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DENSITY FUNCTIONAL THEORY, MOLECULAR GEOMETRY AND VIBRATIONAL SPECTRAL INVESTIGATIONS OF 2-(2- CHLOROPHENYLAMINOTHIAZOL-5-OYL)-N-METHYL-6- CHLOROBENZIMIDAZOLES

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ABSTRACT

The compound 2-(2-chlorophenylaminothiazole-5-oyl)-N-methyl-6-chlorobenzimidazole was characterized by IR spectral data. The optimized molecular geometry, bond lengths, bond angle and dihedral angle of the titled compound have been investigated by Density Functional Theory (DFT) method, using B3LYP method with 3-21G basis set available in Gaussian '09 package. The results indicate that B3LYP method is able to provide satisfactory results for predicting vibrational frequencies and structural parameters. The IR spectra are obtained and assigned by vibrational analysis and found to be reliable compared with the literature observation. The Mulliken population analysis on atomic charges has been computed using DFT calculation. The lowering in the HOMO and LUMO energy gap explains the eventual charge transfer interactions that take place within the molecule.

KEYWORDS

Benzimidazoles, Vibrational analysis, Mulliken charge, Triethylamine, Dipole moment and Gaussian.

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INTRODUCTON

The benzimidazole shares several structural features with indole. In addition, benzimidazoles exhibit several significant biological activities just as indoles. The literature survey shows several examples of compounds having a benzimidazole ring which exhibit remarkable bioactivity. The above survey amply demonstrates the significance of benzimidazole unit us a useful pharmacophore moiety. Such derivatives possess anticancer, anti-inflammatory, anti-bacterial and anti-fungal

activities. Patil *et al.* reported the DFT study on dihydroxyphenylbenzimidazole by using B3LYP/6-31G basis set. In spite of the existing studies, there is still lack of information about structural and energetic properties of 2-(2-chlorophenylaminothiazole-5-oyl)-N-methyl-6-chlorobenzimidazole have been computationally investigated by using Density Functional Theory (DFT).

Plentiful computational methods have been accomplished to correlate the electronic structure and chemical reactivity. Conceptual DFT has been favorably used to unfold chemical reactivity and site selectivity. In order to analyze the chemical reactivity various global and local quantities were utilized. Vibrational spectroscopy is used to identify functional groups and determine the molecular structure of crystals. It also characterizes the bioactivity of the material. Density functional theory (DFT) method is used for the computation of molecular structure, vibrational wave numbers and energies of chemical reactions.

Literature survey by us reveals that no experimental and computational vibrational spectroscopic study on 2-(2-chlorophenylaminothiazole-5-oyl)-N-methyl-6-chlorobenzimidazole is published yet. This inadequacy observed in the literature encouraged us to be making this theoretical and experimental vibrational spectroscopic research based on the molecule to give a correct assignment of the fundamental FT-IR spectra. Therefore the present study aims to give a complete description of the molecular geometry and molecular vibrational assignment of 2-(2-chlorophenylaminothiazole-5-oyl)-N-methyl-6-chlorobenzimidazole.

Experimental

The reagents and solvents used were of AR grade. All the chemicals were purchased from Sigma - Aldrich, Merck specialties Pvt. Ltd. and Himedia Laboratories Pvt. Ltd. The compound 2-(2-chlorophenylaminothiazole-5-oyl)-N-methyl-6-chlorobenzimidazole was prepared according to the following method. A solution of 1-aryl-3-(N,N-dimethylimidoyl) thiourea (1m mol) in DMF (2 ml) was added to a solution of 2-(2-bromoactyl)-N-methyl-6-chlorobenzimidazole (0.254g, 1mmol)

which was prepared from 2-(1-hydroxy ethyl)-6-chlorobenzimidazole in DMF (2ml). The reaction mixture was stirred well and triethylamine (0.15ml, 1mmol) was added. The reaction mixture was heated at 80-85⁰C for 5 minutes. It was then cooled and poured in to ice - cold water with constant stirring. The yellow precipitate thus obtained was filtered, washed with water and dried. The crude product was crystallized from ethanol - water (2:1) to give yellow crystalline solid.

Computational method

Quantum chemical calculations were used to carry out the optimized geometry and vibrational wave numbers with 2009 version of the Gaussian suite program using the B3LYP functional supplemented with 6-31G basis set.

