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MOLECULAR GEOMETRY OF HOMO-LUMO AND DFT CALCULATIONS OF 3-(2-METHYLPHENYLAMINOTHIAZOLE-5-OYL) PYRIDINE

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ABSTRACT

The electronic structure of 3-(2-methylphenylaminothiazol-5-oyl) pyridine was analysed theoretically using B3LYB/6-31G method. The calculations exhibit that the compound non-planar, as observed from the dihedral angles. The electronic spectra of the studied compound are recorded in UV-VIS region, in ethanol as solvent. The identified electronic transitions are facilitated via density functional theory (DFT) computations. Electronic configurations according to every excited state are recognized and the suitable MOs are characterized. The range of delocalization and intermolecular charge transfer was evaluated and considered in terms of natural bond orbital (NBO) analysis. The Mulliken atomic charge describe the charge distribution of atoms. The calculated HOMO-LUMO energy gap unveils that charge transfer arise within the molecule.

KEYWORDS

DFT, NBO, HOMO-LUMO, Mulliken Atomic Charge and Pyridine.

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INTRODUCTON

Pyridine derivatives are highly succeed by great benefaction have acquired a great attention, because this moiety presented in a number of drugs and biologically active compounds naturally transpired and synthetic compounds. Furthermore nitro compounds are amidst the predominant groups of chemicals have been exhibit to be useful building blocks and used in biological, pharmaceutical, and materials science[1]. Pyridine derivatives are complicated in bioactivities with requisition in pharmaceutical drugs and agricultural products[2-7]. Some of the compounds act as anesthetic agents, drugs for obvious brain disease, and prodrugs for handling neuronal damage begin by stroke, to a

few. Pyridines also support analgesics for terrible and chronic pain, treatment for tinnitus, depression, and diabetic neuropathy. And the ring nitrogen of most pyridines undertakes reactions of weak, tertiary amines such as protonation, alkylation and acylation[8]. Pyridine derivatives were known to be suitable ligands for many of the transition metal ions and they are frequently used in the scheme and synthesis of multifunctional compounds[9-12]. Pierrat, *et al*,[3] synthesized pyridine-based compounds from 3-bromopyridine, resulting in pyridine-based synthons and chromophores. Hiremath, *et al*, analysed chloro-5-bromopyridine theoretically[13]. The values of geometrical studies on pyridine and some N-substituted derivatives were analysed[14-21]. Thiazole is an major scaffold in heterocyclic chemistry and 1, 3-thiazole ring is present in many pharmacological energetic substances. Compounds containing thiazole ring have reported as histamine H3 antagonists, with festicidal, anti-cancer, and cardio-depressant activities. Antibacterial activities of substituted thiazoles are prevailing because it enchant (S-C=N) toxophoric unit. Thiazoles have exalt lipid soluble hydrophilicity. Thiazoles are certainly metabolized by regime biochemical reactions and non-carcinogenic. Aminothiazoles and heterocycles represent a potent and selective anticancer agents which display nanomolar inhibitory activity resistant to a range of human breast, leukemia, lung, colon, melanoma, ovarian, renal and prostate cell lines. Aminothiazoles, most especially 2-aminothiazole derivatives have been reported as antiviral, antimicrobial, anti-malarial, anti-inflammatory and anti-tubercular agents[22].

EXPERIMENTAL

The compound (m.f. C16H13N3OS) was assembled in virtuous yield through the reaction of methylphenyl-3-(N, N-dimethylimidoyl) thiourea with DMF and 3-(3-bromoacetyl) pyridine. The resulted compound was stirred continuously, finally triethylamine was added. For 5min, the reaction mixture was heated to 80-85ºC. It was permitted to cool and constant stirring and transferred into ice-cold water. An orange yellow coloured precipitate was obtained and filtered then washed with water clearly and finally dried. The above obtained crude sample was crystallized from benzene and petroleum ether mixture (1:1) then using methanol: water (2:1) mixture to formed orange coloured crystalline solid. DR/JASCO FT-IR 6300 spectrometer using KBr pellets was used to record FT-IR spectrum.

Computational Studies

In Computational Studies, Gaussian 09 software was used for theoretical calculation. The quantum chemical calculations were assisted by DFT method, with Beeke-3-Lee-Yang-Parr (B3LYP) with the standard 6-31G basis set. The optimized geometry to minimum potential energy facet has been formed by resolving self-consistent equation iteratively. Vibrational wave numbers are scientifically calculated by taking the second order derivative of energy used on the same level of theory.

RESULTS AND DISCUSSION

Structure and geometrical properties

The optimized structure of compound (m.f. C16H13N3OS) with labelling of the atoms are represented in Figure No.1. The molecule accommodate three rings (pyridine, thiazole and NH-Ar rings) attached by a keto group.

