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Calculating some electronic and spectroscopic properties of a molecular compound $C_8H_{10}N_2S$

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Original Research

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Abstract:

Some spectroscopic and electronic properties of the bioactive compound were presented using density functional theory (DFT), by depending on Gaussian software and Gauss view 6.0 using the DFT/B3LYP method with 3 - 21G (d, p) basis set. This research concerns the spectroscopic and electronic properties of the 2-ethyl-4-thioamideo pyridine (ETP) compound and UV-Vis and IR are thoroughly studied. The low energy gap between high occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) led to an increase in charge transfer. It was found that the energy gap was 0.14719 eV, and this is due to the calculated band gap decreasing with the formation of charge transfer, which is because of hydrogen bonding between the Several formations. The HOMO-LUMO the calculation presents the fact of electron density transfer. Therefore, The separation energy between HOMO and LUMO is represented as the kinetic stability and also an indicator of the reactivity of the compound.

Keywords: 2-Ethyl-4-Thioamideo pyridine; UV-Vis; IR; HOMO; LUMO

1. Introduction

2-ethyl-4-thioamideo pyridine (ETP) is one drug regimen that remains challenging due to large numbers of patients with hypothyroidism. 2-ethyl-4-thioamideo pyridine (ETP) has been associated with inhibition of thyroid hormone synthesis. That hypothyroidism produced by 2-ethyl-4-thioamideo pyridine (ETP) the molecule examined is an organic compound called 2-ethyl-4-thioamideo pyridine (ETP) ($C_8H_{10}N_2S$) and (N-methyl-N-phenylthiourea), however, is supported by its similar structure to the thiamides, propethiouracil ($C_8H_{10}N_2S$) [1]. From a Return to chart for 137 children retrospectively in Cape Town, it was found that 104 had pulmonary Tuberculosis (TB) and 33 had extrapulmonary TB [2]. Because of the development of precise density functions and its ease of application, density functional theory (DFT) has gained widespread acceptance among researchers in many fields such as physics, materials science, and chemistry [3]. The use of 2-ethyl-4-thioamideo pyridine (ETP) is not recommended for patients who have severe hepatic impairment, gastrointestinal AEs form; the majority of side reactions were reported and 50% of patients were found to be unable to tolerate 1 gram of the drug. Psychotic disorders were also detected and rare cases have been reported as in: blurred vision and optic neuritis, double vision, peripheral neuritis, and pellagra-like syndrome. It is also known; 2-ethyl-4-thioamideo pyridine (ETP) increases LFTs transiently, and causes hepatitis. However the product label also recommends avoiding alcohol, because of the potential psychotic reaction it causes [4]. Menstrual disorders in women have historically been associated with prothionamide [5]. However, 2-ethyl-4-thioamideo pyridine (ETP) and prothionamide in combination with PAS are usually avoided. In general, infrared ray (IR) refers to the visualization of the presence of functional groups in a sample. The process is done by measuring infrared rays have different wavelengths which can be absorbed through several types of bonds. Infrared are the wavelengths and frequencies required to cause the bonds in molecules to vibrate. In order to absorb infrared, the ligands must exhibit a time-related dipole [6]. Using a UV-Vis spectrometer. The absorption spectrum is measured. This spectrophotometer covers many bands of the electromagnetic spectrum, from (ultraviolet to infrared). The device includes two excitation sources: (a) deuterium lamp: for wavelengths in the range (190 - 360) nm, (b) tungsten lamp: for wavelengths in the range (360

- 1100) nm. Both lamps can be used for UV-VIS coverage. The device consists of: a monochromator to determine the wavelength that excites the sample, it also contains a grating, filters according to the required wavelength, a type detector (PMT), and a power supply [7]. According to Koopmans theory: the energy gap represents the difference between HOMO: which is the highest occupied molecular orbital and LUMO: which is the lowest unoccupied molecular orbital [8]. Ionization potential (IP) is the energy needed to remove an electron from an atom or neutral molecule. The energy produced when electrons are added to a molecule or to atom to form a negative ion is known as electron affinity [9, 10]. Study of geometry structure and shape of some complexes as water with different molecules by changing places of bonding with water and determine spectroscopic properties for these molecules by depending on Gaussian program and density functional theory. From previous expression we can determine input data for produced complex.

