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Structural and Thermodynamic functions of 4,5-Difloro-2-nitroaniline by using HF and DFT calculations

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Abstract:

The present study investigates the structural and thermodynamic properties of 4,5-difluoro-2-nitroaniline using computational quantum chemical methods based on Hartree–Fock (HF) and Density Functional Theory (DFT). The molecular geometry, electronic structure, and thermodynamic functions of the compound were theoretically evaluated to understand its stability and physicochemical behaviour. Optimised structural parameters, including bond lengths, bond angles, and dihedral angles, were calculated and compared using the selected computational approaches. In addition, the electric dipole moment (μ), mean polarizability (α), and first hyperpolarizability (β) were determined to assess the molecule's nonlinear optical (NLO) response. Thermodynamic parameters, including heat capacity, entropy, and enthalpy, were evaluated over a range of temperatures to examine the thermal behaviour of the molecule. The calculated results provide useful insights into the relationship between molecular structure, electronic properties, thermal characteristics, and optical response. The study demonstrates the applicability of HF and DFT calculations for predicting important molecular properties of 4,5-difluoro-2-nitroaniline and assessing its potential relevance in materials and molecular science.

Keywords: Structural Properties, Thermodynamics functions4,5-Difloro-2-nitroaniline, Hartree-Fock, Density functional theory

1. INTRODUCTION

Aniline is six membered homoaromatic simplest amine containing – NH_2 functional group. Aniline has significant industrially commodity chemical and also use for fine chemical synthesis. Due to having electron rich benzene ring aniline goes to electrophilic aromatic substitution. After formation of diazonium salt through diazotization reaction this diazonium salt goes to a huge number of nucleophile substitution and form a lot number of compounds used in daily life. They have been broadly used for pharmaceutical manufacturing, electro-optical, chemical dye industries and for other commercial and industrial use, and have been studied extensively [1-3]. Some para substituted compounds of aniline are frequently used local anaesthetics. Among these compounds the amino group plays crucial role in the interaction with the receptor. Therefore, studies of properties as well as the extensive experimental nature of reaction mechanics, [4] and theoretical investigations of substituted aniline have focused on determine the structure and vibrational assignments of aniline and its methyl derivatives [1-8]. Molecular geometry alters due to enhanced interaction between the aromatic ring and the amino group. Substituent group inclusion in aniline also explains the change of charge distribution with in the molecule [9-13]. “It’sgeometry has been reported using semi-empirical [14-15], ab-

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initio methods [14,16-17]. Extensive recent studies on vibrational spectra of substituted anilines assigned [1,5,8,18-20] complete vibrational mode and frequency analyses. G. Karimi et al. reported π conjugation, band gape energy, Ionisation potential electron affinity and red shift in doped state of fluoro substituted aniline [21]. M. George et al. have been investigated π conjugation in the carbon ring system [22].

2. COMPUTATIONAL DETAILS

In the present work the theoretical calculations are carried out for compound 4,5-Difloro-2-nitroaniline. Two different methods are applied for these calculations, Hartree -Fock (HF) and density functional Theory (DFT).For making structure and visualize the geometry the Gauss view molecular visualization program was run while for the calculations of vibrational geometrical, electronic and thermodynamic parameters Gaussian-09 program [23] set was employed. Three parameters that are combined with DFT by Lee, Yang and Parr (LYP) is electron correlation functional [25]. These three-hybrid functional group (B3) parameters by Becke's [26] were used for DFT calculations make one single election density functional method B3LYP. Thermodynamic properties such as, Heat capacity, Entropy, Enthalpy rotational constant also calculated by the HF/6-311 and B3LYP/6-311. Variation of thermodynamics properties with temperature also determined. Mullikan charges of the atoms were also determined of the compound 4,5DF2NA.

