

Spectroscopic and Quantum mechanical investigations of 1-(1,3-Benzodioxol-5-yl) thiourea

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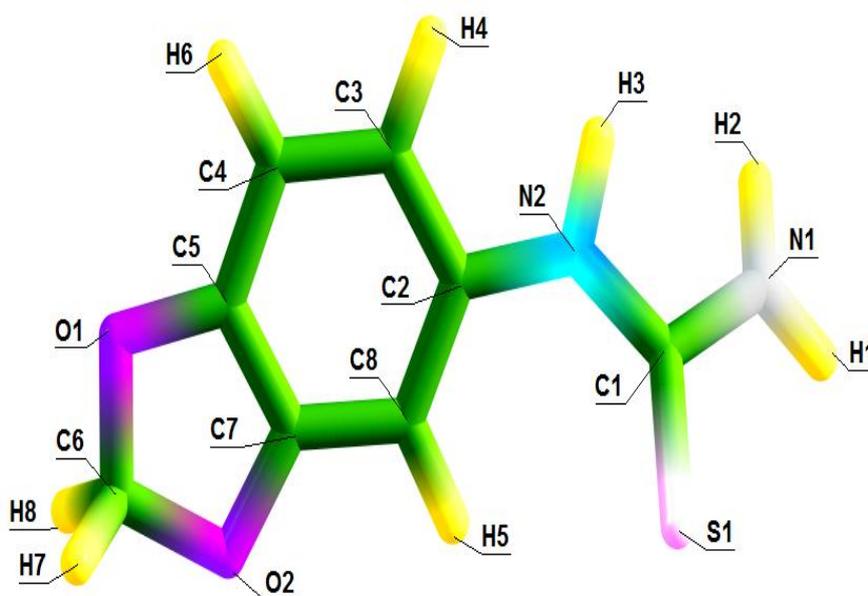
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Abstract

The optimum molecular geometry of 1-(1,3-Benzodioxol-5-yl)thiourea was calculated by the B3LYP method of density functional theory (DFT) using 6-311 ++ G(d,p), mp2/sto-3g basis sets and data source of vibration frequency, polarizability, and thermo-dynamical parameters were set up. By contrast with the theoretical spectra, the vibrational assignment of 1-(1, 3-Benzodioxol-5-yl)thiourea was discussed. In addition, part of significant parameters such as HOMO-LUMO energy gap and hyperpolarizability calculations. This study provides a theoretical support for the spectral detection technology, especially for the analysis of the electronic structure and spectra of of 1-(1,3-Benzodioxol-5-yl)thiourea.

Key words: DFT, 1-(1,3-Benzodioxol-5-yl)thiourea, vibrational spectra



Optimized structure of 1-(1,3-Benzodioxol-5-yl)thiourea

Introduction

Thiourea derivatives have attracted great attention as versatile ligands in numerous applications¹. This is due to its unique properties which enable to coordinate with various transition metal ions as monodentate or bidentate ligands. The methylenedioxy benzene group is present in a number of endothelia receptor antagonists. Endothelins are 21-amino acid bicyclic peptides originally isolated from the supernatant of cultured porcine endothelial cells². There have been many studies about the molecular conformations of indan-like benzene fused ring molecules³⁻⁵. These molecules have received considerable attention due to their interesting conformational properties. 1, 3-benzodioxole has been studied extensively by several spectrographic and theoretical methods owing to its propensity for large amplitude motion⁶⁻¹⁴. It is believed that the molecule has a nonplanar structure in its electronic ground state. While the aromatic ring is planar, the five member ring is puckered, with the oxygen atoms and the CH₂ group on opposite side of the aromatic plane. In the present work, the Quantum mechanical and hyperpolarizability investigations and vibrational spectroscopic analysis of 1-(1,3-Benzodioxol-5-yl) thiourea is reported theoretically.

Materials and Methods

Computational details

Calculations of the title compound were carried out with Gaussian09 software⁹ program using B3LYP/6-311++G(d,p)*, mp2/sto-3g basis sets to predict the molecular structure and vibrational wavenumbers. Calculations were carried out with Becke's three parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. Then frequency calculations were employed to confirm the structure as minimum energy points. At the optimized structure (Fig. 1) of the examined species, no imaginary wavenumber modes were obtained, proving that a true minimum on the potential surface was found. The DFT method tends to overestimate the fundamental modes. The optimized geometrical parameters are given in Table 1. The assignments of the calculated wavenumbers are aided by the animation option of GAUSSVIEW program, which gives a visual presentation of the vibrational modes.