2. Methodology

In this section, we will make a detailed explanation of some theoretical procedures and calculations for the proposed work. In particular, using Gaussian 09 software a comprehensive demonstration of the method using density functional theory (DFT) is described.

2.1 electronic properties

Once the compound used has been engineered to be optimized, more calculations can be done later. In this case, in a procedure similar to the geometric optimization described previously, electronic calculation procedures are listed as follows:
1- The LUMO and HOMO value of a compound can be easily displayed and calculated using the molecular orbital (MO) editor selection tool, a number of orbitals can be given, thus making the desired choice (HOMO-LUMO orbitals were chosen in our case). Using the MO dialog box, you must choose method and also the file destination can be loaded. Subsequently, visualization is determined to visualize the HOMO and LUMO properties of the compound.
2- According to Koopmans theory, the energy gap represents the difference between the HOMO: that is the highest occupied molecular orbital and the LUMO: that is the lowest unoccupied molecular orbital [11].

$$E_g = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} \tag{1}$$

3- Electron affinity related to E_{LUMO} by the following equation [12]:

$$EA = -E_{\mathrm{LUMO}} \tag{2}$$

4- The ionization potential is connected to the EHOMO energy by the following equation [13]:

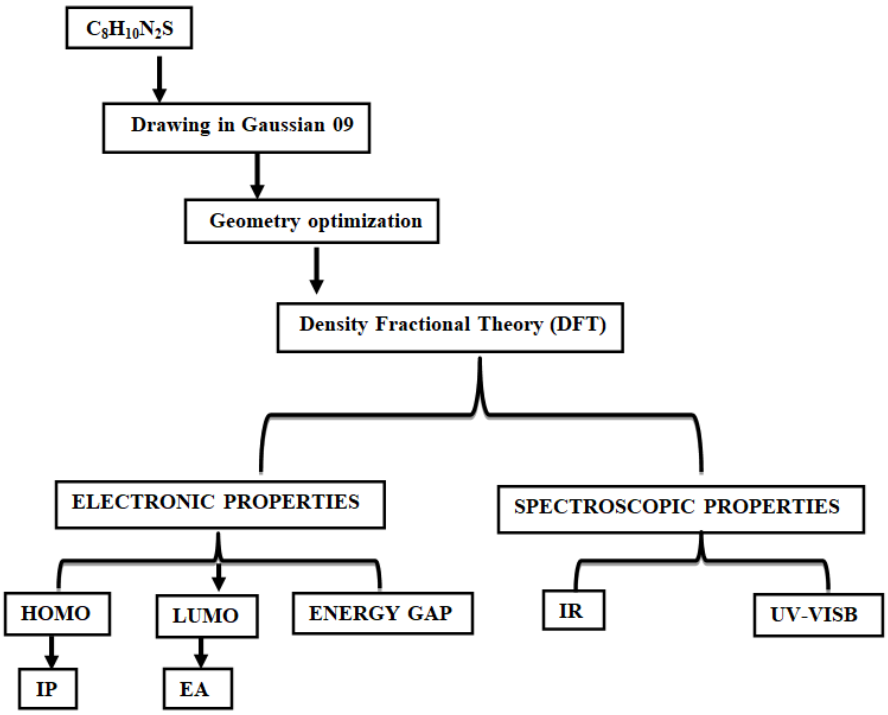
$$IP = -E_{\mathrm{HOMO}} \tag{3}$$

2.2 Spectroscopic properties

1- IR spectra calculation: the infrared spectrum can be calculated using Gaussian view. Where the same engineering optimization procedure is repeated with slight differences. Next steps describe the simulation methods in detail.
2- UV-Vis spectrum calculation: theoretical calculations of UV-visible spectrum of the optimal structure are done using the same methods and basis set.

