Molecular structure, first order hyperpolarizability, NBO and HOMO-LUMO analysis of cinnoline-4-carboxylic acid

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Abstract: In this work, we reported theoretical investigations on molecular structure of cinnoline-4-carboxylic acid (CN4C). The molecular geometry and NLO have been calculated by using density functional theory B3LYP method with 6-311++G(d,p) basis set. The first order hyper polarizability (βα) of this molecular system and related properties (β, μ and Δα) are calculated using B3LYP/6-311++G(d,p) methods based on the finite-field approach. Stability of the molecule arising from hyper-conjugative interactions and charge delocalization has been analyzed using natural bond orbital analysis (NBO). The evaluated HOMO and LUMO energies illustrate that charge transfer within the molecule. Molecular electrostatic potential (MEP) were also performed.

I. INTRODUCTION

Cinnoline derivatives are an important class of compound possessing a wide variety of biological activities such as antibacterial and antifungi activities [1,2]. Investigations on structures of Cinnoline derivatives have attracted the attention due to their peculiar properties and pharmacological uses. Cinnoline and related compounds pointed out that this ring system was the least known of the condensed, bicyclic aromatic heterocycles containing two nitrogen atoms. Some cinnolines have been screened and have received approval as bioactive drugs or are still under clinical trials [3]. Its chemical formula is C9H6N2O2. Literature survey reveals that to the best of our knowledge, there is no DFT studies, vibrational assignments, NLO activity and molecular docking studies for title compound CN4C.

Nowadays, density functional theory (DFT) method becomes the most popular and versatile quantum mechanical modeling method to investigate the electronic structure. Also, the natural bond orbital investigation (NBO) has been performed to get accurate information regarding the hybridization and hydrogen bond interaction energies. In addition to these, the HOMO-LUMO energy gap has been computed to provide the information regarding the charge transfer within the molecule. The other important quantities such as softness (S), hardness (η), electron affinity(A), ionization potential(I), chemical potential (μ), electrophilicity index (ω), electronegativity (χ), are also calculated in the way of molecular orbital framework.

II. COMPUTATIONAL METHODS

Density Functional Theoretical (DFT) quantum chemical computations were carried out at the Becke3-Lee-Yang-parr(B3LYP) level with 6-311++G(d,p) basis set using Gaussian 09 program package [4] to get a clear knowledge of optimized parameters. NBO calculations [5] were performed using NBO 3.1 Program to understand inter and intra-molecular delocalization or hyperconjugation [6-9]. The first hyper polarizabilities and related properties (βtot, μ, Δα) of title compound CN4C were calculated using B3LYP/ 6-311++G(d,p) basis set. The electronic properties such as HOMO and LUMO energies were determined by DFT approach.

III. RESULTS AND DISCUSSION

A. Molecular geometry

The geometrical parameters of the CN4C molecules are listed in Table 1 using DFT/B3LYP method with 6-311++G(d,p) basis set. The optimized molecular structure of cinnoline-4-carboxylic acid is obtained from Gaussian 09W and GaussView 5.0 programs are shown in Fig.1. The theoretical investigation were carried out isolated molecule in the gas phase. This title molecule has nine C - C bond lengths, five C - H bond lengths, two (C - N, C - O) bond lengths and one (N - N, O - H) bond lengths respectively. The highest bond length was calculated for N1 – N2, C6-C7, C7-C8, C8-C9 found to be 1.403 and 1.402 Å respectively. The calculated bond length values for C-C in the benzene ring vary from
1.355-1.402 Å and C-H bond length calculated at 1.070 Å by B3LYP/6-311++G(d,p) basis set. The homonuclear bond lengths (C-C and N-N) are higher and heteronuclear bond lengths (C-H, N-C and C-O) are lower. The important reason for the like charges is repulsive and the forces of unlike charges are attractive.

