molbank

MDPI

Short Note

4-Bromobenzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole)

Timofey N. Chmovzh [1,2], Daria A. Alekhina [1], Timofey A. Kudryashev [1] and Oleg A. Rakitin [1,*]

[1] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prospekt, 119991 Moscow, Russia; tim1661@yandex.ru (T.N.C.); alekhinadariaalex@gmail.com (D.A.A.); tp12345678@yandex.ru (T.A.K.)
[2] Nanotechnology Education and Research Center, South Ural State University, 76 Lenina Avenue, 454080 Chelyabinsk, Russia
* Correspondence: orakitin@ioc.ac.ru; Tel.: +7-499-1355327

Abstract: Bromoderivatives of benzofused 1,2,5-thiadiazoles are important precursors for the synthesis of dyes, which are widely used to design effective photovoltaic materials. In this study, 4-bromobenzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole was selectively obtained from the bromination of benzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole. The structure of the newly synthesized compound was established by means of elemental analysis, high-resolution mass spectrometry, ^{1}H-, ^{13}C-NMR, IR and UV spectroscopy and mass spectrometry.

Keywords: benzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazoles; bromination; 4-bromobenzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole); synthesis

Citation: Chmovzh, T.N.; Alekhina, D.A.; Kudryashev, T.A.; Rakitin, O.A. 4-Bromobenzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole). *Molbank* **2022**, *2022*, M1362. https://doi.org/10.3390/M1362

Academic Editor: Nicholas E. Leadbeater

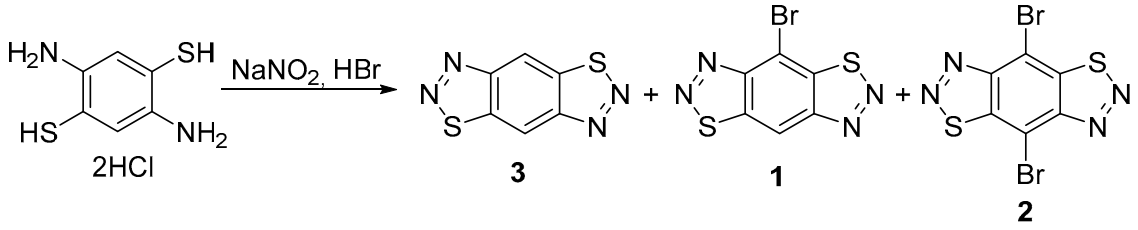
Received: 29 April 2022
Accepted: 10 May 2022
Published: 12 May 2022

1. Introduction

Benzofused 1,2,5-thiadiazoles play an important role as electron-withdrawing building blocks in the synthesis of organic dyes which have various applications in optoelectronics [1–3]. The addition of another electron-acceptor thiadiazole ring to the 2,1,3-benzothiadiazole heterocyclic system leads to the formation of 1*H*,5*H*-benzo[1,2-*c*:4,5-*c*′]bis([1,2,5]thiadiazoles) (BBTs) which have a stronger electron-withdrawing character [4,5] and provide a variety of donor-acceptor materials with a small bandgap [6,7]. Unexpectedly, its benzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole isomers (iso-BBTs), differing only in the order of atoms in the five-membered rings, have been practically unstudied as building blocks. This is because 4-bromo- **1** and 4,8-dibromobenzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazoles **2**, which could serve as efficient intermediates for photovoltaic materials, have never been isolated in pure state or characterized. These compounds have only been identified in an inseparable mixture of benzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole **3** and its mono-bromo **1** and bis-bromo **2** derivatives obtained by the nitrosation of 2,5-diaminobenzene-1,4-dithiol **3** in hydrobromic acid [8]. Herein, we report the selective synthesis of 4-bromobenzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole **1** by the reaction of benzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole **3** with bromine.

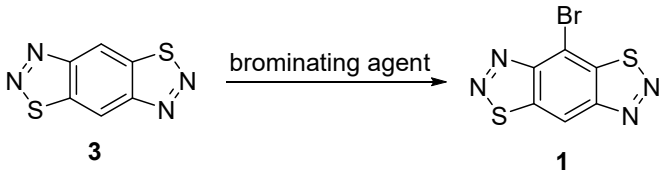
2. Results and Discussion

To synthesize bromoderivatives of benzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole) Fachetti et al. studied the nitrosation of 2,5-diaminobenzene-1,4-dithiol in hydrobromic acid [8]. As a result of this reaction, a mixture of three compounds was formed—tricycle **3**, its 4-mono- **1** and 4,8-bis-bromo **2** derivatives, although the authors failed to isolate and characterize individual compounds (Scheme 1).



