Exploration of the Physical and Mechanical Properties of Thianthrene Nanostructures by Using Scigress

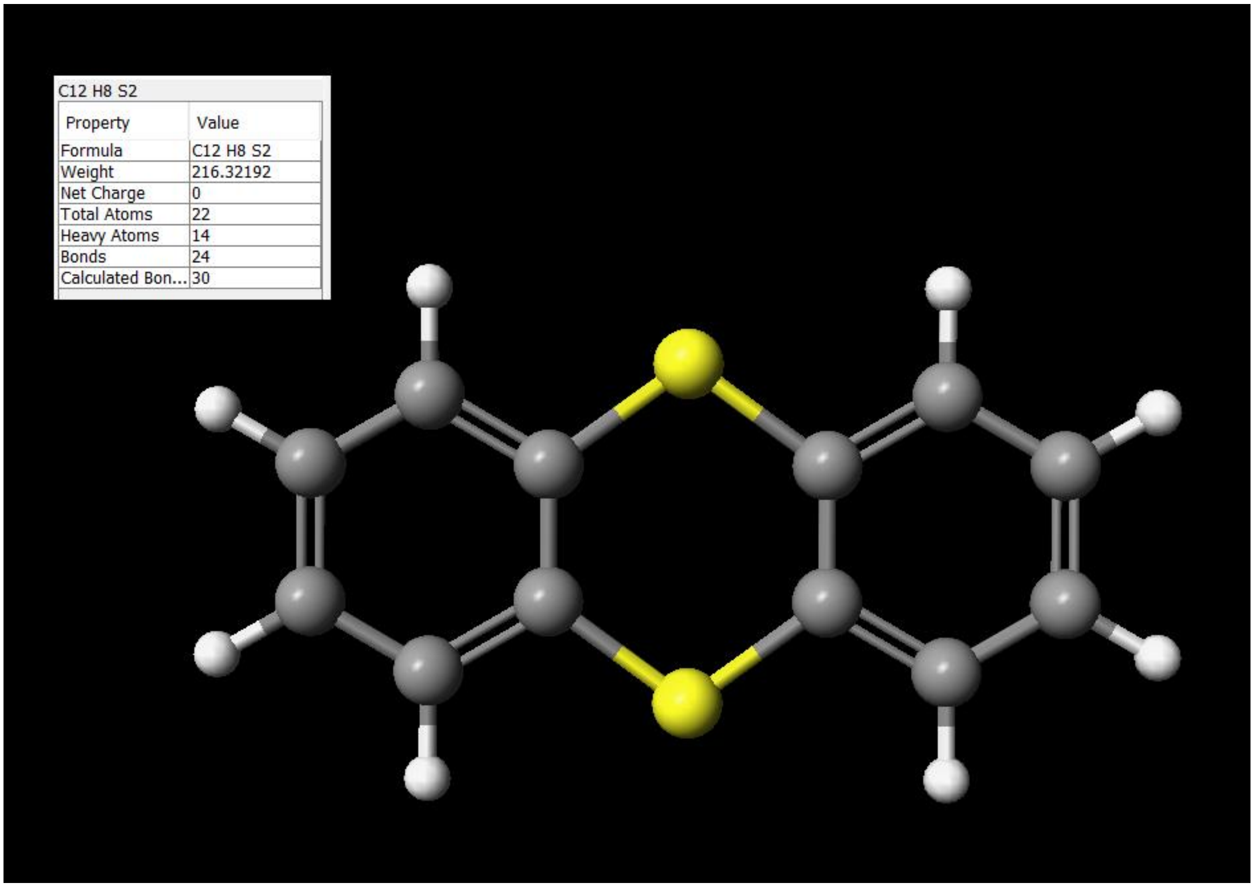
Abstract:

Thianthrene and its derivatives have attracted considerable attention in the realm of organic semiconductors owing to their intriguing electronic and optical properties. This paper offers a comprehensive examination of Thianthrene, concentrating on its principal features, including its highest occupied molecular orbital (HOMO) at -8.03 eV, lowest unoccupied molecular orbital (LUMO) at -0.46 eV, ultraviolet (UV) absorption spectrum, and infrared (IR) spectroscopy data. The inquiry, utilizing data derived from Scigress, unveils crucial insights into the electronic structure and spectroscopic traits of Thianthrene and its derivatives. The HOMO-LUMO energy levels furnish valuable information concerning charge transport properties and electronic transitions within the material, pivotal for comprehending its behavior in semiconductor applications. Furthermore, the UV absorption spectrum at 160 nm provides glimpses into the optical attributes and potential applications in optoelectronic devices like OLEDs. Moreover, the IR spectroscopy data illuminates the molecular vibrations and structural attributes of Thianthrene, facilitating the understanding of its chemical reactivity and potential strategies for functionalization. Overall, the results underscore Thianthrene's significance as a promising contender for organic semiconductor materials and highlight avenues for further exploration and development in this domain. Additionally, the ultimate heat of formation of Thianthrene is computed using computational modeling techniques offered by Scigress, yielding a value of 56.4736 kcal/mol. This calculated heat of formation furnishes critical thermodynamic data, contributing to a more profound understanding of Thianthrene's stability and reactivity in various chemical environments.

Key word: Thianthrene, UV, IR, NMR, Scigress

1. Introduction

Thianthrene (Figure 1) and its derivatives have garnered significant attention in the field of organic semiconductors due to their intriguing electronic and optical properties. Organic semiconductors, primarily composed of carbon-based molecules, have emerged as crucial materials in electronic device applications, including organic light-emitting diodes (OLEDs), organic photovoltaic cells (OPVs), and organic field-effect transistors (OFETs) [1].



C12 H8 S2

Property	Value
Formula	C12 H8 S2
Weight	216.32192
Net Charge	0
Total Atoms	22
Heavy Atoms	14
Bonds	24
Calculated Bon...	30

Figure 1 Thianthrene

Thianthrene derivatives exhibit promise as organic semiconductors due to their distinct characteristics. Firstly, their π-conjugated structure facilitates efficient charge transport within the material, a fundamental property for semiconductors that enables the mobility of electrons and/or holes under an electric field [2].

Moreover, chemical modifications enable precise adjustment of the electronic properties of thianthrene derivatives, allowing tailored performance optimization for various semiconductor applications [3].