3. Results and discussion

This section includes the theoretical results (geometrical, molecular, spectroscopic physical properties and electronic



Scheme 1. Schematic representation of computational details.

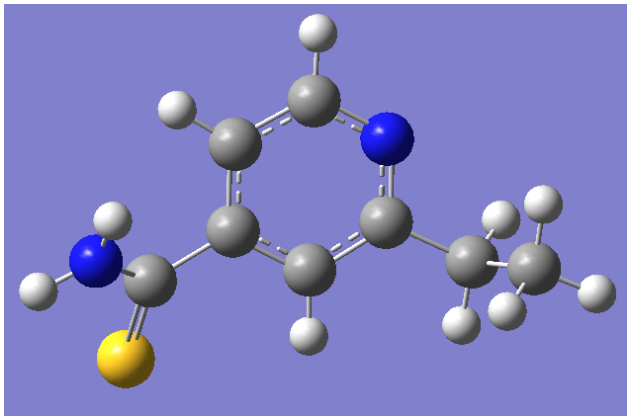


Figure 1. Optimized structure for 2-ethyl-4-thioamideo pyridine (ETP).

properties) for 2-ethyl-4-thioamideo pyridine (ETP) compounds. The results were studied and discussed by theoretical method (DFT) using Gaussian program.

3.1 Molecular structure

Gaussian program was used to calculate the optimal molecular structure of the ETP compounds associated with vibratory compensatory frequencies using the density functional theory (DFT) method and standard split-valence 3 - 21G (d, p) basis set. In addition, the exchange potential can be used for Becke's three-parameter gradient correction and the correlation potential for Lee-Yang-Parr (B3LYP) gradient correction. High stability of the optimized geometry of our compounds it has been confirmed by the wavenumber calculations that showed positive values for all wavenumber obtained.

3.2 Optimized geometry

The results of molecular structure of ETP ($C_8H_{10}N_2S$) compound were displayed in Fig. 1, Table 1. Appears the initial parameters computed by DFT. It is clear from this table and parameters that electronic energy in this method which were - 814.30943 (Hartree) and value of dipole moment 4.2111416 (Debye).

Ionization energy ($IP = -E_{\mathrm{HOMO}}$) is an important description of chemical interactions of molecules and atoms. High ionization energy indicates high chemical inertness and stability, while high interactions of molecules and atoms are known as small ionization energy. The distributions of the HOMO and LUMO energies at this method are shown in Fig. 2.

The ability to accept and give an electron is represented by

Calculation method	DFT
Basis set	3 - 21G (d,p)
Spin	Singlet
Electronic energy	- 814.30943 Hartree
Dipole moment	4.2111416 Debye

Table 1. The initial parameters computed by DFT for 2-ethyl-4-thioamideo pyridine (ETP) compound.

Property	Value (eV)
E_{LUMO}	- 0.07793
E_{HOMO}	- 0.22512
E_g	0.14719
IP	0.22512
EA	0.07793

Table 2. The electronic properties by DFT for 2-ethyl-4-thioamideo pyridine (ETP) compound.

the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), respectively, and band gap energies calculated at DFT method with 3 - 21G (d, p) basis sets are listed in Table 1. The gap value was found 0.14719 eV using DFT method. Table 2 shows the calculated value of LUMO and HOMO , which appear in Figs. 2, 4, and electronic properties for ETP compound. It also shows the difference between orbits called the energy gap. The energy gap is a parameter used to determine a molecular electrical transport property because it represents a measure of electronic conductivity. The Energy band gap (ΔE_{gap}) It is an essential parameter that gives a measure of the stability of the inhibitor molecule toward adsorption on the metal surface.

