

Evaluation of Molecular Structure and Properties of Acetylacetonethiosemicarbazone Using DFT Approach: Exploring Quantum Chemistry for Futuristic Applications

Karnica Srivastava¹, Tahmeena Khan^{2*}

¹Department of Physics, Isabella Thoburn College, Lucknow; ²Department of Chemistry, Integral University, Lucknow

ABSTRACT

Thiosemicarbazone ligands are important Schiff bases and their utility has been studied since a long time. This paper presents the evaluation of molecular structure and properties of 2-(4-oxopent-2-ylidene) hydrazinecarbothioamide (acetylacetonethiosemicarbazone) ligand using the density functional theory (DFT) calculations. B3LYP data set was used for the DFT based evaluation. Primary hyperconjugative interactions were the donation of electron pair from a lone pair orbital LP(1) N₁₅→σ*S₁₂-C₁₄, LP(1)N₁₅→π*N₁₇-C₁₈, and LP(2)O₂₁→σ*C₂₀-C₂₂ leading to the stabilization of the ligand molecule with the energy of 63.91, 28.16, and 22.74 kcal/mol, respectively. The molecular electrostatic potential (MEP) analysis showed that hydrogen atoms act as nucleophilic centers and oxygen (O₂₁) and sulfur (S₁₂) atoms act as the electrophilic centers of ligand, respectively. The non-linear optical (NLO) evaluation showed that the β_o value calculated for ligand is 0.436 × 10⁻³⁰ e.s.u. which was better than the β_o value of urea, that is, 0.1947 × 10⁻³⁰ e.s.u. which is a standard NLO material. Therefore, the ligand molecule might be used as NLO material in future.

Key words: Thiosemicarbazone, Schiff base, Density function theory, Non-linear optical and MEP surface analyses.

1. INTRODUCTION

There has been a constant and significant improvement in the field of medicinal chemistry and drug designing through a computational approach. When working at the quantum mechanical level, the study of biological systems requires such evaluation tools that provide momentous information in a time-effective manner. Computational chemistry and evaluation tools have received considerable attention in the past few years [1]. Quantum chemistry and mechanical simulations are helpful in the characterization of novel compounds and materials. Quantum studies enable us to envisage the structure of a chemical entity with the help of computer-aided software's. The quantum chemistry based simulations may also help in the validation of experimental data. Using a semi-empirical and density functional theory (DFT)-based approach, different properties of a compound can be explored [2]. Thiosemicarbazones are considered to be a great interest due to its antifungal, antibacterial, antiviral, antimalarial, and antitumor activities. The biological activities of thiosemicarbazone are considered to be their ability to form chelates with metals. Hence, the biological activities of metal complexes are different from those of either ligands or the metal ions. In the present manuscript, different properties of acetylacetonethiosemicarbazone are studied through DFT. DFT offers a high level of accuracy in a lesser time and is also cost-effective. DFT has emerged as an important tool for structural elucidation and to comprehend the mechanistic approach [3]. The accuracy of the DFT derived data has been studied extensively. Geometries of small molecules have been accurately predicted by DFT demonstrating its suitability to predict geometries of drug molecules. Various studies have been performed comparing DFT calculations and experimental values which reveal the suitability of the DFT technique [4]. The BP86 functional has been most widely studied in this field. This paper presents the DFT based calculations to elucidate

the structure and understand the important properties of acetylacetonethiosemicarbazone ligand. Thiosemicarbazones are important Schiff bases with an array of medicinal properties [5]. Due to their bi, tri, or multidentate nature, they can bind with metal ions in different oxidation states [6]. They have N, S, or O donor atoms in their structure which coordinates easily and effectively with the metal ions.

2. MATERIALS AND METHODS

The 2-(4-oxopent-2-ylidene) hydrazinecarbothioamide (acetylacetonethiosemicarbazone) ligand is selected for study the molecular structure and its properties which were synthesized and also characterized in the previous published paper [7-10].