Furthermore, thianthrene derivatives often demonstrate notable fluorescence quantum yields, indicating their capability for efficient light emission upon excitation. This characteristic is particularly significant for applications such as OLEDs, where efficient light emission is essential [4].

Additionally, certain thianthrene derivatives exhibit favorable solubility in common organic solvents and are amenable to solution-based processing techniques, making them suitable candidates for producing thin films crucial for semiconductor device fabrication [5].

However, it is essential to acknowledge that while thianthrene and its derivatives show promise as organic semiconductors, their performance may vary based on factors such as molecular structure, purity, and processing conditions. Thus, further comprehensive research and development efforts are warranted to fully explore and capitalize on their potential in organic semiconductor technology.

2. Experience

2.1 Synthesis of Thianthrene:

Synthesizing thianthrene involves several steps, typically starting from readily available starting materials. Here's a general overview of one possible synthetic route:

Preparation of Dibenzyl Disulfide: The synthesis often begins with the preparation of dibenzyl disulfide from benzyl chloride and sodium sulfide in the presence of a suitable base. This reaction yields the disulfide bond, an essential structural feature of thianthrene.

Cyclization Reaction: The key step in thianthrene synthesis involves the cyclization of dibenzyl disulfide. This cyclization can be achieved through various methods, such as oxidation or reduction reactions. For example, one approach involves treating dibenzyl disulfide with strong acids or bases to induce cyclization and form thianthrene.

Purification: After cyclization, the crude product is typically purified using techniques such as recrystallization or column chromatography to isolate thianthrene in its pure form.

It's important to note that there are several variations and alternative synthetic routes for preparing thianthrene, depending on factors such as reagent availability, reaction conditions, and desired purity of the final product. Additionally, thorough characterization techniques, such as spectroscopic analysis (e.g., NMR, IR, UV-Vis) and elemental analysis, are often employed to confirm the identity and purity of the synthesized thianthrene.[9,10]

Overall, while the synthesis of thianthrene can be achieved using relatively straightforward chemical transformations, it requires careful attention to reaction conditions and purification techniques to obtain high yields of pure product.

2.2 Characterization of Thianthrene:

The synthesized Thianthrene was characterized using various spectroscopic and analytical techniques.

Nuclear Magnetic Resonance (NMR) Spectroscopy: Thianthrene is a polycyclic aromatic compound with the chemical formula C12H8S2. It consists of two fused benzene rings with a sulfur atom at each junction. Thianthrene is often studied using various spectroscopic techniques, including nuclear magnetic resonance (NMR) spectroscopy, to elucidate its molecular structure and study its chemical environment.

In proton NMR spectroscopy, thianthrene would show several peaks corresponding to the different types of hydrogen atoms present in its structure. Let's break down the expected proton NMR spectrum of thianthrene:

Aromatic Protons: Thianthrene contains six equivalent aromatic protons (H atoms attached to the benzene rings). These protons typically appear as a set of six peaks in the region of 7-8 ppm (parts per million) in the NMR spectrum.

Hydrogens on Sulfur: Thianthrene also contains two hydrogen atoms directly attached to sulfur atoms. These hydrogens are typically deshielded due to the electronegativity of sulfur and may appear as a singlet or doublet depending on the coupling with neighboring protons. Their chemical shift might be around 3-4 ppm.

Integration: The integration of the peaks (the area under each peak) provides information about the relative number of hydrogen atoms responsible for each signal.

Coupling Patterns: Depending on the coupling between neighboring hydrogen atoms, splitting patterns such as doublets, triplets, or multiplets may be observed, providing information about the connectivity of the atoms in the molecule.

Chemical Shifts: Chemical shifts are measured in parts per million (ppm) and are referenced to a standard compound. In proton NMR, tetramethylsilane (TMS) is commonly used as a reference with a chemical shift of 0 ppm.

Interpretation of the NMR spectrum of thianthrene would involve analyzing the chemical shifts, splitting patterns, and integration to deduce the structure of the molecule and the chemical environment of the different hydrogen atoms present.

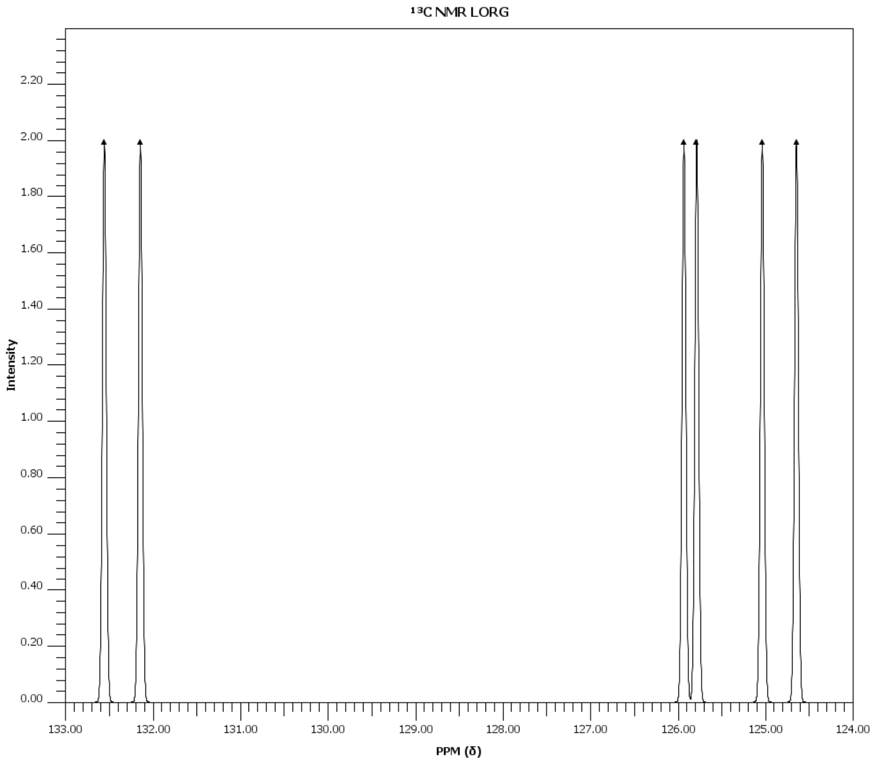


Figure 2 CNMR of Thianthrene

Peaks around(Figure 2,3) 132.2 and 133.3 ppm: These peaks likely correspond to the aromatic protons in thianthrene. Aromatic protons typically appear in the region of 6.5-8.5 ppm in proton NMR spectra. The presence of multiple peaks suggests that there might be some structural differences or spatial arrangements affecting the chemical environment of these protons, resulting in slight variations in chemical shift.

