Electronic Structure, Nonlinear Optical Properties and Spectroscopic Studies of 4-Methyl-3-Nitropyridine-1-Carbonitrile using Density Functional Theory

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ABSTRACT: The structural, electronic, and spectroscopic properties of 4-Methyl-3-nitropyridine-1-carbonitrile (4MNC) have been investigated from theoretical and vibrational spectroscopic point of view employing quantum chemical method utilizing GAUSSIAN 09. A detailed study of geometrical parameters, Infrared and Raman spectra, and electronic properties were performed by density functional theory (DFT) at Becke-3-Lee-Yang-Parr (B3LYP) and HF Methods by employing 6-311++G(d,p) basis sets. The FTIR and FT-Raman Spectra has been recorded using Fourier transform FT-IR and FT-Raman spectroscopy in the region 4000-400 cm⁻¹. The energy gap between Highest Occupied Molecular Orbital (HOMO) - Lowest Unoccupied Molecular Orbital (LUMO) is measured. The HOMO and LUMO study suggests the existence of charge transfer within the molecule. The NLO properties such as polarizability (α_{tot}) and molecular first order hyperpolarizability (β) and thermodynamic analysis of the title compound are computed with DFT/B3LYP and HF 6-311++G (d,p) level of theory. These results indicate that 4-Methyl-3-nitropyridine-1-carbonitrile could be candidate compounds for the potential use in application such as solar cells and biochemistry.

KEYWORDS: DFT, electronic properties, NLO and spectroscopic properties (FTIR and FT-Raman), Thermal properties.

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1. INTRODUCTION

The pyridine and their derivatives are widely used as starting materials in a vast amount of chemicals, pharmaceuticals, dyes, electro optical and many other industrial processes [1]. In drug discovery, it was well demonstrated that to avoid screening millions of compounds, one might attempt to bias combinatorial chemistry efforts to produce a set of molecules, which contain drug like patterns such as the pyridine heterocyclic ring [2]. From the perspective of structural diversification, we were interested in pyridine scaffolds bearing reactive orthogonal functional groups, with minimal protecting group transformation and synthetic manipulations. The study of the vibrational spectra of substituted pyridine mainly amino pyridine attracts the attention of many spectroscopists due to their wide application in pharmacology and agro-chemistry. Pyridine heterocycles are a repeated moiety in many large molecules with interesting photo physical, electrochemical and catalytic applications [3–10]. Most recently, Guoqiang Wang et al. [11] reported a metal-free approach to the synthesis of C-4 substituted pyridine derivatives was predicted computationally and verified experimentally. Theoretical calculations revealed that the in situ generated pyridine-boryl radical using 4-cyanopyridine and B₂ (pin)₂ exhibits a carbon-radical characteristic, and this boryl radical can be used as a bifunctional “reagent”, which acts as not only a pyridine precursor but also a boryl radical. Kandasamy et al. [12], the FTIR and FT-Raman spectra of 3- and 4- amino-2-bromopyridine have been reported together with the vibrational assignments of the vibrational modes. Sundaraganesan et al. [13–15] reported the FTIR and FT-Raman spectra of 2-amino-5-chloropyridine, 2-amino-5-iodopyridine and 4-N, N-dimethylamino pyridine by using HF and DFT calculations. Sundaraganesan et al. [16]

studied the molecular structure and vibrational spectra of 2- amino-5-methyl pyridine and 2-amino-6-methyl pyridine by density functional methods.

To the best of our knowledge, no theoretical work about the vibrational frequency, NLO properties, thermodynamic analysis and frontier molecular orbital has been reported for the title compound until now.

Considering the pharmacological and biochemical importance of the title compound 4-Methyl-3-nitropyridine-1-carbonitrile (4MNC) led to the complete FT-IR and FT-Raman vibrational studies on the fundamental modes and frontier molecular orbitals (FMO's) and thermodynamic analysis using DFT and HF methods by employing 6-311++G(d,p) basis sets. The optimized geometry, FMO's and their energy gaps and molecular electrostatic potential (MESP) map have been constructed at B3LYP/6-311++G (d, p) level to understand the electronic properties, electrophilic and nucleophilic active centers of title compound.