Result and Discussion

Geometrical parameters

The optimized structure of 1-(1,3-Benzodioxol-5-yl)thiourea are shown in the following fig (1). The corresponding minimum energy obtained by b3lyp/6-311+g(d,p) method were fall on -1080.9369747. From the optimized geometry the optimized structural parameters are tabulated on table 1.

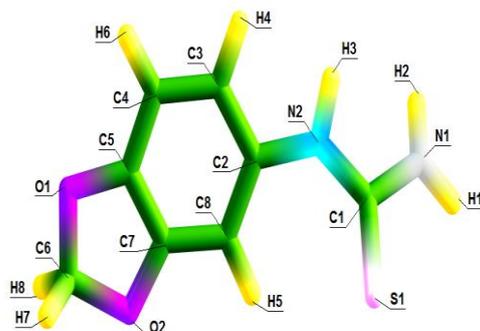


Figure 1: Optimized structure of 1-(1,3-Benzodioxol-5-yl)thiourea

The Geometrical parameters are obtained by computationally. For 1,3-Benzodioxol-5-yl ring the C₈-O₉, C₁₀-O₁₁ bond lengths are 1.375, 1.433 and O₉-C₁₀, O₁₁-C₁₂ bond lengths are 1.433, 1.374. For Thiourea group the C₂-S₃, N₁-C₂ and C₂-N₄ bond lengths are 1.669, 1.374 and 1.370.

For bond angle of Benzodioxol group, the 1, 3 dioxol group at C₁₀ position O₉-C₁₀-O₁₁ is 107.3°, at O₉ position C₈-O₉-C₁₀ is 104.9°, at O₁₁ position C₁₀-O₁₁-C₁₂ is 105.1°.

In the Benzodioxol group, the benzene ring at C₅, C₆, C₇, C₈, C₁₂ and C₁₃ positions the bond angles are C₆-C₅-C₁₃ is 121.1°, C₅-C₆-C₇ is 121.4°, C₆-C₇-C₈ is 116.9°, C₇-C₈-C₁₂ is 121.5°, C₈-C₁₂-C₁₃ is 122.6° and C₅-C₁₃-H₁₈ 121.7°.

For bond angle of Thiourea group at C₂ position, the angles N₁-C₂-S₃ is 121.4°, S₃-C₂-N₄ is 126.0° and N₁-C₂-N₄ is 112.6°.

Bond lenth	value	Bond angle	value
N ₁ -C ₂	1.374	C ₂ -N ₁ -H ₁₄	114.9
N ₁ -H ₁₄	1.008	C ₂ -N ₁ -H ₁₅	119.6
N ₁ -H ₁₅	1.011	N ₁ -C ₂ -S ₃	121.4
C ₂ -S ₃	1.669	N ₁ -C ₂ -N ₄	112.6
C ₂ -N ₄	1.370	H ₁₄ -N ₁ -H ₁₅	115.9
N ₄ -C ₅	1.422	S ₃ -C ₂ -N ₄	126.0
N ₄ -H ₁₆	1.011	C ₂ -N ₄ -C ₅	128.2
C ₅ -C ₆	1.395	C ₂ -N ₄ -H ₁₆	115.7
C ₅ -C ₁₃	1.407	C ₅ -N ₄ -H ₁₆	114.3
C ₆ -C ₇	1.404	N ₄ -C ₅ -C ₆	118.2
C ₆ -H ₁₇	1.084	N ₄ -C ₅ -C ₁₃	120.7
C ₇ -C ₈	1.376	C ₆ -C ₅ -C ₁₃	121.1
C ₇ -H ₁₉	1.082	C ₅ -C ₆ -C ₇	121.4
C ₈ -O ₉	1.375	C ₅ -C ₆ -H ₁₇	119.3
C ₈ -C ₁₂	1.392	C ₅ -C ₁₃ -C ₁₂	116.4
O ₉ -C ₁₀	1.433	C ₅ -C ₁₃ -H ₁₈	121.7
C ₁₀ -O ₁₁	1.433	C ₇ -C ₆ -H ₁₇	119.2
C ₁₀ -H ₂₀	1.089	C ₆ -C ₇ -C ₈	116.9
C ₁₀ -H ₂₁	1.097	C ₆ -C ₇ -H ₁₉	121.5
O ₁₁ -C ₁₂	1.374	C ₈ -C ₇ -H ₁₉	121.6
C ₁₂ -C ₁₃	1.375	C ₇ -C ₈ -O ₉	128.9
C ₁₃ -H ₁₈	1.079	C ₇ -C ₈ -C ₁₂	121.5
		O ₉ -C ₈ -C ₁₂	109.5
		C ₈ -O ₉ -C ₁₀	104.9
		C ₈ -C ₁₁ -O ₁₂	109.4
		C ₈ -C ₁₂ -C ₁₃	122.6
		O ₉ -C ₁₀ -O ₁₁	107.3
		O ₉ -C ₁₀ -H ₂₀	109.5
		O ₉ -C ₁₀ -H ₂₁	109.3
		O ₁₁ -C ₁₀ -H ₂₀	109.5
		O ₁₁ -C ₁₀ -H ₂₁	109.3
		C ₁₀ -O ₁₁ -C ₁₂	105.1
		H ₂₀ -C ₁₀ -H ₂₁	111.9
		O ₁₁ -C ₁₂ -C ₁₃	127.9
		C ₁₂ -C ₁₃ -H ₁₈	121.9