RESULTS AND DISCUSSION

The optimized geometry of 2-(2-chlorophenylaminothiazole-5-oyl)-N-methyl-6-chlorobenzimidazole was obtained at B3LYP level. The molecular structure along with the numbering of atoms is shown in Figure No.1. The theoretical and experimental values were compared and small deviations in some values were observed. There are changes observed in C-H bond length due to variation in the charge distribution on the carbon atom of the benzene ring. The molecule contains benzimidazole ring, phenyl ring, amino group, methyl group and two chlorine atom. The optimized bond length of C-C in phenyl ring fall in the range from 1.3776 Å to 1.4786 Å. The optimized bond length of C-H in methyl group is 1. The optimized geometry of 2-(2-chlorophenylaminothiazole-5-oyl)-N-methyl-6-chlorobenzimidazole was obtained at B3LYP level. The molecular structure along with the numbering of atoms is shown in Figure No.1. The theoretical and experimental values were compared and small deviations in some values were observed. There are changes observed in C-H bond length due to variation in the charge distribution on the carbon atom of the benzene ring. The comparative optimized structural parameters such as bond lengths, bond angles and dihedral angles are presented. The title compound has one C-O bond and its optimized bond length is 1.2637 Å,

nine C-N bonds and its optimized bond length ranges from 1.3333 Å to 1.4752 Å, two C-S bonds and its bond length ranges from 1.8382 Å to 2.8012 Å, one N-H bond and its optimized bond length is 1.0105 Å, eleven C-C bond and its optimized bond length ranges from 1.3871 Å to 2.5130 Å, twelve C-H bonds and its optimized bond length ranges from 1.0791 Å to 1.0830 Å, one C-Cl bond and its optimized bond length value is 1.8329 Å.

Vibrational Spectral Analysis:

The detailed vibrational assignments of fundamental modes of the title compound along with calculated IR intensities are reported. None of the predicted vibrational frequencies have any imaginary frequency implying that the optimized geometry is located at the local minimum point on the potential energy surface. A potential energy surface is a mathematical relationship linking molecular structure and the resultant energy. For a diatomic molecule, it is a two - dimensional plot with the inter-nuclear separation on the x-axis and the potential energy at that bond distance on the y-axis, producing a curve. For larger systems, the surface has as many dimensions as there are degrees of freedom within the molecule. Generally, a non-linear N atomic molecule has $3N-6$ degrees of freedom or internal coordinates. This is because all N atoms can move in three dimensions (x, y and z) giving $3N$ degrees of freedom. However six of those three translations in x, y and z directions and three rotations along x, y and z axes of the molecule as a whole do not produce any change in energy. The title molecule has 38 atoms and it has 96 degrees of freedom⁸.

Methyl Group Vibrations

The assignments of methyl group vibration make a significant contribution to the titled compound. The compound under investigation possesses a CH₃ group. For the assignments of CH₃ group frequencies one can expect that nine fundamentals can be associated to CH₃ group. The C-H stretching is at lower frequencies than those of aromatic ring. The asymmetric stretch is usually at higher wave number than the symmetric stretch. Usually the symmetrical bands are sharper than the asymmetrical bands. Methyl group vibrations are

generally referred to as electron – donating substituent in the aromatic ring system, the anti symmetric C-H stretching mode of CH₃ is expected around 2980 cm⁻¹ and CH₃ symmetric stretching is expected at 2870cm⁻¹⁹⁻¹¹.

C-N Vibrations

The assignment of C-N stretching frequency is a rather difficult task since there are problems in identifying these frequencies from other vibrations. Silverstein¹⁰ assigned C-N stretching vibrations in the region 1382-1266cm⁻¹. In the present work, the observed value at 1358cm⁻¹ and 1199cm⁻¹ in FT-IR spectra is assigned to C-N in- plane bending vibration. In the present study the theoretically computed values belonging to C-N stretching vibrations are good agreement with spectral data.

C-O Vibrations

Generally the C-O vibrations occur in the region 1260-1000cm⁻¹¹². In the present study the C-O stretching vibrations are assigned at 1113cm⁻¹ which is in line with literature.

C-Cl Vibrations

The vibrations belonging to the bond between the ring and halogen atoms were worth the discussion here since the mixing of vibrations are possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of molecule¹³. Generally the C-Cl absorption was obtained in the region 850-550cm⁻¹¹⁴. Most of the aromatic chloro compounds had the strong to medium intensity in the region 385-265cm⁻¹ due to C-Cl bending vibration¹⁵. The FT-IR band identified at 375cm⁻¹ is assigned to the C-Cl bending vibration of the title compound.

C-C Vibrations

The C-C stretching vibrations give rise to characteristic bands in the observed IR spectra, covering the spectral range from 1600 to 1400cm⁻¹.

C-H vibrations

The hetero aromatic compounds and their derivatives are structurally very close to benzene. The C-H stretching vibrations of aromatic and hetero aromatic structures^{16,17} in the region 3100-2900cm⁻¹ is for asymmetric stretching modes of vibrations. This permits the ready identification of the structure. Further in this region the bands are not

much affected due to the nature and position of the substituent's^{18,19}.

