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DFT Study of 3-Methyl Pyridinium Picrate

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Abstract: ***In this study the molecular geometry, vibrational spectra, frontier molecular orbitals, Mulliken charges and thermodynamic properties of the 3-Methyl Pyridinium Picrate compound have been investigated using DFT B3LYP at 6-311G (d, p) basis set. The optimized geometric bond lengths, bond angles and torsional angles obtained by density functional theory show good agreement with experimental data. The observed HOMO and LUMO energies show that charge transfer occurs within the molecule. Picrate oxygen O24 and Pyridinium hydrogen H15 act as donor and acceptor in intermolecular interactions thereby strengthen the molecular system.***

Keywords: DFT calculations, Vibrational mode frequencies, HOMO, LUMO

1. Introduction

Jeganathan Gomathi & Doraisamyraja Kalivani (2015) has synthesized crystallinepicrates of pyridine derivative of 3-Methyl Pyridinium Picrate single crystal. It is reported that the presence of more than one heterocyclic component in a molecule shows the biological response and thermal stability. It ismotivated to analyse the presence of picrate based pyridine bases. In this crystal, the anionic and cationic hydrogen bond units are connected via C-H…O, forming a three dimensional structure [1]. They reported the crystal structure with space group of $P2_1/n$.Theoretical calculations of the molecular structure has been performed using Gaussian 09 software and structural and energy parameters corresponding to the optimum energy have been computed.

2. Theoretical Section

2.1 Computational details

In this study, all theoretical calculations were carried out with the Gaussian 09 program and GaussView 5 molecular visualisation program. The molecular structure and vibrational study of 3-Methyl Pyridinium Picrate molecule was calculated by using B3LYP method with 6-311G (d, p) basis set in ground state. According to the theoretical calculations, 3-Methyl Pyridinium Picrate has a non-planar structure of C_1 point group symmetry. The molecule has 33 atoms and 93 normal modes of vibration active in both IR and Raman. The optimized geometrical parameters namely bond lengths, bond angles and dihedral angles of 3- Methyl Pyridinium Picrate have been reported in Table 1. Optimized bond lengths and angles are larger than the experimental ones since the theoretical calculation were done assuming isolated molecule in gaseous phase. The structural atomic numbering scheme of the molecule is shown in Figure 1. The positive values of all calculated vibrational wavenumbers show that the optimized molecular structure is stable. However, the wavenumber values computed at these levels contain the well-known systematic errors. In order to prevent the well-known systematic errors the computed vibrational wavenumbers were scaled as 0.983 for frequencies less than 1700 cm-1 and 0.958 for frequencies higher than 1700 cm-1 at B3LYP/6-311G(d, p) basis set [2, 3].

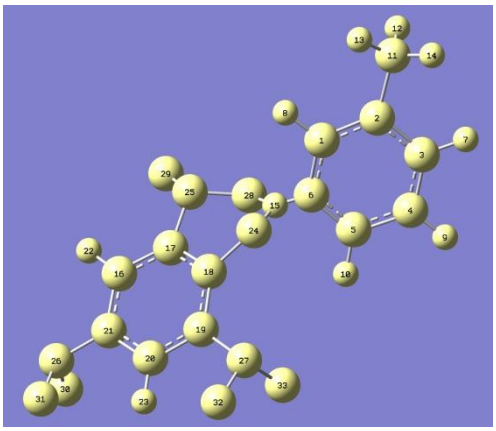

Figure 1: Atomic numbering scheme of molecule

2.2 Bond order analysis

The bond order is related to bond strength, and the bonds with the higher bond order values have short bond length and vice versa. The bond order analysis predicts that the weakest bonds may be cleaved preferentially, and they may possess a relatively low pi bond character. In Table 1, the bond between N6 and H15 shows relatively low pi bond character with bond order value of 0.8848. The C2-C11 has the highest bond order value of 1.5758. The nitro groups O29-N25-O28, O30-N26-O31 and O32-N27-O33 have bond angle of 111.2926, 108.6863 and 109.7084 degree respectively. The optimized geometric bond lengths, bond angles and torsional angles are good in agreement with other investigator [Jeganathan Gomathi & Doraisamyraja Kalivani (2015)]. It is found that the optimized geometrical values are in support of the bond order analysis.