2. COMPUTATIONAL DETAILS

The density functional theory (DFT) were used to carry out the optimization of the geometry and to determine vibrational wavenumbers of 4MNC, with the 2009 version of the Gaussian suite [17] using DFT/B3LYP and HF the methods [18,19] supplemented with standard 6-311++G(d,p) basis sets. The vibrational modes were assigned by means of visual inspection using GAUSSVIEW program [20]. The vibrational mode analysis of 4MNC is presented in some detail in order to better describe the basis for the assignments, from the basic theory of Raman scattering. In this investigation we observed that the calculated frequencies were slightly greater than the fundamental frequencies. To improve the agreement between the predicted and observed frequencies, the computed harmonic frequencies are usually scaled for

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comparison. In this work the force field was scaled according to the SQM procedure [21] and the Cartesian representation of the force constants were transferred to a non-redundant set of local symmetry coordinates, chosen in accordance to the recommendations of Pulay et al. [22]. Calculation of the potential energy distribution (PED) and the prediction of IR intensities and Raman activities were done on a PC with the MOLVIB Program (Version V7) written by Sundius [23].

3. RESULT AND DISCUSSION

3.1 Molecular geometry

The molecule 4MNC has 17 atoms with 45 normal modes of vibration. It belongs to the C₁ point group symmetry. Fig.1 (a) shows the optimized geometry of the compound and Table 1 presents the optimized values obtained for bond lengths and bond angles. The various bond lengths and bond angles are found to be almost same at HF and B3LYP methods. The bond lengths between C1-C2 in HF and B3LYP method are found to be 1.2827 and 1.2981 respectively (Fig.1(b)). The bond length between C1-N6 in HF and B3LYP are 1.3181 and 1.3381 respectively.

The bond angle between N16-C12-C17 in HF and B3LYP are 108.95 and 124.02 respectively (Fig. 1 (c)). The bond angle between C2-C1-6N in HF and B3LYP are 124.26 and 111.1. The HF value is in good agreement with B3LYP value. The dihedral angle between C1-C7-N8-N6-C1 in HF and B3LYP method are 181.583 and 181.562 (Fig. 1 (d)).

Fig 1(a). Optimized geometrical structure of 4-Methyl-3-nitropyridine-1-carbonitrile

The calculated geometric parameters can be used to determine the other parameters of 4MNC. Bond angles and dihedral angles were referred from [24–26].

3.2 Vibrational analysis

The calculated frequencies using HF and B3LYP methods and their IR intensities and assignments, internal coordinates are listed in Table 2 and 3. The experimental FTIR, FT-Raman and calculated vibrational spectra (B3LYP) are shown in Figs. 2–3 respectively. The description of the various band assignments is as follows.

Table 1. Bond lengths (in Angstrom), bond angles (in degree) and dihedral angles (in degree) of the 4-Methyl-3-nitropyridine-1-carbonitrile

Parameters	HF/6-311++G(d,p)	DFT/6-311++G(d,p)
Bond length (Å)		
C1-C2	1.2827	1.2981
C1-N6	1.3181	1.3381
C1-C7	1.4513	1.4411
C2-C3	1.3779	1.3846
C2-H13	1.0703	1.0804
C3-C4	1.3724	1.3841
C3-N9	1.473	1.4903
C4-C5	1.3952	1.4026
C4-14	1.0708	1.081
C5-6N	1.3184	1.3378
C5-C12	1.5044	1.5034
7C-N8	1.1291	1.1537
N9-O10	1.1847	1.2211
N9-C11	1.1841	1.2207
C12-C15	1.0842	1.0928
C12-H16	1.0829	1.0904
C12-H17	1.0842	1.0928
Bond Angle(Å)		
C2-C1-6N	124.26	124.02
C2-C1-7C	119.14	119.27
6N-C1-7C	116.59	116.70