These orbitals, which are crucial for quantum chemistry,

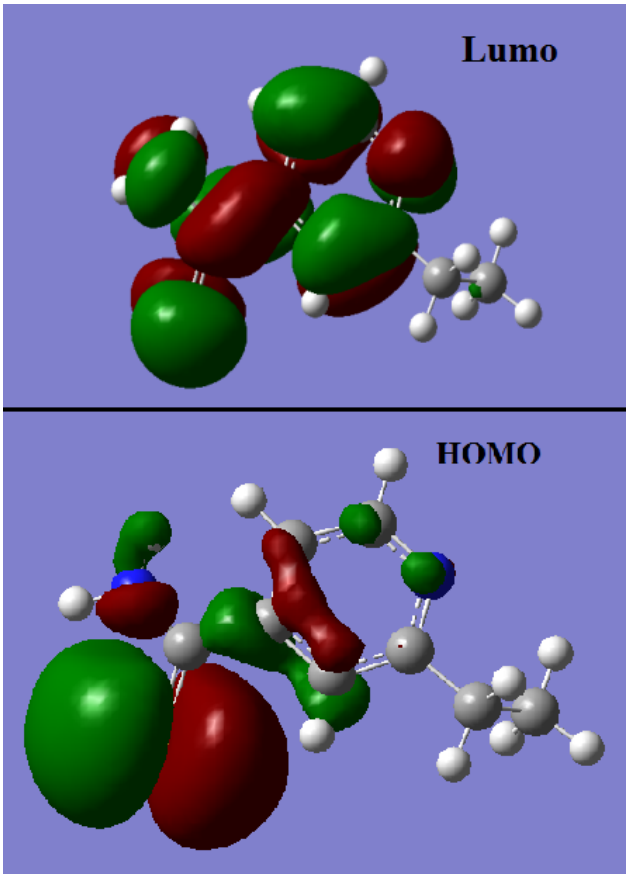


Figure 2. Molecular orbital orientations of LUMO and HOMO with energy gap for 2-ethyl-4-thioamideo pyridine (ETP) by DFT method.

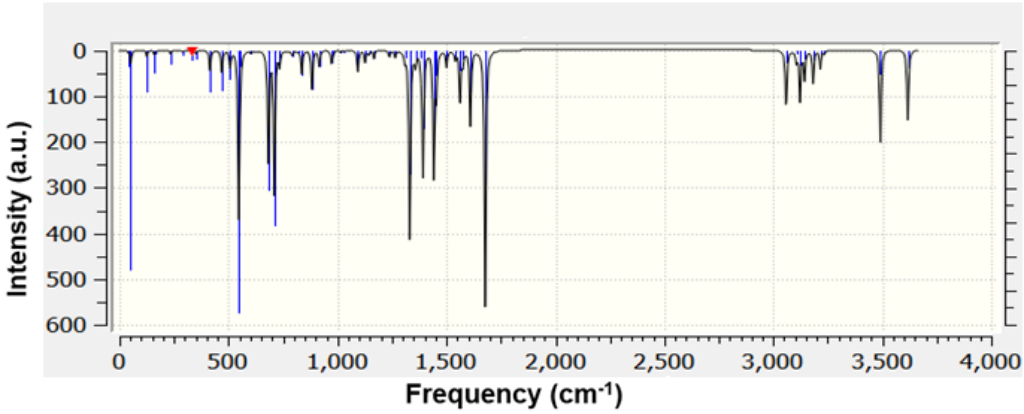


Figure 3. IR spectra of ETP compound as calculated by 2-ethyl-4-thioamideo pyridine (ETP) method.

UV–Vis spectra, and electric and optical characteristics, determine the chemical stability of ETP molecules. There are 123 molecular orbitals in the ETP molecule; 44 of them are filled and HOMO = - 0.07793 eV while the remaining 79 are vacant with LUMO = - 0.07793 eV. Ionization energy indicates chemical inertness and stability, whereas a low ionization energy indicates vital atom and molecular reactivity.