2.1. DFT Calculations

The use of DFT has become one of the most precise tools to study the properties of the molecule [11]. It has been also found that DFT gives more accurate results in comparison to the *ab initio* Hartree-Fock (HF) method [12]. Computational results provide supportive evidence to the experimental observations. DFT method along with Becke's three-parameter (local, non-local, and HF) with Lee *et al.* hybrid correlation functional (B3LYP) [13-15] was adopted to study

*Corresponding author:

E-mail: tahminakhan30@yahoo.com

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the various properties of acetylacetone thiosemicarbazone ligand. Gaussian 09 program employing 6-31G (d and p) was used to study the molecular structure of the ligand and its various properties. Pictorial visualization and confirmation of the calculated data were done using Gauss view software [16].

3. RESULTS AND DISCUSSION

3.1. Geometry Optimization and Energies

The chemical structure of 2-(4-oxopentan-2-ylidene)hydrazinecarbothioamide (acetylacetone thiosemicarbazone) is shown in Figure 1. Ground optimized molecular structure of the ligand is shown in Figure 2. The molecular energy of the optimized structure of the acetylacetone thiosemicarbazone obtained through DFT was -872.93760465 a.u. The optimized geometrical parameters such as bond length, bond angle, and dihedral angles using the DFT method are compared with the experimental geometry obtained using crystal data of ligand are shown in Table 1. The difference between experimental and calculated values of bond length was not more than 1.60 \AA . The bond angle and dihedral angle differed not more than 4.7° and 67.1° , respectively.

3.2. Natural Bond Orbital (NBO) Analysis

NBO analysis has been performed to study the role of intermolecular and intramolecular orbital interaction in the complex, particularly the charge transfer. The analyzes of NBOs such as lone pair (n), bonding (σ), and anti-bonding (σ^*) orbitals can give information about the population of electrons in an atom, bond order between the atoms, the strength of non-covalent interactions, and types of orbital overlapping. Using the second-order perturbation theory, some of the electron donor and acceptor orbital's with their occupancies and interaction stabilization energies $E^{(2)}$ are reported. The higher value of hyper conjugative interaction energy $E^{(2)}$ results in the more intensive interaction between the electron donor to electron acceptor [17]. The hyper conjugative interaction energy was deduced from the second-order perturbation approach (Equation 1).

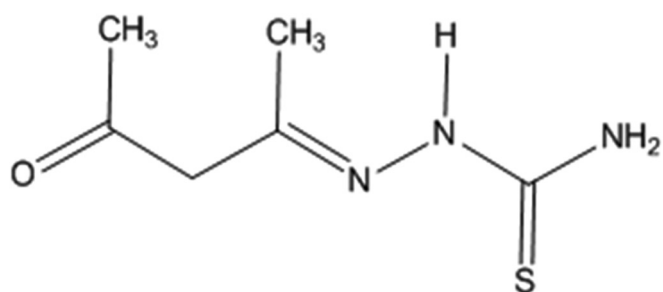


Figure 1: Chemical structure of acetylacetone thiosemicarbazone.

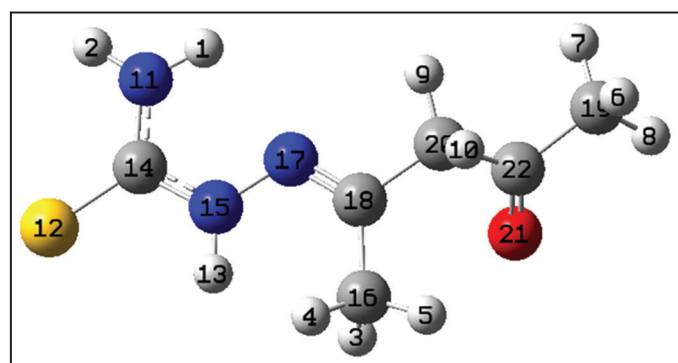


Figure 2: Optimized structure of acetylacetone thiosemicarbazone.

$$E^{(2)} = -q_i \left[\frac{(F_{ij})^2}{\epsilon_j - \epsilon_i} \right] \quad (1)$$

where, q_i is the donor orbital occupancy, ϵ_i and ϵ_j diagonal elements (orbital energies), and F_{ij} is the off-diagonal NBO Fock-matrix element. The second-order perturbation theory analyzes of the Fock matrix, in the NBO basis for acetylacetone thiosemicarbazone, are presented in Table 2.