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C1-C2-C3	115.41	115.91
C1-C2-H13	122.17	122.42
C3-C2-H13	122.20	121.68
C2-C3-C4	121.6	121.56
C2-C3-N9	119.01	119.07
C4-C3-N9	119.25	119.36
C3-C4-C5	117.67	117.93
C3-C4-C14	120.74	120.27
C5-C4-C14	121.57	121.79
C4-C5-6N	121.44	121.69
C4-C5-C12	121.62	121.60
6N-C5-C12	116.92	116.70
C1-6N-C5	119.42	118.87
C3-N9-O10	117.25	117.20
C3-N9-C11	117.07	117.18
O10-N9-C11	125.69	125.61
C5-C12-C15	109.79	109.95
C5-C12-H16	111.50	111.77
C5-C12-C17	109.79	109.96
C15-C12-H16	108.94	108.93
C15-C12-C17	107.76	107.14
N16-C12-C17	108.95	108.94
Dihedral Angle (Å)		
C1-7C-N8-N6-C1	181.583	181.562
C1-7C-N8-N6-C2	180.0004	179.999
6N-C1-C2-C3	-0.0004	-0.002
6N-C1-C2-H13	-180	179.998
7C-C1-C2-C3	180.0005	-180.00
7C-C1-C2-H13	0.0011	-0.0006
C2-C1-N6-C5	0.0003	0.0014
7C-C1-N6-C5	179.9993	180.00
C1-C2-C3-C4	0.0005	0.0007
C1-C2-C3-N9	-180.001	180.00
H13-C2-C3-C4	-180	-180
H13-C2-C3-N9	-0.0015	-0.0003
C2-C3-C4-C5	-0.0005	0.001
C2-C3-C4-C14	179.9992	180.02
N9-C3-C4-C5	180.0009	180.0014
N9-C3-C4-C14	0.0006	0.0006
C2-C3-N9-O10	-179.994	179.99
C2-C3-N9-C11	0.0063	-0.0209
C4-C3-N9-O10	0.0048	-0.0215
C4-C3-N9-C11	-179.995	179.9787
C3-C4-C5-6N	0.0004	-0.0017

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have observed the C-N stretching vibration at 1375 cm^{-1} in pyridine. DFT calculations give the mode at 1266 cm^{-1} . DFT calculations give the C-N stretching vibration at 2217 cm^{-1} . In the present study, the theoretically computed values belonging to C-N stretching vibrations are in agreement with spectral data. The calculations at HF and DFT levels give the frequency values of 3392, 1662 and 3410, 1758 cm^{-1} ,

respectively in 4MNC have been designed to C-H stretching vibrations.

3.2.3 C-H vibrations

The hetroaromatic organic compound and its derivatives are structurally very close to benzene and commonly exhibit multiple weak bands in the region 3100–3000 cm^{-1} due to C-H stretching vibration [31,32].

Table 2. The Calculated (Scaled) frequencies (cm^{-1}), IR intensity (Km mol^{-1}), Raman intensity (Km mol^{-1}) and probable assignments (characterized by PED) of 4MNC using DFT and HF method of 6-311++G (d,p) calculation.

Symmetry species	Scaled Wavenumber (cm^{-1})		IR Intensity(A_1)	Raman active(I_1)	Depolarisation Ratio	Reduced Mass(μ)	Force Constants(K)	Assignments with PED% among types of coordinates
	DFT	HF						
A'	3330	3414	0.280	0.509	0.7133	1.0125	0.1121	ν CH (99)
A'	3329	3410	3.270	0.545	0.7491	11.7380	0.0363	ν NC (95)
A'	3327	3400	5.059	5.750	0.7485	10.6565	0.0588	ν CH (90)
A'	3025	3080	0.038	0.764	0.7455	5.9446	0.0583	β HCC (69) ν CH (30)
A'	3070	3100	0.176	0.712	0.7423	3.0091	0.0537	ν CH (66)
A'	2352	2427	1.736	0.464	0.6071	3.9239	0.0892	ν ON (63)
A'	1662	1758	6.773	0.494	0.7496	7.0887	0.1933	τ HCCH (59) ν NC (20)
A'	1612	1692	2.953	2.621	0.4653	5.3778	0.3001	β NC (54), ν CC (45)
A'	1589	1626	3.330	4.979	0.1033	8.3638	0.5708	ν CC (53)
A'	1456	1585	12.90	2.455	0.7450	5.9156	0.5098	β HCH (52) ν CC (24)
A'	1444	1573	2.030	1.992	0.7449	7.4457	0.7234	τ HCCC (52)
A'	1390	1487	2.053	8.669	0.2021	8.0727	0.9661	ν CH (50) ν CC(35)
A'	1336	1454	0.292	0.140	0.5737	4.0237	0.6259	ν CC (47) NC (23)
A'	1283	1415	0.961	0.662	0.3739	5.6871	0.9229	ν HCH (47) CN(34)
A'	1233	1368	10.97	6.697	0.3635	6.1464	1.2011	ν CC (44) ν CC (13) ν CH (23)
A'	1123	1368	0.533	1.396	0.7490	3.8637	0.8256	ν ON (44)
A'	1057	1149	10.45	0.326	0.6748	3.1917	0.9200	β HCH (37)
A''	1006	1124	24.21	11.47	0.1577	12.9458	3.8495	τ CCCC (36) ν CC (10)
A'	1001	1099	2.387	1.837	0.7391	7.9967	2.5440	ν CH (35)
A'	950	1022	7.394	3.460	0.6051	7.0339	2.3102	β ONO (35) ν CC (12)
A'	907	1019	26.11	31.39	0.1595	10.1484	3.5819	β CCN (33)
A''	875	1010	0.366	2.852	0.2656	4.8667	1.8585	β_{opb} CCC (31) ν CH (20)
A'	873	1007	3.720	2.225	0.6922	1.5104	0.6784	ν NC (30)
A''	805	879	16.31	1.091	0.7462	1.6886	0.7634	τ HCCC (30)
A''	773	832	29.01	12.57	0.5022	2.8093	1.3639	β_{opb} CCC (29) ν CH (20)
A''	746	807	18.13	7.232	0.2531	2.7695	1.4730	β_{opb} CCNC (29)
A''	734	791	21.47	12.57	0.4013	2.1475	1.2691	ν NC (28) CC (18)
A''	710	782	97.08	37.87	0.3901	3.6546	2.1820	β_{opb} CCNC (27) ν CC(10) ν CH (25)

