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*Journal homepage: <http://www.journalijar.com>***INTERNATIONAL JOURNAL  
OF ADVANCED RESEARCH****RESEARCH ARTICLE****Quantum Chemical Calculations of Molecular Structure, Electronic, Thermodynamic and Non-linear optical properties of 2-amino-3-nitro-6-methyl pyridine.****David Pegu, and Ngangbam Bedamani Singh**

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**Key words:***Pyridine derivatives, ab initio,  
Thermodynamic properties***Abstract**

In the present study, we report a theoretical study on molecular structure, electronic and thermodynamical properties of 2-amino-3-nitro-6-methyl pyridine (2A3N6MP) by using ab initio Hartree Fock (HF) and density functional theory (DFT) methods employing B3LYP exchange correlation with 6-311++G(d,p) basis set. The ground state molecular geometrical parameters, have been calculated and compared with available reported values. The calculated HOMO and LUMO energy shows that charge transfer takes place within the molecule and the molecule is chemically soft molecule. The dipole moment, linear polarizability and first hyperpolarizability values were also computed. Finally the temperature dependence thermodynamic properties were also determined and interpreted.

*Copy Right, IJAR, 2013., All rights reserved.***Introduction**

The structural and vibrational spectrum of pyridine and its derivatives have been extensively studied and analyzed in recent years because of their involvement in bioactivities and applications in pharmaceutical, agro chemical and many other industries [1-3]. In particular it has been mentioned that 2-amino pyridine derivatives have attracted considerable interest because they are useful precursors for the synthesis of a variety of heterocyclic compounds possessing a medicinal value [4-7]. Nitro pyridine derivatives have been reported as useful nonlinear optical material which shows large non linear optical properties used in frequency converters [8-9]. Nitropyridine derivatives are also important for its biological activities such as antibacterial or antifungal potency [10]. It has reported recently that the inhibitory properties of 3-nitropyridine derivatives and their salts can be used as therapeutic or preventive agents for hepatitis B and acquired immune deficiency syndrome (AIDS) [11]. Various spectroscopic studies have been reported on methyl substituted pyridine derivatives which have cholesterol lowering properties and as anti-cancer and anti-inflammatory agents [12-14]. The spectroscopic investigation of amino, nitro and methyl substituted pyridine derivatives are studied by many authors by using quantum mechanical ab initio and DFT methods but pyridine derivatives where these three groups are present in the pyridine ring have not been studied yet. Quantum chemical calculation can provide valuable information about structural, electronic, optical, thermodynamics and other related properties of the molecules. Moreover it always has been a difficult task in getting sufficient accuracy and reliability in theoretical prediction of properties of molecules. Therefore, the present investigation was undertaken to study the molecular properties of 2-amino-3-nitro-6-methyl pyridine (2A3N6MP) and to identify useful information of the molecule.

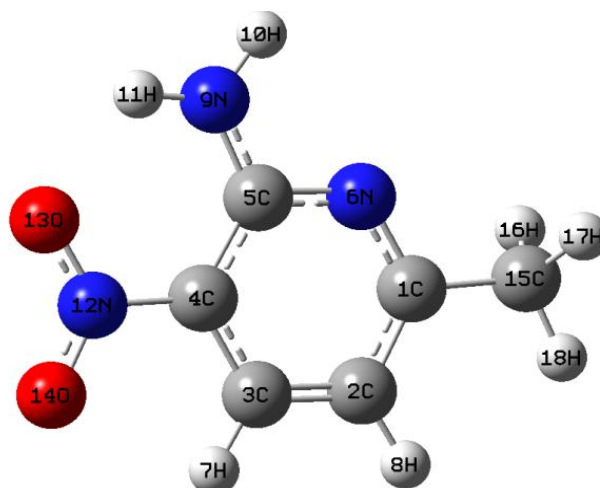
**Computational details**

The molecular geometry optimizations were performed by step by step and finally by HF and density functional theory [15] with Becke's three parameters and the Lee-Yang-Parr functional (B3LYP) [16-18] with the standard 6-311++G(d,p) basis set with Gaussian 09 software package. No symmetry restriction was applied during geometry optimization. The dipole moment, non linear optical properties, frontier molecular orbitals, and thermodynamics properties were also studied using the same method and basis set.