Scheme 1. Nitrosation of 2,5-diaminobenzene-1,4-dithiol.

To selectively obtain bromoderivatives of benzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole), we chose the reaction of unsubstituted tricycle **3** [9] with brominating reagents *N*-bromosuccinimide (NBS) and bromine (Scheme 2). It was shown that NBS does not react with tricycle **3** in $CHCl_3$ and DMF, either at room temperature or when heated at 61 and 100 °C, respectively; starting compound **3** was fully recovered from the reaction mixtures (Entries 1–4, Table 1). Heating compound **3** with excess bromine in HBr at 80 °C for 12 h resulted in a single mono-brominated product (compound **2**) in moderate yield (60%, Entry 5). Increasing the reaction temperature to 110 °C resulted in the same product, **1**, in a lower yield, probably due to partial decomposition of the final compound (Entry 6).



Scheme 2. Synthesis of 4-bromobenzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole) **1**.

Table 1. Bromination of benzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole) **3**.

Entry	Reagent	Solvent	Temperature, °C	Time, h	Yield of 1%
1	NBS	$CHCl_3$	25	24	0
2	NBS	DMF	25	24	0
3	NBS	$CHCl_3$	61	24	0
4	NBS	DMF	110	24	0
5	Br_2	HBr	80	12	60
6	Br_2	HBr	110	12	45

The structure of 4-bromobenzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole) **1** was confirmed by means of elemental analysis, high-resolution mass spectrometry, ^{1}H-, ^{13}C-NMR, IR, UV spectroscopy and mass-spectrometry.

Mono-bromoderivatives of benzofused thiadiazoles are rare and difficult-to-prepare compounds, and they are important precursors for the synthesis of unsymmetrical disubstituted benzothiadiazoles [10]. Thus, the 4-bromobenzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole **1** synthesized by us can be widely explored for the preparation of previously inaccessible various photovoltaic material, such as dye-sensitized solar cells (DSSCs), organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), etc.

3. Materials and Methods

Benzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole) **1** [9] was prepared according to the published method. The solvents and reagents were purchased from commercial sources and used as received. Elemental analysis was performed on a 2400 Elemental Analyzer (Perkin ElmerInc., Waltham, MA, USA). The melting point was determined on a Kofler hot-stage apparatus and was uncorrected. ^{1}H- and ^{13}C-NMR spectra were taken with a Bruker AM-300 machine (Bruker AXS Handheld Inc., Kennewick, WA, USA) (at frequencies of 300 and 75 MHz) in $CDCl_3$ solution, with TMS as the standard. The IR spectrum was measured with a Bruker "Alpha-T" instrument (Santa Barbara, CA, USA) in KBr pellets.

The high-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik Gmbh, Bremen, Germany) using electrospray ionization (ESI). Solution UV–Visible absorption spectra were recorded using an OKB Spektr SF-2000 UV/Vis/NIR spectrophotometer (St. Petersburg, Russia) controlled with SF-2000 software (St. Petersburg, Russia). The sample was measured in a 1 cm quartz cell at room temperature with 7.6×10^{-6} mol/mL concentration in CH_2Cl_2.

Synthesis of 4-bromobenzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole) **1**. (Supplementary Materials).

Bromine (0.5 mL, 20 mmol) was added to a solution of benzo[1,2-*d*:4,5-*d*′]bis([1,2,3] thiadiazole) **3** (250 mg, 1.28 mmol) in HBr (10 mL). The mixture was stirred at 80 °C for 12 h. On completion, the reaction mixture was poured into ice (50 g) and the organic layer was extracted with EtOAc (3 × 35 mL), dried over $MgSO_4$ and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent CH_2Cl_2). Yield: 211 mg (60%), yellow solid, R_f = 0.3 (CH_2Cl_2). Mp > 250 °C. IR spectrum, ν, cm^{-1}: 3083, 2925, 1393, 1289, 1190, 886, 796, 538. ^{1}H-NMR (ppm): δ 9.27 (s). UV-Vis spectra (in CH_2Cl_2), λmax: 240 nm (ε = 1,3702 M^{-1} cm^{-1}). ^{13}C-NMR (ppm): δ 156.5, 156.2, 143.2, 140.6, 113.2, 107.5. HRMS (ESI-TOF), m/z: calcd for $C_6H^{79}BrN_4S_2Ag$ $[M+Ag]^+$, 378.7871, found, 378.7870. MS (EI, 70 eV), m/z (I, %): 274 ($[M + 2]^+$, 70), 273 ($[M]^+$, 6), 272($[M - 1]^+$, 65), 244 (10), 218 (73), 149 (98), 137 (97), 93 (98), 69 (100), 61 (55), 44(50), 32 (53), 18 (96). Anal. calcd. for $C_{28}H_{28}N_6O_2$ (271.8899): C, 26.45; H, 0.37; N, 20.51. Found: C, 26.38; H, 0.30; N, 20.45%.