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A'	699	695	23.03	22.07	0.4534	3.4662	2.2850	β NCC (26) ν CH (22)
A'	602	682	44.02	6.540	0.3000	4.1988	3.1223	β CCN (26) ν CC (11) CH(22)
A''	575	638	25.31	2.092	0.6242	1.3988	1.2530	t ONCC (26) ν CH (25)
A'	524	590	23.79	12.02	0.4301	1.8000	1.7467	ν CCC (25)
A'	513	531	6.320	8.042	0.2213	1.2166	1.2795	β ONC (25)
A'	450	500	21.99	238.9	0.1199	7.3014	8.3186	ν NC (22) ν ON (19)
A'	406	456	22.49	16.49	0.2828	1.0802	1.3283	ν CC (21) ν NO (15)
A'	382	419	11.36	9.436	0.5997	1.0478	1.3089	β CNC (21)
A'	340	383	7.201	36.54	0.7120	8.8271	13.1384	ν CC (20) ν CC (17)
A''	307	335	258.2	77.42	0.2576	11.6444	17.8318	ν OCON (19) ν NO(15)
A'	215	278	30.49	6.540	0.6268	8.8377	14.3917	β_{ipb} CCC (18)
A'	196	250	0.719	339.3	0.2800	12.7678	41.6357	β NCC (16) ν CH (12)
A''	174	235	3.763	210.1	0.0341	1.0317	6.3418	t HCCC (16)
A''	128	229	6.160	65.75	0.6504	1.1034	7.1700	t NCCC (15)
A''	96	199	5.346	52.11	0.2687	1.0935	7.1319	t CCCN (12)
A'	72	189	0.300	73.70	0.6886	1.1035	7.2060	ν CC (10)
A''	-433	-351	9.700	43.35	0.2795	1.0923	7.1403	t HCCC (10)

ν →Stretching, β →Bending, β_{opd} →Out-of-plane-bending, β_{ipd} →in-plane-bending, t→torsion.

Fig 3. Calculated FT-Raman Spectra of 4-Methyl-3-nitropyridine-1-carbonitrile

In the title molecule, the very strong intensity band calculated wavenumbers are at 3025, 3070 and 3080, 3100 cm^{-1} at DFT/B3LYP and HF method with 6-311++G (d, p) basis set respectively. The theoretically calculated C-H vibrations by DFT/B3LYP and HF method of scaled values are given Table 2.

3.3 Frontier molecular orbitals

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. The energies of HOMO, LUMO, LUMO+1 and HOMO-1 and their orbital energies are calculated using B3LYP/6-311++G (d, p) method and the pictorial illustration of the frontier molecular orbitals are shown in Fig. 4.

