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Geometry optimization, Electronic Properties, UV spectra and NLO analysis of 5-nitro- picolinamide by using First principle

Abstract

In the present calculations of molecular geometries 5-nitro- picolinamide in the ground state have been carried with the help of combination of DFT/B3LYP method and 6-311G (d,p) basis set. Theoretical UV-Vis spectrum of 5-nitro- picolinamide is also calculated by using TDDFT calculations with same level of theory. A few electronic parameters are also calculated in the same level theory. The calculated HOMO-LUMO has been used to describe that how title molecule interacts with other species. The NLO analysis is used to study non-linear optical behaviors of the molecule.

Keywords: DFT, TDDFT, HOMO-LUMO, MESP, NLO

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Introduction:

Amides have received huge consideration in current years because of its prospective effect of derivatives of picolonamide as fungicide against R. solani (Kundu A, Saha S. 2014). It is also known that the structural organization is governed basically by means of biological metal ions and activation of definite enzymes due to their wide applications in extensive ranging fields from physical sciences to biological sciences (Rizzotto, M.2012). Picolinamide acts as an inhibitor of poly (ADP-ribose) synthetase (PARP) of nuclei from rat pancreatic cells. Its derivative may use a key role to reduce the C.difficile and act as an antibiotic for C.difficile infection(Speri E.,et.al.,2020) . A complete quantum chemical study may lead to asses every energetic as well as significant mechanistic insight within its formulation periphery.

Density functional theory provides valuable information about structure electronic and biological thermal and properties of compound (Dwivedi A.,et al,2012;2011, Pandey A. K.,et al,2013, Dwivedi A., Kumar A.,2019; Das S., 2018; Aljuboori S., & Mahmood A.2019; Sert Y., 2019). In the current study, an exploration of the properties (e.g. electronic, structural, and vibrational) of 5-nitro- picolinamide have been undertaken. We have

determined the composition and harmonic wave numbers and analyzed at the density functional theory (DFT) level by using the basis set 6-311 G(d, p). The optimized geometry of 5-nitro- picolinamide and its molecular properties e.g. as frontier orbital energy gap, molecular electrostatic potential (MESP) energy map, dipole moment, equilibrium energy, polarisability and first static hyperpolarisability were obtained by calculation and explained. Calculations which are based on Density Functional Theory, make available both qualitative and the quantitative perceptive of energy distribution of each vibrational mode based on distribution of potential energy and show the way to an extra analysis of the data obtained from vibrational spectroscopy as given by various groups . NBO Analysis carried out gives conclusive information about charge transfer.

Computational details

The title molecule is modeled by using Gauss View 3.0 (Frisch A.,2000) and optimized without any symmetry constrain by using G03 program package (M.J. Frisch, et. al. 2003). The optimizations of title molecule were done by using combination of DFT/B3LYP method and 6-311G (d, p) basis set. The HOMO, LUMO, MESP of title molecule is plotted by means of gauss View 3.0. The Electronic parameters and UV spectra of 5-nitro-picolinamide are calculated by TDDFT method on optimized structure by using same level theory. The NBO is analyzed by NBO 3.0 program package (Glendening E.D., et al. 1998).

Geometry Optimization

The optimized geometry having no symmetry with ground state energy -412.170 a,u. The optimized structure of title molecule is presented in Fig.1.The optimized geometry 5-nitro- picolinamide having a nitrobenzene ring with one hydrogen at ortho position is replaced by $–CONH_2$-group.The values of C=C bond length(calculated) of nitrobenzene ring lies in between $1.37A^0$-$1.38A^0$ however bond length of C=N is 1.33 A^0. The calculated bond length in between C=O is $1.22A^0$ however bond length in between N-H is $0.996A^0$-0.995 A^0.

