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Reactive nature, substitution reaction, structural and vibrational properties of 2, 3 Dichloropridine by DFT Study

Abhishek Bajpai[1], Anoop Kumar Pandey[2], Kamal Pandey[3], Apoorva Dwivedi[1*]

[1] Department of Physics, Govt. Kakatiya P. G. College Jagdalpur, Chhattisgarh, India,
[2] Department of Physics, Govt. Danteshwari P.G. College, Dantewada, Chhattisgarh, India
[3]Department of Physics, Govt. Vivekanand P.G. College, Manedragadh, Chhatisgarh, India

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ABSTRACT

Present work deals with the Structural, Vibrational and Electronic properties of the molecular structure of 2, 3 Dichloropridine. The equilibrium geometry, harmonic vibrational frequencies and HOMO-LUMO gap have been calculated by the density functional theory (DFT), employing B3LYP/LANL2DZ as the basis set. A detailed interpretation of the Calculated infrared spectra of 2, 3 Dichloropridine is reported. No experimental spectrum is available so calculated spectra can provide a suitable path for experimental researchers.

Keywords: 2, 3 Dichloropridine, Vibrational Analysis, Polarizability, Hyperpolarizability, electronic properties, DFT.

INTRODUCTION

Pyridine, also called azabenzene and azine, is a heterocyclic aromatic tertiary amine characterized by a six-membered ring structure composed of five carbon atoms and nitrogen which replace one carbon-hydrogen unit in the benzene ring (C_5H_5N). Pyridine is a base with chemical properties similar to tertiary amines. Nitrogen in the ring system has an equatorial lone pair of electrons that does not participate in the aromatic pi-bond. Pyridine and its derivatives are very important in industrial field as well as in bio chemistry. Pyridine and its derivatives are used as solvents and starting material for the synthesis of target compounds such as insecticides, herbicides, medicines, vitamins, food flavorings, feed additives, dyes, rubber chemicals, explosives, disinfectants, and adhesives. Pyridine is also used as a denaturant for antifreeze mixtures, as a dyeing assistant in textiles and in fungicides. 2, 3-Dichloropyridine is an intermediate for the synthesis further pyridine derivatives especially for agrochemical field [1]. As a part of our ongoing research work [2-6], here, the main objective of the present study is to investigate in detail the vibrational spectra of the important biological molecule 2, 3-Dichloropyridine, a derivative of pyridine having commercial interest find application in market areas where bioactivity is important, as in medicinal drugs and in agricultural products such as herbicides, insecticides, fungicides, and plant growth regulators [7].

MATERIALS AND METHODS

Computational methods

All the calculations were performed by the B3LYP [14, 15] method using the LANL2DZ basis set of Density functional theory [16]. All computations were carried out with the GAUSSIAN 09 package [17]. By combining the

results of the GAUSSVIEW'S program [18] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy.

RESULT AND DISCUSSION

Geometry Optimization

The optimized structure parameters and thermodynamic functions-internal thermal energy (*E*), constant volume heat capacity (*Cv*), and entropy (*S*) of 2, 3 Dichloropridine is calculated by B3LYP levels with LANL2DZ basis set and are listed in Table 1 & 2. The model molecular structure is shown in Fig. 1. The optimized geometry of the title compound calculated by the B3LYP method of DFT agrees well with the experimental results. The atomic charges of each atom in the gas phase have also been calculated and have been listed in Table 3. By allowing the relaxation of all parameters, the calculations converged to optimize geometries, which also correspond to the true energy minima, as revealed by the lack of imaginary frequencies in the vibrational mode calculation. Subsequently, the global minimum energy obtained for structure optimization of 2, 3 Dichloropridine with B3LYP/LANL2DZ basis sets is approximately --274.9074 a.u.

The molecule under study 2, 3 Di chloro pridine has 11 atoms with 27 normal modes of the fundamental vibration. A detailed description of vibrational modes can be obtained by means of a normal coordinate analysis (Table 4). The calculated Spectra of title compound is shown in Fig 2.