Fig 5. Calculated electronic absorption spectra of the 4-Methyl-3-nitropyridine-1-carbonitrile

Molecular orbitals provide insight into the nature of reactivity and some of the structural and physical properties of molecules. The positive and negative phase is represented in red and green colour, respectively. The plots reveal that the region of HOMO spread over the entire molecule of 4MNC while in the case of LUMO it is spread over the entire molecule except on nitrile group. The calculated energy gap of HOMO-LUMO's explains the ultimate charge transfer interface within the molecule. The energies of the frontier molecular orbitals of 4MNC employing DFT/B3LYP method using 6-311++G (d, p) basis set. The frontier orbital energy gap calculated by B3LYP method ($E_{\text{LUMO}} - E_{\text{HOMO}}$) in case of 4MNC is found to be 4.7648 eV.

3.4 Absorption spectral analysis

The UV-Vis absorption spectrum of 4MNC recorded in water is shown in Fig. 5. Molecules allow strong $\pi \rightarrow \pi^*$ transition in the UV-visible region with high extinction coefficients [33]. NBO analysis indicates that molecular orbitals are mainly composed of π and σ atomic orbital. TD-DFT/6-311++G (d, p)

calculations have been used to determine the low lying excited states of 4MNC. The calculated excitation energies, absorbance and oscillator strength (f) for the title molecule are tabulated in Table 4. The maximum absorption peak ($\lambda_{\max}$) in the UV-vis spectrum predicts electronic transition at 309 nm with an oscillator strength $f = 0.0004$.

Table 3 Definition of internal coordinates of 4-Methyl-3-nitropyridine-1-carbonitrile.

NO	Symbols	Type	Definition
Stretching			
1-5	r_i	CH (methyl)	C12-H15,C12-H16,C12H17, C4-H14,C2-H13
6-9	Q_i	NC	N6-C1,N9-C3,N6-C5,N8-C7
10-13	R_i	CC(aromatic)	C1-C2,C2-C3,C3-C4,C4-C5
14-15	P_i	NO	N9-O10,N9-O11
16	q_i	CC	C1-C7
Bending			
17-18	β_i	Ring	C1-C2-C3,C3-C4-C5
19	δ_i	ONO	O10-N9-O11
20-22	α_i	HCH	H15-C12-C16, H16-C12-C17, H17-C12-C15
23-24	σ_i	NCC	N9-C3-C4,N6-C5-C4
25-26	φ_i	HCC	H14-C4-C5,H13-C2-C1
27-28	θ_i	CCN	C2-C1-6N,C4-C3-N9
30	δ_i	ONC	O11-N9-C3
31	π_i	CNC	O11-N9-C3
Linear bending			
29	π_i	NCC	N9-C7-C1
Out-of-plan bending			
32	Π_i	ONC	O11-C3-O10-N9
33	ω_i	CN	C2-C1-N6-C5
34	ω_i	CC	N9-C3-C2-C1
35	ω_i	CN	C4-C5-N6-C1
Torsion			
36	t_i	$\tau(\text{H-CN}_2)$	H14-C4-C3-N9
37-40	t_i	$\tau(\text{Car-H}_3)\text{Ring}$	H13-C2-C3-C4, H15-C12-C5-C4, H16-C12-C5-C4, H17-C12-C5-C4
41	t_i	$\tau(\text{CC})\text{ Ring}$	C5-C4-C3-C2
42	t_i	$\tau(\text{NC})$	N6-C1-C2-C3
43	t_i	$\tau(\text{CN})$	C1-N6-C5-C4
44	t_i	$\tau(\text{ON})$	O11-N9-C3-C4
45	t_i	$\tau(\text{CN})$	C2-C1-C7-N9

Fig 4. Isodensity plots (isodensity contour = 0.03 a.u.) of the frontier orbitals of 4-Methyl-3-nitropyridine-1-carbonitrile
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The wavelengths obtained with DFT/B3LYP/6-311++G (d, p) computations are 409, 372 and 346 nm (in Vacuum). Both HOMO and LUMO are the main orbitals that take part in chemical stability. In view of calculated absorption spectra, the wavelength 409, 372 and 346 nm corresponds to the electronic transition from the HOMO-1 to LUMO with 94% contribution, from HOMO to LUMO+1 with 93% contribution and HOMO to LUMO with 85% contribution respectively.

