

Short Note

# Dimethyl 3,7-diamino-4,8-bis((2-methoxy-2-oxoethyl)thio)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxylate

Branislav Pavilek \*, Daniel Végh, Dušan Bortňák, Veronika Šmejkalová, Jozef Kožíšek  and Viktor Milata

Institute of Organic Chemistry, Catalysis, and Petrochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia

\* Correspondence: xpavilek@stuba.sk

**Abstract:** The convenient and multigram synthesis of a linear benzo[*b*]dithiophene (BDT) structure is proposed (dimethyl 3,7-diamino-4,8-bis((2-methoxy-2-oxoethyl)thio)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxylate). The starting materials are commercially available 2,3,5,6-tetrachloroterephthalonitrile and methyl 2-mercaptoacetate, which undergo aromatic substitution, followed by a cyclization reaction in basic conditions to form suitable BDT for potential optoelectronic applications.

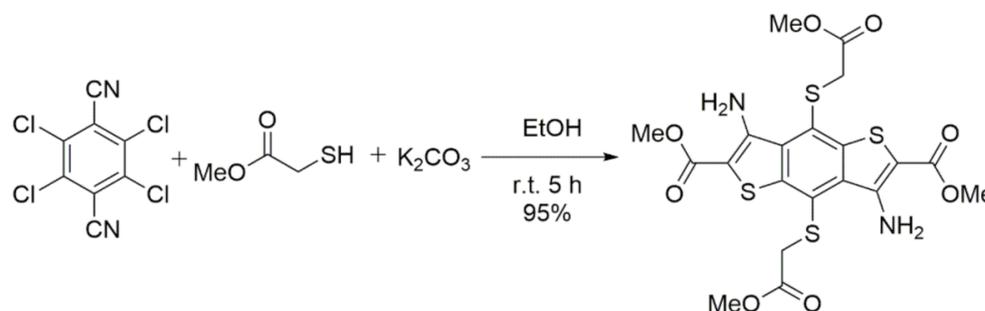
**Keywords:** benzodithiophene; organic semiconductor; cyclization reaction

## 1. Introduction

Due to the ever increasing demand for renewable energy, new organic semiconducting materials are required for optoelectronic applications, such as organic photovoltaics cells (OPCs), organic field-effect transistors (OFETs) [1], etc. One of the most promising building blocks for such a material is linear benzo[*b*]dithiophene [2].

## 2. Results and Discussion

The target BDT molecule is a suitable precursor for the further molecular design of organic semiconducting materials, as it features readily convertible functional groups. The synthesis of BDT is a continuation of previous work of our research group [3], and it pertains to studying the reaction of 2,3,5,6-tetrachloroterephthalonitrile with methyl 2-mercaptoacetate in the presence of potassium carbonate in ethanol (Scheme 1). The reaction mechanism was previously studied on benzo[*b*]thiophenes [4]. Similarly, in this case, the first step of the mechanism could be aromatic substitution via the  $S_NAr$  or  $S_{RN}1$  of methyl 2-mercaptoacetate for chlorine from 2,3,5,6-tetrachloroterephthalonitrile, followed by cyclization via the  $Ad_N$  of carbon nucleophile on the nitrile group in basic conditions.



**Scheme 1.** Preparation of dimethyl 3,7-diamino-4,8-bis((2-methoxy-2-oxoethyl)thio)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxylate (BDT).



**Citation:** Pavilek, B.; Végh, D.; Bortňák, D.; Šmejkalová, V.; Kožíšek, J.; Milata, V. Dimethyl 3,7-diamino-4,8-bis((2-methoxy-2-oxoethyl)thio)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxylate. *Molbank* **2022**, *2022*, M1474. <https://doi.org/10.3390/M1474>

Academic Editor: Fawaz Aldabbagh

Received: 6 October 2022

Accepted: 19 October 2022

Published: 27 October 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

### 3. Materials and Methods

#### 3.1. General Information

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were acquired on a Varian Inova-300 spectrometer (Bratislava, Slovakia) with a frequency of 299.96 MHz for the  $^1\text{H}$  nucleus and 75.43 MHz for the  $^{13}\text{C}$  nucleus. Chemical shifts were recorded in ppm relative to the solvent resonance as the reference. Data were reported as follows: chemical shift, multiplicity (s—singlet; d—doublet; t—triplet; q—quaternary; m—multiplet; br—broad) and coupling constants  $J$  (Hz). The NMR spectra were processed using MestReNova 14.2.2 software (Bratislava, Slovakia).

The IR spectrum was recorded on a Perkin Elmer Spectrum Two apparatus (Bratislava, Slovakia). Wavenumbers were recorded in  $\text{cm}^{-1}$ .

The melting point was measured on a Boetius apparatus (Nagema, Radebeul, Germany,) using a high-precision thermometer TD 121 from VWR. M.P. was left uncorrected.

An elemental analysis was carried out on a FlashEA 1112 (Thermo Scientific, Waltham, MA, USA) from the Thermo electron corporation.