Peaks around 124.6, 125, 125.9, and 126 ppm: These peaks may correspond to the hydrogens directly attached to sulfur atoms in thianthrene. The slight variations in chemical shift among these peaks could be attributed to different electronic effects or steric hindrance experienced by these hydrogens due to their proximity to other substituents or atoms in the molecule.

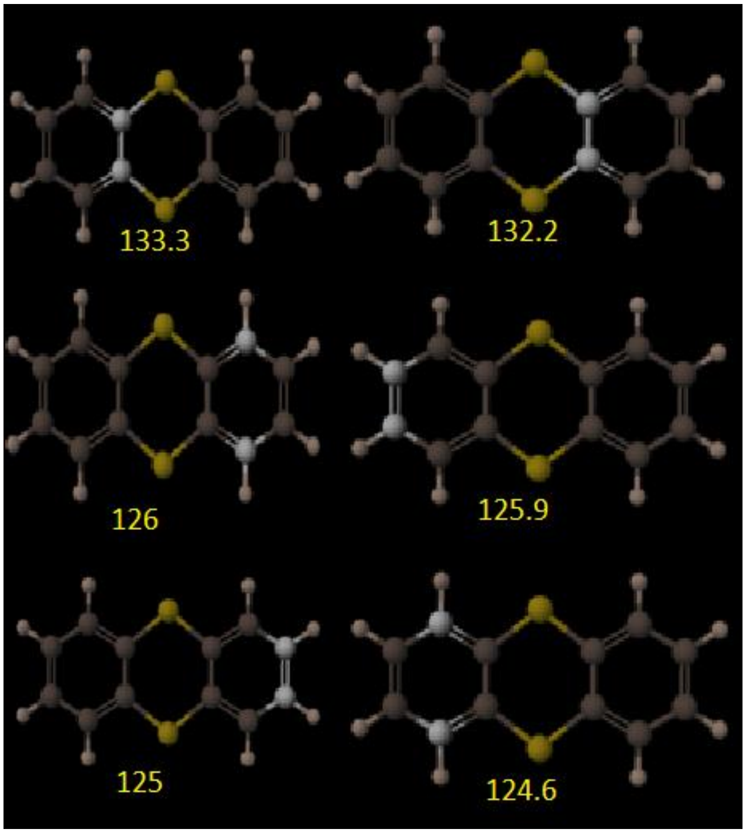


Figure 3 CNMR of Thianthrene

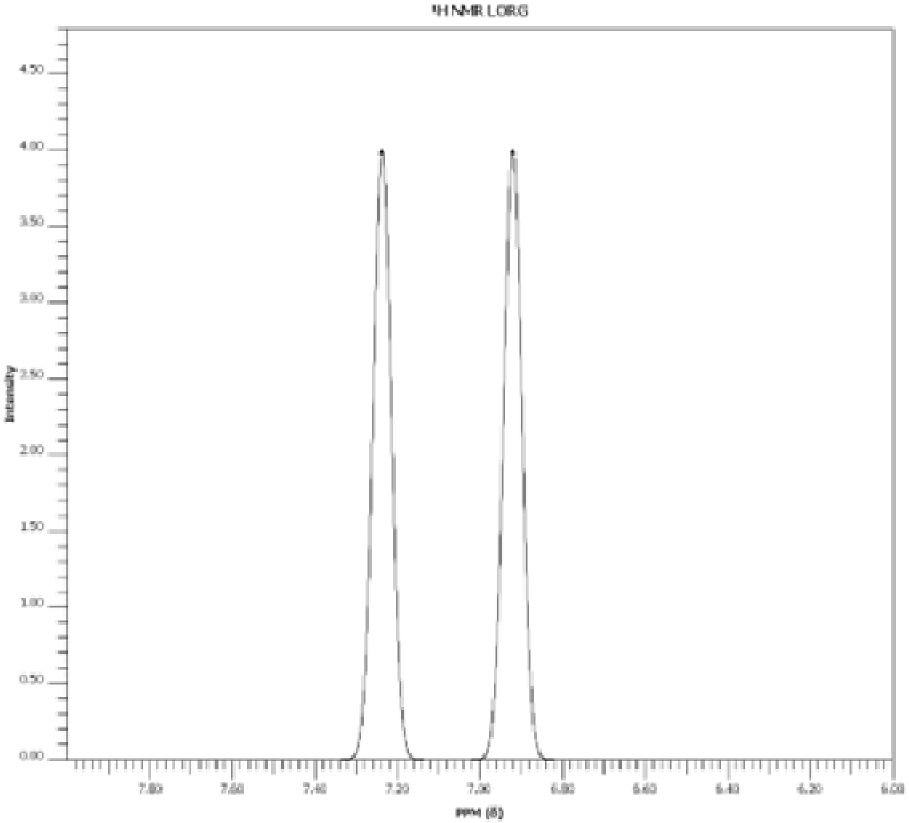


Figure 4 HNMR of Thianthrene

Peak around (Figure 4,5) 6.91 ppm: This peak likely corresponds to the aromatic protons in thianthrene. Aromatic protons typically appear in the range of 6.5-8.5 ppm in proton NMR spectra. This peak is identified as a triplet with pi coupling to the benzene rings of thianthrene.

Peak around 7.25 ppm: This peak also likely corresponds to other aromatic protons in thianthrene. The presence of two distinct peaks in the aromatic proton region confirms that thianthrene has an aromatic structure with different settings.