The intramolecular hyper conjugative interactions are formed by the orbital overlap between σ and π electrons of (C-C) bonds and antibonds lead to the stabilization of the system. The intra-molecular hyper conjugative interaction of $\sigma_{S_{12}-C_{14}} \rightarrow \sigma^*_{S_{12}-C_{14}}$ and $\sigma_{C_{18}-C_{20}} \rightarrow \sigma^*_{N_{15}-N_{17}}$ leads to the stabilization energy of 6.87 and 5.96 kcal/mol. Primary hyper conjugative interactions are the electron donations from a lone pair orbital $LP(1) N_{15} \rightarrow \sigma^*_{S_{12}-C_{14}}$, $LP(1) N_{15} \rightarrow \pi^*_{N_{17}-C_{18}}$, and $LP(2) O_{21} \rightarrow \sigma^*_{C_{20}-C_{22}}$ leading to the stabilization of the acetylacetone thiosemicarbazone with the energy of 63.91, 28.16, and 22.74 kcal/mol, respectively.

3.3. Non-linear Optical (NLO) Properties

NLO phenomena, for instance, the capacity to alter the frequency of light or to intensify one source of light with another, are possibly valid in photonic technology to manufacture components beneficial in computer networks and telecommunication systems. In this context, new inorganic and organic NLO materials have been developed during the past 15 years to reach the best figures of merit. The large hyperpolarizabilities and NLO properties have made organic molecules of great interest as NLO materials [18]. At present, the requirement of NLO materials is more than other materials because of their applications in optoelectronics and photonics. Particularly, the organic NLO crystals are attracted attention as a consequence of the low cost and flexibility of molecular design, which we require for applications with using suitable donors and acceptors. NLO parameters static dipole moment (μ), mean polarizability (α_0), the anisotropy of polarizability ($\Delta\alpha$), and first hyperpolarizability (β_0) are calculated with the help of subsequent equations (2–5).

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (2)$$

$$|\alpha_0| = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3)$$

$$\Delta\alpha = 2^{-1/2} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2 \right]^{1/2} \quad (4)$$

$$\beta = \sqrt{[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]} \quad (5)$$

Hence, the x, y, and z components of α_0 and β_0 of Gaussian 09 output are reported in a.u., the calculated values should be converted into electrostatic units (e.s.u) using the conversion factor as (for α_0 1 a.u. = 0.1482×10^{-24} e.s.u; for β_0 : 1 a.u. = $0.0086393 \times 10^{-30}$ e.s.u.) the values of μ , α_0 , $\Delta\alpha$, and β_0 : of acetylacetone thiosemicarbazone are listed in Table 3.

The magnitude of molecular hyperpolarizability β is one of the key factors in NLO system. Urea is the reference molecule that is used in the study of the NLO properties of molecular systems. Hence, it is used

Table 1: Comparison of experimental and calculated parameters of acetylacetone thiosemicarbazone.