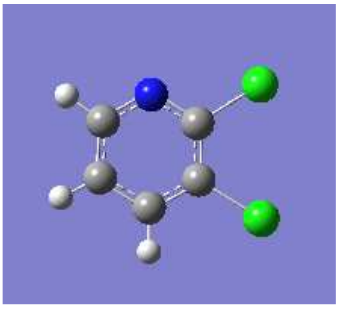

Fig-1 Model molecular structure of 2, 3 Dichloropridine

Table 1 Optimized geometrical parameters of 2, 3 Dichloropridine

Parameters	Calculated (Exp.)	Parameters	Calculated (Exp.)
Bond Lengths			
R(1,2)	1.4056 (1.346)	R(3,7)	1.0852 (0.951)
R(1,6)	1.3557	R(4,5)	1.4093
R(1,8)	1.0857 (0.943)	R(4,11)	1.8036
R(2,3)	1.4077 (1.359)	R(5,6)	1.3333
R(2,9)	1.085	R(5,10)	1.8098 (1.7317)
R(3,4)	1.4037	-	-
Bond Angles			
A(2,1,6)	122.0474	A(4,3,7)	119.7292
A(2,1,8)	121.7984	A(3,4,5)	118.4916
A(6,1,8)	116.1543	A(3,4,11)	118.9864
A(1,2,3)	118.4466	A(5,4,11)	122.522
A(1,2,9)	120.6563	A(4,5,6)	122.473
A(3,2,9)	120.8971	A(4,5,10)	120.7572
A(2,3,4)	119.0142	A(6,5,10)	116.7699
A(2,3,7)	121.2565	A(1,6,5)	119.5272

Table-2 Calculated Thermodynamic Properties of 2, 3 Dichloropridine by (B3LYP)/ LANL2DZ methods

	E (Thermal) (kcalmol^{-1})	CV (cal K^{-1}mol^{-1})	S (cal K^{-1}mol^{-1})
Total	47.741	23.896	83.244
Translational	0.889	2.981	40.866
Rotational	0.889	2.981	29.434
Vibrational	45.964	17.934	12.944

Table 3 Atomic Charges in Gas Phase

Atoms	Charges	Atoms	Charges
C1	-0.312126	H7	0.267160
C2	-0.147465	H8	0.253907
C3	-0.102906	H9	0.240202
C4	0.027913	Cl 10	-0.005075
C5	-0.253718	Cl 11	-0.024352
N6	0.056462		

Table 4 Vibrational assignments of 2, 3 Dichloropridine with B3LYP/LANL2DZ

B3LYP (Calculate)	IR (Int.)	Vibrational Assignments
116	1.749	Ring twist
182	0.104	β(C-C-Cl)
231	2.392	Ring twist
328	1.352	τ(N-C-C-Cl)
392	3.219	τ(Cl-C-C-Cl) + τ(C-C-C-Cl)
435	16.69	τ(C-N-C-Cl)
452	0.369	γ (C-C-H)
512	0.492	γ (C-C-H)
621	7.067	Ring breathing
725	29.50	β(C-C-C)
729	11.64	γ (C-C-C) + γ (C-C-H)
801	59.96	γ (C-C-H)
928	0.014	γ (C-C-H)
974	66.43	Ring Deformation
980	0.568	γ (C-C-H)
1027	13.68	β(C-C-C)
1104	8.222	β(C-C-H)
1125	69.18	β(C-C-C) + β(C-C-H)
1211	2.557	β(C-C-H)
1259	1.398	ν(C-C) + ν(C-N)
1377	142.9	β(C-C-H) +ν(C-C)
1392	15.03	β(C-C-H)
1521	14.74	ν(C-C)
1533	17.77	ν(C-C) + ν(C-N)
3094	2.275	ν(C-H)
3107	7.614	ν(C-H)
3124	10.617	ν(C-H)

Abbreviation: *ν: Stretching, β: -in plane bending, γ: out of plane bending, τ: torsion.*

