CHARGE TRANSFER INTERACTION AND C-H.....O HYDROGEN BONDING ANALYSIS ON WISANINE

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Abstract :The optimized geometries, bonding features and harmonic vibrational frequencies of wisanine have been calculated using density functional theory(DFT) employing B3LYP functional and 6-311G(D,P) basis set. Stability of the molecule arising from hyperconjugative interactions, charge delocalization and C-H....O intramolecular hydrogen bond has been analyzed using natural bond orbital (NBO) analysis by DFT method. The results show that electron density (ED) in the σ* and π* anti-bonding orbitals and second order delocalization energies E(2) confirm the occurrence of intra-molecular charge transfer (ICT) within the molecule. The computed HOMO and LUMO energies demonstrate that charge transfer happens inside of the molecule.

Key words: DFT,NBO,HOMO-LUMO,HYDROGEN BOND

I. Introduction

Wisanine is the major constituent of the amide alkaloids in the root of Piper guineese. Wisanine was the 2-methoxy derivative of 1-piperoylpiperidine [1]. Wisanine have attracted increasing attention due to numerous pharmacological applications in sedative, transquillizing and some anticonvulsant properties[1]. Density functional theory (DFT) approaches using hybrid functional are frequently used to study the structural characteristics, vibrational and electronic properties, interactions among different orbitals, and they are found to yield consistent results. The energies, degrees of hybridization, population of the lone pairs of oxygen, nitrogen atoms, energies of their interaction with the anti-bonding of the rings and the electron density distributions and $E^{(2)}$ energies have been determined by NBO analysis using DFT method to give clear evidence of stabilization originating from the hyper-conjugation of various intra-molecular interactions. The HOMO and LUMO analysis have been used to elucidate information regarding charge exchange within the molecule.

II.Experimental details

The compound under investigation namely wisanine is purchased from Sigma–Aldrich Chemical Company with a stated purity 98% and it was used without any further purification. FT-IR spectrum of this compound was recorded in the region 400–4000 cm^{-1} using a KBr pellet technique at a resolution of 1 cm^{-1}.

III.Computational details

Entire calculations have been executed using the Becke three-parameter hybrid functional [2] with well-designed of Lee, Yang, and Parr[3] (B3LYP) in combination with the 6-311G(d,p) basis set as implemented in the GAUSSIAN 09W [4] program package with the default convergence criteria without any constraint on the geometry[5]. Firstly, the title molecule was optimized, after then the optimized structural parameters were used in the vibrational frequency and calculations of electronic properties. The vibrational wavenumber assignments were carried out by combining the results of the Gauss view 5.08 [6] and VEDA4 programs [7] . The NBO calculations were performed using NBO 3.1 program [8] as implemented in the Gaussian 09 package [9]at the B3LYP/6-311G(d,p) level in order to understand various second order perturbation interactions between the filled orbitals of one subsystem and unfilled orbitals of another subsystem, which is a measure of the intra-molecular delocalization or hyperconjugation. The electronic properties such as HOMO and LUMO energies had been decided by using TD-DFT approach.

IV.Result and Discussion

A. Optimized Geometry

The molecular structure along with numbering of atoms of wisanine is obtained from Gasussian 09 and GAUSSVIEW programs and is shown in Fig.1