Parameters		Experimental	Calculated optimized parameter B3LYP/6-31G (d, p)
Bond length (Å°)			
R1	R (H ₁ -N ₁₁)	1.01	1.01158
R2	R (H ₂ -N ₁₁)	1.0055	1.01224
R3	R (H ₃ -C ₁₆)	1.0962	1.11315
R4	R (H ₄ -C ₁₆)	1.0976	1.11260
R5	R (H ₅ -C ₁₆)	1.0902	1.11378
R6	R (H ₅ -O ₂₁)	2.8629	1.25725
R7	R (H ₆ -C ₁₉)	1.0956	1.11306
R8	R (H ₇ -C ₁₉)	1.0965	1.11258
R9	R (H ₈ -C ₁₉)	1.0905	1.11294
R10	R (H ₉ -C ₂₀)	1.0954	1.11292
R11	R (H ₁₀ -C ₂₀)	1.1012	1.11239
R12	R (N ₁₁ -C ₁₄)	1.3453	1.36927
R13	R (S ₁₂ -C ₁₄)	1.6789	1.57523
R14	R (H ₁₃ -N ₁₅)	1.0135	1.01161
R15	R (C ₁₄ -N ₁₅)	1.3738	1.36925
R16	R (N ₁₅ -N ₁₇)	1.3636	1.35263
R17	R (C ₁₆ -C ₁₈)	1.5076	1.49765
R18	R (N ₁₇ -C ₁₈)	1.2876	1.25947
R19	R (C ₁₈ -C ₂₀)	1.505	1.49658
R20	R (C ₁₉ -C ₂₂)	1.5167	1.50928
R21	R (C ₂₀ -C ₂₂)	1.5339	1.51005
R22	R (O ₂₁ -C ₂₂)	1.2153	1.20760
Bond angle (°)			
A1	A (H ₁ -N ₁₁ -H ₂)	121.8819	120.01941
A2	A (H ₁ -N ₁₁ -C ₁₄)	119.7027	120.01147
A3	A (H ₂ -N ₁₁ -C ₁₄)	118.224	119.96912
A4	A (N ₁₁ -C ₁₄ -S ₁₂)	124.7722	120.04448
A5	A (N ₁₁ -C ₁₄ -N ₁₅)	115.0492	119.96974
A6	A (S ₁₂ -C ₁₄ -N ₁₅)	120.1768	119.98578
A7	A (H ₁₃ -N ₁₅ -C ₁₄)	115.8364	120.02347
A8	A (H ₁₃ -N ₁₅ -N ₁₇)	123.0067	119.98190
A9	A (C ₁₄ -N ₁₅ -N ₁₇)	121.0619	119.99463
A10	A (H ₃ -C ₁₆ -H ₄)	108.2324	109.53237
A11	A (H ₃ -C ₁₆ -H ₅)	106.9885	109.47586
A12	A (H ₃ -C ₁₆ -C ₁₈)	110.9127	109.45286
A13	A (H ₄ -C ₁₆ -H ₅)	108.2121	109.44281
A14	A (H ₄ -C ₁₆ -C ₁₈)	111.1171	109.44566
A15	A (H ₅ -C ₁₆ -C ₁₈)	111.2194	109.47777
A16	A (N ₁₅ -N ₁₇ -C ₁₈)	118.5327	119.98752
A17	A (C ₁₆ -C ₁₈ -N ₁₇)	124.5383	120.00104
A18	A (C ₁₆ -C ₁₈ -C ₂₀)	119.4422	120.01351
A19	A (N ₁₇ -C ₁₈ -C ₂₀)	116.0194	119.98545
A20	A (H ₆ -C ₁₉ -H ₇)	106.9169	109.53983
A21	A (H ₆ -C ₁₉ -H ₈)	110.0164	109.50355

(Contd...)

Table 1: (Continued.)