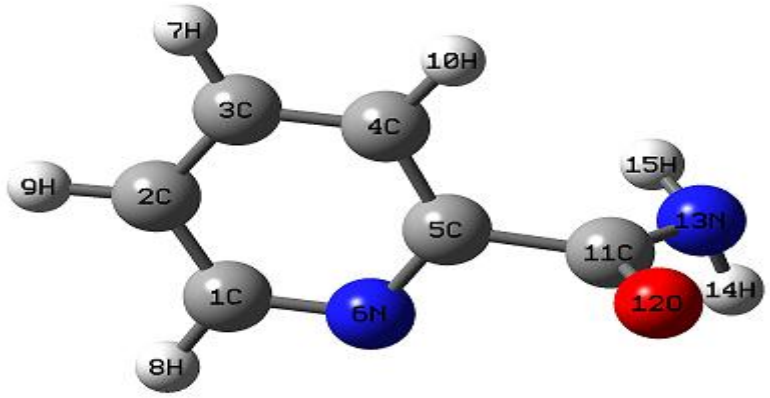


Fig-1 Optimized geometry

Electronic Properties and UV spectra

The HOMO are said to be highest occupied molecular orbitals and LUMO the least unoccupied molecular orbitals are border line molecular orbital. The frontier orbital gap gives valuable information about chemical property and molecular stability. The higher energy gap means molecule is more polarized and consequently molecule shows more reactivity (Gutowski M. et.al.1993, Bose SC.2011) . The calculated gap for title molecule is 4.14eV. The MESP, HOMO, and LUMO plot of molecule are presented in **Fig.2**. Both HOMO and LUMO distributed over whole molecule.

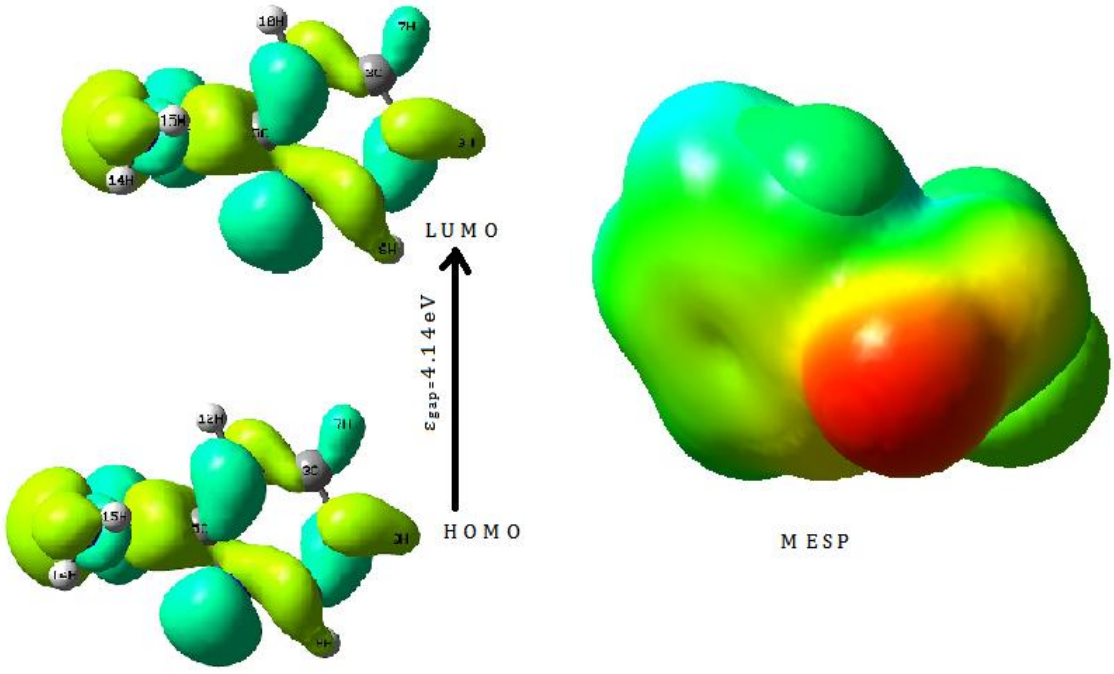


Figure-2 HOMO LUMO and MESP plot of Title molecule

The significance of MESP lies in the reality that it simultaneously exhibits the size of molecule, and the shape as well as +ve, -ve, and neutral electrostatic potential regions in terms of color grading and it is very helpful in studying the molecular structure using its chemical-physical property relationship (Murray JS et.al.1996) . The red color distributed over oxygen however violet color distributed over nitrogen of nitrile group, hence oxygen acts nucleophilic charge center and nitrogen acts as electrophilic charge center.

