International Journal for Rapid Research in Engineering Technology & Applied Science (IJRRETAS)

(Peer-Reviewed, Open Access, Fully Refereed International Journal)

Volume 11 Issue 8, Aug 2025 OPEN ACCESS E-ISSN: 2455-4723 Impact Factor 7.95

Non-linear optical Properties and Thermodynamic functions of 2,5-Dimethoxy-4-nitroaniline by using DFT and HF

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Abstract

In the present work, the non-linear optical properties and thermodynamic functions of 2,5-Dimethoxy-4-nitroaniline have been investigated theoretically using Hartree–Fock (HF) and Density Functional Theory (DFT) methods. The electric dipole moment (μ), mean polarizability (α), anisotropy of polarizability (Δα), and first hyperpolarizability (β) have been calculated to evaluate the non-linear optical (NLO) response of the molecule. The optimized molecular structure, electronic properties, and vibrational characteristics were obtained using appropriate computational methods. The calculated NLO parameters indicate the ability of the molecule to exhibit significant optical non-linearity, which may be attributed to the presence of electron-donating methoxy and amino groups together with the electron-withdrawing nitro group. Thermodynamic functions, including heat capacity, entropy, and enthalpy changes, were also evaluated at different temperatures to understand the thermal behaviour and stability of the molecule. The comparative results obtained from HF and DFT calculations provide useful information about the structural, electronic, optical, and thermodynamic characteristics of 2,5-Dimethoxy-4-nitroaniline and indicate its potential relevance for molecular NLO applications.

Keywords: Non-linear optical Properties, Thermodynamics functions, 2,5-Dimethoxy-4-nitroaniline, Hartree-Fock, Density functional theory

1. INTRODUCTION

Aniline and its derivatives have been exclusively used for chemical dyes industries [1] pharmaceutical sector [2] electro optical world [3]. Nonlinear optical molecules are much more interesting because of their wide applications of optical signal processing, data storage and telecommunication, optical computing [4-8]. Antibacterial activity of some half-substituted compounds has been discussed by Vidhya et al [9-11] for treatment of cancer is of great importance. Cancer is curse for society so its study is too much important in field of research. Aniline is also responsible for bladder cancer [12], forest dieback reported in WHO report in 1995. The beautiful use of anilines and their derivative is to form indigo dye for blue jeans in the dye industry [13-16]. Polyaniline an important derivative of anilines is considered as an emerging conducting polymer in the polymer industries due to its methodical preparation environmental stability and having good electrochemical properties [17-18].For this purpose, details of various studies conducted on aniline and its derivatives are very important. There are molecular geometry changes due to extended interaction of amino group a with an aromatic ring [19-20]. The inclusion of any group for atom by substitution in the parent aniline also leads

to charge distribution variation in the molecule widely affects the geometry and its vibrational parameters [21]. Shanker et al [22] studied 2-chloro-6-methylaniline with Raman and infrared spectra. A detailed study of spectral analysis and NLO, NBO, and HOMO-LUMO of 2, 3-diflouroaniline and 2,4-difluoraniline have been done. Vibrational Spectral and first order hyperpolarizability of - N-Phenylbenzene sulfonamide and 2,5-difluoro nitrobenzene calculated have been [23-25]

2. COMPUTATIONAL DETAILS

After making structure and visualize the geometry the Gauss view molecular visualization program was run while for the calculations of geometrical, and thermodynamic parameters Gaussian- 09 program set was employed [26]. Three parameters that are combined with DFT by Lee, Yang and Parr (LYP) is electron correlation functional. These three-hybrid functional group (B3) [27] parameters by Becke's were used for DFT calculations make one single election density functional method B3LYP [28]. In this work two different theory HF and B3LYP with same basis sets, 6-311++ (d,p) are used for the titled compound. Basis sets are very important in these quantum calculations. Non-linear optical properties have been calculated of the titled compound with HF/6-311 and B3LYP/6-311 by theoretical calculations. Dipole moment, molecular polarizability, the anisotropy of the polarizability and first hyper polarizability have been calculated in all three solvent acetone, ethanol and methanol also calculated with help of these two empirical quantum methods.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 and natural charges of the atoms were also determined of the compound 2,5DM4NA

3. RESULT AND DISCUSSION

3.1 MOLECULAR GEOMETRY : In the titled molecule 2,5DM4NA, the three substituents group are present on the parent molecule aniline. Methoxy group substitution is on second and fifth positions and para position is substituted by nitro group in parent aniline molecule. There is a planer benzene ring containing 24 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 4.1 shows the optimized molecular structure with numbering of atoms

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Figure 1 Optimized geometric structure of 2,5-Dimethoxy-4-nitroaniline with numbering of atoms.