Table 1: Optimized geometrical parameters[b] of 3-Methyl Pyridinium Picarate molecule at B3LYP/6-311G(d, p) level

Definition [a]	3-Methyl Pyridinium Picrate	Definition [a]	3-Methyl Pyridinium Picrate
r(1, 2)	1.396	A(30, 26, 31)	108.6863
r(1, 6)	1.3747	A(19, 27, 32)	110.0735
r(1, 8)	1.1059	A(19, 27, 33)	108.6145
r(2, 3)	1.4057	A(32, 27, 33)	109.7084
r(2, 11)	1.5758	A(15, 28, 25)	120.884
r(3, 4)	1.3929	D(6, 1, 2, 3)	-0.003
r(3, 7)	1.0808	D(6, 1, 2, 11)	178.1794
r(4, 5)	1.404	D(8, 1, 2, 3)	-179.6604
r(4, 9)	1.0577	D(8, 1, 2, 11)	-1.478
r(5, 6	1.3163	D(2, 1, 6, 5)	1.5369
r(5, 10)	1.1069	D(2, 1, 6, 15)	-178.9309
r(6, 15)	0.8848	D(8, 1, 6, 5)	-178.808
r(11, 12)	1.0931	D(8, 1, 6, 15)	0.7242
r(11, 13)	1.0713	D(1, 2, 3, 4)	-1.0891
r(11, 14)	1.0589	D(1, 2, 3, 7)	179.1166
r(15, 24)	1.1436	D(11, 2, 3, 4)	-179.4106
r(15, 28)	1.0611	D(11, 2, 3, 7)	0.7951
r(16, 17)	1.4109	D(1, 2, 11, 12)	-94.3598
r(16, 21)	1.4119	D(1, 2, 11, 13)	26.3804
r(16, 22)	1.0866	D(1, 2, 11, 14)	146.2913
r(17, 18)	1.3251	D(3, 2, 11, 12)	83.7797
r(17, 25)	1.4187	D(3, 2, 11, 13)	-155.4801
r(18, 19)	1.4112	D(3, 2, 11, 14)	-35.5692
r(18, 24)	1.4851	D(2, 3, 4, 5)	0.7506
r(19, 20)	1.417	D(2, 3, 4, 9)	-178.8744
r(19, 27)	1.4665	D(7, 3, 4, 5)	-179.4572
r(20, 21)	1.4093	D(7, 3, 4, 9)	0.9178
r(20, 23)	1.0633	D(3, 4, 5, 6)	0.7712
r(21, 26)	1.4648	D(3, 4, 5, 10)	-179.2183
r(25, 28)	1.3908	D(9, 4, 5, 6)	-179.6115
r(25, 29)	1.3457	D(9, 4, 5, 10)	0.399
r(26, 30)	1.3453	D(4, 5, 6, 1)	-1.8904
r(26, 31)	1.3468	D(4, 5, 6, 15)	178.6046
r(27, 32)	1.3727	D(10, 5, 6, 1)	178.0987
r(27, 33)	1.3732	D(10, 5, 6, 15)	-1.4063
A(2, 1, 6)	122.5943	D(1, 6, 15, 24)	-95.843
A(2, 1, 8)	118.3456	D(1, 6, 15, 28)	84.1882
A(6, 1, 8)	119.0592	D(5, 6, 15, 24)	83.6841
A(1, 2, 3)	115.8315	D(5, 6, 15, 28)	-96.2847
A(1, 2, 11)	125.7024	D(6, 15, 24, 18)	-147.4622
A(3, 2, 11)	118.4421	D(28, 15, 24, 18)	32.508
A(2, 3, 4)	120.7076	D(6, 15, 28, 25)	-155.6583
A(2, 3, 7)	119.133	D(24, 15, 28, 25)	24.3719
A(4, 3, 7)	120.159	D(21, 16, 17, 18)	-2.3461
A(3, 4, 5)	119.8746	D(21, 16, 17, 25)	177.8297
A(3, 4, 9)	119.0511	D(22, 16, 17, 18)	177.1912
A(5, 4, 9)	121.0733	D(22, 16, 17, 25)	-2.633
A(4, 5, 6)	119.7176	D(17, 16, 21, 20)	-1.3369
A(4, 5, 10)	118.3031	D(17, 16, 21, 26)	179.2271
A(6, 5, 10)	121.9793	D(22, 16, 21, 20)	179.1248
A(1, 6, 5)	121.2446	D(22, 16, 21, 26)	-0.3113
A(1, 6, 15)	116.5066	D(16, 17, 18, 19)	5.5708
A(5, 6, 15)	122.2471	D(16, 17, 18, 24)	-171.4731
A(2, 11, 12)	108.4068	D(25, 17, 18, 19)	-174.579
A(2, 11, 13)	109.1032	D(25, 17, 18, 24)	8.3771
A(2, 11, 14)	110.6339	D(16, 17, 25, 28)	-144.1936
A(12, 11, 13)	110.7902	D(16, 17, 25, 29)	-22.7797
A(12, 11, 14)	108.9017	D(18, 17, 25, 28)	35.9569
A(13, 11, 14)	109.0042	D(18, 17, 25, 29)	157.3708
A(6, 15, 24)	120.7778	D(17, 18, 19, 20)	-5.0555
A(6, 15, 28)	121.8981	D(17, 18, 19, 27)	174.2578
A(24, 15, 28)	117.3241	D(24, 18, 19, 20)	171.4264
(17, 16, 21)	117.2296	D(24, 18, 19, 27)	-9.2603
A(17, 16, 22)	121.4944	D(17, 18, 24, 15)	-50.4226