Table 1: optimized geometrical parameters

For bond angle of Thiourea group at C₂ position, the angles N₁-C₂-S₃ is 121.4°, N₁-C₂-N₄ is decreases by 112.6° and this asymmetry reveals the interaction between the thiol group. For urea group S3-C₂-N₄ is increased by 6°, N₁-C₂-N₄ is reduces by 7.4° and asymmetry reveals the urea group.

Frequency	IR		Raman		Assignment
	b3lyp/6-311+g(d,p)	mp2/sto-3g	b3lyp/6-311+g(d,p)	mp2/sto-3g	
602.2575	2.5781	18.4476	4.6614	7.4229	
624.4101	5.0868	41.7303	5.3934	4.1471	C-H band
662.78	14.6769	1.2315	2.647	1.7961	
717.4696	1.8947	3.4896	7.4462	6.0381	
729.2528	10.4493	26.6546	17.7948	12.0817	
750.3589	22.9252	52.0689	9.2077	19.78	C-H band
808.849	17.6345	39.8604	5.514	5.1215	C-H band
822.5655	20.5612	5.298	14.011	2.1609	
839.323	4.4759	4.8879	22.0359	4.3366	
868.5547	21.4247	199.3382	4.5335	26.0169	C-H band
920.7254	1.2564	0.6832	0.3841	1.3208	
948.8464	55.9259	23.137	0.7712	3.6514	
965.0694	5.7994	23.2262	4.9378	5.6943	
1058.324	132.9061	14.3155	2.0692	0.5726	C=S Stretch
1065.173	38.3491	6.4477	16.4498	2.8857	
1119.266	13.0623	11.1956	14.2525	2.6735	C-O-C Stretch
1142.962	8.8531	50.1603	0.6343	6.8011	C-O-C Stretch
1157.294	14.9648	72.9873	5.7297	8.2713	C-O-C Stretch
1210.895	65.1559	124.419	12.6242	3.0884	C-O-C Stretch
1227.434	167.3336	0.0098	4.1928	7.6292	
1251.796	158.4409	31.5093	1.9262	2.2649	C-N Stretch
1296.304	23.2811	52.5162	23.4152	9.0326	C-N Stretch
1299.461	113.963	7.2448	87.3257	12.2568	C-N Stretch
1376.361	123.2188	69.0637	6.6302	15.9518	C-H bending
1401.805	377.2873	4.2063	4.2345	8.6631	
1424.453	2.5793	149.3392	11.5062	42.9088	CH ₂ Stretch
1478.893	41.9918	75.9427	61.2207	5.8716	
1520.793	289.9063	279.8599	23.1944	3.5071	C=C Stretch
1539.286	35.5578	17.2606	12.5857	1.9582	
1552.691	166.4308	17.7765	19.5598	35.5402	C=S Stretch
1634.376	147.3505	10.3142	8.0394	4.7371	
1652.443	10.604	0.5307	55.2365	77.8828	
1664.833	9.8713	2.4208	32.2219	18.4366	
3000.521	126.674	2.5918	254.1482	85.5503	
3123.665	30.9038	1.2936	158.11	65.9217	
3174.545	7.4592	2.0843	68.1196	38.615	
3207.649	2.5699	1.3621	145.3898	72.297	
3236.393	0.4157	2.6268	44.6322	29.6171	
3553.229	37.7315	23.8851	233.4671	107.9873	CH ₂ stretch
3581.807	24.0858	9.4584	177.2181	85.1077	CH ₂ stretch
3684.410	47.2835	1.9604	69.4739	48.9404	

Table 2: Selected IR, Raman wavenumbers and assignments

Vibrational analysis

The observed IR, Raman bands and calculated wavenumbers and assignments are given in Table 2.