It is observed the highest value of dipole moment for titled compound is 10.3619 Debye for B3LYP/6-311++G (d, p) in methanol comparative two other solvent. It is also observed the highest dipole moment for the μY component for 2,5-dimethoxy-4-nitroanilineall three solvents. All the values of dipole moment are reported in the table 4.1. The polarizabilities and hyper polarizabilities are calculated in atomic units (a. u) after that it change to in the electrostatics units (esu) (α: 1 a. u=0.1482x10^{-24} esu, β, 1 a. u=8.6393x10^{-33}esu).The values of mean polarizability (α) and anisotropy polarizability (Δα) for the title molecule in the same table by using B3LYP/6-311++G(d, p) in three solvents also reported. Moreover, addition of methoxy or nitro, group to the parent molecules increases, the mean polarizability; due to molecular charge distribution. The calculated values of anisotropy polarizability (Δα) are 3.3541x 10^{-24}esu., 3.269 x 10^{-24}esu.,and 2.8532x 10^{-24}esu. in ethanol methanol and acetone respectively using B3LYP/6-311++G(d, p) for 2,5-dimethoxy-4-nitroaniline.

Another important parameter of the titled compound, the first static hyperpolarizability values calculated and presented in Table 3.4.5 β_{total} is9.1163 x 10^{-31}esu, 9.0826 x 10^{-31}esu, and 8.6752x 10^{-31}esuin ethanol methanol and acetone respectively using B3LYP/6-311++G(d, p) for 2,5-dimethoxy-4-nitroaniline.

The large value of β calculated by the B3LYP and HF methods show that the studied compound is a good NLO material. The theoretical calculation of β components is very useful as this clearly indicates the direction of charge delocalization. The smallest β_{zzz} value indicates charge delocalization is along the bond axis and the involvement of σ orbitals in intra-molecular charge transfer process [29-33].

Table 3.1. The values of calculated static electronic polarizabilities α (a.u.), first hyperpolarizability β (a.u.) components for 2,5-dimethoxy-4-nitroaniline using B3LYP/6-311++G(d, p)

Parameters	Component	Ethanol	Methanol	Acetone
Dipole Moment (Debye)	μx	-6.1519	-6.1826	-5.4145
	μy	8.2222	8.2620	7.4996
	μz	0.9351	0.9402	0.5968

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	μtotal	10.3114	10.3619	9.2691
Polarizability (a.u.)	αxx	-76.8028	-76.8179	-82.2071
	αyy	-75.9215	-75.2863	-74.6844
	αzz	-83.9471	-83.9462	-83.5402
	αxy	17.8267	17.8674	14.1404
	αxz	-0.6360	-0.6376	0.6092
	αyz	3.4445	3.4529	2.2247
	⟨α⟩	-78.8904	-78.6835	-80.1439
	⟨α⟩ ($\times 10^{-24}$ esu)	-11.7625	-11.6608	-11.9521
	Δα	21.4512	22.0584	21.0067
	Δα ($\times 10^{-24}$ esu)	3.3541		

3.2 THERMODYNAMIC PROPERTIES

Table 4.2(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 2,5-dimethoxy-4-nitroaniline using B3LYP/6-311++G(d, p)

Thermodynamic Parameters (298K)	**HF/6-311++G (d, p)**	**B3LYP/6-31++G (d, p)**
Zero-Point Energy , E0	124.30080	115.4910
Rotational Constants X	0.93278	0.9828675
Rotational Constants Y	0.56064	0.5462777
Rotational Constants Z	0.35388	0.3641859
ENTROPY (S)		
Total	113.418	117.497
Translational	41.755	41.755
Rotational	31.830	31.890
Vibrational	39.833	43.851
THERMAL ENERGY (E)		
Total	132.378	124.040
Translational	0.289	0.889
Rotational	0.289	0.889
Vibrational	130.601	122.262

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SPECIFIC HEAT (CV)		
Total	47.090	50.400
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	41.029	44.438