Supplementary Materials: The following supporting information can be downloaded at: copies of ^{1}H-, ^{13}C-NMR, IR, HMRS, UV–Vis and mass-spectra for compound **1**.

Author Contributions: Conceptualization, O.A.R. and T.N.C.; methodology, O.A.R.; software, T.N.C.; validation, O.A.R.; formal analysis, investigation, D.A.A. and T.A.K.; resources, O.A.R.; data curation, O.A.R.; writing—original draft preparation, O.A.R.; writing—review and editing, O.A.R.; visualization, O.A.R.; supervision, O.A.R.; project administration, O.A.R.; funding acquisition, O.A.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funding by the Russian Science Foundation, grant number 22-23-00252.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of compounds **1**–**3** are available from the authors.

References

1. Neto, B.A.D.; Lapis, A.A.M.; da Silva Júnior, E.N.; Dupont, J. 2,1,3-Benzothiadiazole and Derivatives: Synthesis, Properties, Reactions, and Applications in Light Technology of Small Molecules. *Eur. J. Org. Chem.* **2013**, *2013*, 228–255. [CrossRef]
2. Rakitin, O.A. Recent developments in the synthesis of 1,2,5-thiadiazoles and 2,1,3-benzothiadiazoles. *Synthesis* **2019**, *51*, 4338–4347. [CrossRef]
3. Rakitin, O.A. Fused 1,2,5-thia- and 1,2,5-selenadiazoles: Synthesis and application in materials chemistry. *Tetrahedron Lett.* **2020**, *61*, 152230. [CrossRef]
4. Ono, K.; Tanaka, S.; Yamashita, Y. Benzobis(thiadiazole)s Containing Hypervalent Sulfur Atoms: Novel Heterocycles with High Electron Affinity and Short Intermolecular Contacts between Heteroatoms. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1977–1979. [CrossRef]
5. Chmovzh, T.N.; Knyazeva, E.A.; Mikhalchenko, L.V.; Golovanov, I.S.; Amelichev, S.A.; Rakitin, O.A. Synthesis of 4,7-dibromo derivative of ultrahigh electron-deficient [1,2,5]thiadiazolo [3,4-*d*]pyridazine heterocycle and its cross-coupling reactions. *Eur. J. Org. Chem.* **2018**, *41*, 5668–5677. [CrossRef]
6. Wang, Y.; Kadoya, T.; Wang, L.; Hayakawa, T.; Tokita, M.; Mori, T.; Michinobu, T. Benzobisthiadiazole-based conjugated donor–acceptor polymers for organic thin film transistors: Effects of π-conjugated bridges on ambipolar transport. *J. Mater. Chem. C* **2015**, *3*, 1196–1207. [CrossRef]
7. Du, X.; Qi, J.; Zhang, Z.; Ma, D.; Wang, Z.Y. Efficient Non-Doped Near Infrared Organic Light-Emitting Devices Based on Fluorophores with Aggregation-Induced Emission Enhancement. *Chem. Mater.* **2012**, *24*, 2178–2185. [CrossRef]

8. Bianchi, L.; Zhang, X.; Chen, Z.; Chen, P.; Zhou, X.; Tang, Y.; Liu, B.; Guo, X.; Facchetti, A. New Benzo[1,2-*d*:4,5-*d*′]bis([1,2,3]thiadiazole) (iso-BBT)-Based Polymers for Application in Transistors and Solar Cells. *Chem. Mater.* **2019**, *31*, 6519–6529. [CrossRef]
9. Facchetti, A.; Chen, Z.; Brown, J.E. Semiconducting Compounds and Related Devices. U.S. Patent, 0110666, 2017.
10. Konstantinova, L.S.; Knyazeva, E.A.; Rakitin, O.A. Recent Developments in the Synthesis and Applications of 1,2,5-Thia- and Selenadiazoles. A Review. *Org. Prep. Proced. Int.* **2014**, *46*, 475–544. [CrossRef]