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A Theoretical Studies of 2-(4-bromophenyl)-2-(4-chlorophenylamino) acetonitrile by density functional theory

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Abstract: In the present study, we have performed extensive theoretical calculations to investigate the structural and vibrational properties of 2-(4-bromophenyl)-2-(4-chlorophenylamino)acetonitrile (**1**). The molecular geometry, harmonic vibrational frequencies and bonding features of the molecule **1** at the ground state have been studied. The assignment of the fundamental vibrations modes have been done on the basis of the potential energy distribution (PED).

Keywords: DFT, Vibrational Analysis, FTIR, Molecular Orbital

I. INTRODUCTION

Alpha-aminonitriles are the versatile precursors of a wide range of pharmaceutically relevant natural and unnatural molecules of interest; they are the key precursors of diverse α -amino-acids finding applications in synthesizing proteins and also as chiral building blocks in the pharmaceutical industry. Alpha-aminonitriles constitute key parts of several pharmaceutically important bioactive molecules such as clopidogrel, prasugrel, saframycin A, manzacidin A-C, ecteinascidin 743, and phtalascidin [1, 2]. Furthermore, they are also regarded as versatile intermediates for the preparation of 1, 2-diamines, and nitrogen or sulfur-containing heterocycles such as imidazoles and thiadiazoles [1].

II. RESULTS AND DISCUSSION

All quantum chemical calculations of the title compound are carried out with Gaussian 09 suite of program [3] using the B3LYP/6-311+G(d,p) levels of theory to predict the molecular structure and vibrational wave numbers.

A. Molecular Structure and Optimized Geometry

The optimized geometry for ground state lower energy conformer is shown in **Figure 1**. The selected optimized parameters of the title compound calculated at B3LYP/6-311++ G (d, p). The molecule possesses C_1 symmetry.

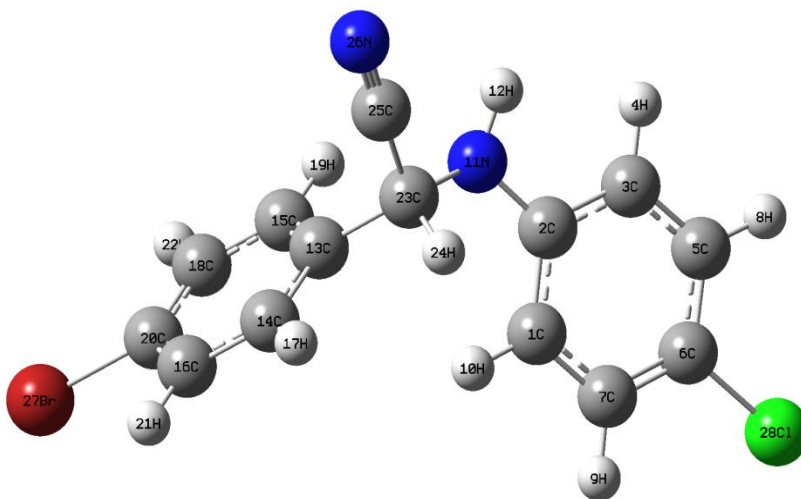


Figure1. Optimized structure of title compound

B. Vibrational Analysis

The selected theoretical and experimental vibrational modes of the title compound, calculated using B3LYP/6-311++G(d, p) method. The vibrational band assignments have been done on the basis of normal co-ordinate analysis. The maximum number of

potentially active observable fundamentals of a nonlinear molecule which contains N atoms is equal to $(3N-6)$ modes of vibrations [6, 7]. The molecule consists of 27 atoms hence undergoes 75 normal modes of vibration.

