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Synthesis, Characterization, and Computation of Benzodithienothiadiazole-based Small Molecular Fragments (DT-BTD)

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Abstract: *Benzodithienothiadiazoles (DT-BTDs) are a class of small molecular fragments with rigid planar conjugated structures, which are simple and easy to synthesize with high yields. There is currently an essential structure for constructing efficient polymer materials. unit. Synthesis, characterization, and calculation of small molecule fragments based on benzodithienothiadiazole are comprehensive experiments using organic chemistry research methods. This paper aims to improve students' essential operational and analytical ability in organic synthesis to apply experimentally. It is combined with the textbook content to deepen the understanding of the textbook content. In addition, the infrared spectroscopy, ultraviolet spectroscopy, and hydrogen nuclear magnetic resonance spectroscopy of DT-BTD molecules, infrared spectroscopy, and ultraviolet spectroscopy calculations using Gaussian software are supplements to the current undergraduate experimental teaching in computational chemistry. This experiment is conformed to the innovative undergraduate experimental design, which can comprehensively improve undergraduates' experimental literacy. It can broaden their knowledge and cultivate the ability to independently use modern instrumental analysis methods.*

Keywords: *Benzodithienothiadiazoles; Organic synthesis; Gaussian calculations*

1. Introduction

As a kind of clean energy can be seen everywhere. However, it is difficult to use effectively, and "light" has always attracted people's attention. The development of light and optical application technology has significantly progressed human civilization. Light-based and light-based technologies are of multi-dimensional importance to the lives of the peoples of the world and the global society. In the field of luminescence, organic materials have attracted increasing attention due to their wide variety, good tunability, rich colors, high color purity, and relatively flexible molecular design. According to theoretical predictions, when the energy band gap of the polymer approaches 0 eV, the polymer exhibits intrinsic metal-like conductivity. However, for a long time, the energy conversion efficiency of polymer solar cells is not high because the common polymer spectral response range cannot effectively cover the solar spectrum. Therefore, the energy band gap Eg of the polymer was provided lower than the maximum luminous flux of sunlight (1.8 eV) so that the absorption spectrum overlaps with the solar spectrum, which has become the focus of attention to the greatest extent.

π-conjugated copolymers or oligomers composed of alternately mixed donor and acceptor units can reduce the electronic band gap, which has become the most popular and effective band gap engineering of π-conjugated polymers as a strategy [1-2]. Therefore, it is obtained new donor and acceptor molecules is a very efficient and fast method for band gap research because it can form new π-conjugated systems with various band gaps and properties. Benzodithiophene (BDT) derivatives are essential as commonly used fragments in polymer donors. The core unit of benzodithiophene derivatives has a rigid planar conjugated structure, which improves the π-electron delocalization ability of acceptor materials. Moreover, it is enhanced the intermolecular π-π stacking interaction, which is convenient for regulating molecular energy level and optical band gap and has higher electron mobility. BDT is highly planar, and BDT-based polymers generally have high mobility and low HOMO energy level. Therefore, BDT groups have become an important structural unit for constructing high-efficiency polymer materials [3]. Benzothiadiazole (BBTz) is an essential electron-deficient group, and the benzothiadiazole group as an acceptor unit is copolymerized with different donor units, which obtains a series of conjugated donor polymers [4]. Synthesis and functionalization of benzodithienodithiazole-based small-molecule

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fragments (DT-BTD) provide a novel π-conjugated polymer donor and acceptor units for π-conjugated polymers. The development of the field has provided, and it has broad application prospects in the fields of organic light-emitting diodes (OLEDs), chemical biosensors, organic solar cells, and cell imaging.

2. Experimental part

2.1. Experimental preparation

The experimental reagents were used.

Ferric chloride, dichloromethane (DCM), petroleum ether (Pe), hydroxylamine hydrochloride, anhydrous ethanol, stannous chloride, concentrated hydrochloric acid, dichlorodisulfide, N, -N dimethylformamide (DMF), chloroform, silica gel.

The experimental setup was performed.