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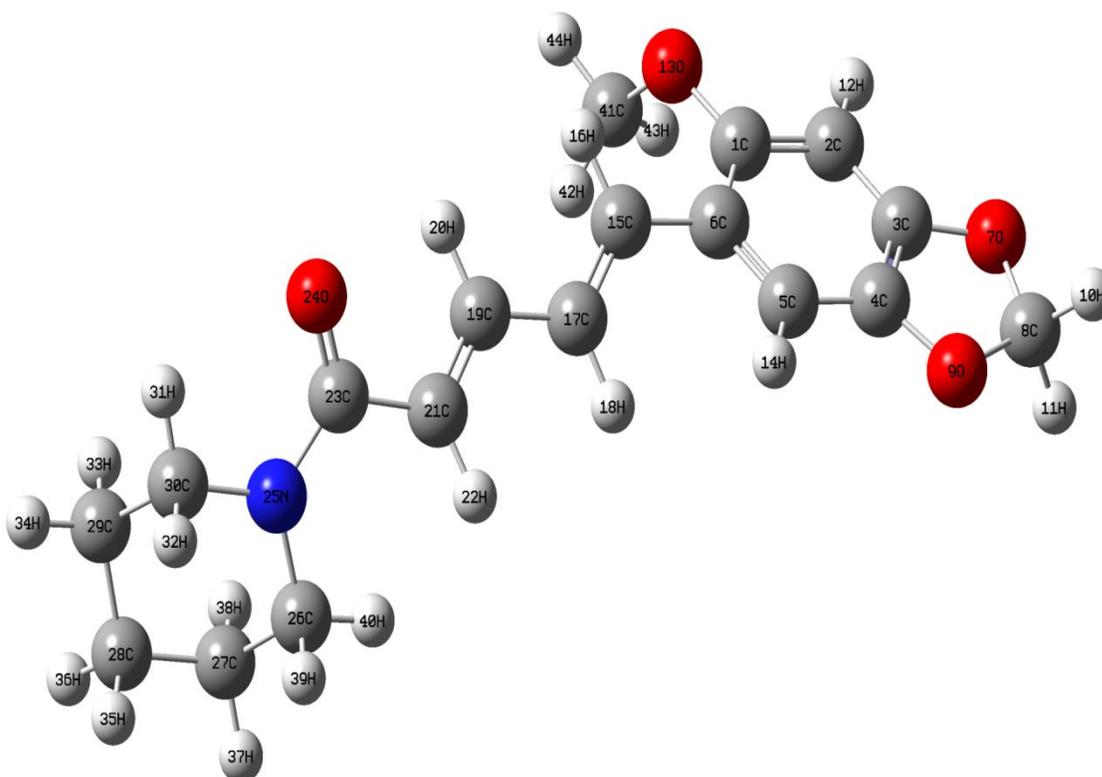
Figure - 1: Optimized molecular structure of wisanine

The most optimized structural parameters (bondlength and bondangle) calculated by DFT/B3LYP with 6-311G(d,p) basis sets are compared with experimental data and are presented in Table 1. From the theoretical values, it is found that some of the calculated parameters are slightly deflected from the experimental values, due to fact that the theoretical calculations belong to molecule in the gaseous state and the experimental results belong to molecule in solid state. The bond lengths of C_{21}-C_{23}, C_{17}-C_{19} and C_6-C_{15} found in the range 1.439-1.486Å are observed to be longer due to the single bond character whereas the bond lengths of C_{19}=C_{21} and C_{15}=C_{17} found in the range1.348-1.353Å are shorter due to the double bond nature. The C–N bond distances are slightly shorter than the C–C bond distances while C–N–C bond angles are slightly larger than C–C–N bond angles [10]. The C_{26}-N_{25} and C_{30}-N_{25} bond nearly 1.461 Å by B3LYP method, which is coincide with literature value ~1.461 Å [11]. In the present study, the calculated bond angles C_{26}-N_{25}-C_{30}, N_{25}-C_{30}-C_{29} and C_{26}-C_{27}-C_{28} are 113.8°, 110.8° and 111° respectively. Piperidine ring essentially adopts chair conformation, with all substituents equatorial as evident from the torsional angles N_{25}–C_{26}–C_{27}–C_{28}, N_{25}–C_{30}–C_{29}–C_{28} are -54.17° and 54.41° by B3LYP method, respectively.

