**A DFT Study of (2Z,3Z)-1,4-dithiane-2,3-dionedioxime**

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| **Abstract**In this study, electronic structures vicinal dioxime were studied by DFT calculations. Structural and electronic parameters of the complexes were determined by using Gaussian 09 program. First of all, geometric parameters (bond length, bond angle, torsion angle) of the most stable form of the complex were determined with mPW1PW91 iop(3/76=0572004280) / gen [S: cc-pvqz, C and H: 6-31+g(d,p), N: 6-31+g(2d), O: cc-pvqz] level. The theoretical frontier molecular orbital descriptors such as electronegativity, chemical potential, softness, electrophilicity index, and electron affinity of the title compound were calculated with the same level. In addition, the total and partial density of state distribution (TDOS, PDOS) of the molecular orbitals, molecular electronic potential surface map (MEP) and nonlinear optical properties (NLO) of the compound were determined. |
| Keywords: Vicinal dioxime, Density Fuctional Theory, MEP, Nonlinear optics. |

1. **Introduction**

Vicinal dioximes refer to a class of organic compounds that contain two oxime (nitrogen-oxygen) functional groups positioned on adjacent carbon atoms in a molecule. The presence of these adjacent oxime groups contributes to the amphoteric nature of vicinal dioximes (vic-dioximes). Vic-dioximes have diverse applications across multiple branches of chemistry: coordination chemistry, biological research, analytical, organic and medicinal chemistry. Vic-dioximes serve as intermediate compounds in organic synthesis, contributing to the construction of various organic molecules. Vic-dioximes, particularly in the form of metal complexes, hold potential applications in medical chemistry [1]. They could be used as drug carriers or contrast agents. Due to their ability to mimic specific biological functions [2], vic-dioximes are employed in biological research [3, 4]. They can model reactions found in biological systems, such as the reduction of vitamin B12 [5]. Coordination compounds, including those involving vic-dioximes, can be utilized in analytical chemistry [6]. They may serve in sensors designed to detect or identify specific metals [7].

However, the detailed Density Functional Theoretical (DFT) studies on the complete structural and electronic studies of the title compound have not appeared yet in the literature for a derivative of vic-dioxime molecule, (2Z,3Z)-1,4-dithiane-2,3-dionedioxime (Fig.1.). Determination of the structural and electronic characteristics of a small molecule derivative of vic-dioximes will serve as an introductory study for the ongoing complexes with this molecule. Therefore, in this study, DFT investigations of vic-dioxime molecules have been conducted. DFT calculations were performed in order to clarify molecular structures, frontier molecular orbitals (FMOs), map of molecular electrostatic potential (MEP) and nonlinear optical properties (NLO) of the title molecules.

1. **Calculations**

The quantum chemical calculations were performed using Gaussian 09 software [8] by DFT level using the Lee-Yang-Parr correlation functional mPW1PW91 methods [9] with iop(3/76=0572004280) / gen [S: cc-pvqz, C and H: 6-31+g(d,p), N: 6-31+g(2d), O: cc-pvqz] level. Superior basis sets yielding better results for each atom have been selected based on the information available in the literature. Computed molecular structures of the conformers were drawn with the CYLview program [10].

Electronic parameters, along with the distribution of partial and total density of states, were computed and illustrated on the molecular electronic surface map at an equivalent level. To assess the contributions of the moieties to frontier orbitals, calculations have been performed for both total and partial density of states (TDOS and PDOS). To quantify the contributions of the moieties to frontier orbitals, the total and partial density of states have been calculated. The determination of the contribution of groups to molecular orbitals, along with the calculated percentage contributions, is achieved by analysing TDOS and PDOS graphs generated using the GaussSum program [11]. The groups of C=N, O-H, and other atoms have been partitioned.

Molecular electrostatic potential V(r) is defined by the electronic density function: and ZA is the charge on the nucleus A, located at RA [12–14].

 (1)

To examine and gather data regarding regions of varying charge within the molecule, theoretical calculations were employed to analyze the map of molecular electrostatic potential.

The parameters determining the nonlinear optical properties have been calculated using the following equations: the dipole moment (µ), the polarizability (αtot) and the first hyperpolarizability (βtot)

µ = (µx2+ µy2 + µz2)1/2 (2)

αtot = 1/3 (αxx + αyy + αzz) (3)

βtot = (βx+βy+βz)1/2 (4)

In the context, βi is characterized as

βi = (βiii+ βijj+ βikk) i, j, k = x, y, z. (5)

where the x, y, and z components of came from the output of a Gaussian 09.

1. **Results and Discussion**
	1. **Structural properties**

In order to determine the possible conformations of (2Z,3Z)-1,4-dithiane-2,3-dionedioxime, all possible conformers of the three tautomeric forms of the title compound were fully optimized at the MPW1PW91 iop(3/76=0572004280) / gen [S: cc-pvqz, C and H: 6-31+g(d,p), N: 6-31+g(2d), O: cc-pvqz] level. The relative abundances (the population of the different conformers) of the possible conformers were calculated using the

 

**Figure 1.** The geometric structures of three different conformers of the title molecule. The structure were drawn using CYLview 1.0b [10].

Boltzmann distribution equation:

 (5)

According to the Boltzman distribution, conformer number **1** is the 99 percent most stable conformer (Table 1.)