HOMO-LUMO energy gap

The HOMO –LUMO energy gap of a molecule will play an important role in determining its bioactive properties²⁰. The total energy, HOMO-LUMO energy, energy gap and dipole moment have influence on the stability of a molecule. We have performed optimization in order to investigate the energetic behavior and dipole moment of title compound. The total energy, and dipole moment have been calculated with B3LYP/6-31G level. The energy gap between the highest occupied and lowest unoccupied molecular orbital's, is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. The analysis of wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from HOMO to LUMO. The HOMO energy characterizes the ability of electron giving and the LUMO energy characterizes the ability of electron accepting and the gap between HOMO and LUMO characterizes the molecular chemical stability.

The energy gaps are largely responsible for the chemical and the spectroscopic properties of the molecules²¹. All the HOMO and LUMO are placed symmetrically. The positive phase is red and the negative one is green. Moreover lower in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.

The dipole moment in a molecule is another important electronic property which results from non-uniform distribution of charges on the various atoms in a molecule. It is mainly used to study the intermolecular interactions involving the Vander Waals type dipole - dipole forces, etc., because bigger the dipole moment, stronger will be the intermolecular interactions²²⁻²⁴.

Mulliken Analysis

The atomic charge in molecule is fundamental to chemistry. For instance, atomic charge has been used to describe the process of electro negativity equalization and charge transfer in chemical reactions²⁵.

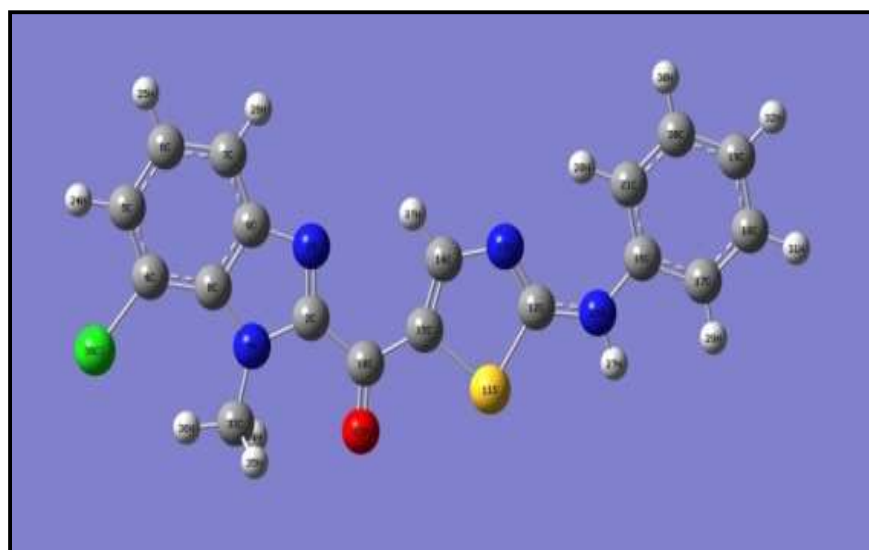
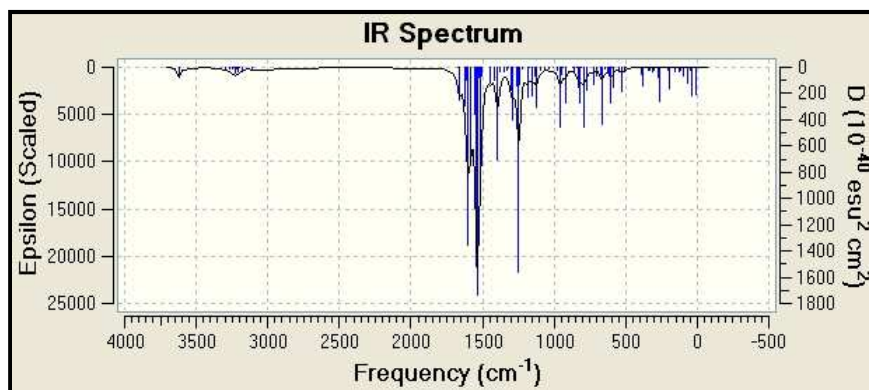
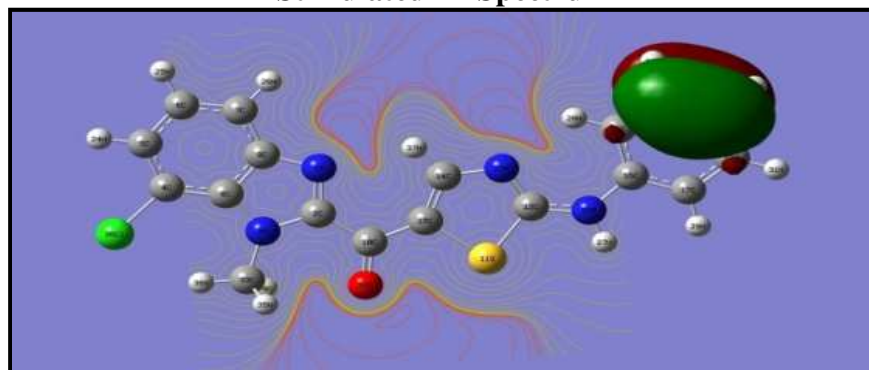