Table 1: Selected bond lengths, bond angles and dihedral angles of wisanine

Bond Length (Å)	Exp. value	wisanine	Bond Angle(°)	Exp. value	wisanine	Dihedral Angle (°)	Exp. value	wisanine
C_6-C_{15}	1.459	1.455	N_{25}-C_{30}-C_{29}	109.97	110.88	N_{25}–C_{26}–C_{27}–C_{28}	-54.34	-54.17
C_{17}-C_{19}	1.437	1.439	N_{25}-C_{26}-C_{27}	109.83	111.03	N_{25}–C_{30}–C_{29}–C_{28}	56.12	54.41
C_{21}-C_{23}	1.476	1.486	C_{26}-C_{27}-C_{28}	111.6	111			
C_{15}=C_{17}	1.333	1.353	C_{26}-N_{25}-C_{30}	112.54	113.8			
C_{19}=C_{21}	1.332	1.348						
C_{26}-N_{25}	1.459	1.461						
C_{30}-N_{25}	1.454	1.465						
C_{26}-C_{27}	1.518	1.536						
C_{29}-C_{30}	1.512	1.532						

B. Vibrational Spectral analysis
The objective of the vibrational analysis is to find the vibrational modes connected with the molecular structure of the title compound. The recorded infrared spectra for the compound in the solid phase are shown in Fig. 2.
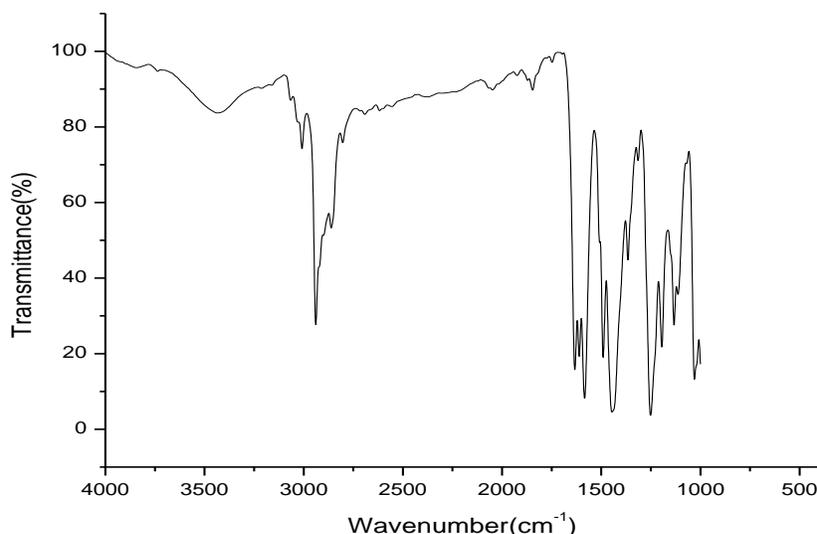
Fig 2.FTIR spectrum of wisanine

The aromatic CH stretching vibrations of hetroaromatic structures are expected to appear in the frequency range of 3100-3000cm^{-1} , with multiple weak bands. The nature of the substituent cannot affect the bands in this region[12-14]. The calculated value of this mode for the title molecule have been found to be 3067, 3067 and 3008cm^{-1} at the DFT-B3LYP level show agreement with FTIR band at 3065 and 3003cm^{-1}.

The C-N stretching vibration usually lies in the region 1200 to 1400 cm-1 [15]. The theoretically computed C-N stretching mode at 1255cm^{-1} is well correlated with experimental data.

A strong absorption band observed in these compounds due to C=O stretching vibration is observed in the region 1750-1600 cm^{-1}[16]. If a carbonyl group is part of a conjugated system, then the wavenumber of the carbonyl stretching vibration decreases, the reason being that the double bond character of the C=O group is less due to the π-electron conjugation being localized. For the title compound, the C=O stretching vibrational mode is observed as a strong band at 1633cm^{-1} in FT-IR and the corresponding DFT calculation give this mode at 1634 cm^{-1}.