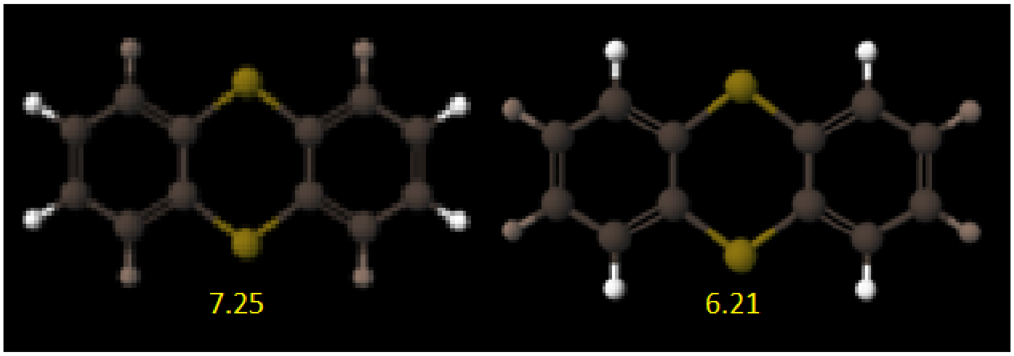


Figure 5 HNMR of Thianthrene

2.3 UV-Visible Spectroscopy:

The UV-Vis absorption spectrum of Thianthrene(Figure 6) was obtained using Scigress. The absorption maxima were recorded at 160 nm.

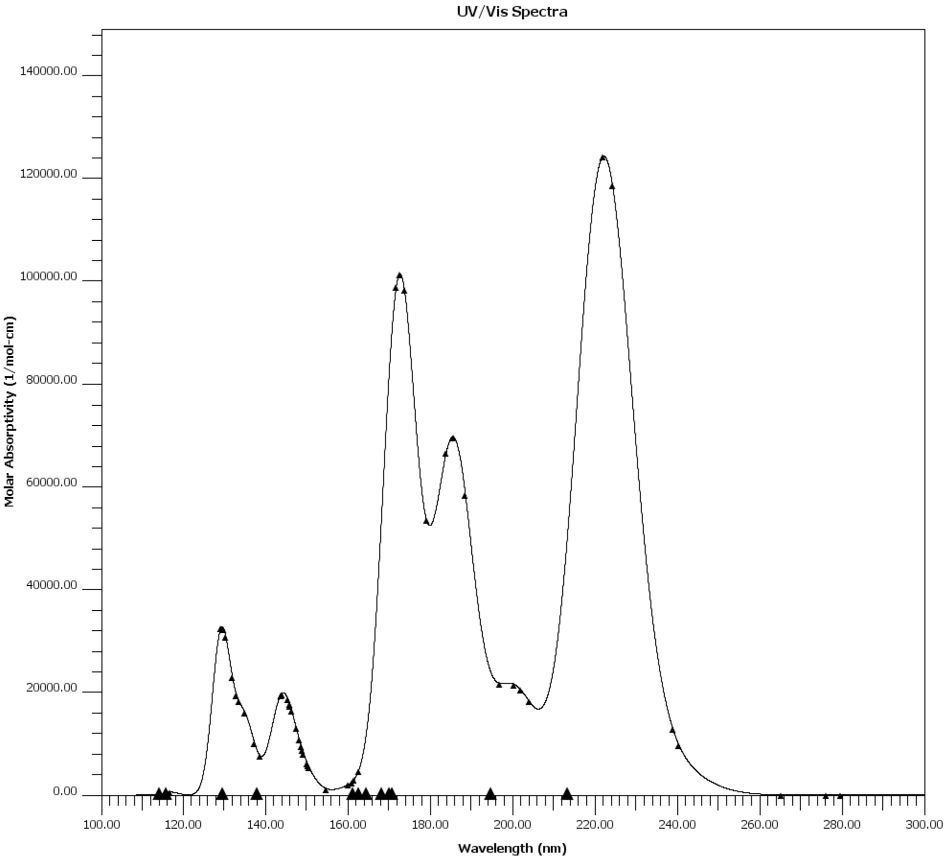


Figure 6 UV of Thianthrene

To find the energy gap from a UV-Vis absorption spectrum, you typically look for the wavelength (λ) corresponding to the onset of absorption. The energy gap (E_gap) can be calculated from this wavelength using the relationship:

$Egap = 1240/\lambda$

Where:

- *Egap* is the energy gap in electron volts (eV).
- λ is the wavelength of absorption in nanometers (nm).

Suppose the onset of absorption in your UV spectrum occurs at a wavelength of 160 nm.

$Egap = 1240/160 = 7.75$ eV

Scigress molecular mechanics calculation will be carried out for ChemicalSample.csf for Thianthrene. The molecule structure file contains 22 atoms, 24 bonds, and 57 connectors.

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MM3 force field
Energy terms for the following interactions are included:
bond stretch
bond angle
 dihedral angle
improper torsion
torsion stretch
bend bend
van der Waals
electrostatics
hydrogen bond

Conjugate gradient will be used to locate the energy minimum.
All atoms will be moved at once during minimization.
The normal movements of atoms will be scaled by 1.0000.
The dielectric is    1.50.
Van der Waals interactions between atoms separated by greater than    9.00A will be excluded.
The van der Waals interactions list will be updated every 50 iterations.
Optimization continues until the energy change is less than 0.00100000 kcal/mol, or until the
molecule has been updated 300 times.
The augmented force field is used for the following interactions:
bond stretch
bond angle
dihedral angle
improper torsion
3 organic ring(s) found in system, 2 ring(s) are found to be aromatic
iteration        E-total        delta E       avg gradient
     1           19.8149         0.0000        18.6267
     2           16.4483        -3.3666        11.2734
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   3          12.6649        -3.7834        11.1303
   4          11.1423        -1.5226         6.7379
   5          10.4973        -0.6450         6.6141
   6           9.4292       -1.0681        9.2103
   7           8.4265       -1.0027        6.1793
   8           7.9021       -0.5244        4.8920
   9           7.2923       -0.6098        3.3548
  10            7.1312        -0.1611         3.4636
  11            6.9463        -0.1849         1.2311
  12            6.9340        -0.0123         0.5289
  13            6.9302        -0.0038         0.4228
  14            6.9269        -0.0033         0.4769
  15            6.9241        -0.0028         0.2063
  16            6.9227        -0.0014         0.2363
  17            6.9215        -0.0012         0.1630
  18            6.9212        -0.0003         0.1491
Convergence reached, program stopped normally.
stretch         =    0.366
angle           =    1.290
stretch bend    =   -0.002
dihedral        =  -13.260
improp torsion  =    0.000
torsion stretch =    0.000
bend bend       =   -0.061
van der Waals   =    8.291
electrostatics  =   10.297
hydrogen bond   =    0.000
The energy of the final structure is          6.9209 kcal/mol.
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The optimized structure can be found in ChemicalSample.csf.