Several Global reactivity descriptors are calculated and reported Table-1 which are given as

Energy band gap = $\varepsilon LUMO - \varepsilon HOMO$)

Electronegativity (χ) = -½ $\varepsilon LUMO + \varepsilon HOMO$) ----(1)

Chemical potential $\mu = -\chi$,

Global hardness η = ½ $\varepsilon LUMO - \varepsilon HOMO$) ---- (2)

Global softness S = $\frac{1}{2\eta}$ ---------- (3)

Global electrophilicity index $\omega = \frac{\mu 2}{2\eta}$ -------- (4)

(Parr R.G. et al.1989, 1983, Pearson R.G., 1989 , Geerlings P.,et.al.2003)

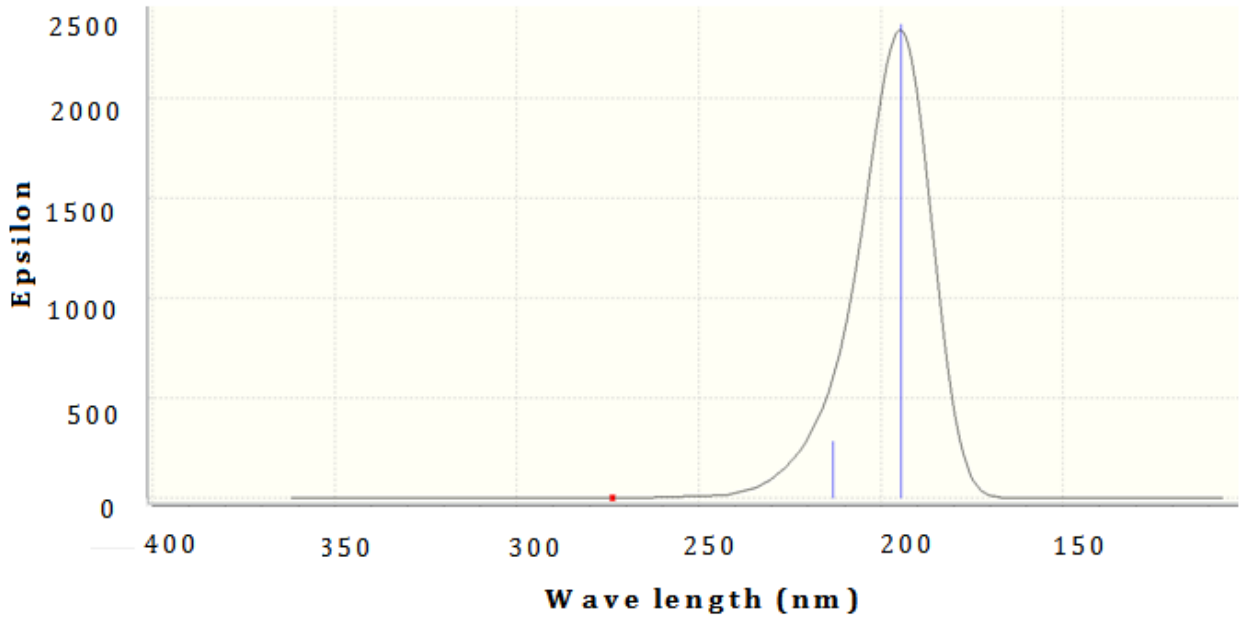
Table 1: Calculated Electronic parameter of title compound