C. NBO Analysis

The NBO analysis is carried out by describes all possible interactions between 'filled' (donor) Lewis-type NBOs and 'empty' (acceptor) non-Lewis NBOs, and estimating their energy by 2nd order perturbation theory. NBO analysis has been performed on the molecule at the DFT/B3LYP/6-311G(d,p)level in order to elucidate the intra-molecular, rehybridization and delocalization of electron density within the molecule, which are presented in Table 2. The larger the $E^{(2)}$ value, the more intensive is the interaction between electron donors and acceptors. For wisanine, $\sigma(C_1-C_2)$ of the NBO conjugated with $\sigma^*(C_3-O_7)$ leads to an enormous stabilization of 25.06kJ/mol and $\sigma(C_5-C_6)$ of the NBO conjugated with $\sigma^*(C_4-O_9)$ leads to an enormous stabilization of 27.32kJ/mol respectively. This strong stabilization denotes the larger delocalization. The intramolecular C–H.....O hydrogen bonds are exposed by the interactions between the oxygen lone-pair LP(2) O_{24} and the antibonding orbital $\sigma^*(C_{30}-H_{31})$ whose contribution (3.56 kcal/mol) are smaller but definitely not negligible and can be used as a measure of intramolecular delocalization.

Table 2 : Second order perturbation theory of Fock Matrix in NBO basis for wisanine

Donor NBO (i)	E.D (e)	Acceptor NBO (j)	E.D (e)	$E^{(2)}$ KJmol^{-1}
$\sigma(C_1-C_2)$	1.973 -0.707	$\sigma^*(C_3-O_7)$	0.029 0.340	25.06
$\sigma(C_2-C_3)$	1.969 -0.73	$\sigma^*(C_3-C_4)$	0.041 0.540	21.25
$\sigma(C_3-C_4)$	1.976 -0.716	$\sigma^*(C_4-C_5)$	0.020 0.596	24.02
$\sigma(C_5-C_6)$	1.964 -0.678	$\sigma^*(C_4-O_9)$	0.031 0.331	27.32
$\sigma(C_{15}-H_{16})$	1.973 -0.497	$\sigma^*(C_5-C_6)$	0.021 0.545	19.87
		$\sigma^*(C_{17}-H_{18})$	0.022 0.440	22.63

$\sigma(C_{15}-C_{17})$	1.824 -0.258	$\sigma^*(C_1-C_6)$	0.029 0.537	8.95
$\sigma(C_{17}-H_{19})$	1.975 -0.66	$\sigma^*(C_6-C_{15})$	0.022 0.507	16.65
$\sigma(C_{21}-C_{23})$	1.974 -0.638	$\sigma^*(N_{25}-C_{30})$	0.028 0.358	17.11
$\sigma(C_{23}-O_{24})$	1.991 -0.341	$\sigma^*(N_{25}-C_{26})$	0.029 0.356	10.58
$\sigma(C_{30}-H_{31})$	1.979 -0.487	$\sigma^*(N_{25}-C_{26})$	0.029 0.356	17.74

ED means Electron Density

$E^{(2)}$ means energy of hyper conjugative interaction

D. Atomic charges

The calculations of partial atomic charges are useful part of quantum mechanical calculations because of atomic charges explain the changes of dipole moment, molecular electronic structure as well as molecular polarizability. Also transfer of atomic charges in molecule can explain the chemical reactivity of molecule. The calculated atomic charge values from the natural population analysis (NPA) procedures using the B3LYP 6-311G(d,p) method. This calculation depicts the charges of the all atom in molecule wisanine. Very similar values of positive charges noticed for the five hydrogen pairs forming the CH_2 groups connected with carbon atoms of the piperidine ring. For the hydrogen atoms, the differences in calculated charge are relatively smaller. It is worth mentioning that the biggest value of charge is noticed for H_{31} which are involved in hydrogen bonding. The charge increased at the hydrogen atom taking part in hydrogen bonding(as supported by NBO analysis) is also a clear evidence of hydrogen bonding.
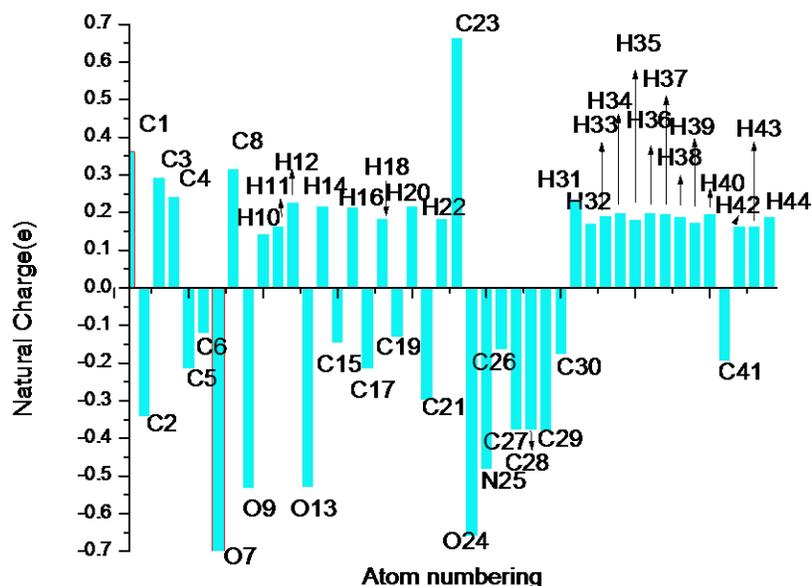