**Table 1.** Calculated lattice parameters, bulk modulus (B), pressure derivatives of bulk modulus (B’) formation for DyAg compound.

|  |  |  |
| --- | --- | --- |
| **Conformers** | **Total Energy (a.u.)** | **Percentage %** |
| **1** | -1212.266634 | 0.99 |
| **2** | -1212.266743 | 0.01 |
| **3** | -1212.271549 | 0.01 |

* 1. **Molecular orbital studies**

The molecular characteristics of the specified compound were determined by calculating frontier molecular orbital descriptors using Koopmans equations [15, 16]. These equations involve parameters such as chemical potential (μ), chemical hardness (η), global softness (S), and electrophilicity index () to assess the reactivity and stability of the complexes. A comprehensive list of these descriptors for the compound can be found in Table 2. (μ=(EHOMO+ELUMO)/2, η=(EHOMO-ELUMO)/2, S=1/η and = μ2/2η).

As seen, although IP is 6.10 ev, softness is 0.22 ev-1, ΔEHOMO-LUMO was calculated as -4.52eV.

**Table 2.** Calculated molecular orbital discriptors of the compound.

|  |  |
| --- | --- |
| **Molecular Properties (eV)** | **Ligand** |
| ELUMO | -1.58 |
| EHOMO | -6.10 |
| ΔEHOMO-LUMO | -4.52 |
| Ionisation Potential (IP) | 6.10 |
| Electron Affinity (EA) | 1.58 |
| Chemical Hardness (η) | 2.26 |
| Electronegativity (χ) | 3.84 |
| Chemical Potential (μ) | -3.84 |
| Softness (S) ev-1 | 0.22 |
| Electrophilicity index (ω) | 3.26 |

**Table 3.** The calculated contributions percentage of molecular orbitals HOMO-LUMO

|  |  |  |  |
| --- | --- | --- | --- |
|  | **OH** | **C=N** | **OTHER** |
| LUMO | 12 | 79 | 9 |
| HOMO | 19 | 29 | 51 |

It can be seen in Table 3. and Fig. 2. that while LUMO is on C=N, HOMO is on the ring.



**Figure 2.** The distribution of both partial and total density of states PDOS and TDOS for the compound.

* 1. **Molecular electronic potential surface map**

To explore the nucleophilic characteristics of the moleculein question, map of molecular electronic potential (MEP) surface was obtained for its ground state geometry using the same level. Map illustrates negative and positive charge contributions, with varying colors indicating different electrostatic potential values. The color scale, ranging from red(negative) to blue (positive), highlights the transition from negative to positive potential regions. The map of MEP shows that the negative potential sites are on electronegative atoms as well as the positive potential sites around the hydrogen atoms. The negative regions of the studied molecule are found around the O11, O13, N9 and N10 atoms (Fig. 3a), therefore electrophilic attack can happen to oxygen and nitrogen atoms. As can be seen from the contour picture, the potential line is in the form of denser lines in this region (Fig. 3b).



1. **b) **

**Figure 3.** Molecular electrostatic potential of the title compound a) map and b) contour

* 1. **Nonlinear optical properties**

To assess nonlinear optical effects in the compound, the electric dipole moment , average polarizability Δαtot, and first hyperpolarizability βtot were determined using the mPW1PW91 iop(3/76=0572004280) / gen [S: cc-pvqz, C and H: 6-31+g(d,p), N: 6-31+g(2d), O: cc-pvqz] level computational method. The components of these properties, as theoretically computed, are detailed in Table 3. Average polarizability was calculated as 5, and hyperpolarizability was found to be 24. Average polarizability was calculated as Δα = 244.71 (a.u.), Δα= 3.63×10−23 esu and hyperpolarizability was found to be βtot=237.47 (a.u.) and βtot = 20.52×10−31 esu. Table 3 clearly illustrates that the hyperpolarizability is influenced by the x value.

**Table 3.** The calculated electric dipole moment (), the average polarizability (Δα) and hyperpolarizability (β) of the compound.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **µ** |  |   | **β** |   |
| *µx* | 0.60 |  | *βxxx* | 93.18 |
| *µy* | -1.55 |  | *βxxy* | 58.12 |
| *µz* | 0.08 |  | *βxyy* | 83.36 |
| ***µ (D)*** | **1.67** |  | *βyyy* | -47.19 |
| **α** |   |  | *βxxz* | -3.43 |
| *αxx* | 137.07 |  | *βxyz* | 3.22 |
| *αxy* | -6.18 |  | *βyyz* | -0.43 |
| *αyy* | 114.02 |  | βxzz | 59.70 |
| *αxz* | 0.07 |  | βyzz | -25.32 |
| *αyz* | -0.06 |  | βzzz | -15.41 |
| *αzz* | 69.71 |  | βx | 236.25 |
|  |  |  | βy | -14.40 |
| **<α> (a.u.)** | **106.93** |  | βz | -19.27 |
| **Δα (a.u.)** | **244.71** |  | **βtot (a.u.)** | **237.47** |
| **Δα (×10−23 esu)** | **3.63** |   | **βtot (×10−31 esu)** | **20.52** |

α: (1 a.u.) = 0.1482 × 10−24 esu; β; (1 a.u.) = 8.6393 × 10−33 esu

1. **Conclusion**

In summary, our theoretical investigation was carried out structural conformations, frontier molecular orbitals (FMOs), map of molecular electrostatic potential (MEP) and nonlinear optical properties of the title molecule as a continuation of this study, the investigation into the molecule with metal complexes is ongoing.

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