Parameters		Experimental	Calculated optimized parameter B3LYP/6-31G (d, p)
Bond angle(°)			
A22	A (H ₆ -C ₁₉ -C ₂₂)	111.085	109.42401
A23	A (H ₇ -C ₁₉ -H ₈)	109.2729	109.46112
A24	A (H ₇ -C ₁₉ -C ₂₂)	109.7944	109.43164
A25	A (H ₈ -C ₁₉ -C ₂₂)	109.7025	109.46712
A26	A (H ₉ -C ₂₀ -H ₁₀)	106.3363	109.56421
A27	A (H ₉ -C ₂₀ -C ₁₈)	109.6184	109.47211
A28	A (H ₉ -C ₂₀ -C ₂₂)	109.2117	109.42987
A29	A (H ₁₀ -C ₂₀ -C ₁₈)	110.5407	109.47074
A30	A (H ₁₀ -C ₂₀ -C ₂₂)	107.1123	109.39270
A31	A (C ₁₈ -C ₂₀ -C ₂₂)	113.7329	109.49765
A32	A (C ₁₉ -C ₂₂ -C ₂₀)	115.9864	119.99943
A33	A (C ₁₉ -C ₂₂ -O ₂₁)	122.146	120.02194
A34	A (C ₂₀ -C ₂₂ -O ₂₁)	121.8676	119.97863
Dihedral angle (°)			
D1	D (H ₁ -N ₁₁ -C ₁₄ -S ₁₂)	-177.5068	180.00000
D2	D (H ₁ -N ₁₁ -C ₁₄ -N ₁₅)	2.9793	0.00000
D3	D (H ₂ -N ₁₁ -C ₁₄ -S ₁₂)	-2.4388	0.00000
D4	D (H ₂ -N ₁₁ -C ₁₄ -N ₁₅)	178.0472	180.00000
D5	D (N ₁₁ -C ₁₄ -N ₁₅ -H ₁₃)	-178.3797	180.00000
D6	D (N ₁₁ -C ₁₄ -N ₁₅ -N ₁₇)	-1.8198	0.00000
D7	D (S ₁₂ -C ₁₄ -N ₁₅ -H ₁₃)	2.0821	0.00000
D8	D (S ₁₂ -C ₁₄ -N ₁₅ -N ₁₇)	178.6421	180.00000
D9	D (H ₁₃ -N ₁₅ -N ₁₇ -C ₁₈)	-4.6779	0.00000
D10	D (C ₁₄ -N ₁₅ -N ₁₇ -C ₁₈)	179.0145	180.00000
D11	D (H ₃ -C ₁₆ -C ₁₈ -N ₁₇)	67.084	60.00156
D12	D (H ₃ -C ₁₆ -C ₁₈ -C ₂₀)	-113.0311	-119.99844
D13	D (H ₄ -C ₁₆ -C ₁₈ -N ₁₇)	-53.3553	-60.04643
D14	D (H ₄ -C ₁₆ -C ₁₈ -C ₂₀)	126.5296	119.95357
D15	D (H ₅ -C ₁₆ -C ₁₈ -N ₁₇)	-173.976	180.00000
D16	D (H ₅ -C ₁₆ -C ₁₈ -C ₂₀)	5.9089	0.00000
D17	D (N ₁₅ -N ₁₇ -C ₁₈ -C ₁₆)	-0.6069	0.00000
D18	D (N ₁₅ -N ₁₇ -C ₁₈ -C ₂₀)	179.5046	180.00000
D19	D (C ₁₆ -C ₁₈ -C ₂₀ -H ₉)	-172.8648	119.96609
D20	D (C ₁₆ -C ₁₈ -C ₂₀ -H ₁₀)	-55.9643	-119.91973
D21	D (C ₁₆ -C ₁₈ -C ₂₀ -C ₂₂)	64.5655	0.00000
D22	D (N ₁₇ -C ₁₈ -C ₂₀ -H ₉)	7.0297	-60.03391
D23	D (N ₁₇ -C ₁₈ -C ₂₀ -H ₁₀)	123.9302	60.08027
D24	D (N ₁₇ -C ₁₈ -C ₂₀ -C ₂₂)	-115.54	180.00000
D25	D (H ₆ -C ₁₉ -C ₂₂ -C ₂₀)	51.2148	59.99181
D26	D (H ₆ -C ₁₉ -C ₂₂ -O ₂₁)	-128.8352	-120.00819
D27	D (H ₇ -C ₁₉ -C ₂₂ -C ₂₀)	-66.8337	-60.03909
D28	D (H ₇ -C ₁₉ -C ₂₂ -O ₂₁)	113.1163	119.96091
D29	D (H ₈ -C ₁₉ -C ₂₂ -C ₂₀)	173.0674	180.00000
D30	D (H ₈ -C ₁₉ -C ₂₂ -O ₂₁)	-6.9826	0.00000

(Contd...)

Table 1: (Continued.)