A(21, 16, 22)	121.2744	D(19, 18, 24, 15)	132.9415
A(16, 17, 18)	125.6398	D(18, 19, 20, 21)	1.661
A(16, 17, 25)	126.0033	D(18, 19, 20, 23)	-178.9995
A(18, 17, 25)	108.3567	D(27, 19, 20, 21)	-177.6669
A(17, 18, 19)	118.0763	D(27, 19, 20, 23)	1.6727
A(17, 18, 24)	112.6849	D (18, 19, 27, 32)	151.0789
A(19, 18, 24)	129.1587	D(18, 19, 27, 33)	-88.7924
A(18, 19, 20)	119.2107	D(20, 19, 27, 32)	-29.6087
A(18, 19, 27)	121.4387	D(20, 19, 27, 33)	90.52
A(20, 19, 27)	119.3471	D(19, 20, 21, 16)	1.5308
A(19, 20, 21)	121.1525	D(19, 20, 21, 26)	-179.0284
A(19, 20, 23)	119.4393	D(23, 20, 21, 16)	-177.809
A(21, 20, 23)	119.4049	D(23, 20, 21, 26)	1.6318
A(16, 21, 20)	118.4611	D(16, 21, 26, 30)	90.4925
A(16, 21, 26)	121.1781	D(16, 21, 26, 31)	-149.4497
A(20, 21, 26)	120.3584	D(20, 21, 26, 30)	-88.9329
A(15, 24, 18)	114.5485	D(20, 21, 26, 31)	31.1249
A(17, 25, 28)	106.4528	D(17, 25, 28, 15)	-64.1651
A(17, 25, 29)	111.2634	D(29, 25, 28, 15)	174.4397
(28, 25, 29)	111.2926		
A(21, 26, 30)	109.6388		
A(21, 26, 31)	110.9497		

[a]For atomic numbering scheme, see Figure 1.[b]Bond lengths (r) in Angstrom, bond angles (A) and dihedral angles (D) in degree.