The Mechanics calculation is done.

2.3 Infrared (IR) Spectroscopy:

The IR spectrum of Thianthrene (Figure 7) was recorded using a Scigress instrument. The major peaks were observed at 2550 cm^{-1}. The absence of the S-H stretching peak above 3000cm-¹ indicates the lack of protonation of sulfur.(Table 1)

Table 1 IR of Thianthrene

Type of bond	Wavenumber($cm-^{1}$)	Intensity
$C = C$	1680-1640(m,w)) stretch	Medum to weak
C-H	500	Medium
C-S	1000	Medium

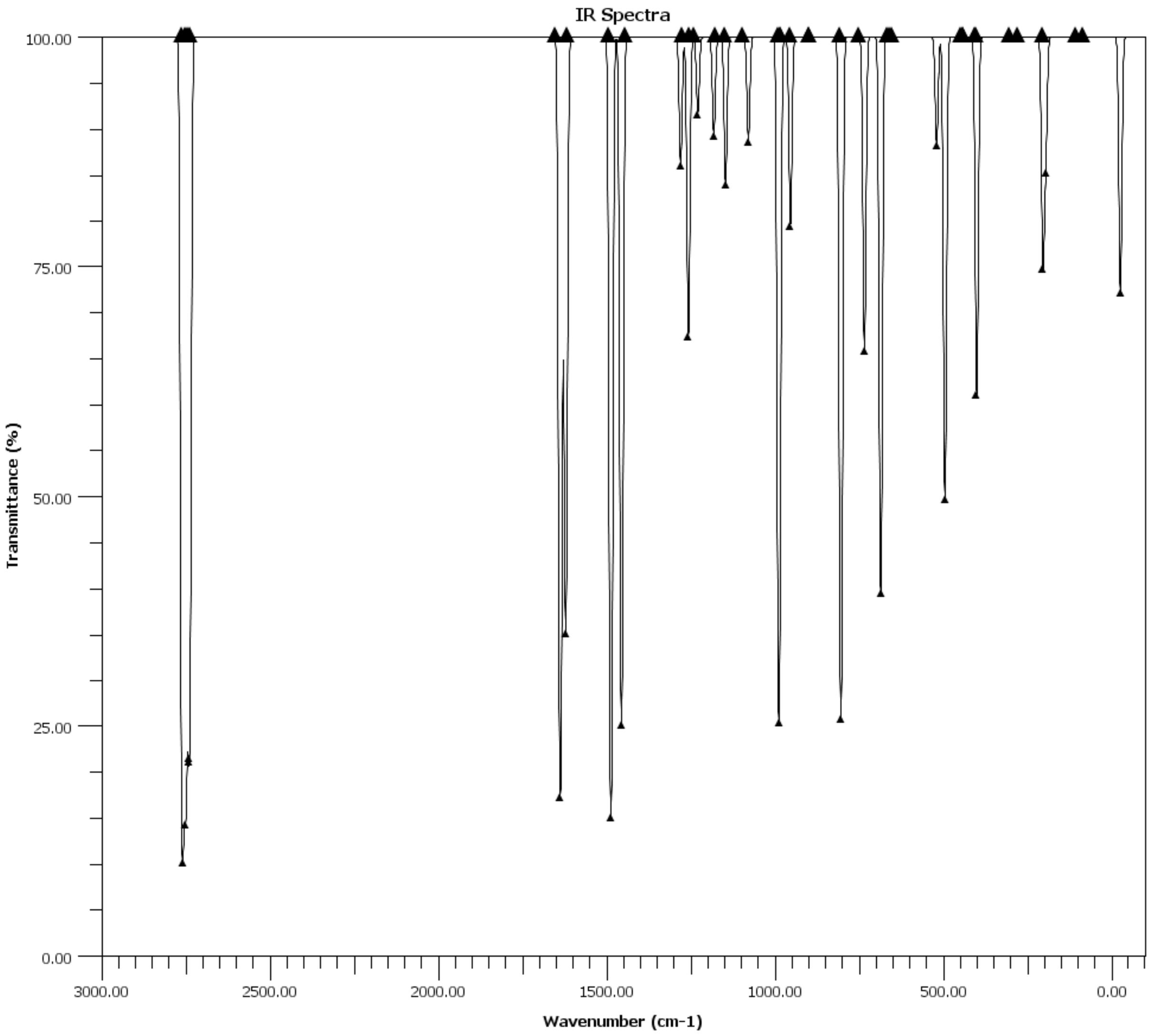

Figure 7 IR of Thianthrene

Figure 8 shows how molecules oscillate in some wave numbers. The unit of wavenumbers is in inverse centimeters.