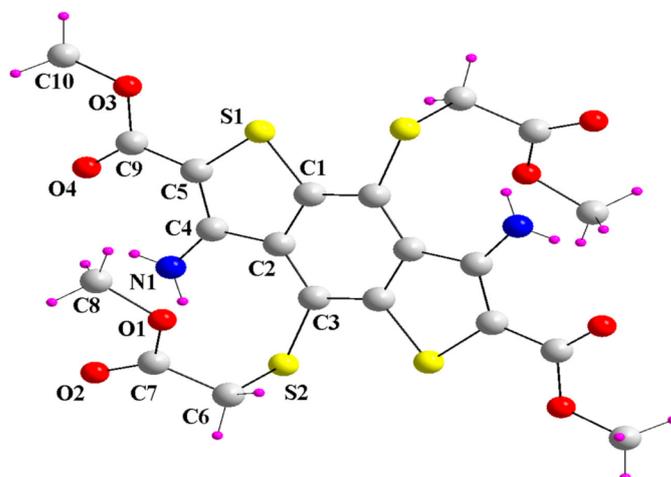
The single-crystal X-ray analysis was performed on an Oxford Diffraction Gemini R four-circle diffractometer (Oxford Diffraction Ltd., Abingdon, UK) with CrysAlis [5], using Cu-K $\alpha$  radiation for BDT at 100(1) K. Data reduction was performed with CrysAlis RED [5]. The structure was solved with the charge-flipping algorithm superflip [6] using OLEX2 [7]. A refinement was carried out on  $F^2$ , and scattering factors incorporated in SHELXL-2013 [8] were used. All nonhydrogen atoms were refined with anisotropic thermal parameters. Crystal data, data collection procedures, structure determinations and refinements were summarized in Table 1 and Figure 1. The positions of the H atoms were geometrically optimized and constrained to ride on their parent atoms, with a bond length of C–H = 0.96 Å (CH<sub>3</sub>); the N–H hydrogen was obtained from Fourier synthesis. Hydrogen's temperature factors were  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$ . The DIAMOND program package was used for the molecular structure drawing [9]. Cambridge Crystallographic Data Centre (CCDC) 2203334 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (accessed on: 24 August 2022) or from the Cambridge Crystallographic Data Centre, 12 Uni-on Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

**Table 1.** Crystal data and structure refinement for BDT.

Compound	BDT
Empirical formula (g/mol)	$\text{C}_{10}\text{H}_{10}\text{NO}_4\text{S}_2\text{C}_{14}$
Temperature (K)	100(1)
Wavelength (Å)	1.54184
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	$a = 6.3851(3)$ Å, $\alpha = 73.558(3)^\circ$ $b = 9.5602(3)$ Å, $\beta = 79.571(3)^\circ$ $c = 10.0541(4)$ Å, $\gamma = 81.722(3)^\circ$
Formula weight	272.31
Volume (Å <sup>3</sup> )	576.11
Z/calculated density (Mg/m <sup>3</sup> )	2/1.570
Absorption coefficient (mm <sup>-1</sup> )	4.247
F(000)	282
Crystal size (mm)	$0.267 \times 0.038 \times 0.026$
Theta range for data collection	4.637 to 73.894°
Index ranges	$-7 \leq h \leq 7$ $-11 \leq k \leq 11$ $-12 \leq l \leq 11$
Reflections collected	8848

Table 1. Cont.

Compound	BDT
Independent reflections	2270 ( $R_{\text{int}} = 0.0310$ , $R_{\text{sigma}} = 0.0231$ )
Completeness to $2\Theta = 25.000^\circ$	99.95 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	2270/0/194
Goodness-of-fit on F <sup>2</sup>	1.024
Final R indices ( $I > 2\sigma(I)$ )	$R_1 = 0.0325$ $wR_2 = 0.0876$
R indices (all data)	$R_1 = 0.0375$ $wR_2 = 0.0917$
Extinction coefficient	n/a
Largest diff. peak and hole ( $e.\text{\AA}^{-3}$ )	0.31 and $-0.24$



**Figure 1.** The molecular structure of BDT, showing the atom-labeling scheme. Displacement ellipsoids were drawn at the 30% probability level.

### 3.2. Dimethyl

#### 3,7-diamino-4,8-bis((2-methoxy-2-oxoethyl)thio)benzo[1,2-b:4,5-b']dithiophene-2,6-dicarboxylate

A 250 mL three-necked round-bottom flask was equipped with a thermometer, dropping funnel and condenser. The flask was charged with 2,3,5,6-tetrachloroterephthalonitrile (2.66 g, 10 mmol, 1 eq.) and potassium carbonate (6.92 g, 50 mmol, 5 eq.) in 80 mL of ethanol. The dropping funnel was filled with methyl 2-mercaptoacetate (5.31 g, 50 mmol, 5 eq.) in 80 mL of ethanol. A solution of methyl 2-mercaptoacetate was added dropwise into the stirring reaction mixture at room temperature. The colorless reaction mixture turned yellow, and the orange precipitate was formed. After the addition of methyl 2-mercaptoacetate was completed, the reaction mixture was heated to reflux for 5 h. The reaction was monitored with TLC (ethyl acetate:isohexane 1:1,  $R_f$  for BDT was 0.4). After cooling, the formed precipitate was filtered off and washed with cold water and ethanol, resulting in 5.16 g (95%, 9.5 mmol) of crude product. The crude product was crystallized from dimethyl carbonate to form red needles (m.p. 211 °C).