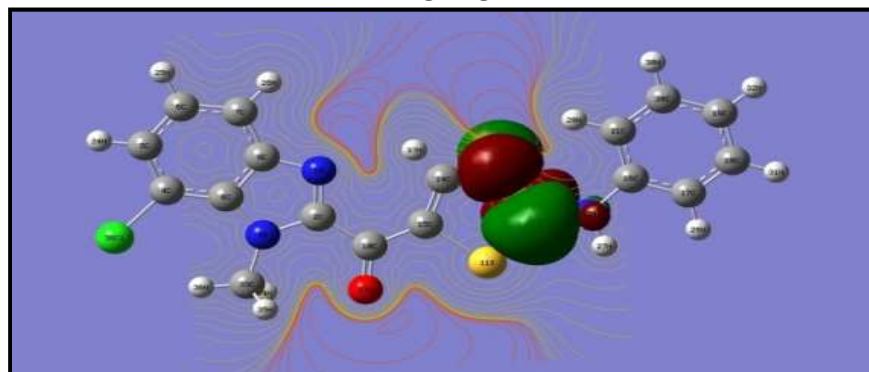
Figure No.1: Optimized geometrical structure of 2-(2-chlorophenylaminothiazol-5-oyl)-1-methyl-6-chlorobenzimidazole



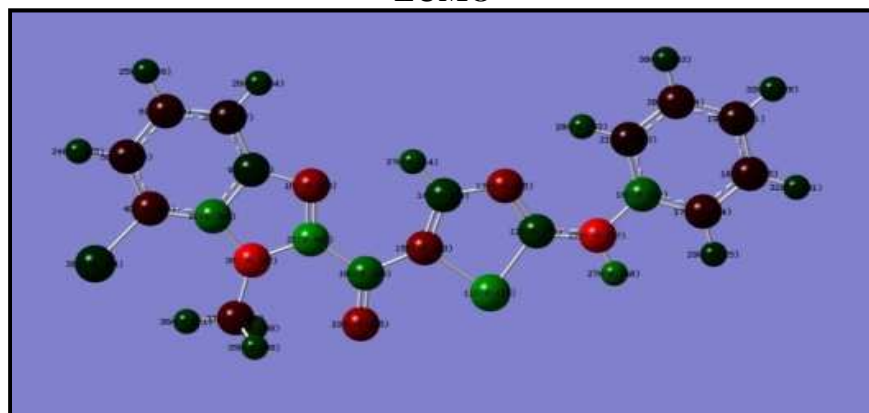
Stimulated IR Spectrum



HOMO



LUMO



Mulliken charge distribution of 2-(2-chlorophenylaminothiazole-5-oyl)-N-methyl-6-chlorobenzimidazole

CONCLUSION

We have carried out DFT calculations on the structure and vibrational spectrum, HOMO, LUMO analysis of 2-(2-chlorophenylaminothiazole-5-oyl)-N-methyl-6-chlorobenzimidazole comparison between the calculated and experimental structural parameters indicates that B3LYP results are in good agreement with experimental values. Vibrational frequencies and infrared intensities are calculated by DFT (B3LYP) levels of theory utilizing 6-31G method agree very well with experimental results. From the vibrational discussion, it was concluded that the substitution of H atom by Cl atom distorts the ring geometry to small extent and the planarity of the molecule. On the basis of agreement between the calculated and observed results, assignments of fundamental vibration modes of 2-(2-chlorophenylaminothiazole-5-oyl)-N-methyl-6-chlorobenzimidazole are examined and some assignments were proposed. This study demonstrates that scaled DFT calculations are powerful approach for understanding the vibrational spectra of medium sized organic compounds. The C=C stretching vibrational frequencies are observed well within the expected range compared to the literature values. Among alkanes C-H stretching vibrations, only some are expected in asymmetric range while others in symmetric range. But in the present case, all the observed bands for stretching lay in asymmetric range. These show that the vibrations of methyl group are not much affected by other substituents in the ring. The lowering of the HOMO-LUMO energy gap value has substantial influence on the charge transfer and bioactivity of the molecule.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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