250ml double-mouth flask, 250ml single-mouth flask, spherical condenser, tee joint, chromatographic column, 250ml partition funnel, 250ml conical flask, oil bath, iron stand, ground-mouth glass stopper, extraction flask, Brinell funnel, silica gel plate, capillary tube, syringe, rubber-tipped dropper, nitrogen bottle, oil pump, etc.

Experimental instruments are used: analytical balance, constant temperature heating magnetic stirrer, ultrasonic cleaner, triple UV analyzer, rotary evaporator, vacuum pump, cooling water circulation pump, blast drying oven, characterization instrument, infrared spectrometer, nuclear magnetic resonance instrument, UV spectrometer

The calculation software is applied.

GaussView 5.0 and Gaussian 09W were used for the calculation of this experiment.

2.2. Experimental ideas

Aromatic diketones are starting materials for synthesizing planar conjugated structures, which can be derived from synthetic monomers for many conjugated materials. The ketone functional groups in aromatic diketones can be easily transformed into other new functional groups that can give different properties and characteristics to the molecule. Furthermore, most of these transformations only need to be done in one or two steps [5]. To construct efficient π-conjugated polymer donor and acceptor units, we used benzo[1,2-b:6,5-b] dithiophene-4,5-dione (BDTD) as the intermediate, based on which a thiadiazole group was introduced, a small molecular fragment DT-BTD was synthesized, which is beneficial to further study of molecular properties and has broad application prospects.

The target molecule is dithiophene [3',2':3,4;2",3":5,6] benzo[1,2-c] [1,2,5] thiadiazole (DT- BTD), retrosynthetic analysis of the target molecule, as shown in Figure 1.

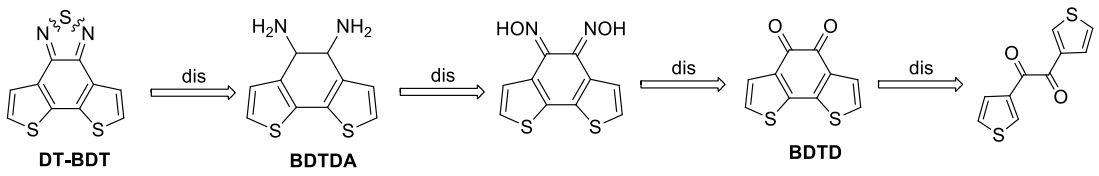

Figure 1: Retrosynthetic analysis of target molecules

In the second step of the reverse reaction analysis, Pd/C was used as the catalyst, and hydrazine, which was used as the raw material for the reaction. According to the content of the textbook, the hydrochloric acid solution of stannous chloride, which is familiar to students, can be used as the reducing agent in this step of the reduction reaction [6], and other organic impurities will not be introduced while improving the reaction process.

Therefore, this reaction is mainly carried out in three steps, and the reaction process is described in Figure 2.

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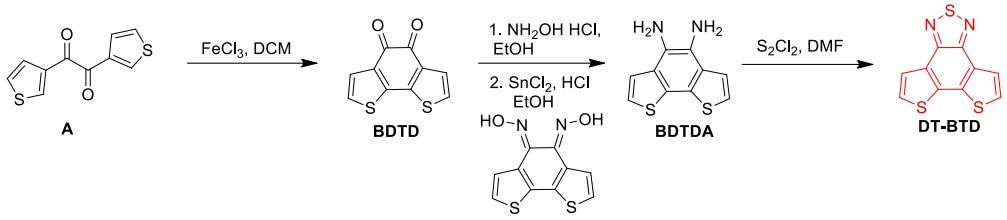

Figure 2: Synthetic route of DT-BTD

2.3. Experimental method

2.3.1. Synthesis of Benzo[1,2-b:6,5-b] dithiophene-4,5-dione (BDTD)

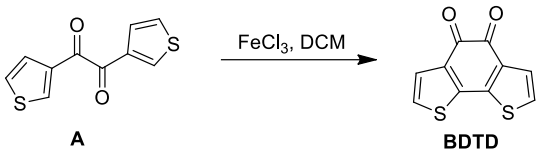

Figure 3: Synthesis of Benzo[1,2-b:6,5-b] dithiophene-4,5-dione (BDTD)