## Results and Discussion

### Geometrical Parameters

Molecular geometry is a sensitive indicator of intra and intermolecular interactions. The accurate determination of geometrical deformation in substituted pyridine rings is an important tool for investigating the nature of the interactions between the ring and the substituent's [19-21]. The geometry of 2-amino-3-nitro-6-methyl pyridine was optimized at HF and DFT (B3LYP) levels using 6-311++G (d,p) basis set. At the optimized geometry for the title molecule no imaginary frequency modes were obtained, so there is a true minimum on the potential energy surface. The optimized molecular structure with symbols and numbering of the title molecule is obtained from Gaussian 03W [22] and Gauss View programs [23] as shown in the Fig. (i). The molecule contains  $\text{NH}_2$ ,  $\text{NO}_2$  and  $\text{CH}_3$  groups connected with the pyridine ring. The comparative optimized geometrical parameters such as bond lengths, bond angles and dihedral angles are presented in the Table (i). Since crystal structure of 2A3N6MP is not available, the optimized theoretical results have compared with similar structural compounds. It is observed that most of the optimized bond lengths and bond angles are slightly shorter, as well as longer than the experimental values in both HF and B3LYP method. The inconsistency between the theoretical and experimental results is due to the fact that, theoretical calculation belongs to isolated molecules in gaseous phase and the experimental results belonging to molecules in solid state. Comparing the bond angles and bond length of DFT/B3LYP with those of HF, as a whole the formers are bigger than the later and HF calculated values correlates more nearer to the experimental values. It is found that most of the optimized theoretical bond lengths are in good agreement with experimental bond length but bond angles are slightly longer or shorter than that of experimental values. In the ring C-C bond length varies from 1.313 to 1.425 Å due to different substituent in the pyridine ring. The computed value of the bond length in  $\text{NO}_2$  and  $\text{NH}_2$  group is different from the experimental value; may be due to the involvement of intermolecular interaction of these groups in the crystalline state. It is observed that the C-C bond length at the position of methyl group substitution is much more influenced than the amino and nitro group. The calculated C-C-C bond angles between the ring carbon atoms are significantly deviated at both levels of calculations in the position of substituted pyridine ring. From the dihedral angles it is found that both  $\text{NO}_2$  and  $\text{NH}_2$  are coplanar with the pyridine ring.



**Fig. (i)** Optimized molecular structure and atomic numbering of 2-amino-3-nitro-6-methyl pyridine.

**Table (i)** Selected optimized geometrical parameters of 2A3N6MP in comparison with XRD data.

Parameters	HF/ 6311++G(d, p)	B3LYP/ 6311++G(d, p)	<sup>a</sup> Experimental 2A5MP	<sup>b</sup> Experimental pyridine
C1-C2	1.39830	1.40708	1.400	1.395
C1-N6	1.31321	1.32950	1.338	1.340
C2-C3	1.37012	1.37969		1.394
C3-C4	1.38839	1.39481		1.394
C4-C5	1.41367	1.42547		1.395
C5-N6	1.33301	1.34826		1.340
C2-H8	1.07213	1.08187		1.081
C3-H7	1.07205	1.08162	0.980	1.081
C4-N12	1.44880	1.44051	1.4832	
N12-O13	1.19690	1.23946	1.2419	
N12-O14	1.18879	1.22692	1.2902	
C4-C3	1.38839	1.3948		
C5-N9	1.33860	1.34762	1.338	1.340
N9-H10	0.99189	1.00690	0.9186	
N9-H11	0.98986	1.00785	0.9506	
C3-H7	1.07205	1.08187	1.0409	
C2-H8	1.07213	1.08187	0.9530	
C1-C15	1.50351	1.50404	1.506	
C15-H16	1.08448	1.09313		
C15-H17	1.08457	1.09319	1.090	
C15-H18	1.08280	1.09058	1.070	
N6-C1-C2	119.64570	120.01117		123.6
C1-C2-C3	119.00175	119.00596		118.5
C2-C3-C4	119.92278	119.67791		
C3-C4-C5	117.61676	118.32287		118.1
C4-C5-N6	122.78562	122.45480		123.3
O13-N12-O14	123.09033	123.41829	121.8500	
C5-C4-N12	122.86372	122.98100	121.9700	
N6-C5-C9	115.67018	115.16230	115.2700	
H10-N9-H11	121.51900	122.62965	109.1300	
N6-C1-C15	116.02153	116.02223	116.005	
C1-C15-C16	109.55541	109.97819	111.0	
C1-C15-C17	109.55041	109.96859	106.0	
C1-C15-C18	111.72178	111.83845		
C1-C2-H8	121.10573	120.68441	120.549	
C2-C3-H7	121.32534	121.94639	121.436	
C6-C1-C15	116.02153	116.22920	123.0	
C2-C1-C15	121.19279	121.31599	118.0	
C5-C4-N12-O13	-0.12695	-0.03814	4.0600	
C3-C4-N12-O13	179.97012	179.91085	-175.6600	
H10-N9-C5-N6	-0.11750	-0.16949	-0.0195	
H11-N9-C5-N6	-179.88111	-179.79566	179.5900	
N6-C1-C15-H16	-58.55703	-58.66769		
N6-C1-C15-H17	59.10784	59.21353		
N6-C1-C15-H18	-179.74234	179.74434		