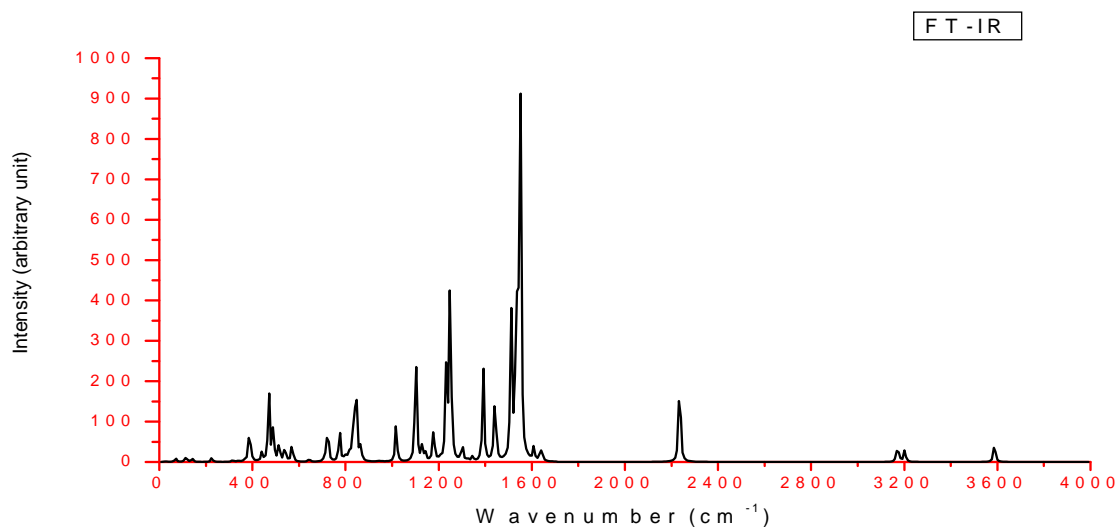


Figure2. Cal. IR plot of the title compound,

The N-H stretching of the title compound is observed at 3351 cm^{-1} , whereas this is calculated as 3408 cm^{-1} . As expected, this is a pure stretching mode and also evident by its PED, i.e. 100%. The weak band of N-H scissoring vibration is calculated at 1607 cm^{-1} and 537 cm^{-1} which represent the N-H scissoring and torsion mode of vibrations, respectively. The aromatic structure of the title compound **1** shows the presence of C-H stretching vibration in the region $3077\text{--}3040\text{ cm}^{-1}$, which is also the characteristic region for the identification of C-H stretching vibration [12, 13] and is assigned well with the peak in the region $2847\text{--}3065\text{ cm}^{-1}$ in FTIR spectra. These vibrations are not found to be affected due to the nature and position of the substituent. Rocking mode of methylene vibration is calculated to be 1306 cm^{-1} . The C-H in plane bending frequencies for the alpha-aminonitrile appear in the range $1287\text{--}1018\text{ cm}^{-1}$ and are very useful for the characterization purpose [14]. The C-H in plane bending vibration appear as strong bands in the FTIR spectrum at $1192, 1130, 1128\text{ cm}^{-1}$ and $1116, 1018\text{ cm}^{-1}$ in FTIR spectrum. The C-H out of plane bending vibrations are strongly coupled vibrations occurring in the region $1000\text{--}750\text{ cm}^{-1}$ [15] and corresponding FTIR spectra observed at 937 cm^{-1} and 833 cm^{-1} . In aromatic hydrocarbon, skeletal vibrations involving carbon-carbon stretching within ring are observed in the region $1614\text{--}1524\text{ cm}^{-1}$. The C-C aromatic stretching vibrations gives rise to characteristics bands in the spectral range from $1643\text{--}1577\text{ cm}^{-1}$. Therefore, the C-C stretching vibrations of alpha-aminonitrile are found in the region $1636\text{--}1142\text{ cm}^{-1}$ and in FTIR spectrum at 1509 cm^{-1} and 1487 cm^{-1} . Most of the ring vibrational modes are affected by the substitution in the aromatic ring of alpha-aminonitrile. Other mode of vibrations such as scissoring and torsion are found at lower frequencies. The stretching vibration of the triply-bonded groups occurs between $2500\text{ and }2000\text{ cm}^{-1}$. The group $\text{C}\equiv\text{N}$ gives rise to a strong absorption in the 2173 cm^{-1} . The $\text{C}\equiv\text{N}$ stretching vibrations in the title molecule are found at 2250 cm^{-1} in the FTIR spectra. The in-plane and out of plane bending such as scissoring and torsion, $\text{C}\equiv\text{N}$ vibrations have also been identified at lower frequencies and presented in the assignment table.

