnetic field [V M Geskin et al., 2003, M Nakano et al., 2002, Shajikumar et al., 2017]. Hyperpolarizability ($\beta$) provides the direct approach from the finite field method which plays an important role in the various significant activities like signal transferring, fiber optic cables optical changing, optical controlling and optical logical circuits in many telecommunication areas [Shajikumar et al., 2017, D Sajan et al., 2013]. The optical properties of the molecule can be obtained from the values of second order polarizability [E. GladisAnitha et al., 2015] or first order hyperpolarizability ($\beta_0$), anisotropic tensor ($\Delta\alpha$), linear polarizability ($\alpha$) and dipole moment ($\mu$). Dipole moment ($\mu$) and first order hyperpolarizability ($\beta_0$) calculated for urea using the same basis set is 1.3732 Debye and 0.3728 x 10$^{-33}$ esu respectively. NLO parameters of the title compound can be calculated as follows:

Dipole moment, $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$

Linear polarizability, $\alpha = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$

First order hyperpolarizability,

$$\beta_0 = \left[ (\beta_{xxx} + \beta_{xxy} + \beta_{xxz})^2 + (\beta_{xyy} + \beta_{yyz} + \beta_{yzy})^2 + (\beta_{zzz} + \beta_{zzy} + \beta_{zyz})^2 \right]^{1/2}$$

Since urea is one of the exemplary molecule for studying the NLO activity, the calculated values of first order hyperpolarizability, and dipole moment of the molecule are assessed with urea.
The dipole moment and first order hyperpolarizability of the title molecule is 3.483 Debye and 4110.074 x 10^-33 esu respectively. Dipole moment of the title molecule is 2.53 times and first order hyperpolarizability is 11 times greater than urea. Hence we propose that the investigated compound under study is an efficient material for future NLO applications.

<table>
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<th>Parameters</th>
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<td>10.6593936</td>
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<td>α0</td>
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<tr>
<td>B</td>
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<td>4110.074 x 10^-33 esu</td>
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**Table 7: Thermodynamic Parameters of 3B4MBN**

<table>
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<tr>
<th>Thermal Parameters</th>
<th>B3LYP/6-311++g(d,p)</th>
</tr>
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<tbody>
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<td>SCF(a.u)</td>
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</tr>
<tr>
<td>Zero point vibrational Energy(Kcal/Mol)</td>
<td>67.9002</td>
</tr>
<tr>
<td>Rotational Constant(GHz)</td>
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</tr>
<tr>
<td>Rotational Temperature(kelvin)</td>
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</tr>
<tr>
<td>Vibrational</td>
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<tr>
<td>Vibrational</td>
<td>71.889</td>
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<tr>
<td>Total</td>
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<tr>
<td>Transitional</td>
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<tr>
<td>Rotational</td>
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<tr>
<td>Vibrational</td>
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<tr>
<td>Dipole moment (Debye)</td>
<td>3.483 Debye</td>
</tr>
<tr>
<td>Lumo(eV)</td>
<td>-1.76</td>
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<tr>
<td>Homo(eV)</td>
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<tr>
<td>Energy gap(eV)</td>
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<td>Total</td>
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<td>Transitional</td>
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<td>Gibbs Free Energy</td>
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<td>Enthalphy</td>
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**VI. CONCLUSION**

Detailed investigation of the structural, vibrational and optical property of the compound under study has been performed by DFT using suitable basis set. The optimized structure and geometrical parameters for conformational studies of the compound was determined theoretically using the same basis set. Calculated FTIR and FT-Raman frequencies are in good agreement with the experimental frequencies. HOMO- LUMO gap helps in the determination of chemical reactivity and stability of the compound. The title compound exhibit good electronic property which was proved by frontier molecular orbital, and NBO analysis. NBO analysis shows the intramolecular charge transfer between the bonding and antibonding orbitals. Mulliken population analysis was done to study the electronic charge distribution of the molecules.
The energy gap, polarizabilities, hyperpolarizabilities, excitation energies, atomic charges, electrostatic potential and certain thermodynamic parameters were determined using theoretical method. First order hyperpolarizability calculated for the compound is 11 times greater than urea. Hence the compound under study is an efficient material for future NLO applications.

REFERENCES


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