The isotropic (or average) linear dipole moment and

\[ \mu = \frac{\alpha \beta}{3} \]

where \( \alpha \) is the linear polarizability, \( \mu_0 \) is the permanent dipole moment and \( \beta_{ij} \) are the first hyperpolarizability tensor components. The isotropic (or average) linear polarizability is defined as:

\[ \alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \]

The first order hyperpolarizability is a third rank tensor that can be explained by 3x3x3 matrix. The 27 components of 3D matrix can be abridged to 10 components owing to the Kleinman symmetry [12]. Components of the first hyperpolarizability can be calculated using the following equation:

\[ \beta_{ij} = \beta_{ij}^{(0)} + \sum_{k} \left( \beta_{ij}^{(1)} + \beta_{ij}^{(2)} + \beta_{ij}^{(3)} \right) \]

Using the x, y and z components of \( \beta \), the magnitude of the first hyperpolarizability tensor can be calculated by:

\[ \beta_{tot} = \sqrt{\beta_{xx}^2 + \beta_{yy}^2 + \beta_{zz}^2} \]

The entire equation for reckoning the magnitude of \( \beta \) from

| Parameters | Bond length(Å) | Parameters | Bond angle(°) |
|------------|----------------|------------|--------------|
| N1-N2      | 1.403          | N2-N1-C10  | 120.1        |
| N1-C10     | 1.337          | N1-N2-C3   | 120.8        |
| N2-C5      | 1.341          | N1-C16-N5  | 119.6        |
| C3-C4      | 1.356          | N1-C16-C9  | 120.3        |
| C3-H14     | 1.070          | N2-C3-C4   | 120.4        |
| C4-C5      | 1.399          | N2-C3-H14  | 119.8        |
| C4-C11     | 1.355          | C4-C3-H14  | 119.8        |
| C5-C6      | 1.401          | C5-C4-C5   | 119.8        |
| C5-C10     | 1.397          | C5-C4-C11  | 120.1        |
| C5-C7      | 1.402          | C5-C4-C11  | 120.1        |
| C6-H15     | 1.070          | C4-C5-C6   | 120.4        |
| C7-C8      | 1.402          | C4-C5-C10  | 119.4        |
| C7-H16     | 1.070          | C4-C11-O12 | 120.0        |
| C8-C9      | 1.402          | C4-C11-O13 | 120.0        |
| C8-H17     | 1.070          | C6-C5-C10  | 120.1        |
| C9-C10     | 1.401          | C5-C6-C7   | 119.9        |
| C9-H18     | 1.070          | C5-C6-H15  | 120.1        |
| C11-O12    | 1.258          | C5-C16-C9  | 120.1        |
| C11-O13    | 1.301          | C7-C6-H15  | 120.1        |
| O13-H19    | 0.960          | C6-C7-C8   | 120.0        |
|            |                | C6-C7-H16  | 120.0        |
|            |                | C6-C7-H16  | 120.0        |
|            |                | C7-C8-C9   | 120.0        |
|            |                | C7-C8-H17  | 120.0        |
|            |                | C9-C8-H17  | 120.0        |
|            |                | C9-C9-C10  | 119.9        |
|            |                | C9-C9-H18  | 120.0        |
|            |                | C10-C9-H18 | 120.0        |
|            |                | O12-C11-O13| 120.0        |
|            |                | C11-O13-H19| 120.0        |

Table 1: Geometrical parameters optimized in carboxylic acid (CN4C) bond length (Å) and bond angle (°) with 6-311++G(d,p) basis set.