3.3 IR spectra calculation

The fundamental wavenumbers of our molecule were calculated by DFT method with B3LYP and GGA-PBE levels at 3 - 21G (d, p) basis set. However, Fig. 3 demonstrates infrared spectra that were theoretically examined using the Gaussian program, according to the function density method DFT/B3LYP level by using 3 - 21G (d, p) basis set.
Due from 21 atoms in our compound, the molecule exhibits 57 regular vibrational modes (from freedom degree 3N-6, where N no. of atoms) that are involved in infrared absorption (Fig. 3), where appeared high intensity at 1650 cm^{-1}.

3.4 UV-Vis spectrum calculation

Visible light behaves like ultraviolet light in many of its manifestations, and both are produced by the absorption of electronic excitation in molecules Fig. 4. Many of the instruments used in visible spectroscopy are the same as those used in UV spectroscopy, so they were studied together. Quantum chemical calculations were used in the specific investigation of the electronic properties of our compounds. One of the important topics that has been investigated is the excited states in the ultraviolet-visible absorption spectra using the DFT/B3LYP method with 3 - 21G (d, p) basis set of the our compounds. Fig. 3 shows the absorption spectra of UV-visible of the ETP compound, which were calculated theoretically using DFT /B3LYP. The electronic spectra of the title compound show maximum absorption band in 300 nm which is acceptance value in the UV/Visible range.

4. Conclusion

The structural and spectroscopic parameters for our compounds are obtained by using density functional theory. The infrared, UV-visible of the these compounds are simulated by the B3LYP method in conjunction with the 3 – 21G basis set and analysis of calculated geometry parameters is very helpful in determination of unambiguous position of

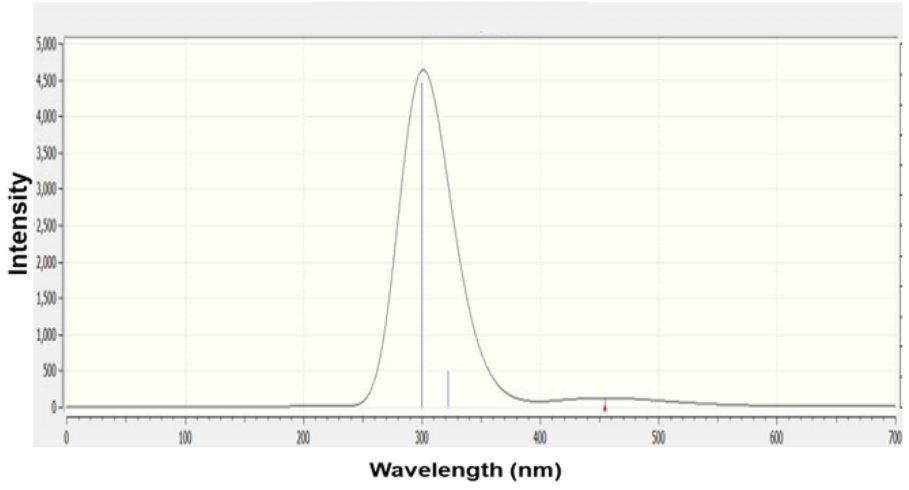


Figure 4. UV-Vis spectrum for 2-ethyl-4-thioamideo pyridine (ETP) compound as calculated by DFT method.

atoms and in turn to determine the most stable geometry. This computational work of our studied compounds were investigated important points represented by spectroscopic and electronic parameters such as IR, UV-Vis and electronic energy, HOMO and LUMO energies , energy gap, electron affinity, ionization potential, these good agreement in the results because many calculations after that depend on energy gap. All values of our compounds are positive which shows that the compounds are stable. Theoretical calculations is another conclusion which made for gas phase of molecule better than in solid state as we tried in our calculation in DFT method.