For Thiourea group C=S stretching vibration has been assigned by various authors to frequencies ranging from less than 800 cm^{-1} to greater than 1500 cm^{-1} ¹⁵. The region of absorption for the C=S vibration obviously depends on the type of compound in which this group occurs, specifically on what atoms are bonded to the carbon atom of the thiocarbonyl group, where nitrogen atoms are attached to the thiocarbonyl derivatives, there seem to be three regions in the infrared in which a C=S vibration, coupled with other vibrations, may be observed. This appears to be a useful concept, although, of the three arbitrary regions, viz. $1570-1395\text{ cm}^{-1}$, $1420-1260\text{ cm}^{-1}$, and $1140-940\text{ cm}^{-1}$, the lowest should be extended to 700 cm^{-1} to include absorptions which have recently been shown to exhibit a contribution from C=S stretching.

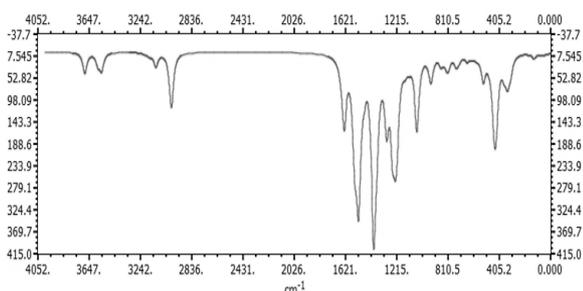


Figure 2: FTIR Theoretical spectrum of FT-IR

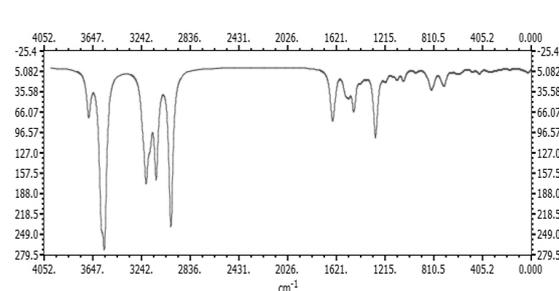


Figure 3: FTIR Theoretical spectrum of FT-RAMAN

The identification of C–N vibrations is found to be difficult tasks because of the mixing of several vibrations possible in this region. Our calculation 1264.812 , 1286.1476 and 1294.1433 cm^{-1} frequency corresponding to a mixed mode stretching frequencies due to C–NH₂¹⁶.

The thiourea which is under investigation has NH₂ group and hence asymmetric and symmetric NH stretch vibrations are possible. The NH¹⁷ stretching frequency of aromatic compounds occurs in the region $3300-3500\text{ cm}^{-1}$ are assigned to NH₂ asymmetric AND symmetric group of vibrations. The bands at 3460 cm^{-1} and 3380 cm^{-1} are due to N-H stretching modes of vibrations appear in group are found to be stronger when compared to N-H ring vibrations.

For methylene groups, the CH₂¹⁸ vibrations are observed in the region $2800-3000$, $1200-1400$, $875-1150$ and $600-950\text{ cm}^{-1}$. The vibrations of the CH₂ group (the asymmetric stretch CH₂, symmetric stretch CH₂, the scissoring vibration and wagging vibration) appear in the regions $2940-3005$, $2870-2940$, $1420-1480$ and $1320-1380\text{ cm}^{-1}$. Theoretically observed the IR spectrum of the title compound, the stretching bands of the CH₂ groups is at 3553.229 , 3581.807 cm^{-1} .

The C-C stretch vibrations occur nearly at 1600 cm^{-1} . The peak observed at 1710 cm^{-1} is due to C=C stretching vibrations¹⁹.

The asymmetric and symmetric C-O-C stretching vibrations are expected to appear at $1150-1250$ and $1000-1050\text{ cm}^{-1}$. In the present case the DFT calculations give these modes at 1119.266 , 1142.962 , 1157.294 , 1210.895 and 1227.434 cm^{-1} ²⁰. The bands at 1142.962 , 1157.294 , 1210.895 (IR) and 1119.266 , 1210.895 cm^{-1} (Raman) are assigned as C-O-C symmetric stretching modes.