<sup>a</sup> X-ray data from Ref.[24].<sup>b</sup> X-ray data from Ref. [25].

### Non Linear Optical Properties:

Some of the nitro substitute pyridine materials show efficient nonlinear optical properties that can be used in various non linear optical devices. It is well known that the higher values of dipole moment, polarizability, and hyperpolarizability are important for more active NLO properties. In this study dipole moment, polarizability and the second order polarizability or first hyperpolarizability of the titled molecule were investigated by using HF and B3LYP method at 6-311++ G(d, p) basis set. The complete equations for calculating the magnitude of total static dipole moment ( $\mu$ ), the anisotropy of the polarizability ( $\Delta\alpha$ ) and first hyperpolarizability ( $\beta$ ), using the  $x$ ,  $y$ ,  $z$  components are defined as follows:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\Delta\alpha = \frac{1}{\sqrt{2}} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2 \right]^{1/2}$$

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

Here,

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

**Table (ii)**

Electric dipole moment  $\mu$  (Debye), mean polarizability  $\Delta\alpha$  (in esu) and first order hyperpolarizability  $\beta$  (in esu) value of 2-amino-3 nitro-6 methyl pyridine calculated by HF/6-311++G(d,p) and B3LYP/6-311++G(d,p).

	HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)	HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)
$\mu_x$	-0.9789	-0.9183	$\beta_{xxx}$	-79.2642
$\mu_y$	-1.3471	-1.4361	$\beta_{xxy}$	65.7913
$\mu_z$	-0.0851	-0.0747	$\beta_{xyy}$	374.4273
$\mu$	1.66738	1.706235	$\beta_{yyy}$	7.8568
$\alpha_{xx}$	108.6509	124.707	$\beta_{xxz}$	-9.4361
$\alpha_{xy}$	6.1848	12.6013	$\beta_{xyz}$	2.9765
$\alpha_{yy}$	122.3588	144.219	$\beta_{yyz}$	43.0419
$\alpha_{xz}$	6.3932	8.0172	$\beta_{xzz}$	-9.0793
$\alpha_{yz}$	-1.0124	-0.7827	$\beta_{yzz}$	-41.6483
$\alpha_{zz}$	55.3886	58.348	$\beta_{zzz}$	0.1774
$\Delta\alpha$	61.285	77.979	$\beta$	306.4074
$\Delta\alpha(\text{esu})$	$9.0824 \times 10^{-24}$	$11.5564 \times 10^{-24}$	$\beta(\text{esu})$	$27.0843 \times 10^{-31}$

Theoretically calculated values of various components of first hyperpolarizability, mean polarizability and dipole moment by using HF and B3LYP method at 6-311++G(d,p) basis set are shown in the Table (ii). The calculated NLO parameters in B3LYP / 6-311++G(d,p) method are found to be higher than the HF / 6311++G(d,p) method. The components of polarizability and hyperpolarizability tensors were obtained from frequency job output file of Gaussian 03. The electronic dipole moment  $\mu_i$  ( $i = x, y, z$ ) and total dipole moment ( $\mu$ ) for the title compound are also listed. However,  $\alpha$  and  $\beta$  values of Gaussian output are in atomic units (a. u.), so they have been converted into electrostatic units (esu) as ( $\alpha$ ; 1 a.u. =  $0.1482 \times 10^{-24}$  esu and  $\beta$ ; 1 a.u. =  $8.6393 \times 10^{-33}$  esu). The dipole moment reflects molecular charge distribution in three given direction which can be used to describe charge movement across the molecule. The calculated value of dipole moment was found to be 1.706235 Debye. The highest value of dipole moment is observed for component  $\mu_y = -1.4361$ . The calculated anisotropy of polarizability ( $\Delta\alpha$ ) of 2A3N6MP is calculated as  $11.5564 \times 10^{-24}$  esu. The magnitude of the molecular hyperpolarizability  $\beta$  is one of the