Ethical approval
This manuscript does not report on or involve the use of any animal or human data or tissue. So the ethical approval is not applicable.

Authors Contributions
All the authors have participated sufficiently in the intellectual content, conception and design of this work or the analysis and interpretation of the data (when applicable), as well as the writing of the manuscript.

Availability of data and materials
The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

Conflict of Interests
The author declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] J. Whitlow, A. Paul, and A. Polini. "Bioactive materials: definitions and application in tissue engineering and regeneration therapy. In book: Biocompatible Glasses". *Springer*, :1–17, 2016.

[2] D. K. Kafi and A. N. Ayyash. "Density functional theory and molecular docking study to lutein molecule for COVID-19 protease inhibitors.". *Applied Nanoscience*, **13**:1–12, 2023.

[3] C. R. S. Kumar. "Approach of density functional theory to molecules using Gaussian. ". *International Journal of Pure and Applied Physics*, **15**:1–13, 2019.

[4] J. Sun, R. Haunschild, B. Xiao, I. W. Bulik, G. E. Scuseria, and J. P. Perdew. "Semilocal and hybrid meta-generalized gradient approximations based on the understanding of the kinetic-energy-density dependence.". *The Journal of Chemical Physics*, **138**: 044113, 2013.

[5] M. P. Stevens. "Polymer chemistry.". *Oxford University Press*, , 1990.

[6] J. M. Bakker, L. Mac Aleese, G. Meijer, and G. von Helden. "Fingerprint IR spectroscopy to probe amino acid conformations in the gas phase.". *Physical Review Letters*, **91**:203003, 2013.

[7] S. Sebastian and N. Sundaraganesan. "The spectroscopic (FT-IR, FT-IR gas phase, FT-Raman and UV) and NBO analysis of 4-Hydroxypiperidine by density functional method.". *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **75**:941–952, 2010.

[8] M. Miar, A. Shiroudi, K. Pourshamsian, A. R. Oliaey, and F. J. J. O. C. R. Hatamjafari. "Theoretical investigations on the HOMO–LUMO gap and global reactivity descriptor studies, natural bond orbital, and nucleus-independent chemical shifts analyses of 3-phenylbenzo [d] thiazole-2 (3 H)-imine and its para-substituted derivatives: Solvent and substituent effects. ". *Journal of Chemical Research*, **45**:147–158, 2021.

[9] M. M. Kadhim and R. M. Kubba. "Theoretical investigation on reaction pathway, biological activity, toxicity and NLO properties of diclofenac drug and its ionic carriers. ". *Iraqi Journal of Science*, **61**:963–951, 2020.

[10] T. A. Julboev, M. M. Sultonov, and K. Abduvaliyeva. "Teaching chemistry computer software to students of chemistry in pedagogical higher education institutions.". *European Journal of Research and Reflection in Educational Sciences*, **9**:2056–5852, 2021.

[11] A. Zarrouk, H. Zarrok, R. Salghi, B. Hammouti, S. S. Al-Deyab, R. Touzani, and T. B. Hadda. "A theoretical investigation on the corrosion inhibition of copper by quinoxaline derivatives in nitric acid solution. ". *International Journal of Electrochemical Science*, **7**: 6353–6364, 2012.

[12] M. Saranya, S. Ayyappan, R. Nithya, R. Sangeetha, and A. Gokila. "Molecular structure, NBO and HOMO-LUMO analysis of quercetin on single layer graphene by density functional theory. ". *Digest Journal of Nanomaterials and Biostructures*, **13**:97–105, 2018.

[13] M. K. Awad, M. R. Mustafa, and M. M. A. Elnga. "Computational simulation of the molecular structure of some triazoles as inhibitors for the corrosion of metal surface. ". *Journal of Molecular Structure: Theochem*, **959**:66–74, 2010.