Figure 2, 3 shows the theoretical FTIR and RAMAN spectrum of 1-(1,3-Benzodioxol-5-yl)thiourea

Frontier molecular orbital analysis:

The molecular orbital theory is employed extensively to describe chemical activities. Not only does the molecular orbital theory become an ever-present set of tools used to explain chemical actions, such as reactivity and kinetics, but it also provides an indispensable theoretical construct for the description of other phenomenon

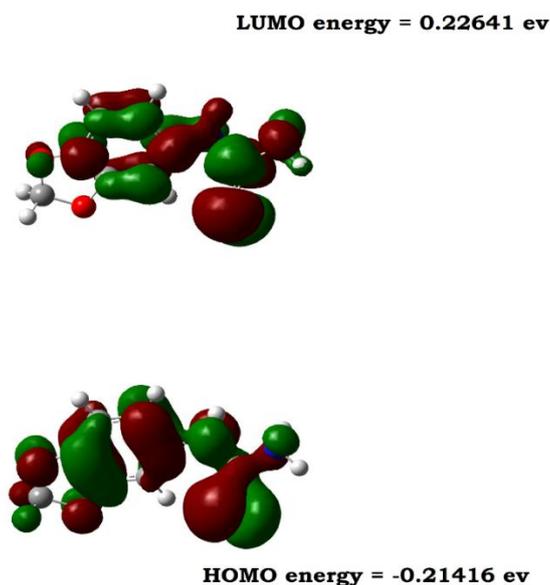


Figure 4: HOMO – LUMO energy diagram of 1-(1,3-Benzodioxol-5-yl)thiourea

involving molecular electronic structure including charge- transfer processes, photo excitation, magnetism, and molecular electronics. In fact, it is rather common to extract trends in molecular behaviour based on simple molecular orbital properties. For example, molecules with large HOMO-LUMO gaps are generally stable and un reactive; while those with small gaps are generally reactive. Thus the stability of a molecule can be affected by the factors of total energy, dipole moment and energy gap between HOMO-LUMO levels. The computed values of HOMO-LUMO of 1-(1,3-Benzodioxol-5-yl)thiourea are -0.22641 and -0.21416 respectively. The intra molecular charge transfer (ICT) from HOMO-LUMO occurs through π -conjugated path. Here LUMO is an electron acceptor and HOMO represents the ability to donate an electron. The energy gap is a factor to determine the molecular electrical transport property because it is a measure of electron conductivity. The boundary orbital picture is given in Figure 4.

The filled orbital (HOMO) is located in the entire molecule except hydrogen atoms in 1-(1,3-Benzodioxol-5-yl) thiourea whereas the unfilled orbitals (LUMO) are localized except methyl and hydrogen atoms.

IONIZATION ENERGY AND ELECTRON AFFINITY I = 0.21416; A = -0.22641
HARDNESS $\eta = - (0.21416 + 0.22641)/2 = 0.220285$
CHEMICAL POTENTIAL $\mu = 1/2(-0.21416 + 0.22641) = 0.006125$
GLOBAL ELECTROPHILICITY POWER $\omega = 8.515 \times 10^{-5}$

Table 3: Calculated ionization energy, hardness, chemical potential and global electrophilicity power

Using HOMO and LUMO orbital energies, the ionization energy and electron affinity can be expressed as: $I = -E_{HOMO}$, $A = -E_{LUMO}$, $n = (-E_{HOMO} + E_{LUMO})/2$ and $\mu = 1/2(E_{HOMO} + E_{LUMO})$ proposed the global electrophilicity power of a ligand as $\omega = \mu^2/2n$. The hardness n and chemical potential²¹ μ are given by the following relations $n = (I \square A)/2$ and $\mu = \square (I + A)/2$ where I and A are the first ionization potential and electron affinity of the chemical species²². The calculated values are given in the Table 3.

Predication of first hyperpolarizability

The first hyperpolarizability (β_o) of the 1-(1,3-Benzodioxol-5-yl)thiourea and the related property (β_o) were calculated using the *B3LYP/6-311++G(D,P)* basis set, based on the finite field approach.