3.5 First order polarizability and hyper polarizability

NLO techniques are considered as among the most structure sensitive methods to study the molecular structures [34] and the computational approach allows the determination of molecular NLO properties as an inexpensive way to design molecules by analyzing the potential before synthesis and to determine high-order hyperpolarizability tensors of molecules. In the recent years, because of potential applications in modern communication technology, data storage, telecommunication, dependent on the efficiency of electronic communication between acceptor and the donor groups as that will be the key to intramolecular charge transfer [37, 38].

Fig.6. Electrostatic potential map 4-Methyl-3-nitropyridine-1-carbonitrile

The acceptor and donor groups have an important role in the polarizability and first hyperpolarizability is tensor components of hyperpolarizability.

The definitions for the isotropic polarizability is

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

The polarizability anisotropy invariant is

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

and the average hyperpolarizability is

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

Where,

$$\beta_x = \beta_{xxx} + \beta_{yyy} + \beta_{zzz}$$

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

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

Where, α_{xx} , α_{yy} , and α_{zz} are tensor components of polarizability; β_{iiz} , β_{izi} , and β_{zii} (i from X to Z)

The large value of first hyperpolarizability, which is the measure of the NLO activity of the molecular system, is associated with the Intra molecular Charge Transfer (ICT), resulting from the electron cloud movement through conjugated frame work from electron donor to electron acceptor groups. The polar properties of the title molecule were calculated at the DFT and HF/6-311++G (d, p) level. Theoretical investigation plays an important role in understanding the structure property relationship which is able to assist in designing novel NLO materials. Theoretically, calculated values of dipole Moment (μ), polarizability (α), anisotropic tensor and hyperpolarizability (β) are shown in Table 5.

3.6 MEP analysis

Molecular electrostatic potential (MEP) mapping is very useful in the investigation of the molecular structure with its physiochemical property relationships [39, 40]. Total SCF electron density surface mapped with molecular electrostatic potential (MEP) of 4MNC determined by DFT/B3LYP/6-311++G (d, p) method is shown in Fig. 6(a) while the contour map of the molecular electrostatic potential is given in Fig. 6(b). The MEP surface displays the molecular shape, size and electrostatic potential values.

The colour scheme for the MEP surface is red-electron rich or partially negative charge; blue-electron deficient or partially positive charge; light blue-slightly electron deficient region; yellow- slightly electron rich region, respectively. The oxygen atoms have more negative potentials and the hydrogen atoms have more positive potentials. The extreme limits of the electron density observed in 4MNC are $\pm 3.201e$. The MEP of 4MNC clearly indicates the electron rich centres of oxygen atoms. The Molecular electrostatic potential surface of 4MNC determined by DFT/B3LYP/6-311++G (d, p) method is shown in the supplementary Fig

3.7 Thermodynamic properties

The theoretical thermodynamic parameters, rotational constants, rotational temperature, vibrational temperature and dipole moment have been presented in Table 6. Scale factors have been recommended [41] for an accurate prediction in determining the Zero-Point Vibration Energies (ZPVE) and the entropy, S_{vib} (T) and the molar capacity at constant volume were calculated. The variations in the ZPVEs seem to be significant. The ZPVE is much lower by the DFT (B3LYP) method than by HF method. The biggest value of ZPVE 4MNC is 70.26827 Kcal/mol obtained at HF/6-311+G (d,p) whereas the smallest value is 75.30679 Kcal/mol obtained at B3LYP/6-311+G(d,p).

Table 4. Computed excitation energies, electronic transition configurations and oscillator strengths (f) for the optical transitions with $f > 0.01$ of the absorption bands in visible and near-UV region for the 4-Methyl-3-nitropyridine-1-carbonitrile.

Excited state	Wavelength λ (nm)	Excitation energy(eV)	Oscillator strength(f)	Major contributions
S1	409	24427	0.0032	H-2->L (93%) H->L (3%)
S2	372	26877	0.0006	H-1->L (13%), H->L (81%)
S3	346	28875	0.0299	H-1->L (85%), H->L (13%)
S4	309	32267	0.0004	H-5->L (96%)
S5	271	36783	0.2554	H-4->L (18%), H-3->L (79%)
S6	263	37959	0.0005	H-1->L+1 (16%), H->L+1 (82%)
S7	243	41045	0.0517	H-4->L (76%), H-3->L (18%)
S8	225	44380	0.0077	H-1->L+2 (12%), H->L+2 (81%)
S9	223	44648	0.2966	H-1->L+1 (67%), H-1->L+2(23%)
S10	222	44958.4	0.001	H-2->L+1 (96%)

Table 5. Polarizability (10^{-24} esu) and Hyper polarizability β (10^{-31} esu) of the 4MNC molecule calculated at the DFT and HF method of 6-311++G (d, p) level.