3. RESULT AND DISCUSSION

3.1 MOLECULAR GEOMETRY

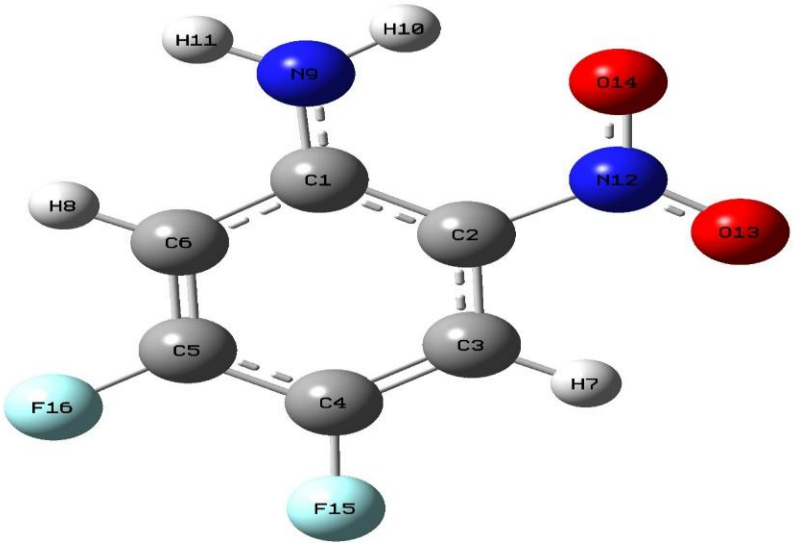

Figure 3.1 Optimized geometric structure of 4,5-Difloro-2-nitroaniline with numbering of atoms.

The structure and scheme with number of atoms of the compound 4,5-difluoro -2-nitro aniline was explained in the present study. For the geometrical demonstration of the title compound, Cs point group symmetry has been taken account for this. In this research study Cartesian coordinate analysis of theoretical force constant took into consideration.The computation have

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been started with 168 symmetry adapted basis functions ,168 symmetry adapted Cartesian basis functions ,332 primitive gaussians ,for 44 alpha and 44 beta electrons with nuclear repulsion energy ;686.6262 hartree assuming C_s point group symmetry of the optimized structure of title compound .To find out the optimized structure, conformation and orientation of -NO_2 and F atom in aniline molecule polarised set 6-31++G(d,p) and 6-3111++G(d,p) are used in this investigation .In the titled molecule 4,5-difluoro-2-nitroaniline, the three substituents group are present on the parent molecule aniline. Flouro group substitution is on fourth and fifth positions and ortho position is substituted by nitro group in parent aniline molecule. There is a planer benzene ring containing 16 atoms including substituted groups. The optimized structure of titled compound and structural parameters [Bond length and Bond angle] are obtained by two different quantum theories HF and DFT-B3LYP with two different basis sets 6-31++G(d,p) and 6-311++G(d,p). Figure 3.1 shows the optimized molecular structure with numbering of atoms. The optimized bond length between C-C of benzene rings lie in the range from 1.351 to 1.4131 Å in HF and from 1.3785 to 1.4295 in DFT-B3LYP, that is in good range of experimentally obtained data of aniline [12,13,20]. The N-H bond length is almost equal in both theories by using different basis sets. The C-F bond length shows a considerable increase in comparison to C-H in benzene ring. The bond angles calculated by various theoretical methods shows the similar trend as bond length. The C-C-C bond angles of the benzene ring and fluorine substitutions are significantly larger than others. Rest of the angles of benzene ring other than substituted position are close to $120^{o.}$ Angles between C-C-N of both substituent groups containing nitrogen atom are larger than 120^{o} due to steric hindrances of these larger size group, that is in good range of experimentally obtained data of aniline [12,13,25]. Bond angles other than these substitutions are less than 120^{o} in the above two theories HF and DFT. Both the empirical theories show dihedral angle between ring and bulky substituents (-NH_2, -NO_2) are near about 180^{o}. This indicates that ,these substitutions are tilted almost perpendicular to benzene ring plane. This is due to the bulky and steric hindrance of substituents (-NH_2, -NO_2).

3.2 THERMODYNAMIC PROPERTIES

Table 3.2(a): Theoretically computed Zero-Point Vibrational Energies (kcal/ mol), Rotational Constants (GHz), Dipole moment (Debye's), Entropies (cal/mol-Kelvin) Thermal Energy(kcal/mol) and Specific Heat(cal/mol-Kelvin) for 4,5-Difloro-2-nitroaniline using B3LYP/6-311++G(d, p)

Parameter		HF		DFT	
		HF/6-31+G (d, p)	HF/6-311++G (d, p)	B3LYP/6-31+G (d, p)	B3LYP/6-31++G (d, p)
Zero-Point Energy		69.85868	65.41412	65.84548	64.61489
Rotational Constants	X	1.70379	1.66222	1.69312	1.65130
	Y	0.69559	0.63292	0.68539	0.66980
	Z	0.49398	0.45840	0.48314	0.47651