ε_{HOMO}	ε_{LUMO}	ΔE	χ	μ	η	S	ώ
-6.98	-2.84	4.14	4.91	-4.91	2.09	0.240	5.79

The UV spectrum of title molecule is done by using TDDFT method with same level theory. The TDDFT calculation has done on optimized structure of title molecule. The calculated UV spectra and transition orbitals of title molecule is shown in Fig.3(a),and 3(b).The calculated electronic transitions E (eV), oscillatory strength (f), λ_{max} (nm) are calculated and collected in Table-2. The calculated UV spectra shows two prominent absorption peak corresponds at 213nm and 194nm wavelengths. These transitions are due to HOMO-4→LUMO(31%), HOMO-3→LUMO(21%), HOMO-4→LUMO+7(21%) and HOMO-2→LUMO+1(17%), HOMO→LUMO(80%), HOMO-3→LUMO+1(3%) respectively.

Table 2: The values of electronic transitions(calculated): E (eV), oscillatory strength (f), λ_{max} (nm) of title molecule

S.N.	Transitions	E (eV)	Oscillatory Strength(f)	λ_{max} calculated	% Contribution	Assign ment
1	$HOMO-4 \rightarrow LUMO$ $HOMO-3 \rightarrow LUMO$ $HOMO-4 \rightarrow LUMO+7$	1.24	00.0068	213	31% 21% 21%	$n_p \rightarrow n_p^*$
2	$HOMO-2 \rightarrow LUMO+1$ $HOMO \rightarrow LUMO$ $HOMO-3 \rightarrow LUMO+1$	2.71	0.0568	194	17% 80%	$n_p \rightarrow n_p$



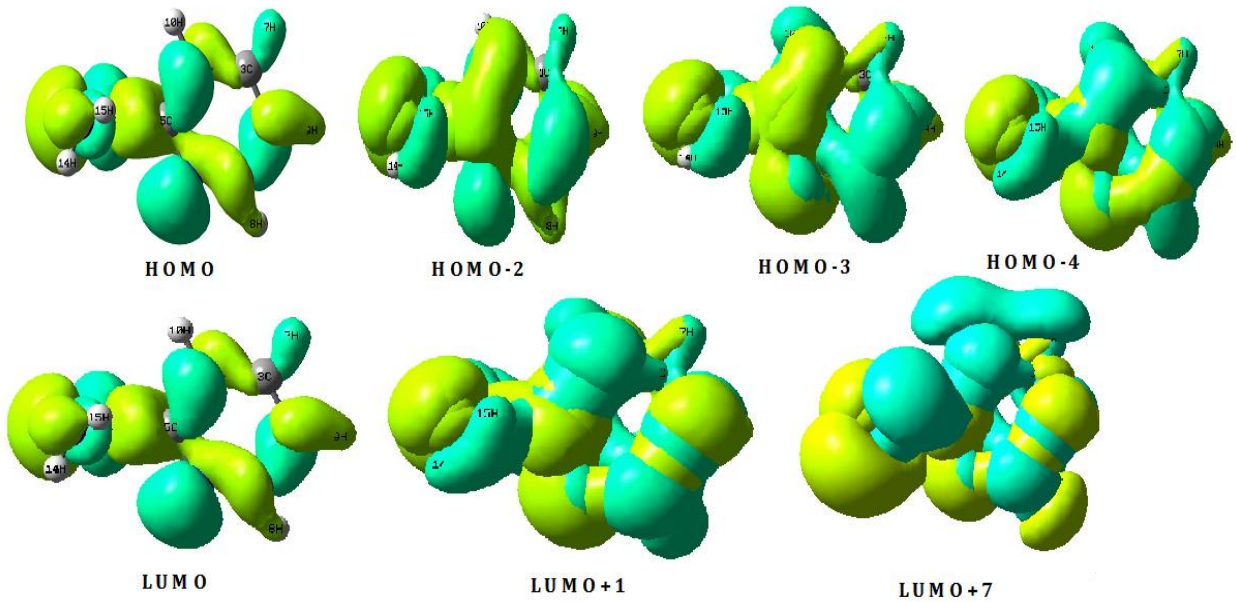


Fig-3(a) Calculated UV spectra (b) Transitions orbitals

NLO analysis

The calculations of Hyperpolarizability and Polarizability have been made by means of a grouping of the DFT / B3LYP method and a 6-311G base group (d, p). Buckingham defined the total μ(dipole moment), mean value of polarizability in a two dimensional cartesian coordinate frame and hyperpolarizability in three dimensional Cartesian coordinate frame by