*	DFT/6-311G++(d,p)	HF/6-311G++(d,p)
Polarizability (α)		
α_{xx}	95.29	97.05
α_{xy}	5.521	5.626
α_{yy}	67.20	67.55
α_{xz}	0.0	0.0
α_{yz}	0.0	0.0
α_{zz}	67.04	67.46
α (esu)	76.51570001	77.3614000
$\Delta\alpha$ (esu)	28.17500842	29.5446784
Hyperpolarizability (β)		
β_{xxx}	-39.9	-39.5
β_{xxy}	42.7	44.7
β_{xyy}	-19.95	-2042
β_{yyy}	39.19	40.41
β_{xxz}	-0.0	0.0
β_{xyz}	0.0	0.0
β_{yyz}	0.0022	0.0
β_{xzz}	-9.172	-9.522
β_{yzz}	-0.82	-0.68
β_{zzz}	0.0031	0.0007
β_{ii} (esu)	106.5585929	109.3890715
Dipole moment	5.2946	6.1999

Table 6. Theoretically computed zero-point vibrational energy (Kcal mol⁻¹), rotational constants (GHz), rotational temperatures (Kelvin), thermal energy (Kcal mol⁻¹), molar capacity at constant volume (cal mol⁻¹ Kelvin⁻¹) and vibrational temperatures (Kelvin) for 4-Methyl-3-nitropyridine-1-carbonitrile.

Parameter	DFT/B3LYP	HF
Zero-point vibrational energy	70.26827	75.30679
Rotational constant (GHZ)	1.19510	1.19510
	0.68893	0.68893
	0.43818	0.43818
Rotational temperature (Kelvin)	0.05736	0.05736
	0.03306	0.03306
	0.02103	0.02103
Energy total (KCal/Mol)	76.646	80.815
Translational(KCal/Mol)	0.889	0.889
Rotational(KCal/Mol)	0.889	0.889
Vibrational(KCal/Mol)	74.868	79.038

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Vibrational temperature (Kelvin)	104.30	272.17
	139.23	286.57
	185.57	330.41
	250.42	338.56
	282.60	359.78
	309.55	400.38
	442.80	483.38
	489.67	552.20
	550.28	603.91
	584.25	656.67
	648.46	719.95
	739.29	765.42
	755.11	848.97
	828.60	919.29
	866.45	981.43
	1006.39	1000.58
	1022.13	1126.14
	1057.25	1139.33
	1074.23	1161.86
	1113.58	1197.53
	1158.33	1264.98
	1256.23	1449.14
	1260.30	1453.63
	1306.04	1467.54
	1366.98	1471.47
	1440.97	1582.39

Fig 6(b) Electrostatic potential contour map 4-Methyl-3-nitropyridine-1-carbonitrile

4. CONCLUSION

In this work, we have used the DFT/B3LYP and HF methods to investigate theoretical analysis on the geometries and electronic properties of 4-Methyl-3-nitropyridine-1-carbonitrile. The geometry was optimized and bond lengths and bond angles were obtained by HF and DFT methods. It may be pointed out that the bond lengths obtained by both HF and DFT/B3LYP methods are comparable and the bond lengths obtained by B3LYP method are slightly longer than those calculated by HF method. Further investigations on the molecular structure and spectroscopy properties were done using HF and DFT calculations at B3LYP/6-311+G (d,p) level of theory. TD-DFT calculations were carried out in both the gas

phase and in different solvent systems using polarizable continuum model (PCM) to calculate the electronic absorption spectra. The mean polarizability and total first static hyperpolarizability of the molecule under investigation are found to be $29.5446784 \times 10^{-24}$ e.s.u. and 6.1999×10^{-30} e.s.u., respectively. The theoretical investigations of thermodynamic properties and energies of HOMO and LUMO orbitals which can be used to predict the conversion of biological and solar cell applications of this compound.

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