important key factors in a NLO system. The first hyperpolarizability ( $\beta$ ) value of the title compound is equal to  $58.7641 \times 10^{-31}$  esu. The hyperpolarizability value was dominated by the component  $\beta_{xyy} = 462.487$ . Domination of particular component indicates a substantial delocalization of charges in this direction. The dipole moment, mean polarizability and first hyperpolarizability of 2A3N6MP by B3LYP/ 6311++G(d,p) are 1.706235 D and  $11.5564 \times 10^{-24}$  esu and  $58.7641 \times 10^{-31}$  esu respectively, which are greater than urea. (For urea  $\alpha = 9.68774 \times 10^{-24}$  esu; and  $\beta = 7.803 \times 10^{-31}$  esu and  $\mu = 1.5285$  D obtained by B3LYP / 6-311++ G(d,p) method). The value of first hyperpolarizability value is significantly 8 times greater than those of urea which indicates the molecule as NLO material.

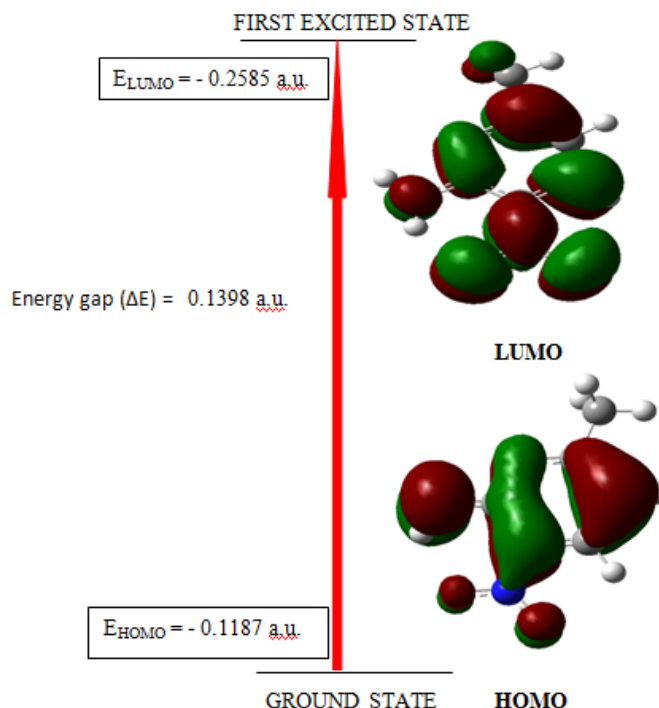
#### Frontier molecular orbitals:

Frontier molecular orbitals play an important role in electric and optical properties as well as chemical reaction. Both highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are the main orbitals taking part in chemical stability [26]. The energy gap between HOMO and LUMO reflects the kinetic stability, chemical reactivity, molecular polarizability and also determines the softness or hardness of the molecule. A molecule with smaller frontier molecular orbitals is associated with high chemical reactivity, low kinetic stability, more intermolecular interactions due to which the molecule is termed as soft molecule. The HOMO, LUMO and HOMO-LUMO energy gap of 2-amin-3-nitro-6-methyl pyridine in the HF and DFT level in 6-311++G(d,p) basis set has been calculated. Surfaces for the frontier orbitals were drawn for the title compound in the Fig. (ii). By careful observation of HOMO-LUMO plot we can provide insight into the nature of reactivity, and some of the structural and physical properties of molecules. The positive phase of the molecule is represented in red color and negative phase in green color. From HOMO-LUMO plot it has been observed that HOMO is localized mainly on the nitro group and the pyridine ring. On the other hand LUMO is delocalized on the entire compound except one of C-H of the methyl group. The value of energy separation between HOMO and LUMO is 0.1398 a.u. or 3.8041 eV for 2A3N6MP which makes it a soft and more polarizable molecule. The lower value of HOMO-LUMO energy gaps of the title compound reflects increased charge transfer within the molecule. The other related molecular properties have been also calculated in both level of theory. The Ionisation energy (E) and electron affinity (A) can be expressed in terms of HOMO and LUMO orbital energies as  $I = -E_{\text{HOMO}}$  and  $A = -E_{\text{LUMO}}$ . The global hardness which is associated with the stability of the molecule can be expressed as  $\eta = 1/2(E_{\text{LUMO}} - E_{\text{HOMO}})$ . The electronic chemical potential ( $\mu$ ) in terms of electron affinity and ionization potential is given by  $\mu = 1/2(E_{\text{HOMO}} + E_{\text{LUMO}})$ . The global electrophilicity index,  $\omega = \mu^2/2\eta$  is also shown in the Table (iii).