$$\mu = (\mu x^2 + \mu y^2 + \mu z^2)^{1/2} \quad (5)$$

$$< \alpha > = \frac{1}{3}[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] \quad (6)$$

$$\beta_{Total} = (\beta^2 x + \beta^2 y + \beta^2 z)^{1/2}$$

$$= [(\beta xxx + \beta xyy + \beta xzz)^2 + (\beta yyy + \beta yxx + \beta yzz)^2 + (\beta zzz + \beta zxx + \beta zyy)^2]^{1/2} \text{—(7)}$$

The calculated (Table 3) Polarizability of title molecule shows that molecule more polarize along x and y axis. The value of β_{XXY} and β_{XXZ} contains major part of hyperpolarizability. The calculated value of hyperpolarizability of 5-nitro- picolinamide is almost 3/2 greater than that of urea. Analysis of NBO indicates that the electron cloud moment of π–electron from the donor to the receiving atom is responsible for the polarization in the molecule.

Table 3 : Calculated Polarizability and Hyper Polarizability of 5-nitro- picolinamide

S. N	Parameter	Polarizibility	S. N	Parameter	Hyper Polarizibility
1	α_{xx}	84.908	1	β_{xxx}	-0.1470
2	α_{yy}	73.862	2	β_{yyy}	-6.934
3	α_{xzz}	19.155	3	β_{zzz}	1.0441
4	α_{xy}	1.826	4	β_{xyy}	-0.0088
5	α_{xz}	-0.004	5	β_{xxy}	-34.864
6	α_{yz}	0.001	6	β_{xxz}	-61.3815
	<α>	**-59.31 a.u.**	7	β_{XZZ}	0.0068
-	-	-	8	β_{YZZ}	2.521
-	-	-	9	β_{YYZ}	7.543
-	-	-	10	β_{XYZ}	-0.0056
-	-	-		β_{Total}	**73.69 a.u.**
1 a.u. = $8.3693X10^{-33}$e.s.u.					

Thermodynamic Property

According to vibrational analysis Enthalpy (H^0_m), Entropy (S^0_m), Heat Capacity ($C^0_{p.m}$) are major thermodynamic functions. In this communication we have calculated these major parameters by using grouping of DFT/B3LYP method and base 6-311G (d, p) in between 100K-500K temperature range. The calculated graph in between temperature and these parameters are plotted . These are temperature and Enthalpy (H^0_m), Entropy (S^0_m), and Heat Capacity ($C^0_{p.m}$). We have find a good correlation in between these parameters with temperature. The calculated correlation of these parameters with variation of temperature after quadratic fitting of order two are given below

$$H^0_m=104.77- 0 .00081T- 0.000177T^2 (R^2=0.99961)—(8)$$

$$C^0_{p.m}=-3.38+0.3211T-0.00066 (R^2=0.99941) —(9)$$

$$S^0_m=74.124+0.267T-0.000041 T^2 (R^2=0.99975) —(10)$$

The above correlation equations are helpful in thermochemistry for computation in thermo energy and also valuable for additional work for 5-nitro- picolinamide

Conclusion

The electronic properties such as molecular orbital energies and their distributions (HOMO-LUMO clouds, molecular electrostatic potential energy map) were calculated by using combination of DFT/B3LYP method and 6-311G base group (d,p). The ultravoilet spectrum of concerned molecule shows two prominent absorption peaks. The molecular electrostatic potential (MESP) energy map plot shows that Oxygen behaves most

nucleophilic and Nitrogen is most electrophilic charge centre. The calculated HOMO-LUMO gap of title molecule shows that title molecule is less chemically reactive. The calculated optical parameters point out that title molecule is good NLO agent in future.

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