Parameters		Experimental	Calculated optimized parameter B3LYP/6-31G (d, p)
Bond angle(°)			
D31	D (H ₉ -C ₂₀ -C ₂₂ -C ₁₉)	50.2187	60.00805
D32	D (H ₉ -C ₂₀ -C ₂₂ -O ₂₁)	-129.7314	-119.99195
D33	D (H ₁₀ -C ₂₀ -C ₂₂ -C ₁₉)	-64.5493	-60.03248
D34	D (H ₁₀ -C ₂₀ -C ₂₂ -O ₂₁)	115.5006	119.96752
D35	D (C ₁₈ -C ₂₀ -C ₂₂ -C ₁₉)	173.0118	180.00000
D36	D (C ₁₈ -C ₂₀ -C ₂₂ -O ₂₁)	-6.9383	0.00000

Table 2: Second-order perturbation theory analysis of Fock matrix in NBO basis for acetylacetone thiosemicarbazone.

Donor NBO (i)	ED (i)/e	Acceptor NBO (j)	ED (j)/e	E (2) ^a Kcal/mol	E (j)-E (i) ^b	F (i, j) ^c
σH ₁ -N ₁₁	1.98672	π*S ₁₂ -C ₁₄	0.02023	4.93	0.96	0.062
σH ₂ -N ₁₁	1.98858	σ*C ₁₄ -N ₁₅	0.05775	4.67	1.11	0.065
σH ₃ -C ₁₆	1.97483	π*N ₁₇ -C ₁₈	0.18321	4.55	0.53	0.046
σH ₅ -C ₁₆	1.98759	σ*N ₁₇ -C ₁₈	0.01718	5.21	1.12	0.068
σH ₇ -C ₁₉	1.97108	π*O ₂₁ -C ₂₂	0.08155	5.55	0.53	0.049
σH ₁₀ -C ₂₀	1.95609	π*O ₂₁ -C ₂₂	0.08155	5.41	0.53	0.048
σS ₁₂ -C ₁₄	1.98231	σ*S ₁₂ -C ₁₄	0.49859	6.87	0.22	0.039
σC ₁₈ -C ₂₀	1.97344	σ*N ₁₅ -N ₁₇	0.03307	5.96	1.01	0.069
LP (1) N ₁₁	1.71349	σ*S ₁₂ -C ₁₄	0.49859	76.10	0.21	0.119
LP (2) S ₁₂	1.88269	σ*N ₁₁ -C ₁₄	0.04716	10.37	0.66	0.075
LP (2) S ₁₂	1.88269	σ*C ₁₄ -N ₁₅	0.05775	10.76	0.62	0.074
LP (1) N ₁₅	1.66380	σ*S ₁₂ -C ₁₄	0.49859	63.91	0.22	0.110
LP (1) N ₁₅	1.66380	π*N ₁₇ -C ₁₈	0.18321	28.16	0.28	0.083
LP (1) N ₁₇	1.92032	σ*H ₁₃ -N ₁₅	0.03371	9.38	0.83	0.080
LP (1) N ₁₇	1.92032	σ*C ₁₆ -C ₁₈	0.03115	11.15	0.79	0.085
LP (2) O ₂₁	1.88796	σ*C ₁₉ -C ₂₂	0.05409	20.45	0.65	0.104
LP (2) O ₂₁	1.88796	σ*C ₂₀ -C ₂₂	0.07347	22.74	0.63	0.108

NBO: Natural bond orbital

commonly as a threshold value for comparative purposes. The β_o value urea is 0.1947×10^{-30} e.s.u and β_o value calculated for ligand is 0.436×10^{-30} e.s.u. Therefore, the calculated result shows that acetylacetone thiosemicarbazone has a good response and might be used as NLO material in future.

3.4. Frontier Molecular Orbitals Analysis

Frontiers orbital's such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and their energies are used to predict the most reactive positions in the conjugated systems and hence also provide to define several types of reactions. HOMO and LUMO orbital's correspond to the chemical stability of the molecule. HOMO energy leads to ionization potential while LUMO energy leads to electron affinity. The electronic parameters, such as HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), and energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$), were described through theoretical calculations. HOMO-LUMO energy gap is an important index used to determine the electron transport properties [19]. The HOMO-LUMO of acetylacetone thiosemicarbazone and its energy gap is shown in Figure 3.