Normal mode analysis-

Bands due C–H stretching vibrations are calculated at 3124, 3107, and 3094 cm^{-1} respectively in the calculated spectrum. This is the usual range of C-H stretching vibration. Intense band due to C-C stretching vibration is found at 1533 cm^{-1} in the calculated spectrum. A high intense band due to the combination of in plane bending of (C-C-H) and stretching of (C-C) is observed at 1377 cm^{-1} in the calculated spectrum. An intense band due to ring deformation is at 974 cm^{-1} in calculated spectrum. An intense band due to out of plane bending of (C-C-H) is at 801 cm^{-1} in the calculated spectrum. An intense band due to in plane bending of (C-C-C) is at 725 cm^{-1} in calculated spectrum. An intense band due to torsion of (C-N-C-Cl) is at 435 cm^{-1} in calculated spectrum. In lower region, due to ring twist and torsion in the ring, bands are at 231, 328, and 392 cm^{-1} having appreciable IR intensity. Furthermore, the study of low frequency vibrations is of great significance, because it gives information on weak intermolecular interactions, which takes place in enzyme reactions [8]. Knowledge of low frequency mode is also essential for the interpretation of the effect of electromagnetic radiation on biological systems [9]. Although no experimental FTIR

spectrum is available in the present case so the whole frequency assignments including lower region has been discussed throughout the calculated spectra. The aim of this paper is to obtain direct information on lower and higher frequency vibrations of such biological molecule. In the absence of experimental vibrational spectra of the title compounds, the theoretically calculated spectra should provide an important path for experimentalists. The measurements were made for the gas phase.

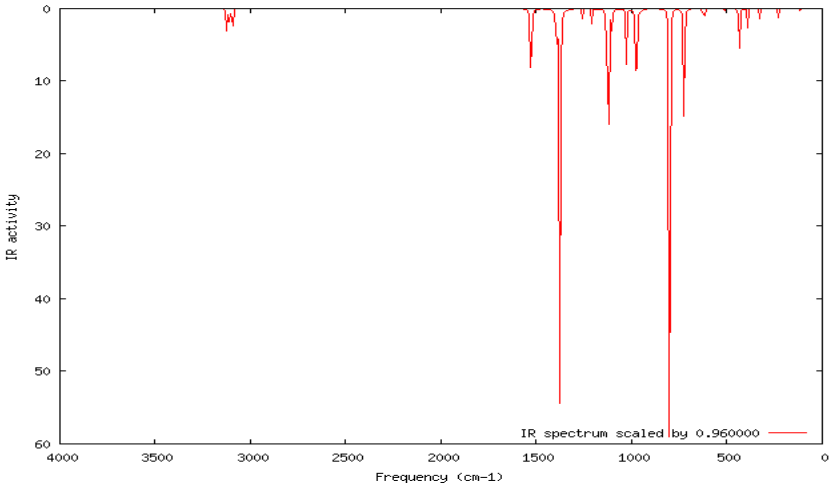

Fig-2 Calculated IR spectra of 2, 3 Dichloropridine

Electronic properties, Dipole moment, Polarizability and Hyper Polarizability

The difference between highest occupied molecular orbital and lowest unoccupied molecular orbital is called energy band gap or frontier orbital energy bandgap. As the gap is small, the molecule has strong chemical reactivity. The calculated value of the frontier orbital energy gap, 2, 3 Dichloropridine is 5.75 eV. The HOMO is found to be concentrated over the whole molecule, but the LUMO lies mainly over the ring in the molecule but little over chlorine atoms. MESP have been shown to correlate well with experimentally based quantities such a pka and other donor and acceptor values [10]. MESP can confirm the electrostatic potential region distribution of size and shape of molecules. Electro static potential contour plot predict the substitution of electrophiles and neucleophiles. For electrostatic potential contour plots, the electro negative region (red) is towards the outer part. The electronegative lines (in between -0.08a.u. and -0.02a.u.) form a closed contour. The energy equal to the shielded potential energy surface is required for any substitution reaction near the electro negative region. Thus it can be asserted that MESP values have been shown to be well related to biological properties. [11-13]. The plots of the HOMO, LUMO, MESP and contour plot for the title compound are shown in Figs.3 and 4. As we see a greater contribution of α_{zz} in the title compound which shows that molecules are elongated more towards X direction and more contracted in the X direction. $\beta_{xxx,}$ β_{yyy} contribute lager part of hyperpolarizibility in the title compound. This shows that Y axis and X-axis are more optically active in this direction. The calculated values of energy gap, Dipole moment, polarizibility and hyperpolarizibility are given in table 5 and 6 respectively.