To a 500 mL two-necked flask, anhydrous FeCl3 (19.465 g, 120 mmol, 3 equiv) and diketone A (8.8914 g, 40 mmol, 1 equiv) were added in portions, as shown in Figure 3. Oxygen was purged, 250 mL of dry DCM was syringed into a two-necked flask, and the reaction mixture was stirred at room temperature for 2 hours. The mixture was quenched with 100 mL of cold water and stirred for an additional 5 minutes. After the resulting liquid mixture was poured into a separatory funnel and extracted three to four times with DCM, the organic phase was retained, and the DCM was removed by rotary evaporation. The filtered solid was washed with copious amounts of deionized water and stirred in 200 mL of water until a fine powder formed. Then, the solution was then filtered and rewashed with plenty of water. Moreover, the resulting solid was air-dried for 10 minutes, washed with 200 mL of petroleum ether, and dried under a vacuum. The black solid was added to 200 mL of DCM to dissolve, then 100 mL of silica gel was added. The mixture was stirred until the solids were dispersed on the silica gel, then the entire mixture was transferred to a chromatographic column. The column was then flushed with Pe: DCM=1:3 eluent until all dark purple solids were recovered. After product recovery, a green stain remained on the column. After removal of the organic solvent, the resulting solid was stirred in petroleum ether for 15 minutes, vacuum filtered, and air dried. The black solid was dried under a vacuum, and the product was weighed to obtain 8.627 g with a yield of 97.8%.

2.3.2. Synthesis of Benzo[1,2-b:6,5-b^,] dithiophene-4,5-diamine (BDTDA)

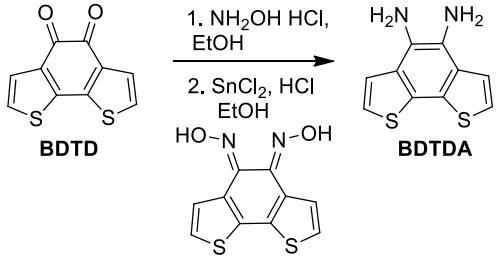

Figure 4: Synthesis of Benzo[1,2-b:6,5-b^,] dithiophene-4,5-diamine (BDTDA)

Under a nitrogen atmosphere, a 250 mL two-necked flask equipped with a stirring magnet was added BDTD (2 g, 9.0799 mmol, 1 equiv), hydroxylamine hydrochloride (1.577 g, 2.5 equiv), and 100 mL absolute ethanol. The flask was fitted with a reflux condenser, and the mixture was heated to reflux (75–80 ℃) and stirred for 2 hours, as shown in Figure 4.

Stannous chloride (7.6 g, 40.0 mmol) was dissolved in concentrated hydrochloric acid (18 mL), and the solution was added to the reaction system under ice bath conditions. After stirring for ten minutes, the system was heated to reflux (80-85 ℃) for 3 hours. The mixture is suction filtered under reduced pressure and washed 2-3 times with water. The filter residue was added to 100 mL of saturated aqueous sodium bicarbonate solution for neutralization, the filtrate and filter residue was extracted with DCM, and the extracts were mixed and dried over anhydrous sodium sulfate. The solution was rotary evaporated to give a beige powdery solid (1.210 g, 79%).

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2.3.3. Synthesis of benzodithienothiadiazole (DT-BTD)

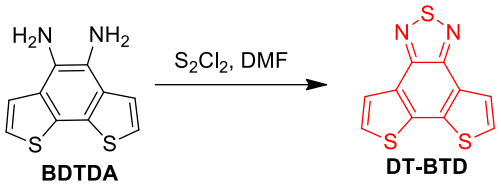

Figure 5: Synthesis of benzodithienothiadiazole (DT-BTD)