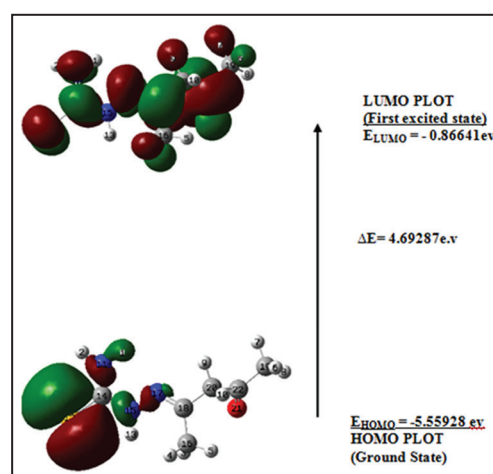


Figure 3: HOMO-LUMO plot for acetylacetone thiosemicarbazone with orbitals involved in electronic transitions. HOMO: Highest occupied molecular orbital, LUMO: Lowest unoccupied molecular orbital.

The value of the energy gap indicates molecular stability. The energy gap also predicts the intramolecular charge transfer.

3.5. Molecular Electrostatic Potential Surface (MEPS)

The MEPS serves as a useful quantity to explain the polarization and charge transfer effects within the molecule. It also explains the hydrogen bonding and reactivity of molecules. It can be used to analyze the electrophilic and nucleophilic sites [20] within the molecule where chemical reactions are likely to take place. It gives a pictorial method to recognize the relative polarity of the molecule. MEPS is also calculated at the same level of theory. MEP $V(r)$

Table 3: Calculated dipole moment (μ), polarizability (α_0), anisotropy of the polarizability ($\Delta\alpha$), and the mean first-order hyperpolarizability (β_0) using B3LYP/6-31G (d, p).

Property	Acetylacetone thiosemicarbazone
μ_x	5.8909 Debye
μ_y	-2.4858 Debye
μ_z	-2.7353 Debye
μ	0.6698 Debye
α_{xx}	-86.8755 a.u.
α_{yy}	-62.9367 a.u.
α_{zz}	-76.4883 a.u.
α_{xy}	2.1307 a.u.
α_{xz}	-4.2672 a.u.
α_{yz}	-2.5615 a.u.
α_0	11.17924×10^{-24} e.s.u.
$\Delta\alpha$	77.24969×10^{-24} e.s.u.
β_{xxx}	144.2089 a.u.
β_{xyy}	-9.3021 a.u.
β_{xzz}	6.2839 a.u.
β_{yyy}	-18.1292 a.u.
β_{xyx}	-44.9642 a.u.
β_{yzz}	-1.034 a.u.
β_{zzz}	-1.9244 a.u.
β_{xxz}	-23.9011 a.u.
β_{yyz}	-0.7612 a.u.
β_{xyz}	-5.297 a.u.
β_0	0.436×10^{-30} e.s.u.

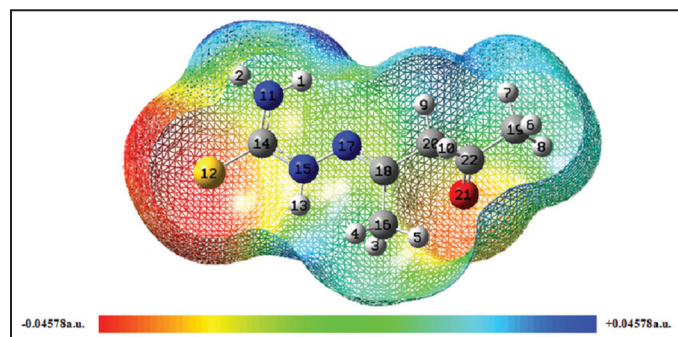


Figure 4: Molecular electrostatic potential surface formed by mapping of total density over electrostatic potential in the gas phase of acetylacetone thiosemicarbazone.

generated through the molecules, electrons, and nuclei are given by the expression:

$$V(r) = \sum_A \frac{Z_A}{|R_A - \vec{r}|} - \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} dr' \quad (6)$$

where Z_A is the charge on nucleus A, located at R_A and $\rho(r')$ is the electronic density function for the molecule. It correlates with the dipole moment, electronegativity, partial charges, and the site of chemical reactivity of the molecule. Different values of the electrostatic potential at the surface are represented by different colors: Red represents the region of negative electrostatic potential, blue represents the region of most positive electrostatic potential, and green color represent the region of zero potential. Potential increases in the following order red < orange < yellow < green < blue. The color code of the MEP map of acetylacetone thiosemicarbazone lies in the range between -0.04578 a.u. and $+0.04578$ a.u. MEP surface of the ligand is shown in Figure 4.