**Table(iii)**

Comparison of HOMO, LUMO, energy gaps ( $E_{\text{Homo}} - E_{\text{Lumo}}$ ) and related molecular properties of 2A3N6MP

Molecular Properties	HF/6-311 ++ G (d, p)	B3LYP/6-311 ++ G (d, p)
$E_{\text{Homo}}$	-0.36971	-0.2585
$E_{\text{Lumo}}$	0.02303	-0.1187
Energy gap ( $\Delta E$ )	0.39274	0.1398
Ionosation Potential (I)	0.36971	0.2585
Electron affinity (A)	-0.02303	0.1187
Global Hardness ( $\eta$ )	0.19637	0.0699
Chemical Potential ( $\mu$ )	-0.17334	-0.1886
Global Electrophilicity ( $\omega$ )	0.07651	0.25443



**Fig. (ii)** The atomic orbital HOMO-LUMO plot of 2-amino-3-nitro-6-methyl pyridine at B3LYP/6-311++G(d,p).

#### Thermodynamics properties:

The various thermodynamical parameters like rotational constant, zero point vibrational energy, total energy at room temperature and pressure are presented in the Table (iv). It has been observed that most of the values in HF/6-311+G(d,p) methods are greater than the B3LYP/ 6-311+G(d,p). The changes in the total entropy of the investigated molecule at different methods are only marginal. Scale factors have been recommended to determine accurate prediction of the zero-point vibrational energy, entropy and heat capacities with the values of this table. The values of the thermodynamics functions such as entropy, heat capacity, total energy at different temperatures are listed in the Table (v). It is found that the values are increasing with temperatures ranging from 100 to 700 K due to the fact that molecular vibrational intensities are increasing with temperatures. All the theoretically calculated thermodynamic data provide helpful information for the further study on the 2-amino-3-nitro-6-methyl pyridine.

**Table (iv):** Thermodynamic functions of 2-amino-3-nitro-6-methyl pyridine obtained by HF and B3LYP level with the standard 6-311++G(d,p) basis set.

Thermodynamic parameters	HF/6-311+G(d,p)	B3LYP/ 6-311+G(d,p)
Zero point vibrational energy (Kcal/Mol)	90.80556	84.39993
Rotational constants (GHz)	2.40038	2.35752
	0.837274	0.82046
	0.62310	0.61093
Rotational temperature(Kelvin)	2.40038	0.11314
	0.83724	0.03938
	0.62310	0.02932
Total energy (kcal mol <sup>-1</sup> )	96.728	90.668
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	94.950	88.890
Heat Capacity at const. volume (cal mol <sup>-1</sup> K <sup>-1</sup> )	34.610	36.821

Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	28.497	30.859
Entropy (cal mol <sup>-1</sup> K <sup>-1</sup> )	96.961	100.196
Translational	40.987	40.987
Rotational	29.930	29.988
Vibrational	26.045	29.222

**Table (v):** Thermodynamic properties for 2A3N6MP at different temperatures at B3LYP/6-311++ G(d,p)

T(K)	S <sup>0</sup> <sub>m</sub> (Cal /mol <sup>-1</sup> k <sup>-1</sup> )	C <sup>0</sup> <sub>p,m</sub> (Cal /mol <sup>-1</sup> k <sup>-1</sup> )	H <sup>0</sup> <sub>m</sub> (Kcal /mol <sup>-1</sup> )
100	71.530	15.529	85.481
150	86.934	20.830	87.566
200	85.550	26.273	86.934
250	93.824	31.705	89.016
298.150	88.718	30.610	72.503
350	106.836	42.087	92.714
400	113.034	46.822	94.938
450	119.038	51.159	97.389
500	124.844	55.084	100.047
550	130.53	58.64	102.891
600	131.086	57.520	99.693
700	140.659	62.670	105.711
750	150.963	69.477	115.76

## Conclusion

The computed optimized geometric parameters of the molecule were compared and analyzed with available experimental data. The calculated frontier molecular orbitals and related parameters shows that eventual charge transfers takes place within the molecule and the molecule is chemically reactive. The first order hyperpolarizability and related properties was examined and the results show that the molecule can be used as material for NLO applications. Furthermore, the results of the thermodynamics parameters of the compound increase with increasing temperature owing to the intensities of the molecular vibrations increases with rise in temperature.

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