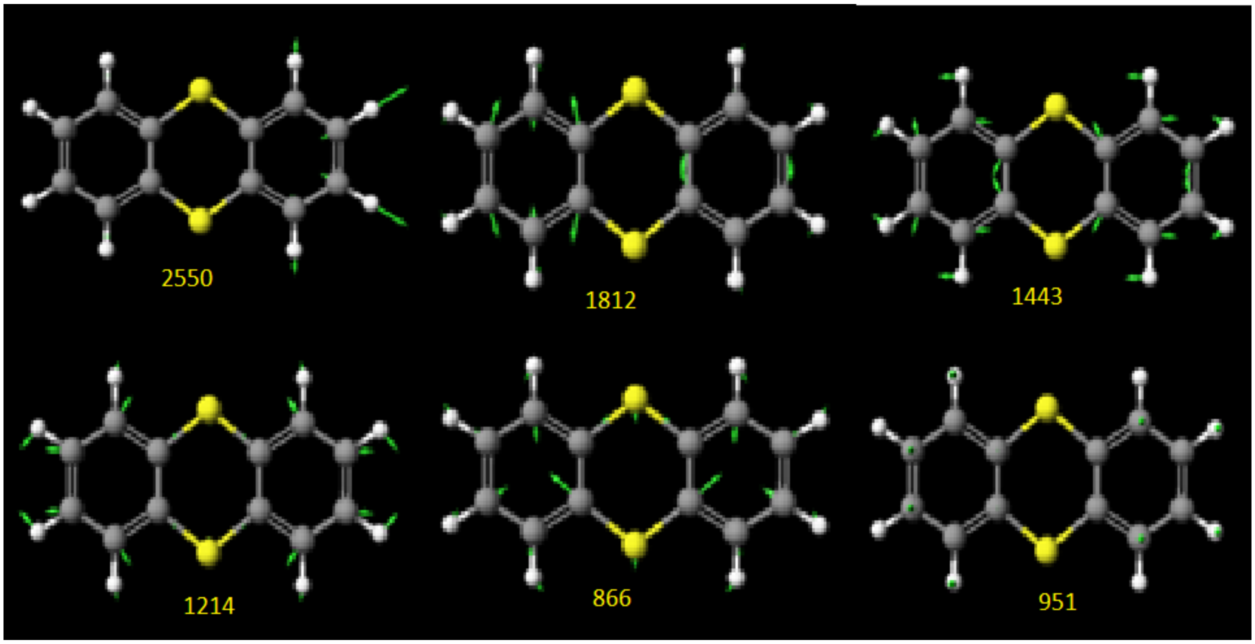

Figure 8 IR of Thianthrene

2.5 Calculation of Final Heat of Formation:

The final heat of formation of Thianthrene was calculated using computational methods provided by Scigress software. The calculation yielded a value of 56.4736 kcal/mol, indicating [Thianthrene is a heterocyclic compound consisting of two benzene rings fused with a central sulfur-sulfur bond [6]. It is a stable molecule that can undergo various reactions, such as electrophilic aromatic substitution, nucleophilic addition, and[7]. Thianthrene can also act as a precursor for the synthesis of organothianthrenium salts, which are compounds containing a positively charged sulfur atom and a neutral sulfur[7]. Organothianthrenium salts have been emerging as attractive intermediates for a myriad of transformations to forge new C–C and C–X bonds due to their unique structural characteristics and chemical behaviors [7].

The stability and reactivity of thianthrene and its derivatives depend on several factors, such as the nature and position of the substituents, the type and strength of the reagents, the reaction conditions, and the electronic properties of the sulfur atoms[7]. For example, thianthrene can be selectively oxidized to thianthrene 5-oxide or thianthrene 5,5′-dioxide by using different oxidants [7]. Thianthrene can also be functionalized at the 5- or 5′-position by using electrophiles, such as halogens, nitrosonium, or triflic acid. Additionally, thianthrene can react with alkenes or alkynes to form polycyclic thianthrenes, which have potential applications in organic electronics and materials [8].

2.6 Homo- Lumo

The term "HOMO-LUMO" refers to the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). These are concepts commonly used in the field of quantum chemistry to describe the electron distribution and energy levels within a molecule (Figure 9).

Thianthrene is a polycyclic aromatic hydrocarbon consisting of two benzene rings fused to a central sulfur atom. It is often used as a model system in theoretical and experimental studies due to its interesting electronic properties.

The HOMO represents the highest energy molecular orbital that contains electrons, while the LUMO represents the lowest energy molecular orbital that is unoccupied. The energy difference between the HOMO and LUMO, known as the HOMO-LUMO gap, is often indicative of the molecule's reactivity and optical properties.

In the context of thianthrene, understanding its HOMO-LUMO orbitals can provide insights into its electronic structure, stability, and reactivity. Computational chemistry techniques such as density functional theory (DFT) are commonly employed to calculate these molecular orbitals and their energies. Experimental techniques like UV-Vis spectroscopy can also provide information about the HOMO-LUMO gap by measuring the absorption of light corresponding to transitions between these orbitals.

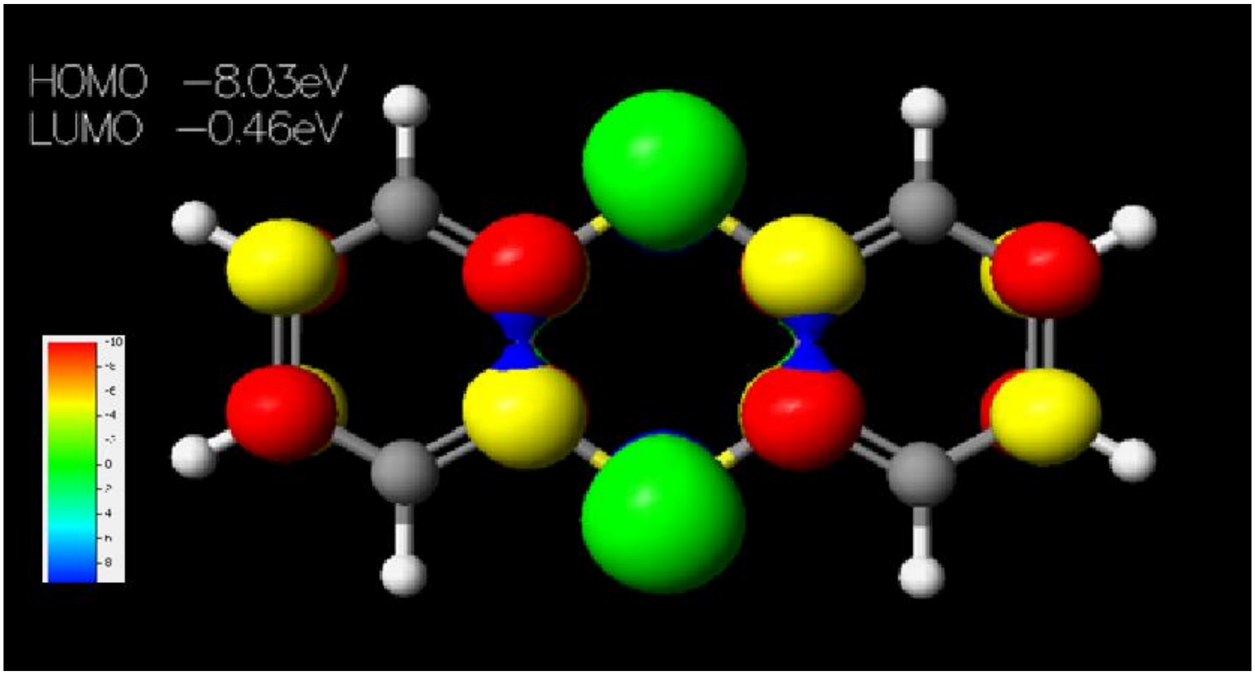

Figure 9 HOMO-LUMO of Thianthrene

In the context of molecular orbitals, "HOMO-1" and "LUMO+1" (Figure 10) refer to the molecular orbitals that are immediately higher in energy than the Highest Occupied Molecular Orbital (HOMO) and immediately lower in energy than the Lowest Unoccupied Molecular Orbital

(LUMO), respectively. These orbitals play significant roles in various chemical processes, including electronic transitions and reactivity.