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Dipole Moment				
μ_x	-1.0810	1.1011	1.1323	-1.0917
μ_y	4.0813	4.0082	3.8809	4.1484
μ_z	-0.0811	-0.2656	-0.4180	-0.0801
μ_{Total}	4.1512	4.1652	4.0643	4.2904

ENTROPY

Total	96.916	100.445	96.832	96.867
Translational	41.369	41.369	41.369	41.369
Rotational	30.685	30.878	30.703	30.790
Vibrational	24.861	28.918	24.914	24.707

ENERGY (THERMAL ENERGY)

Total	75.836	71.655	74.356	70.708
Translational	0.889	0.889	0.889	0.889
Rotational	0.889	0.889	0.889	0.889
Vibrational	74.058	69.878	72.814	68.931

SPECIFIC HEAT (Cv)

Total	35.485	36.887	36.314	37.351
Translational	2.981	2.981	2.981	2.981
Rotational	2.981	2.981	2.981	2.981
Vibrational	29.523	30.926	30.614	31.390

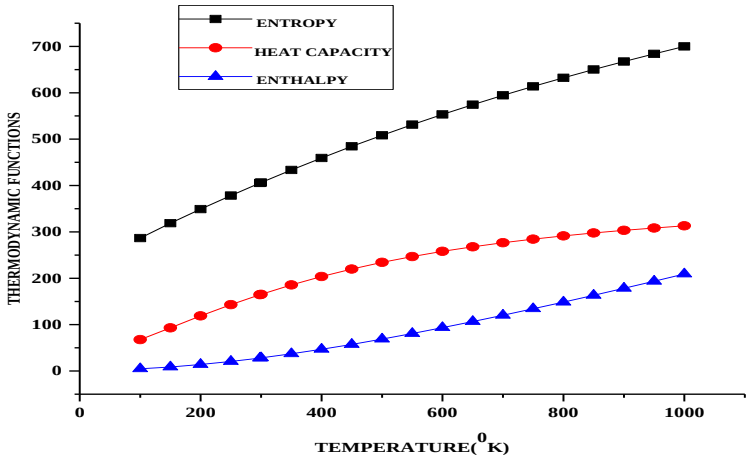

Fig. 3.2 Variation of Entropy, Heat capacity and Enthalpy at different temperatures of 4,5-Difloro-2-nitroaniline using B3LYP/6-311++G(d,p)

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Table 3.2(b): Thermodynamic properties Entropy, Heat capacity and Enthalpy at different temperatures of 4,5-Difloro-2-nitroaniline using B3LYP/6-311++G(d, p)

Temperature (K)	Entropy {S} (J/mol·K)	Heat Capacity {Cp} (J/mol·K)	Enthalpy {H} (kJ/mol)
100.00	286.660	67.608	4.689
150.00	318.833	93.103	8.699
200.00	349.167	118.854	14.002
250.00	378.328	143.108	20.559
298.15	405.399	164.592	27.974
300.00	406.420	165.379	28.280
350.00	433.457	185.592	37.062
400.00	459.448	203.754	46.805
450.00	484.400	219.931	57.405
500.00	508.328	234.249	68.767
550.00	531.260	246.883	80.802
600.00	553.229	258.028	93.430
650.00	574.280	267.879	106.583
700.00	594.458	276.615	120.199
750.00	613.812	284.396	134.228
800.00	632.393	291.359	148.625
850.00	650.248	297.618	163.353
900.00	667.422	303.207	178.377
950.00	683.958	308.394	193.671
1000.00	699.897	313.056	209.209

Thermodynamics functions are calculated by both the quantum chemical model Hartree fock (HF) and density functional theory (DFT) using 6-311++G(d,p) basis sets. The results were computed the thermodynamic properties such as enthalpy, entropy, heat capacity, free energy, along with translational, vibrational, and rotation contribution [26-29]. At this stage, it seems that the HF method gives overestimated results in comparison to DFT. Variation of thermodynamics parameters of the title compound 4,5 DF2NA with temperature is also computed by density functional theory. The numerical values of these thermodynamics' parameters, thermal energy, heat capacity at constant volume, entropy zero-point vibrational energy along rotational constants in the ground state at 2980K are listed in Table3.2(a).For the computation of these properties' molecular weight, a moment of inertia, fundamental vibration frequencies, and temperature are needed. Using Vibrational frequencies computed by DFT, these thermodynamics properties we calculated with the help of a computer program at different temperatures ranging from 100 - 1000 K. Variation of these properties with temperature are shown in Figure 3.2, and data are listed in Table3.2(b).It is seen that all the properties listed in table and shown in figure increased linearly with low-temperature range. After that crave become flatten and increases less rapidly. This is due to that at lower