C. HOMO-LUMO surfaces analysis

The frontier molecular orbital, highest occupied molecular orbitals (HOMOs) and lowest molecular orbitals (LUMOs) offer a reasonable qualitative prediction of the excitation properties and the ability of electron transport [16, 17]. The HOMO primarily acts as an electron donor and LUMO acts as an electron acceptor and are the main orbital which takes part in chemical stability [18]. The frontier molecular orbital gap has been used as a measure for the bioactivity, since the intra-molecular charge transfer determining the bioactivity depends on this energy gap. The HOMO and LUMO plots of title compound are shown in **Figure 3**. The energy gap between frontier molecular orbital of title compound is 3.98 eV .

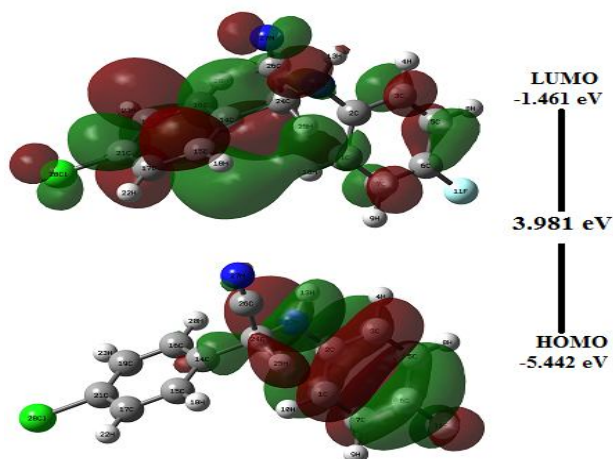


Figure 3. HOMO-LUMO Plot of the alpha-aminonitrile

D. Molecular Electrostatic Potential Surface Analysis

The molecular electrostatic potential (MESP) is related to the electron density and is a very useful to understanding sites for electrophilic (negative region) and nucleophilic (positive region) reactions [17, 18]. MESP is also well suited for analyzing process based on the “recognition” of one molecule by another, as in drug receptor, and enzyme-substrate interactions, because it is through this interaction that the two entities first feel each other [19, 20]. To predict reactive sites for electrophilic and nucleophilic attack, for the investigated molecule, MESP is calculated at the B3LYP/6-311++G (d, p) and shown in Figure 4. The different values of the electrostatic potential at the surface are represented by different colors and potential increases in the order red<orange<yellow<green<blue. The color code of these maps is in range between -0.04315 a.u. and 0.04315 a.u. in the title compound, where blue indicates the most electropositive i.e. electron poor region and red indicates the most electronegative region i.e. electron rich region. From the MESP it is evident that the most electropositive region is located over nitrogen bonded with hydrogen, which effectively acts as electron poor and most electronegative region is located over nitrogen, triple bonded with carbon which is electron rich region.

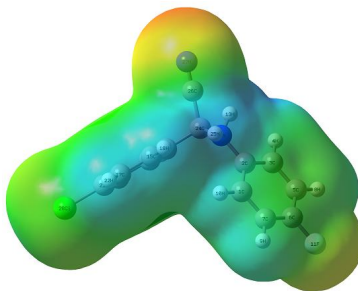


Figure4. Molecular Electrostatic Potential Surface of the alpha-aminonitrile

III. CONCLUSIONS

In the present work, with the help of DFT calculations we have calculated the geometrical parameters, vibrational frequencies, HOMO-LUMO and MESP surfaces of a synthetic alpha-aminonitrile compound, 2-(4bromophenyl)-2-(4-chlorophenylamino) acetonitrile (1).

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