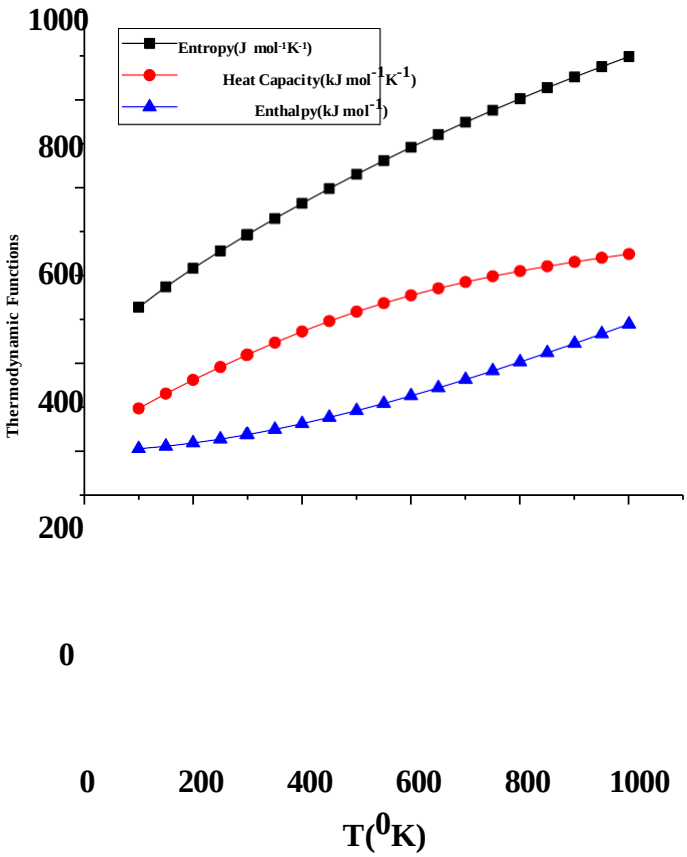

Fig. 3.2: Variation of Entropy, Heat capacity and Enthalpy at different temperatures of 2,5-dimethoxy-4-nitroaniline using B3LYP/6-311++G(d, p).

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

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TEMPERATURE (K)	ENTROPY {S} (J/mol.K)	HEAT CAPACITY {Cp} (J/mol.K)	ENTHALPY {H} (kJ/mol)
100.00	327.737	97.993	6.354
150.00	373.925	131.618	12.106
200.00	416.091	162.647	19.472
250.00	455.560	191.989	28.343
298.00	491.715	219.187	38.246
300.00	493.074	220.211	38.652
350.00	529.066	247.223	50.344
400.00	563.758	272.647	63.348
450.00	597.249	296.163	77.577
500.00	629.582	317.638	92.930
550.00	660.784	337.101	109.307
600.00	660.883	354.690	126.609
650.00	719.912	370.587	144.748
700.00	747.911	384.983	163.643
750.00	774.925	398.057	183.224
800.00	801.001	409.968	203.429
850.00	826.187	420.853	224.204
900.00	850.528	430.830	245.500
950.00	874.071	439.996	267.273
1000.00	896.858	448.436	289.487

Another important parameter of the title compound 4,5DF2NA, 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 [34-36]. At this stage it is seems that HF method gives overestimated results in comparison of DFT. Variation of thermodynamics parameters of the title compound 2,5 DM4NA with temperature are 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 with rotational constants in ground state at 298^0K are listed in Table.4.2(a) For computation of these properties molecular weight, 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 computer program at different temperatures ranging from 100- 1000

K. Variation of these properties with temperature are shown in Figure 4.2 and data are listed in Table 3.2(b). It is seen that all the properties listed in table and shown in figure increased almost linearly in low temperature range. After that crave become flatten and increases less rapidly. Entropy of any system is the measurement of randomness. As the temperature of system rises the randomness in molecular arrangement of the system increased and lead to increase in entropy. This is due to that at lower temperature range only translation vibration part of the molecule take part in motion. As the temperature increases the other portion of molecular motion (Vibrational, Rotational) also make the contribution in excitation. That trend is reflected in the curve of entropy. At higher range of temperature curve shows a little bit positive deviation from linearity. The heat capacity curve is also linear in a small range of 200 K to 400 K and after that it starts to became flatten. While enthalpy curve shows the vice versa trend of heat capacity.

4. Conclusion

The calculated NLO properties provide a chance to the compound used as non-linear optical material due to its wide used in paint, dye, biological and chemical industries. Thermodynamic 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.

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