Fig -3 HOMO (left) and LUMO (right) pictures of 2, 3 Dichloropridine

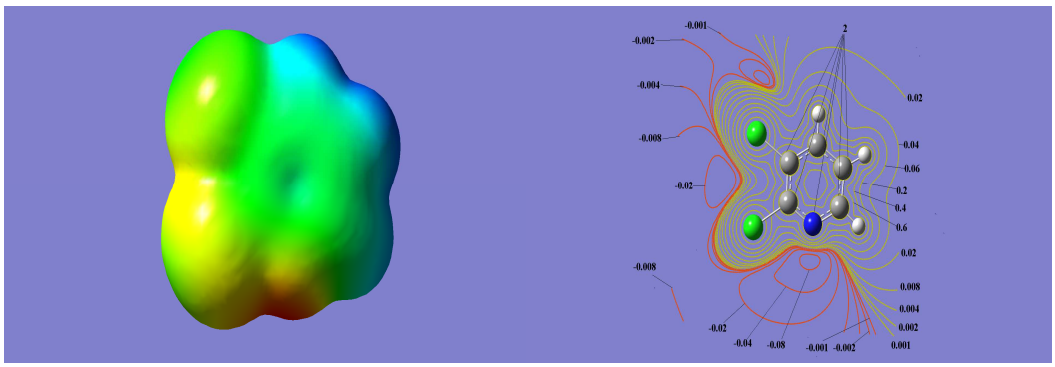

Fig -4 MESP (left) and Contour (right) pictures of 2, 3 Dichloropridine

Table 5 Lowest Energy, HOMO- LUMO Gap (Frontier orbital energy gap) and Dipole Moment of 2, 3 Dichloropridine by (B3LYP)/ LANL2DZ methods

Parameters	DCP
Energy (in au)	-274.9074
HOMO (in e V)	-7.47
LUMO (in e V)	-1.72
Frontier orbital energy gap (in e V)	5.75
Dipole moment (in Debye)	4.36

Table 6 Polarizability and Hyper Polarizability of 2, 3 Dichloropridine

Polarizability	Values	Hyper Polarizability	Values
α_{XX}	-50.6630	β_{XXX}	11.1534
α_{XY}	2.8095	β_{XXY}	1.1758
α_{YY}	-60.2405	β_{XYY}	-1.3450
α_{YZ}	0.0005	β_{YYY}	19.0056
α_{ZZ}	-59.6889	β_{XXZ}	0.0032
α_{XZ}	0.0010	β_{XYZ}	-0.0003
<α>	56.8641	β_{YYZ}	-0.0020
-	-	β_{XZZ}	-9.7578
-	-	β_{YZZ}	-1.2930
-	-	β_{ZZZ}	-0.0043
-	-	β_{Total}	18.8885

CONCLUSION

This paper reports a comprehensive computational structural study on 2, 3 Dichloropridine. The frequency assignments for 2, 3 Dichloropridine have been done for the first time by employing Density functional theory (DFT) with LANL2DZ as the basis set. Normal modes analysis provides detailed description of the vibrational spectra of the molecules in question. The values of hyperpolarizability indicate a possible use of these compounds in electro-optical applications. The lower value of frontier orbital energy gap and a higher dipole moment suggests a reactive nature of title compound. The present work might encourage the need for an extensive study by the experimentalists interested in the vibrational spectra and the structure of these compounds. The results reported in the present paper can help guide future experimental investigations on the origin of the biological activity of these molecules.

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