According to the result, blue shade is mainly over hydrogen atoms which are nucleophilic center and red shade is localized over oxygen (O_{21}) and sulfur (S_{12}) atoms which are the major electrophilic center of acetylacetone thiosemicarbazone, respectively.

4. CONCLUSION

The synthesis and characterization of 2-(4-oxopent-2-ylidene)hydrazinecarbothioamide (acetylacetone thiosemicarbazone) were reported in the previous paper. The present manuscript is used to evaluate the molecular structure and different properties of the acetylacetone thiosemicarbazone using quantum chemical calculation such as DFT. According to NBO calculation, the intramolecular interaction such as $\sigma_{S_{12}-C_{14}} \rightarrow \sigma^*_{S_{12}-C_{14}}$ and $\sigma_{C_{18}-C_{20}} \rightarrow \sigma^*_{N_{15}-N_{17}}$ and primary hyper conjugative interactions such as $LP(1)N_{15} \rightarrow \sigma^*_{S_{12}-C_{14}}$, $LP(1)N_{15} \rightarrow \pi^*_{N_{17}-C_{18}}$, and $LP(2)O_{21} \rightarrow \sigma^*_{C_{20}-C_{22}}$ stabilize the acetylacetone thiosemicarbazone with the energy of 63.91, 28.16, and 22.74 kcal/mol, respectively. The calculated value of hyperpolarizability (β_0) was 0.436×10^{-30} e.s.u. which indicates that acetylacetone thiosemicarbazone has the potential to be used for NLO applications. The HOMO and LUMO energy provide information regarding ionization potential and electron affinity. From the MEPS, it was seen that the negative potential (red) is localized over oxygen (O_{21}) and sulfur (S_{12}) atoms which act as electrophilic centers and the positive region (blue) is localized over hydrogen (H) atoms which act as nucleophilic center. Thus, the present investigation may provide a complete reliable structural study of acetylacetone thiosemicarbazone, which may be further used to analyze similar ligands for designing new drugs in future.

5. CONFLICT OF INTEREST

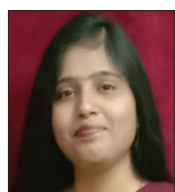
None declared.

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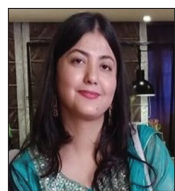
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*Bibliographical Sketch



Dr. Karnica Srivastava, is currently working as an Assistant Professor, in the Department of Physics, Isabella Thoburn College, Lucknow. She has done her Ph.D. from the Department of Physics, University of Lucknow. Her research work was based on Studying the Structural Properties of Pharmaceutical cocrystals using Vibrational spectroscopy and Quantum Chemical Calculation. She has been a recipient of UGC-BSR scholarship. She has published 12 research papers in International reputed journals and 3 chapters in Conference proceeding. She has received awards for Best oral presentation in International Conference and for Best research papers. She has participated in 20 conferences, 14 workshops and 11 seminars/webinars.



Dr. Tahmeena Khan is currently working as an Assistant Professor, in the Department of Chemistry, Integral University. A gold medallist in her master's course, she holds a specialization in Inorganic Chemistry. She specialized in Magnetic Resonance Spectroscopy and Magnetic Resonance Imaging for her M.Phil. and worked on automated 3D structure determination of proteins for dissertation. For her doctoral degree, she worked on mixed ligand-metal and mixed metal-ligand complexes of thiosemicarbazones and their therapeutic properties. She holds thirteen years of teaching experience and has supervised several dissertations of M.Sc. students. She has a number of research papers and chapters to her credit, and has edited two international books and two conference proceedings.