Fig.3 :The histogram of calculated Natural charges for wisanine

E. HOMO–LUMO analysis

The analysis of frontier molecular orbitals interprets one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The HOMO-LUMO energy gap for wisanine was computed at the B3LYP/6-311G(d,p) level of theory. The eigen values of LUMO and HOMO and their energy gap reflect the chemical activity of the molecule. Generally, if the energy gap between the HOMO and LUMO decreases, it is easier for the electrons of the HOMO to be excited. The energy of HOMO, to easier it is for LUMO to accept electrons when the energy of LUMO is low. Surfaces for the frontier orbitals were drawn to understand the bonding scheme of the present compound. The features of these MO can be seen in fig.4. Positive and Negative regions are shown by red and green colors, respectively.From the figure the HOMO is localized on the benzodioxol part of the molecule and LUMO is localized on the centre part of the

molecule. The calculated energy value of the HOMO and LUMO are -0.29319eV and -0.22605eV . The value of energy separation between the HOMO and LUMO is-0.06714eV.
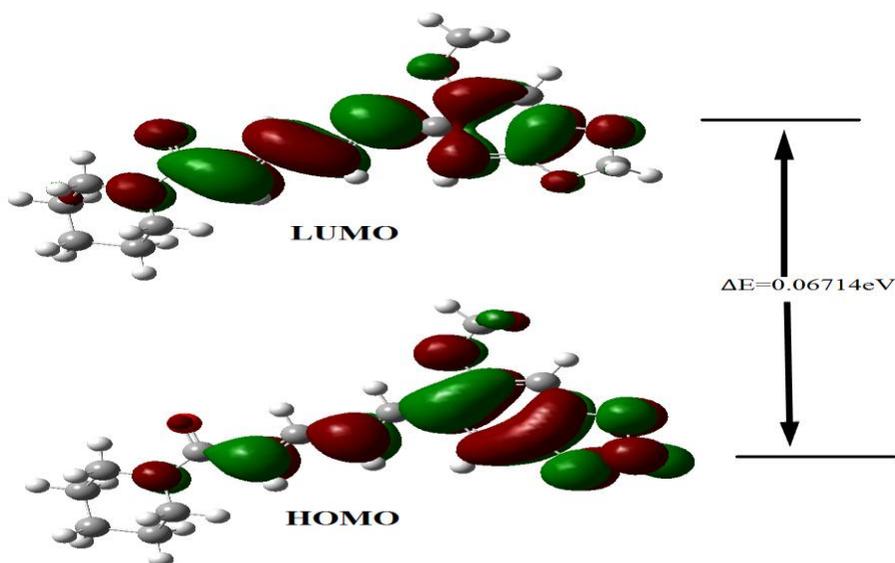

Fig.4: Atomic orbital compositions of the frontier molecular orbital for wisanine

V. CONCLUSION

The ground state geometry and vibrational wavenumbers are determined and analyzed using B3LYP with 6-311G(d,p) basis set. The calculated wavenumber agree well with the observed wavenumbers. The strength of the C-H...O hydrogen bond interactions were obtained from NBO analysis. Partial atomic charges are evaluated using natural population analysis. The lowering of the HOMO–LUMO energy gap value has significant influence on the intramolecular charge transfer within the molecule

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