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temperature range only the translation vibration part of the molecule takes part in motion. As the temperature increases, the other portion of molecular motion (Vibrational, Rotational) also makes a contribution in excitation. The entropy of the title molecule is the function of the measurement of disorderness. As the temperature rises the molecular motion increased and leads to an increase in entropy. This data can be used to calculate the other thermodynamics properties and predict the pathway of any related chemical reaction according to the law and relationship of thermodynamics in thermochemical field.

3.3MULLIKEN CHARGES

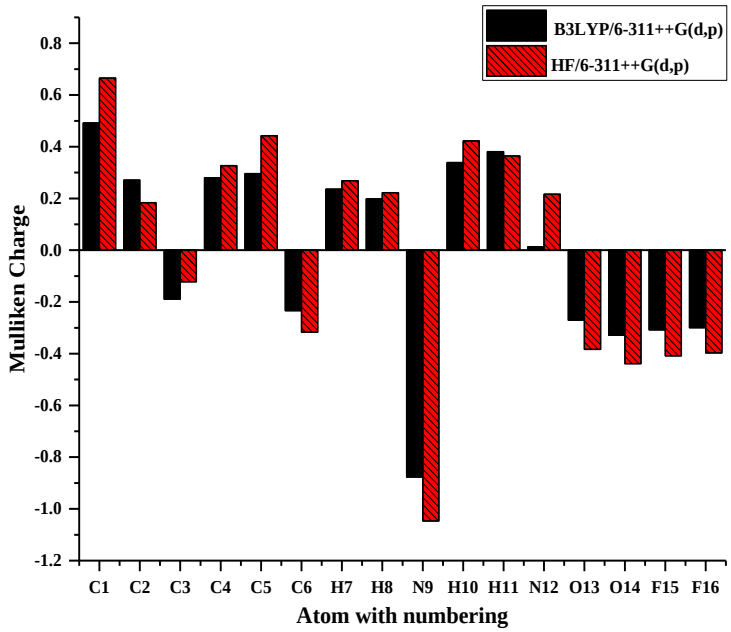

Fig:3.3 Mulliken Charges of 4,5-Difloro-2-nitroaniline with B3LYP/6-311++G(d,p)and HF/6-311++G(d,p)

[C-Carbon, H-Hydrogen, N-Nitrogen, F-Fluorine, O-Oxygen]

The Mulliken atomic charges that are based on the LCAO (Linear combination of atomic orbitals) method are partial atomic charges. It is calculated by Mulliken population analysis. these charges are basis set dependent and computed by using a complete basis set. These calculations have been carried out by computational chemistry. In the present study the Mulliken charges of 4,5-diflouro-2-nitroaniline computed from the HF and DFT quantum chemical models are shown in Fig :3.3. The negative and positive charges of an atom of 4,5DF2NA also have been shown in the figure:3.3. In the present study, the charge on C3 and C6 are negative while the other carbon atoms of the ring acquire a positive charge. This is due to the positive resonance effect ofNH2 –group. There is another important observation also there C3 is less negative to C6. The reason of this is due to the –NO2 group has a tendency of

negative resonance effect. N9 of –NH2 group is more negative to a comparison of N12 of -NO2 group. A valid reason for this is due to +I effect of hydrogen and -I effect of oxygen.

4. CONCLUSION

In the present investigation of the molecule 4,5-difloro-2-nitroaniline a detailed geometrical, have been done with the help of both empirical quantum chemical method Hartree Fock and density functional theory. This is the first time that optimized structure, bond length, bond angle, thermodynamic parameters, mulliken charges is produced for the title compound 4,5-difloro-2-nitroanilineThe parameters, bond length, bond angle, obtained from molecular geometry are very well correlated to the data available in literature for aniline.

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