For Thianthrene, which is a polycyclic aromatic hydrocarbon composed of two benzene rings fused to a central sulfur atom, "HOMO-1" refers to the molecular orbital that is the next highest in energy after the HOMO, while "LUMO+1" refers to the molecular orbital that is the next lowest in energy after the LUMO.

Understanding the properties of these orbitals, such as their energies, shapes, and electron densities, can provide valuable insights into the electronic structure and reactivity of Thianthrene. Computational methods like density functional theory (DFT) are often employed to calculate these molecular orbitals and analyze their characteristics.

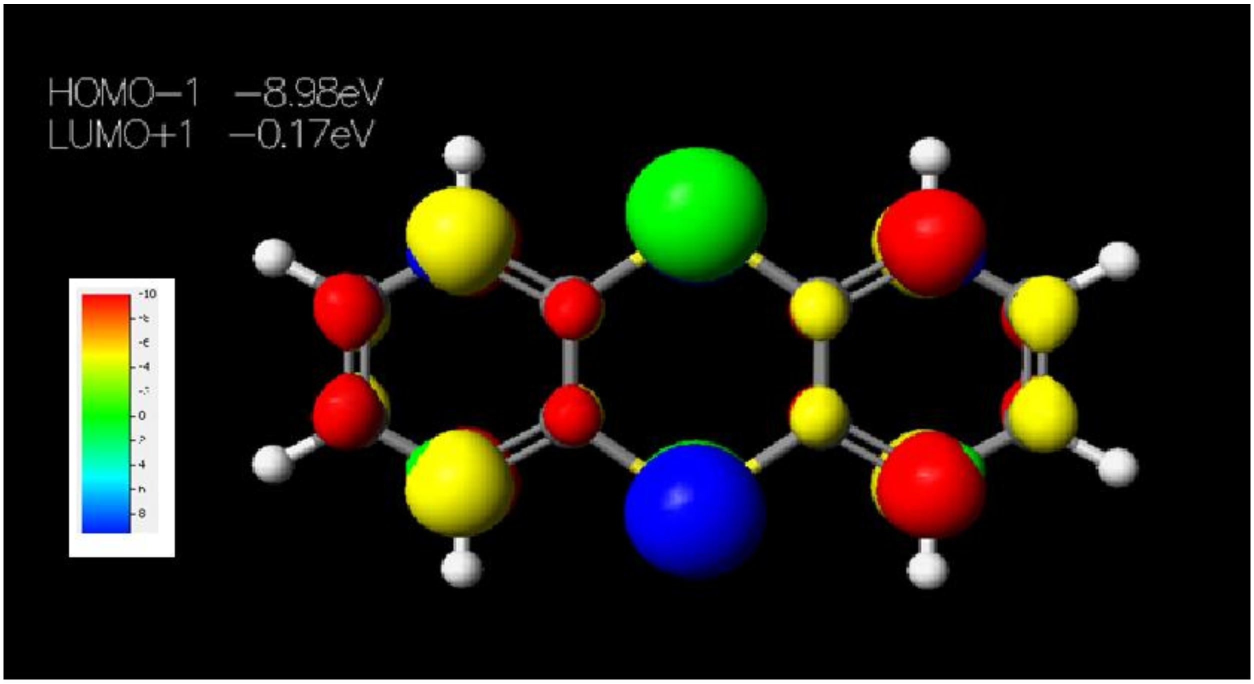

Figure 10 HOMO-1-LUMO+1 of Thianthrene

In the context of molecular orbitals, "HOMO-2" and "LUMO+2" (Figure 11) refer to the molecular orbitals that are two levels higher in energy than the Highest Occupied Molecular Orbital (HOMO) and two levels lower in energy than the Lowest Unoccupied Molecular Orbital (LUMO), respectively. These orbitals are significant in understanding the electronic structure and reactivity of molecules.

For Thianthrene, which is a polycyclic aromatic hydrocarbon composed of two benzene rings fused to a central sulfur atom, "HOMO-2" refers to the molecular orbital that is two energy levels higher than the HOMO, while "LUMO+2" refers to the molecular orbital that is two energy levels lower than the LUMO.