Gaussian 09W program output is given a follows:

\[ \beta_{tot} = \sqrt{(\beta_{xx} + \beta_{yy} + \beta_{zz})^2 + (\beta_{yy} + \beta_{xx} + \beta_{zz})^2 + (\beta_{zz} + \beta_{xx} + \beta_{yy})^2} \]

The calculations of the total molecular dipole moment (\( \mu \)), linear polarizability (\( \alpha \)) and first-order hyperpolarizability (\( \beta \)) from the Gaussian output have been explained in detail previously [13], and DFT has been widely used as an efficient method to investigate the

Figure 1: Optimized geometrical structure with atoms numbering of CN4C

B. Hyperpolarizability geometric calculations

The first order hyperpolarizability (\( \beta_{total} \)) of the CN4C along with related properties (\( \mu, \alpha \) and \( \Delta \alpha \)) are investigated by DFT/ Becke-3-Lee-Yang-Parr method with 6-311++G(d,p) basis set, is based on the finite-field approach. NLO activity arises from the interactions of electromagnetic fields in different media to produce latest fields changed in phase, frequency, amplitude or other propagation characteristics from the incident fields. Nonlinear optical effects (NLO) is at the forefront of the recent investigation because of its significance in bestowing the key functions of optical modulation, optical logic, optical memory, optical switching and frequency shifting for the presently growing technologies in areas such as telecommunications, signal processing, and optical interconnections [10,11].

The non-linear optical response of an isolated molecule in an electric field \( E(\omega) \) can be represented as a Taylor series enlargement of the total dipole moment, \( \mu_{tot} \), induced by the field:

\[ \mu_{tot} = \mu_0 + \alpha_{ij} E_j + \beta_{ij}^{(1)} E_j E_k + \ldots \]

Where the linear polarizability, \( \mu_0 \) is the permanent dipole moment and \( \beta_{ij}^{(1)} \) are the first hyperpolarizability tensor components. The isotropic (or average) linear polarizability is defined as:

\[ \alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \]

The calculations of the total molecular dipole moment (\( \mu \)), linear polarizability (\( \alpha \)) and first-order hyperpolarizability (\( \beta \)) from the Gaussian output have been explained in detail previously [13], and DFT has been widely used as an efficient method to investigate the

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organic non-linear optical materials [14,15]. In addition, the polar properties of the CN4C were computed at the DFT (B3LYP) level using Gaussian 09W program package.

| Parameters | B3LYP/6-311++G(d,p) | Parameters | B3LYP/6-311++G(d,p) |
|------------|---------------------|------------|---------------------|
| \( \mu_x \) | -2.3846             | \( \beta_{xx} \) | 137.5768             |
| \( \mu_y \) | -1.4185             | \( \beta_{yy} \) | -100.8850            |
| \( \mu_z \) | 0                   | \( \beta_{zz} \) | 92.05543             |
| \( \mu \) (D) | 2.7746              | \( \beta_{ij} \) (D) | -1019.3400           |
| \( \alpha_{xx} \) | 178.0215            | \( \alpha_{jj} \) | -63.7273             |
| \( \alpha_{xy} \) | -11.8985            | \( \alpha_{ij} \) | -185.4690            |
| \( \alpha_{yx} \) | 140.2307            | \( \alpha_{ji} \) | -157.8390            |
| \( \alpha_{zz} \) | 0                   | \( \alpha_{00} \) | 8.5535               |
| \( \alpha_{ij} \) | 61.0276             | \( \alpha_{00} \) | -301.3370            |
| \( \alpha_{00} \) (e.s.u) | 1.3736X10^{-20}     | \( \beta_{ij} \) (e.s.u) | 12.5990X10^{-30}    |
| \( \alpha_{00} \) (e.s.u) | 4.8198X10^{-23}     | \( \beta_{ij} \) (e.s.u) | 3.0000X10^{-26}    |

Urea is the ideal molecule utilized in examining the NLO properties of the compound. For this reason, urea was used often as a threshold value for comparative purpose. The calculated dipole moment and hyperpolarizability values obtained from B3LYP/6-311++G(d,p) methods are collected in Table 2. The first order hyperpolarizability of CN4C with B3LYP/6-311++G(d,p) basis set is 12.5990 \times 10^{-30} esu. From the computation, the high values of the hyperpolarizabilities of CN4C are probably attributed to the charge transfer existing amid the benzene rings within the molecular skeleton. This is evidence for the nonlinear optical (NLO) property of the molecule.