To a 25 mL, round-bottom flask equipped with a stirring magnet and blanketed with nitrogen was added DMF (2 mL) and sulfur chloride (0.6 mL, 0.9801 g, 7.2624 mmol, 4 equiv). The flask was cooled to 0 ℃, then the mixture was stirred, and the diamino compound BDTDA (previously dissolved in 10 mL of dry DMF) was added dropwise via syringe, as shown in Figure 5. The mixture was allowed to warm to room temperature and stirred for 2 hours. The reaction mixture was quenched with 15 mL of water, stirred for 5 minutes, suction filtered, and air-dried for 5 minutes. The resulting sticky solid was triturated with a spatula, transferred to a round bottom flask, and dissolved with a small amount of DCM. Then, the silica gel was added to the DCM solution, and the DCM was removed by rotary evaporation. The resulting silica gel was transferred to a chromatographic column and covered with a layer of anhydrous sodium sulfate. Rinse the column with petroleum ether (250 mL). Spot the plate to confirm that all sulfur by-products have eluted, then place a new filter bottle under the funnel. The silica was rinsed with a 1:20 mixture of DCM: Pe, and spot plate detection ensured complete separation of oxygen-containing impurities from the product. The product was yellow and had noticeable fluorescence. Increase the eluent polarity until all yellow product comes out. The solvent was removed by rotary evaporation. The yellow fine needle-like solid was collected by filtration, washed with ethanol, air-dried, and placed under vacuum to obtain 0.370 g of the product with a yield of 82%.

2.3.4. Characterization and calculation of DT-BTD

Molecules were drawn into GaussianView software and optimized with Gaussian 09W. The optimized model was analyzed by ultraviolet and infrared, which were set to opt freq and td (nstate=20), exported as .out files, and dragged into GaussianView to observe the molecular structure. It was determined as a planar conjugated structure. The model that has completed the infrared analysis was opened, right-click, and find the Vibrations option in Results to view the infrared spectrum data. Click on Sprctrum to view the infrared spectrum. In the same way, open the model that has completed the UV-Vis spectral analysis, right-click, and find the UV-Vis option in Results to view the UV-Vis spectral data. Click on Sprctrum to view the UV-Vis spectrum. The data peaks can be found by exporting the data and plotting with origin.

The samples were detected by infrared and ultraviolet-visible spectroscopy using a Nicolet iS10 Fourier transform infrared spectrometer with a KBr tablet and a UH5300 UV-Vis spectrophotometer using chloroform as a solvent, and the samples were dissolved in deuterated chloroform. Moreover, samples were sent for H NMR spectroscopy. The nuclear magnetic resonance instrument was a BRUKER ASCEND/AVANCE III-400 superconducting nuclear magnetic resonance instrument (with CDCl3 TMS purchased from Bailingwei Technology Co., Ltd. as the internal standard).

3. Results and discussion

3.1. Yield analysis

Table 1: Yield analysis

Reaction steps	Reactants and dosage	Products and Output	Single-step recovery rate	Total Reaction Yield
Step 1	1,2-bis(thiophen-3-yl)-1,2-dione 8.8914g	BDTD 8.672g	97.8%	63%
Step 2	BDTD 2g	BDTDA 1.210g	79%	
Step 3	BDTDA 0.4g	DT-BTD 0.370g	82%	

1,2-bis(thiophen-3-yl)-1,2-dione was used as the raw material for synthesizing DT-BTD in a three-step reaction with an overall yield of 63%. The high yield is suitable for undergraduate teaching

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experiments.

3.2. Characterization results

NMR hydrogen spectroscopy is a basic method for analyzing the structure of organic compounds. In NMR hydrogen spectroscopy, the number of characteristic peaks reflects the type of chemical environment of hydrogen atoms in organic molecules. The intensity ratio of different characteristic peaks (i.e., the height ratio of characteristic peaks) reflects the ratio of the number of hydrogen atoms in different chemical environments; the structure of organic compound molecules can be effectively determined by NMR hydrogen spectroscopy.

The target molecule DT-BTD has a conjugated double bond, which will have a strong UV absorption between 200-300 nm, and the double bond C=N containing heteroatoms will have a weak UV absorption between 200-400 nm. Some other atoms and functional groups in the molecule will also produce the corresponding UV characteristic absorption peaks. Meanwhile, the C-H bond near 2900 cm-1, the C=C double bond near 1645cm-1, and other functional groups have infrared characteristic absorption peaks, and their relative structures can be determined by infrared spectroscopy.