2.3 Vibrational assignments

The vibrational spectra for 3-Methyl Pyridinium Picrate were compared with the existing experimental data.IR and Raman spectraare presented in Figure 2 and 3. Spectroscopic identification of NO_2 group is generally made by the observation of strong IR absorptions due to its stretching frequencies (symmetric and anti-symmetric). In the compound, the nitro groups have been reported to give rise to experimental bands in the 1570-1470 cm^{-1} and 1370 – 1340 cm^{-1}region [4]. Two bands have been observed due to anti symmetric modes (in the 1570-1470 cm^{-1} region) and one band due to symmetric modes (1370 – 1340 cm^{-1} region).The nitro group asymmetrical stretching frequency appears with maximum at 1529 cm^{-1}[5]. The scissoring mode of NO_2 vibrations gives rises to only weak infrared bands in the region 800 – 890 cm^{-1}. In the spectrum, the scissoring mode of NO_2 vibration appears at 807 cm^{-1} in IR and 836 cm^{-1} in Raman spectra. The CO stretching coordinate has a frequency 1631 cm^{-1} in IR and 1664 cm^{-1} in Raman spectra. In higher frequency region almost all vibrations belong to C-H stretching. C-H stretching (3171 cm^{-1} in Raman spectra and 3120 cm^{-1} in IR spectra) lies some higher region than benzene. This can be possibly due to the presence of meta directing NO_2 which creates deficiency of electron at meta position and hence the carbon ring extracts electron from the hydrogen atom and it reduces the bond strength of C-H. The ring C-C stretching vibration is calculated at 1588 cm^{-1} and 1546 cm^{-1} which are in good agreement with the experimental data. According to our calculations, the bands at 1289 cm^{-1} in IR and 1270 cm^{-1} in Raman were assigned to N-H bending mode [6].

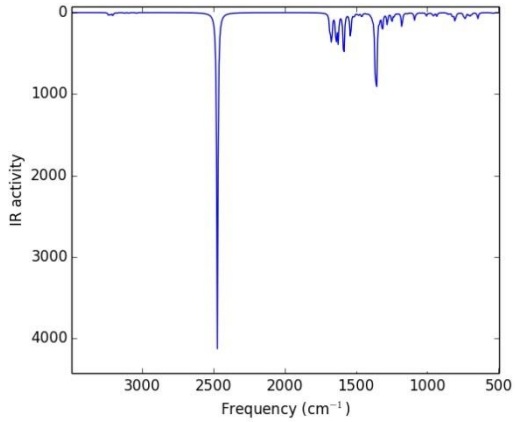

Figure 2: IR spectrum of 3-Methyl Pyridinium Picrate

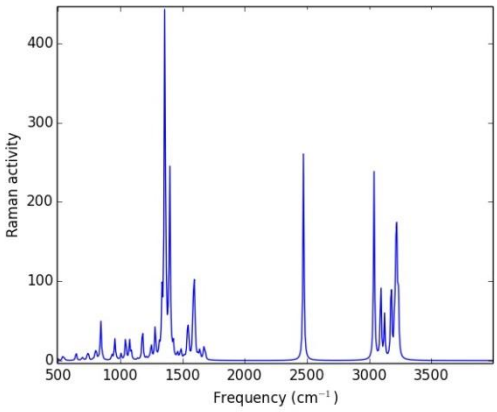

Figure 3: Raman spectrum of 3-Methyl Pyridinium Picrate

2.4 Molecular orbital analysis

The highest occupied molecular orbitals and the lowest unoccupied molecular orbitals are named as Frontier molecular orbitals (FMOs). The frontier molecular orbital analysis furnishes a platform for understanding the phenomenon of charge transfer through optical molecular