**C. NBO analysis**

NBO study provides the most accurate result possible ‘natural Lewis structure’ picture of \( \varphi \), because all orbital information are mathematically chosen to include the highest possible percentage of the electron density. A helpful of the natural bond orbital method is that it gives information about intra- and intermolecular interactions in both filled. The second-order Fock matrix was carried out to evaluate the donor-acceptor interactions in the NBO analysis [16]. The interactions result is a loss of occupancy from the localized NBO of the romanticize Lewis structure into an empty non-Lewis orbital. For each acceptor (j), donor (i) and the stabilization energy E(2) associated with the delocalization \( i \rightarrow j \) is predicted as

\[
E_2 = \Delta E_{ij} = q_i \frac{F(i,j)^2}{E_i - E_j}
\]

Where q\(_i\) is the donor orbital occupancy, E\(_i\) and E\(_j\) are diagonal elements and F(i,j) is the off diagonal NBO Fock matrix elements.

![Figure 2: Atomic orbital HOMO – LUMO composition of the frontier molecular orbital for CN4C](image-url)

NBO analysis provides an inter and intra molecular bonding and interaction among bonds, and also provides a suitable basis for examining charge transfer or conjugative interaction in molecular systems. The interacting stabilization energy, some electron acceptor orbital and donor orbital resulted from the second-order micro-disturbance theory are reported [17,18]. The higher the E(2) value, the molecular interaction between electron donors and electron acceptors is more intensive and the greater the extent of conjugation of the entire system. Delocalization of electron density amid occupied Lewis-type (bond or lone pair) NBO orbitals and properly unoccupied (antibond or Rydberg) non-Lewis NBO orbitals resemble to a stabilizing donor-acceptor interaction. NBO analysis has been performed on the title molecule at the B3LYP/6-311++G(d,p) level in order to elucidate the intra molecular, rehybridization and...
delocalization of electron density within the molecule. The strong intramolecular hyperconjugative interaction of 