	HyperPolar for au	HyperPolar for $\times 10^{-33}$ esu
β_{xxx}	69.9449593	604.2754869
β_{xyy}	22.3149193	192.7852823
β_{xyx}	-63.8468645	-551.5922165
β_{yyx}	28.8975118	249.6542737
β_{xzz}	82.6570453	714.0990115
β_{xzy}	-64.7006671	-558.9684733
β_{yzy}	74.8739161	646.8582234
β_{xzz}	-55.8083695	-482.1452466
β_{yzz}	59.2946229	512.2640356
β_{zzz}	23.772256	205.3756513
β_o	218.0683	1883.957

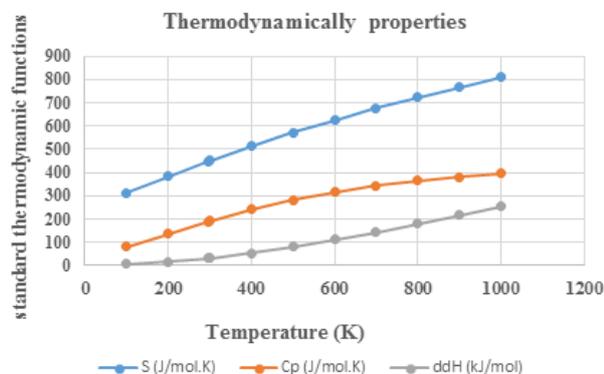
Table 4: calculated values of hyperpolarizability

The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. Theoretically calculated values of hyperpolarizability (β_o) are 1883.957×10^{-33} esu as shown in the Table 4. We can conclude that the title complex is an attractive object for future studies of non-linear optical application.

Thermo dynamical properties

On the basis of vibrational analyses and statistical thermodynamics, the standard thermodynamic functions: heat capacity ($C_{p,m}^0$), entropy (S_m^0) and enthalpy (H_m^0) were calculated²³ using perl script THERMO.PL²⁴ and are listed in Table 5.

T (K)	S (J/mol.K)	C_p (J/mol.K)	ddH (kJ/mol)
100.00	312.70	80.22	5.64
200.00	384.82	135.17	16.36
298.15	449.11	190.03	32.34
300.00	450.29	191.03	32.69
400.00	512.31	241.21	54.37
500.00	570.75	282.68	80.64
600.00	625.33	315.75	110.62
700.00	676.06	342.13	143.57
800.00	723.19	363.49	178.88
900.00	767.05	381.11	216.14
1000.00	807.99	395.85	255.01



Graph 1: Thermodynamical Property of title compound

Table 5: Calculated standard thermodynamic functions

From the table graph 1 is drawn taking standard thermodynamic functions are in x axis and Temperature (K) in y axis. As observed from Table & Graph, the values of $C_{p,m}^0$, S_m^0 and H_m^0 all increase with the increase of temperature from 100 to 1000 K, which is attributed to the enhancement of the molecular vibration as the temperature increases.

Conclusion

The present investigation thoroughly reports the vibrational spectra, both infrared and Raman of 1-(1,3-Benzodioxol-5-yl)thiourea. All the vibrational bands observed in the FT-IR and FT-Raman spectra of this compound are assigned to the various modes of vibration. Most of the modes have wave numbers in the range suggested by previous assignments found in literature in the case of related molecules. The bond lengths lie between the values for the single and double bonds are typical of aromatic compounds. The HOMO–LUMO energy gap calculated at the B3LYP/6-311G(d,p) level reveals the chemical activity and kinetic stability of the molecule. The thermodynamic calculations reveal that all the thermodynamic parameters increase with increase in temperature.