Vibrational Analysis

C–H Vibrations

The modes of vibrations of aromatic compounds are evaluated as separate C–H or ring C–C vibrations. Anyhow, as with some complex molecules, vibrational interface arise and these symbols only specify the foremost vibration. Substituted benzene was large number of active bands, that is, bands those position is crucially affected by the mass and electronic parameters mesomeric or inductive effects, of the substituents. According to the literature[23], in infrared spectra, most of the mono and polynuclear aromatic compound containing three or four peaks in the region 3000–3100cm−1[24], these peaks indicating stretching vibrations of the C–H bonds. Consequently, in the present study, four C–H stretching vibrations was observed at 3030, 3040, 3050 and 3020cm−1. These reserved frequencies are in line with the literature values.

The in-plane and out-of-plane bending vibrations of C-H stretching vibrations generally recline in the range of 1000–1300cm−1 and 950–800cm−1[25], respectively. Four C–H in-plane bending vibrations are notified at 1260, 1280, 1100 and 1160cm−1 and two C–H out-of-plane bend-ing vibrations are identified at 930 and 910cm−1. Based on the literature, in-plane and out-of-plane bending vibrational assignments are established well within their characteristic regions.

Methyl group vibrations

The methyl group vibration assemble a crucial contribution to the spectra. The C–H vibrations secure that the place of methyl group in the benzene ring. The asymmetric C–H vibration of methyl group is generally occurring in the region 2975 to 2920cm−1 and symmetric C–H vibrations for the methyl group is present in the region of 2870–2840cm−1.

C–C vibrations

Conventionally the C=C stretching in aromatic compounds are observed in the region between 1430–1650cm−1. The C=C stretching vibrations of 3-(2-methylphenylaminothiazol-5-oyl) pyridine are observed at 1590, 1480 and 1450cm−1. The stretching vibrational bands for C-C bond are observed at 1470, 1400 and 1410cm−1.

Amino group vibrations

Primary amine, commonly the N–H stretching vibrations are arise in the region 3500–3300cm−1. The amino group have two vibrations; one is existence asymmetric and other is symmetric. Frequency of asymmetric vibration is higher than that of sym-metric one. In the present work, the asymmetric and symmetric vibrations of N–H determine the bands at 3460cm−1and 3380cm−1, respectively. The considered stretching vibrations that recline in the range 3468 and 3383cm−1 by B3LYP/6-31G (d, p) method absolutely correlate with the literature value.

C–N vibrations

The C–N stretching vibration is quite difficult to venture since there are complication in these frequencies from other vibrations. The C–N stretching frequency between 1386–1266cm−1 for aromatic amines. In this work, the C–N stretching is discovered at 1310cm−1.

C–CH3 vibrations

The C–CH3 vibrations typically combine with C–H in-plane bending vibration. In 3-(2-methylphenylaminothiazol-5-oyl) pyridine a strong band is identified at 1200cm−1 for C–CH3 stretching. The C–CH3 in-plane bending vibration is observed at 330cm−1 and out-of-plane bending is identified to 210cm−1. Based on the literature [63, 64], all the C–CH3 vibrations drift float slightly from the envisage range. This is adequate to the clash of amine group. It should be modulation that the frequencies calculated with the B3LYP/631-G (d, p) method of the C–CH3 and CH3 in-plane modes at 337cm −1 and 160cm−1 are in consensus with experimental values.

C–O vibrations

The C–O vibration and the absorption provoked by such C–O stretching is very strong. The C–O stretching vibrations of the little substituents repose in the region 1095–1310cm−1 and in carboxylic acids, the C–O stretching vibrations emerge at 1725 with ±65cm−1. In the present compound C–O stretching vibrations are perceived at 1300 and 1270cm−1 with weak intensity in infrared and Raman. The frequencies are evidently lesser than the cited values, which are expected as the bond is present in between the naphthalene and methyl group. The C–O in-plane bending are identified at 710 and 712cm−1 and out-of-plane bending vibrations at 388 and 284cm−1. All these vibrations are occurred with very weak intensity in Raman.

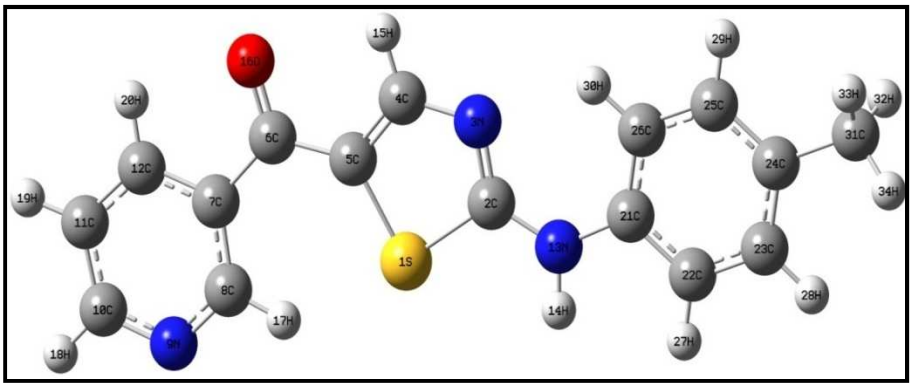

Figure No.1: Optimized structure of 3-(2-methylphenylaminothiazol-5-oyl) pyridine