| Donor(s) | Type | EDE | Acceptor(s) | Type | EDE | \( V_{E}(1) \) (kJ mol\(^{-1}\)) | \( V_{E}(1)-E(1) \) (a.u.) | \( \%P_{LP}(a.u.) \) |
|----------|------|-----|-------------|------|-----|----------------|-----------------|----------------|
| N\(_{2}\), N\(_{4}\) | \( \sigma \) | 1.9441 | C\(_{11}\)-C\(_{10}\) | \( \sigma^* \) | 0.0251 | 3.190 | 1.340 | 0.069 |
| N\(_{2}\), C\(_{6}\) | \( \sigma \) | 1.9874 | C\(_{11}\)-C\(_{10}\) | \( \sigma^* \) | 0.0249 | 2.360 | 1.390 | 0.051 |
| C\(_{6}\) | \( \sigma \) | 0.4243 | 3.060 | 1.410 | 0.059 |
| N\(_{2}\), C\(_{16}\) | \( \pi \) | 1.6421 | N\(_{2}\)-C\(_{16}\) | \( \pi^* \) | 0.3169 | 12.840 | 0.310 | 0.057 |
| C\(_{6}\) | \( \pi \) | 1.4516 | C\(_{11}\)-C\(_{10}\) | \( \pi^* \) | 0.2191 | 15.950 | 0.320 | 0.067 |
| C\(_{6}\)-H\(_{12}\) | \( \sigma \) | 1.9744 | N\(_{1}\)-N\(_{2}\) | \( \sigma^* \) | 0.0220 | 5.980 | 0.880 | 0.065 |
| C\(_{6}\)-C\(_{1}\) | \( \sigma \) | 1.9832 | C\(_{11}\)-C\(_{10}\) | \( \sigma^* \) | 0.0312 | 5.160 | 1.320 | 0.074 |
| C\(_{6}\)-C\(_{1}\) | \( \pi \) | 1.5576 | N\(_{2}\)-C\(_{16}\) | \( \pi^* \) | 0.4029 | 22.540 | 0.270 | 0.071 |
| C\(_{6}\) | \( \pi \) | 0.3149 | 26.420 | 0.270 | 0.079 |
| C\(_{6}\)-C\(_{1}\) | \( \pi \) | 0.2794 | 18.370 | 0.270 | 0.066 |
| C\(_{6}\)-C\(_{1}\) | \( \sigma \) | 0.2986 | 30.280 | 0.280 | 0.086 |
| C\(_{6}\)-C\(_{1}\) | \( \pi \) | 0.1736 | C\(_{11}\)-C\(_{10}\) | \( \pi^* \) | 0.4516 | 21.580 | 0.300 | 0.075 |
| C\(_{6}\)-C\(_{1}\) | \( \pi \) | 1.7002 | N\(_{2}\)-C\(_{16}\) | \( \pi^* \) | 0.2191 | 15.160 | 0.340 | 0.061 |
| N\(_{1}\) | \( \pi \) | 0.9452 | C\(_{11}\)-C\(_{10}\) | \( \pi^* \) | 0.0429 | 9.120 | 0.940 | 0.083 |
| N\(_{1}\) | \( \pi \) | 1.9484 | N\(_{2}\)-C\(_{16}\) | \( \pi^* \) | 0.0313 | 7.450 | 0.890 | 0.073 |
| O\(_{2}\) | \( \pi \) | 1.8815 | C\(_{11}\)-C\(_{10}\) | \( \pi^* \) | 0.0538 | 11.240 | 0.850 | 0.088 |
| O\(_{2}\) | \( \pi \) | 1.9611 | C\(_{11}\)-C\(_{10}\) | \( \pi^* \) | 0.0795 | 24.110 | 0.680 | 0.115 |
| O\(_{2}\) | \( \pi \) | 1.7857 | C\(_{11}\)-O\(_{1}\) | \( \pi^* \) | 0.2968 | 54.430 | 0.330 | 0.123 |
| N\(_{2}\)-C\(_{16}\) | \( \pi^* \) | 0.4029 | C\(_{11}\)-C\(_{10}\) | \( \pi^* \) | 0.4516 | 206.940 | 0.020 | 0.085 |
| N\(_{2}\)-C\(_{16}\) | \( \pi^* \) | 0.3169 | C\(_{11}\)-C\(_{10}\) | \( \pi^* \) | 0.4516 | 271.730 | 0.010 | 0.091 |
| C\(_{6}\)-C\(_{1}\) | \( \pi^* \) | 0.2794 | C\(_{11}\)-C\(_{10}\) | \( \pi^* \) | 0.4516 | 131.340 | 0.020 | 0.074 |
| C\(_{6}\)-H\(_{12}\) | \( \sigma \) | 1.6458 | H\(_{10}\) | \( \lambda^* \) | 0.6636 | 102.440 | 0.840 | 0.375 |
| O\(_{2}\) | \( \lambda^* \) | 1.9611 | H\(_{10}\) | \( \lambda^* \) | 0.6636 | 17.180 | 0.910 | 0.125 |
| O\(_{2}\) | \( \lambda^* \) | 1.5005 | H\(_{10}\) | \( \lambda^* \) | 0.6636 | 612.850 | 0.790 | 0.637 |

**Note:** Calculated with B3LYP/6-311++G(d,p) basis set (Fig. 2) and the result are given in Table 4.

**Figure 3:** Total electron density mapped with molecular electrostatic potential surface of CN4C

**D. HOMO – LUMO energy**

The fundamental importance of HOMO and LUMO understanding the chemical stability and reactivity of many organic molecules. The energy gap between the HOMOs and LUMOs is the congested parameters in deciding molecular electrical transport properties assist in the measure of electron conductivity [19]. The HOMO energy illustrates the ability of electron donor unit, the LUMO illustrate the ability of the electron acceptor unit. HOMO and LUMO is related to the ionization potential and electron affinity. The energy difference between HOMO and LUMO energy is called as energy gap that is important stability for structure [20]. The total energy, HOMO and LUMO energies, the energy gap (\( \Delta E \)), the ionization potential (I), the electron affinity (A), the absolute electronegativity (\( \gamma \)), the absolute hardness (\( \eta \)) and softness (S) for the CN4C molecule have been calculated as follows:

\[ V_{E}(1) = V_{E}(1) - E(1) \text{ (a.u.)} \]

\[ \%P_{LP}(a.u.) = \frac{P_{LP}}{\text{Total Energy}} \times 100 \]