excitations [7, 8]. The chemical hardness and reactivity of an optical material can be predicted from HOMO-LUMO energy gap. The calculated energies of HOMO an LUMO of 3-Methyl Pyridinium Picrate are -6.54 eV and -3.07 eV respectively. The energy gap is found to be 3.47 eV. The ionization energy (I) and electron affinity (A) can be expressed through HOMO and LUMO orbital energies as I = - E_{HOMO} = 6.54 eV and A = - E_{LUMO}= 3.07eV. The global hardness (η) is predicted by the relation η = (I-A)/2 = 1.735 eV. The electron affinity can be used in combination with ionization energy to give electronic chemical potential μ = -(E_{HOMO} + E_{LUMO})/2 = 4.805 eV. The global electrophilicity index (ω), introduced by Parr et al. [9] is calculated in terms of chemical potential and the hardness as ω = -(μ^2/2η) = -6.65 eV and assess the lowering of energy due to maximal electron flow between donor and acceptor. The inverse of the hardness is expressed as the global softness S=(1/ η) = 0.576. Considering the chemical hardness, if one molecule has large HOMO-LUMO gap, it is a hard molecule or small HOMO-LUMO gap it is a soft molecule.

2.5 Mulliken atomic charges

The calculation of effective atomic charges plays a dominant role in the application of quantum mechanical calculations to molecular systems. The electronic charge on the individual atoms in a molecule decides the bonding pattern. The atomic charge values were obtained by the Mulliken population analysis [10]. The bar diagram of Mulliken charge distribution is shown in Figure 4.All oxygen atoms have negative charge. Among all the oxygen atoms, O24 possesses the highest negative charge 0.475. Similarly all the hydrogen atoms have a net positive charge. In particular, the hydrogen atom H15 has large net positive charge. This is due to the presence of N6–H15…O24 strong intra molecular bonding. All the nitrogen atoms except N6 have positive charges. The positive nitrogen atoms (N25, N26, N27) are combined with the negative charge of Oxygen atoms (O28, O29, O30, O31, O32, O33) in nitro group.

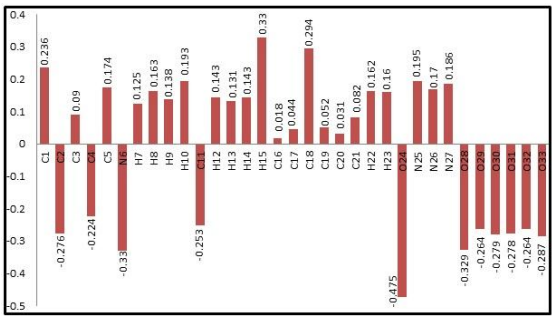

Figure 4: Mulliken charge distribution

2.6 Thermodynamic properties

The total energy of a molecular system is the sum of translational, rotational, vibrational and electronic energies. The molecular partition function is the product of the translational, rotational, and electronic partition functions of the molecule [11]. The thermochemical analysis is carried out at room temperature of 298.15 K and one atmospheric pressure. Several calculated thermodynamic parameters are presented in Table 2. The variations in the zero point vibration energies seem to be insignificant. The total energies are found to decrease with the increase of the basis set dimension. The value of dipole moment is 14.9296 Debye. The total entropy at room temperature is found to be 158.178 cal mol^{-1} K^{-1}.

Table 2: The calculated thermodynamic parameter of 3-Methyl Pyridinium Picarate employing B3LYP/6-311G(d, p) method

SCF energy (a.u)	-1208.89947147
Total energy (thermal), Etotal (kcal mol^{-1})	156.382
Heat capacity at const. volume, Cv (cal mol^{-1} K^{-1})	73.786
Entropy, S (cal mol^{-1} K^{-1})	158.178
Vibrational energy, Evib (kcal mol^{-1})	154.604
Zero-point vibrational energy, E0 (kcal mol^{-1})	143.42439
Rotational constants (GHz)	
A	0.44195
B	0.13849
C	0.11003
Dipole Moment (Debye)	14.9296

3. Conclusions

In the present study, we report the results of optimized geometry, vibrational spectra, molecular orbital analysis and Mulliken charge analysis of the title compound. The assignments of the fundamental vibrational modes of the title compound are examined. The geometrical parameters are found to be slightly differed from the experimental data. The amino atom in the pyridine is found to be the agent for crystal packing interactions in the hydrogen bonds and mainly for the stability of the crystal structure in the solid state.

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