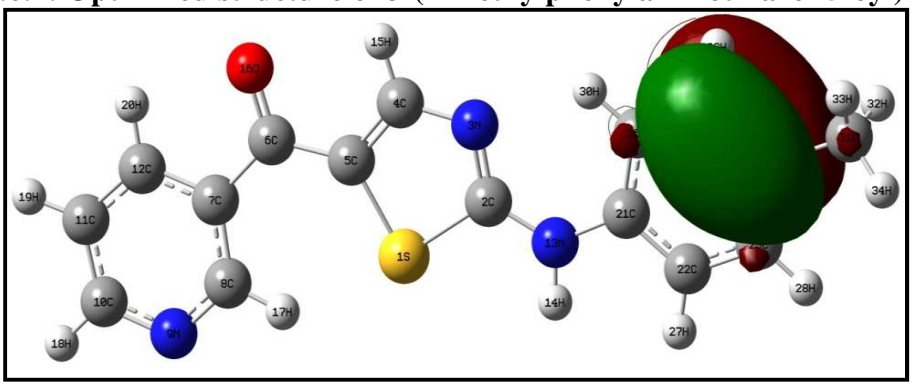

Figure No.2: HOMO of 3-(2-methylphenylaminothiazol-5-oyl) pyridine

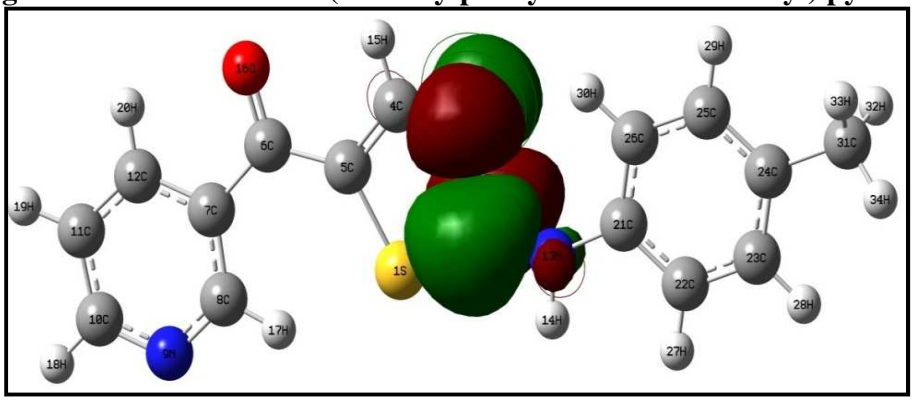

Figure No.3: LUMO of 3-(2-methylphenylaminothiazol-5-oyl) pyridine

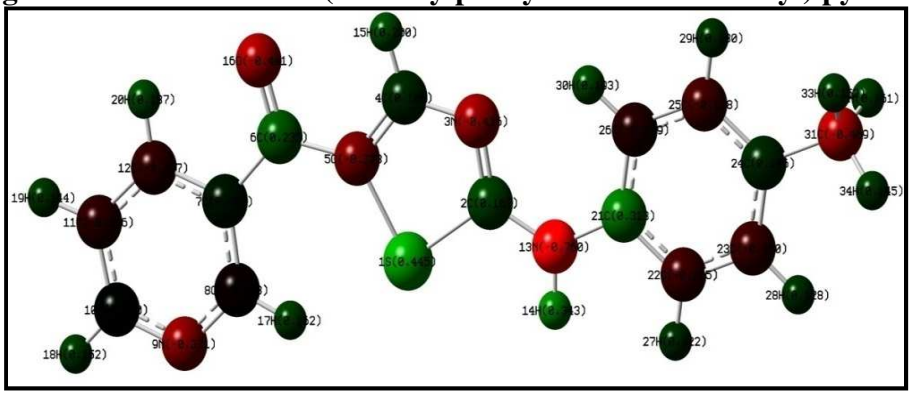

Figure No.4: Mulliken Charges of 3-(2-methylphenylaminothiazol-5-oyl) pyridine

CONCLUSION

In summary, 3-(2-methylphenylaminothiazol-5-oyl) pyridine was studied using FT-IR spectra. The geometry of 3-(2-methylphenylaminothiazol-5-oyl) pyridine was optimized by DFT- method using B3LYP/6-31G basis set. The optimized geometry of the compound was obtained from *ab initio* and DFT calculations. Mulliken atomic charge shows charge distributions. HOMO-LUMO energy gap is so small. Therefore, low energy is needed to transfer the charge from HOMO-LUMO.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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