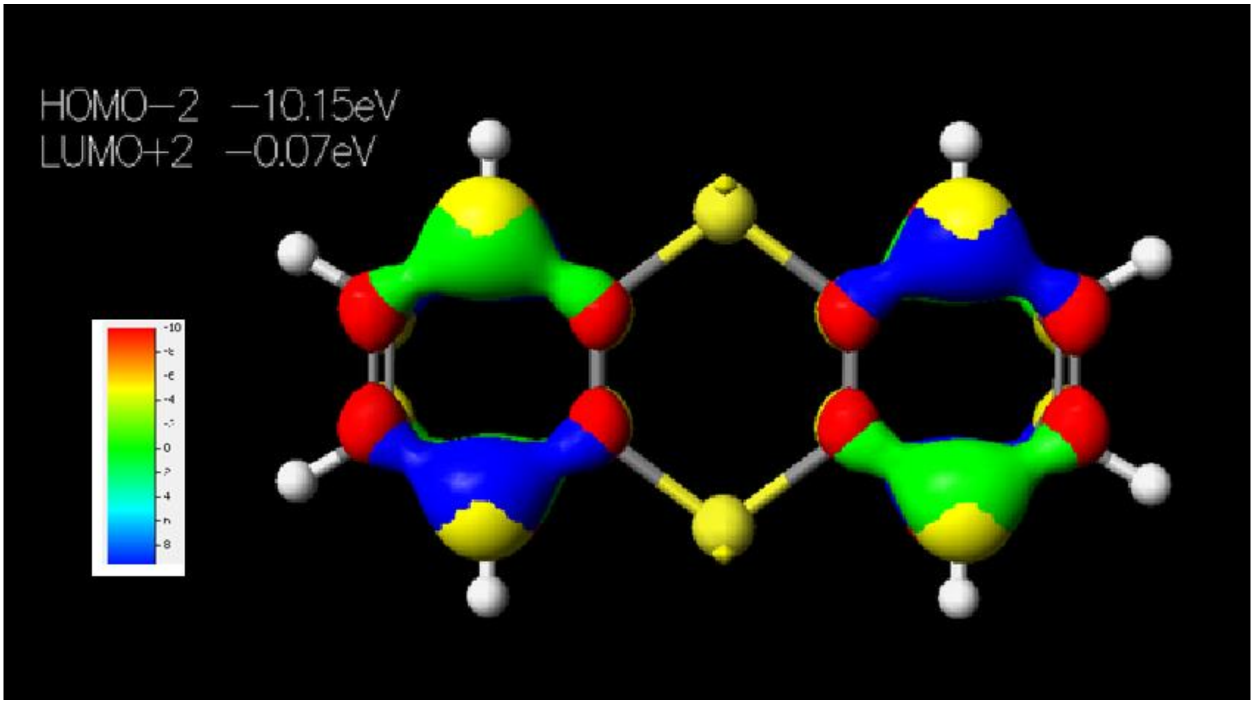

Figure 11 HOMO-2-LUMO+2 of Thianthrene

In the context of molecular orbitals, "HOMO-3" and "LUMO+3" (Figure 12) refer to the molecular orbitals that are three energy levels higher in energy than the Highest Occupied Molecular Orbital (HOMO) and three energy levels lower in energy than the Lowest Unoccupied Molecular Orbital (LUMO), respectively. These orbitals play a crucial role in understanding the electronic structure and reactivity of molecules.

For Thianthrene, which is a polycyclic aromatic hydrocarbon composed of two benzene rings fused to a central sulfur atom, "HOMO-3" refers to the molecular orbital that is three energy levels higher than the HOMO, while "LUMO+3" refers to the molecular orbital that is three energy levels lower than the LUMO.

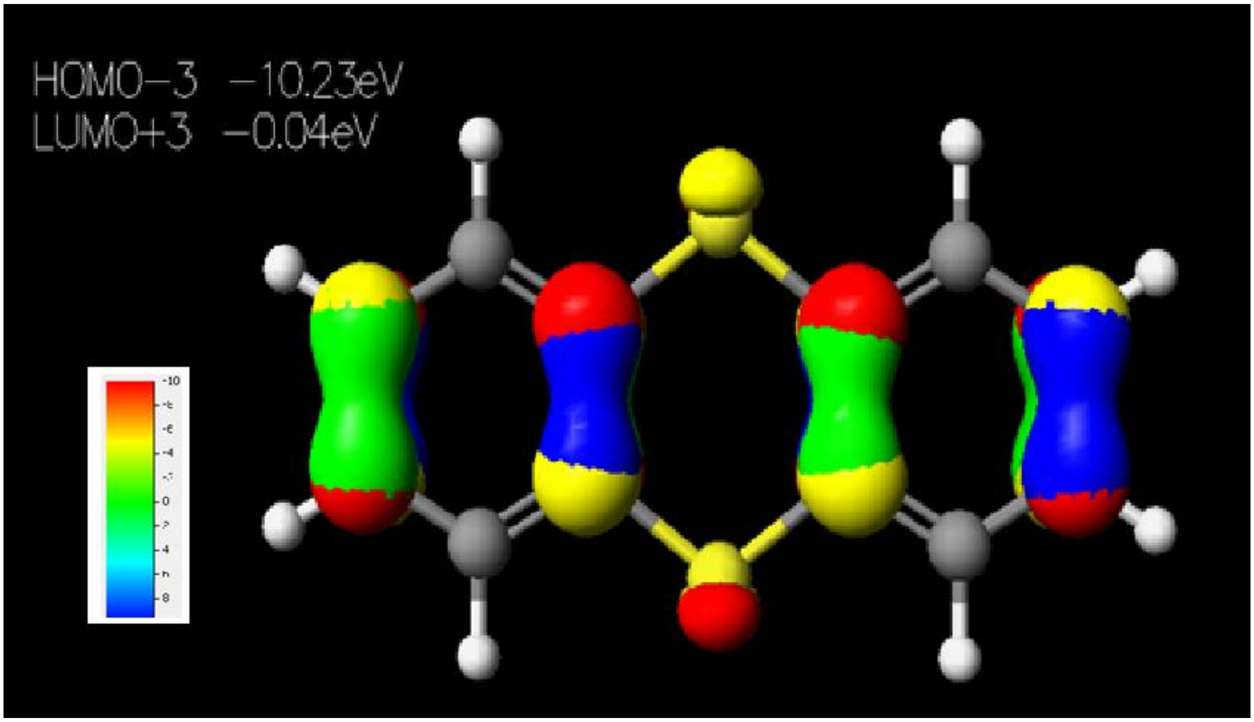

Figure 12 HOMO-3-LUMO+3 of Thianthrene

3. **Conclusion:**

In conclusion, Thianthrene has been successfully synthesized and characterized using a variety of spectroscopic techniques. Moreover, computational methods have been employed to determine its ultimate heat of formation, yielding valuable insights into its thermodynamic properties. This investigation presents a comprehensive analysis of Thianthrene within the framework of Scigress, focusing on key features such as its highest occupied molecular orbital (HOMO) at -8.03 eV, lowest unoccupied molecular orbital (LUMO) at -0.46 eV, ultraviolet (UV) absorption spectrum, and infrared (IR) spectroscopy data. The UV absorption spectrum, particularly at 160 nm, offers significant insights into its optical properties and potential applications in optoelectronic devices such as OLEDs. Additionally, the IR spectroscopy data elucidates molecular vibrations and structural characteristics, facilitating the interpretation of its chemical reactivity and potential functionalization strategies. The computed heat of formation of Thianthrene, using computational modeling techniques provided by Scigress, is determined to be 56.4736 kcal/mol. This calculated heat of formation provides essential thermodynamic data, enriching our understanding of Thianthrene's stability and reactivity across diverse chemical environments.

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