The NMR hydrogen, UV-Vis, and IR spectra were analyzed together to obtain the specific structures of the products, as shown in Figure 6, Figure 7, and Figure 8, respectively.

In this experiment, GaussianView 5.0 was used to plot the molecular structure. The molecular structure optimized in advance by Gaussian 09W was used to calculate the infrared and ultraviolet spectra. It was used to verify the correctness of the obtained molecular structure by comparing it with the test results.

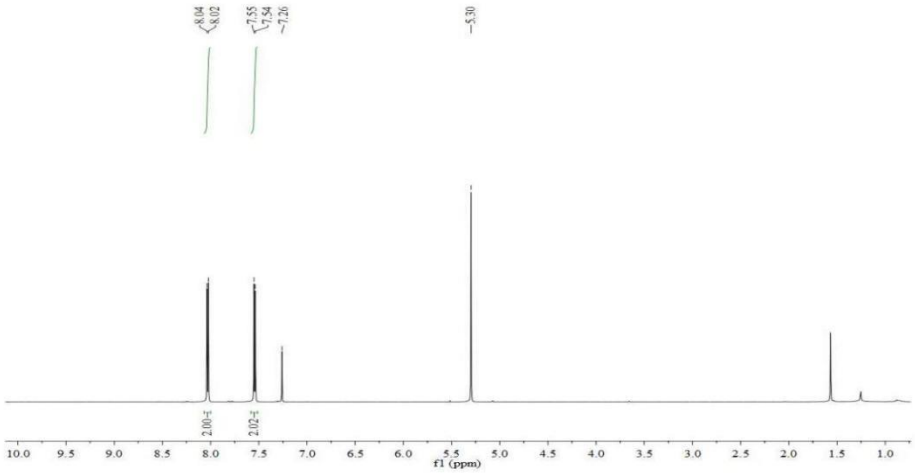

Figure 6: DT-BTD Nuclear Magnetic Resonance Hydrogen Spectroscopy

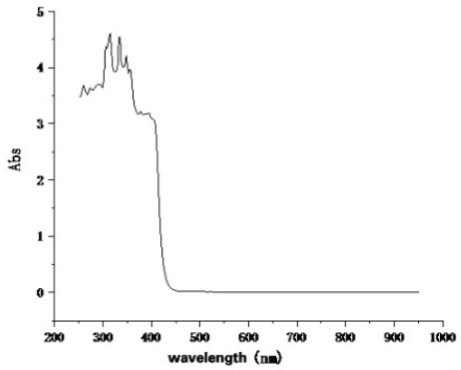

Figure 7: UV-Vis absorption spectra measured.

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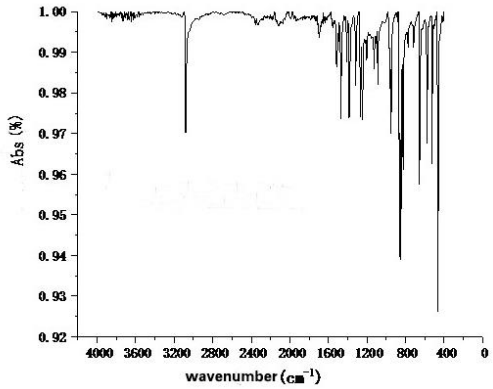

Figure 8: Infrared spectrum of DT-BTD measured with trichloromethane as solvent by potassium bromide press method

3.3. Calculation results

The molecular graph obtained after bringing the calculated results into the coordinates is an approximate planar structure, import the data into the origin, and make plots shown in Figure 9.