References

1. Diego M. Gil, M.E. Defonsi Lestard, O. Estévez-Hernández, J. Duque, E. Reguera *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 145 (2015) 553–562.
2. Yanagisawa, M. Kurihara, H. Kimura, S. Tomobe, Y. Kobayashi, M. Mitsui, Y. Goto, K. Masaki, T.A., *Nature* 332: 411 (1988).
3. Laane, J., *J. Phys. Chem.* **104A**: 7715 (2000).
4. Caminati, W., Damiani, D., Favero, L.B., *Mol. Phys.* **79**: 699 (1993).
5. Leal, L.A., Alonso, J.L., Lister, D.G., Lopez, J.C., *Mol. Phys.* **81**: 1205 (1994).
6. Duckett, J.A., Smithson, T.L., Wieser, H., *Chem. Phys. Lett.* **64**: 261 (1979).
7. Caminati, W., Melandri, S., Corebelli, G., Favero, L.B., Meyer, R., *Mol. Phys.* **80**: 1297 (1993).
8. Sakurai, S., Meinander, N., Morris, K., Laane, J., *J. Am. Chem. Soc.* 121: 5056 (1999).
9. Panicker et al., *Orient. J. Chem.*, Vol. 28(2), 1037-1041 (2012).
10. Mounir A. Salem, Magda I. Marzouk and Naglaa F. Mahmoud *J. Serb. Chem. Soc.* 79 (9) 1059–1073 (2014).
11. C.yohannan Panicker, Hema Tresa Varghese and Y. Sheena Mary *Orient. J. Chem.*, Vol. 28(2), 1037-1041 (2012).
12. Yang Shu, Xiang JunFeng, Yang QianFan, Zhou QiuJu, Zhang XiuFeng, Li Qian, Tang YaLin & XU GuangZhi *March 2011 Vol.56 No.7*: 613–617.
13. M. Agostinha R. Matos, Clara C. S. Sousa, and Victor M. F. Morais *J. Chem. Eng. Data* 2007, 52, 1089-1094.
14. Jaebum Choo *Journal of Molecular Structure* 597 (2001) 232- 240.
15. Gaussian 09: Frisch, M. J. Trucks, G. W. Schlegel, H. B. Scuseria, G. E. Robb, M. A. Cheeseman, J. R. Scalmani, G. Barone, V. Mennucci, B. Petersson, G. A.; Nakatsuji, H. Caricato, M. Li, X. Hratchian, H. P. Izmaylov, A. F. Bloino, J. Zheng, G. Sonnenberg, J. L. Hada, M. Ehara, M. Toyota, K. Fukuda, R. Hasegawa, J. Ishida, M. Nakajima, T. Honda, Y. Kitao, O. Nakai, H. Vreven, T. Montgomery, J. A., Jr. Peralta, J. E. Ogliaro, F. Bearpark, M. Heyd, J. J. Brothers, E. Kudin, K. N. Staroverov, V. N. Kobayashi, R. Normand, J. Raghavachari, K. Rendell, A. Burant, J. C. Iyengar, S. S. Tomasi, J. Cossi, M. Rega, N. Millam, N. J. Klene, M. Knox, J. E. Cross, J. B. Bakken, V. Adamo, C. Jaramillo, J. Gomperts, R. Stratmann, R. E. Yazyev, O. Austin, A. J. Cammi, R. Pomelli, C. Ochterski, J. W. Martin, R. L. Morokuma, K. Zakrzewski, V. G. Voth, G. A. Salvador, P. Dannenberg, J. J. Dapprich, S. Daniels, A. D. Farkas, Ö. Foresman, J. B. Ortiz, J. V. Cioslowski, J. Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
16. D. AI. Wiles, B. A. Ginkasa, X D T. Suprlnchuk *Canadian Journal of Chemistry*. Volume 45, 469 (1907).
17. M. Honda, A. Fujii, E. Fujimaki, T. Ebata and N. Nikami., *J Phys Chem.*, 2003, 107A, 3678.

18. D. Sajan, J. Binoy, B. Pradeep, K. Venkatakrisnan, V.Ksrths, I.Joe, V. Jayakumar, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 60 (2004) 173- 180.
19. Ilango G, Arivazhagan M, Joseph Prince J & Balachandran N, Indian J Pure & Appl Phy, 46 (2008) 698.
20. Mizi Fan, Dasong Dai and Biao Huang (2012). Fourier Transform Infrared Spectroscopy for Natural Fibres, Fourier Transform - Materials Analysis, Dr Salih Salih (Ed.), ISBN: 978-953-51-0594-7.
21. Pratim K. Chattaraj, Andre´s Cedillo and Robert G. Parr J. Chem. Phys. Vol 103. No 17 1 November 1995.
22. Ralph G. Pearson Proc. Natl. Acad. Sci. USA 83 (1986).
23. Xian-Wei Li, Etsuro Shibata and Takashi Nakamura Materials Transactions, Vol. 44, No. 5 (2003) pp. 1004 to 1013.
24. Davood Nori-Shargh, Fatemeh-Rozita Ghanizadeha, Maryam Malek Hosseinib, Farzad Deyhimic, Journal of Molecular Structure: THEOCHEM Volume 808, Issues 1–3, 30 April 2007, Pages 135–144.