<sup>1</sup>H NMR (DMSO, 300 MHz):  $\delta$  = 3.30 ppm (s, 6 H), 3.34 ppm (s, 6 H), 3.69 ppm (s, 4 H), 7.29 ppm (br, 4 H) (See Supplementary Materials).

<sup>13</sup>C NMR (DMSO, 75 MHz):  $\delta$  = 168.68, 164.49, 149.62, 146.21, 130.37, 124.31, 98.5, 52.22, 51.63, 37.26.

Anal. Calcd. (%) for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>8</sub>S<sub>4</sub>: C 44.11; H 3.70; N 5.14; O 23.50; S 23.55. Found: C 44.02; H 3.79; N 5.22; O 23.43; S 23.48.

IR (cm<sup>-1</sup>): 3448.7; 3335.7; 2948.4; 1734.9; 1672.6; 1592.0; 1522.7.

X-ray analysis: The crystal structure of BDT was deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 2203334.

#### 4. Conclusions

In conclusion, the convenient and multigram synthesis of a linear benzo[b]dithiophene heterocycle is described with corresponding spectral, and crystallographic data for this structure. The title compound could be utilized as a building block for organic semiconducting materials, as it features readily convertible functional groups suitable for further molecular design.

**Supplementary Materials:** The following are available online. <sup>1</sup>H, <sup>13</sup>C NMR spectra and IR of dimethyl 3,7-diamino-4,8-bis((2-methoxy-2-oxoethyl)thio)benzo[1,2-b:4,5-b']dithiophene-2,6-dicarboxylate.

**Author Contributions:** Conceptualization, D.V.; methodology, V.Š.; validation, D.B.; formal analysis, J.K.; writing—original draft preparation, B.P.; writing—review and editing, D.V.; visualization, B.P.; supervision, V.M.; project administration, V.M.; funding acquisition, J.K. and V.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was financially supported by the Science and Technology Assistance Agency under contract no. APVV-17-0513, and the Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0718/19). We are grateful to the HPC center at the Slovak University of Technology in Bratislava, which is a part of the Slovak Infrastructure of High-Performance Computing (SIVVP project, ITMS code 26230120002, funded by the European region development funds, ERDF), for the computational time and resources provided.

**Data Availability Statement:** The presented data are available in this article.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript or in the decision to publish the results.

#### References

1. Perepichka, I.F.; Perepichka, D.F. *Handbook of Thiophene-Based Materials: Applications in Organic Electronics and Photonics*; John Wiley and Sons: Hoboken, NJ, USA, 2009; ISBN 9780470057322.
2. Rasool, A.; Zahid, S.; Shehzad, R.A.; Salim Akhter, M.; Iqbal, J. Designing of Benzodithiophene (BDT) Based Non-Fullerene Small Molecules with Favorable Optoelectronic Properties for Proficient Organic Solar Cells. *Comput. Theor. Chem.* **2021**, *1203*, 113359. [[CrossRef](#)]
3. Végh, D.; Milata, V. Synthesis of Highly Fluorinated 3,4-Substituted-1-Benzo[b]Thiophene and Benzo[1,2-b:4,5-b']Dithiophene Derivatives as Potential Biologically Active Compounds and Novel Opto-Electronic Materials. In *Proceedings of the FloHet-2015 Florida Heterocyclic And Synthetic Conference, Gainesville, FL, USA, 1–4 March 2015*; ARKAT USA, Inc.: Gainesville, FL, USA, 2015; p. 90.
4. Beugelmans, R.; Bois-Choussy, M.; Boudet, B. Etude Des Reactions de Srn1—Partie 10: Action de Sulfanions Sur Les Halogenures d'aryle Fonctionnalisés. Synthèse Directe de Benzothiophenes et Thienopyridines. *Tetrahedron* **1983**, *39*, 4153–4161. [[CrossRef](#)]
5. Oxford Diffraction. *CrysAlis PRO and CrysAlisRed*; Oxford Diffraction Ltd.: Abingdon, UK, 2016.
6. Palatinus, L. The Charge-Flipping Algorithm in Crystallography. *Acta Crystallogr. B* **2013**, *69*, 1–16. [[CrossRef](#)] [[PubMed](#)]
7. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339–341. [[CrossRef](#)]
8. Sheldrick, G.M. IUCr A Short History of SHELX. *Acta Cryst.* **2007**, *64*, 112–122. [[CrossRef](#)] [[PubMed](#)]
9. Brandenburg, K.; Berndt, M. *DIAMOND*; Crystal Impact GbR: Bonn, Germany, 1999.