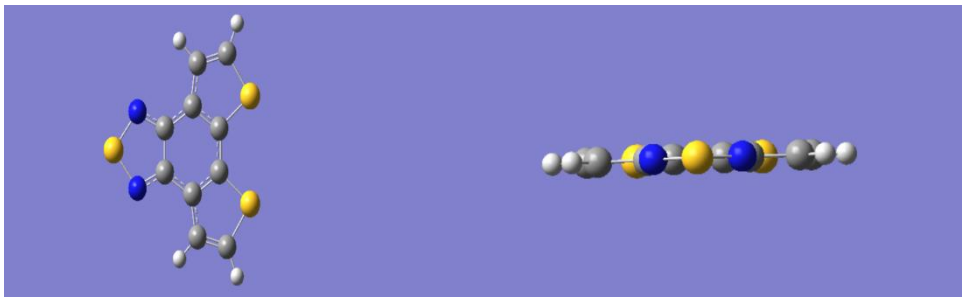

Figure 9: Perform UV-Vis Spectrum prediction on the molecule

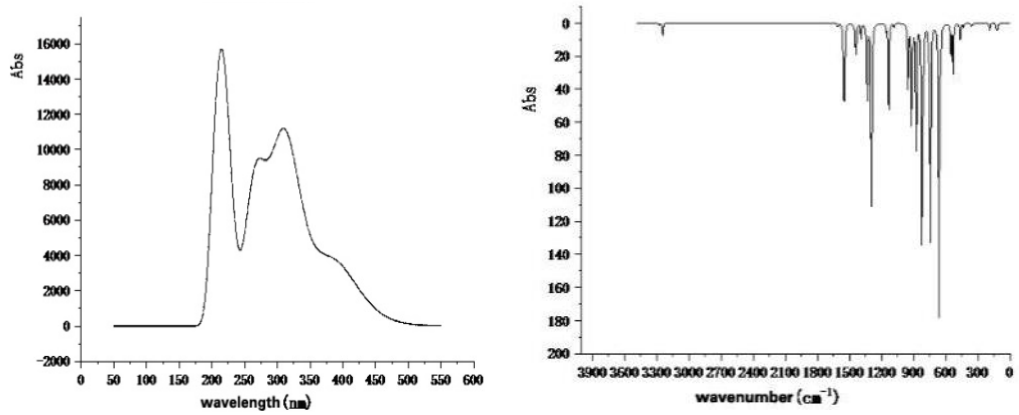

Figure 10: Theoretical calculations of UV-Vis and IR spectra

The data were analyzed by fitting the peaks to the theoretical calculations of UV-Vis spectra, and it was observed that the peak positions after fitting were at 213 nm, 321 nm, and 402 nm, respectively, as shown in Figure 10. Due to the instrumentation problem and the relatively high number of spurious peaks below 250 nm, the positions of the peaks measured theoretically and experimentally after 250 nm were in close agreement, which proved the correctness of the obtained product structure. From the theoretical IR spectra, the molecule has a weak absorption peak at about 3244 cm-1 and strong absorption peaks at 467 cm-1, 665 cm-1, 744 cm-1, 824 cm-1, 1423 cm-1, 1652 cm-1. The used data was in general agreement with the measured data.

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4. Conclusion

This experiment is referred to the literature, and it was improved and optimized based on the literature. It was combined with the textbook content to improve experimental step 2, which designed a high-yield synthetic route. It involves organic synthesis, comprehensive product processing operations, and training students to read the literature. According to the literature, it was carried out as an independent investigation, which was suitable for two people to cooperate to complete as a senior undergraduate students. It is also suitable for senior undergraduates as the teaching experiment to improve their comprehensive experimental ability.

According to the NMR hydrogen spectra, the results obtained are DT-BTD. The results obtained through theoretical calculations are consistent with the actual situation of IR and UV spectra. It can prove the optimized structure's correctness and help students accurately understand molecules' planar conjugated structure. While cultivating their ability to solve the spectra, the essential operation of using computational chemistry software is applied.

This experiment contains the basic operations and knowledge of undergraduate organic chemistry laboratory courses. Moderate improvement increases the difficulty and exercises the students' literature review and independent investigation ability. It is helpful to improve the experimental skills and research ability of organic chemistry undergraduates. The changes in product morphology in each step are apparent, and the final product molecules provide strong fluorescence, which reflects the experiment's interesting nature.

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