By using HOMO and LUMO energy values for a molecule, electronegativity and chemical hardness can be calculated as follows:
\[ \chi = \frac{(1+A)}{2} \text{ (Electronegativity)} \]
\[ \mu = \frac{-}(1+A)\text{/2 (Chemical potential)} \]
\[ \eta = \frac{(1-A)}{2} \text{ (Chemical hardness)} \]

**Table 4**
Calculated energy values of title compound by B3LYP/6-311++G(d,p) method.

| Basis set | B3LYP/6-311++G(d,p) |
|-----------|---------------------|
| \(E_{\text{HOMO}}\) (eV) | -7.4815 |
| \(E_{\text{LUMO}}\) (eV) | -3.8030 |
| Ionization potential | 7.4815 |
| Electron affinity | 3.8030 |
| Energy gap (eV) | 3.6785 |
| Electronegativity | 5.6422 |
| Chemical potential | 5.6422 |
| Chemical hardness | 1.8392 |
| Chemical softness | 0.2718 |
| Electrophilicity index | 8.6543 |

\[
\omega = \mu^2/2\eta \text{ (Electrophilicity index)}
\]

Where \(I\) and \(A\) are ionization potential and electron affinity; \(I = -E_{\text{HOMO}}\) and \(A = -E_{\text{LUMO}}\) respectively [21]. The HOMO and LUMO are delocalized over the entire molecule. The lowest unoccupied molecular orbital (LUMO) energy is -3.8030 eV and the highest occupied molecular orbital (HOMO) energy is -7.4815 eV. According to DFT calculation, the frontier orbital energy gap of CN4C is found to be 3.6785 eV. This smaller energy gap of HOMO-LUMO explains the eventual charge transfer occurs within the molecule, which influences its high polarizability and biological activities.

**E. Molecular electrostatic potential (MEP)**

At any given point \(r(x, y, z)\) in the vicinity of a molecule, the molecular electrostatic potential, \(\nu(r)\) is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at \(r\) [22,23]. The molecular electrostatic potential (MEP) is related to the electronic density and a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions [24,25]. In the present study, 3D plots of molecular electrostatic potential (MEP) of CN4C are illustrated in Fig. 3. The different value of electrostatic potential at the surface is represented by different colors. Potential increases in the order red < orange < yellow < blue. The color code of these maps in the range between -9.853 eV and +9.853 eV in compound, where blue indicates the strongest attraction and yellow indicates repulsion. As can be seen from the MEP of the title compound while region having the negative potential are over the electronegative atoms (Nitrogen, Oxygen atom), the region having the positive potential are over the hydrogen atom. From this result, we can say that the H atom indicates the strongest attraction and Nitrogen, Oxygen atoms the repulsion.

**IV CONCLUSION**

The optimized molecular structure, Natural bond orbital and electronic properties of cinnoline-4-carboxylic acid are calculated by DFT method using B3LYP/6-311++G(d,p) basis set. The optimized geometric parameters (bond lengths and bond angles) are theoretically determined by DFT theory. The lowering of the HOMO-LUMO energy gap value has substantial influence on the intermolecular charge transfer and bioactivity of the molecule. The NBO analysis indicates the intermolecular charge transfer between the bonding and antibonding orbitals. The electronic dipole moment, polarizabilities and the hyperpolarizabilities of the compound studied. The MEP map shows the negative potential sites are on Nitrogen and Oxygen atoms as well as the positive potential sites around the hydrogen atoms.

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