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Short Note

4,7-Bis(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)-[1,2,5]thiadiazolo[3,4-*c*]pyridine

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Abstract: Donor-acceptor-donor (D-A-D) type molecules are of interest as components in organic light emitting diodes (OLEDs). In this communication, 4,7-bis(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)-[1,2,5]thiadiazolo[3,4-*c*]pyridine was obtained by two successive reactions—aromatic nucleophilic substitution S_NAr and Buchwald-Hartwig cross-coupling reaction. The structure of newly synthesized compounds was established by elemental analysis, high resolution mass-spectrometry, ^1H, ^{13}C NMR, IR and UV spectroscopy and mass-spectrometry. The luminescent properties of the title compound were studied.

Keywords: donor-acceptor-donor molecules; [1,2,5]thiadiazolo[3,4-*c*]pyridines; aromatic nucleophilic substitution; Buchwald-Hartwig cross-coupling reaction; luminescent properties

Citation: Chmovzh, T.N.; Rakitin, O.A. 4,7-Bis(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)-[1,2,5]thiadiazolo[3,4-*c*]pyridine. *Molbank* **2022**, *2022*, M1441. https://doi.org/10.3390/M1441

Academic Editor: Nicholas E. Leadbeater

Received: 31 August 2022
Accepted: 6 September 2022
Published: 8 September 2022

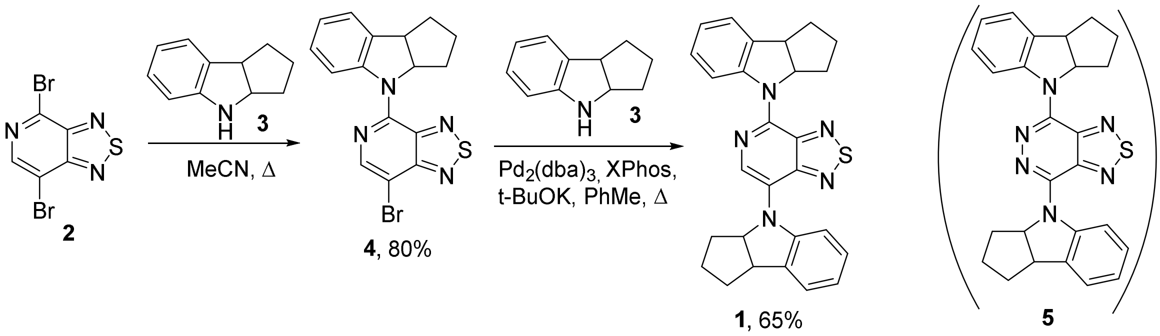
1. Introduction

In recent decades, there has been a great attention to the design of small organic molecules containing donor (D) and acceptor (A) fragments due to their possible application in various electronic devices, such as organic solar cells (OSCs) [1,2], n-type organic field effect transistors (OFETs) [3,4] and luminescent materials emitting in the visible and infrared regions [5,6]. Special attention in the construction of OLEDs is given to structures of the donor-acceptor-donor (D-A-D) type [7]. Recently various building blocks based on a fused 1,2,5-thiadiazole ring, such as benzo[*d*][1,2,3]thiadiazole [8], benzo[1,2-*d*:4,5-*d′*]bis([1,2,3]thiadiazole [9] and [1,2,5]thiadiazolo[3,4-*d*]pyridazine as an electron acceptors with ultrahigh electron deficiency have been used for the preparation of D-A-D luminophores [7], and low-bandgap conjugated polymers [4] have been reported. However, according to SciFinder and Reaxys searches there are more than 200 D-A-D [1,2,5]thiadiazolo[3,4-*c*]pyridines, there are no examples of when donor fragments were attached to thiadiazolopyridine ring by nitrogen. To obtain such compounds we combined two synthetic procedures: aromatic nucleophilic substitution S_NAr and Buchwald-Hartwig cross-coupling reaction, as it was employed for the synthesis of 4,7-bis(dodecylthio)-[1,2,5]thiadiazolo[3,4-*c*]pyridine from 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine [10]. Herein, we report the preparation of 4,7-bis(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)-[1,2,5]thiadiazolo[3,4-*c*]pyridine **1** from 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine **2** and the investigation of its luminescent properties.

2. Results and Discussion

4,7-Dibromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine **2** was investigated in the reaction of nucleophilic aromatic substitution of S_NAr with 1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole **3**. It was shown that when dibromide was treated with 2 equiv of amine **3** at room temperature in CH_2Cl_2 or MeCN, the formation of monoamino derivative **4** was observed. The reaction in acetonitrile proceeded much more smoothly than in the less polar dichloromethane.

We have shown that by the refluxing of amine **3** with dibromide **2** in acetonitrile, an increase in the yield of monosubstituted derivative **4** up to 80% was observed (the yield of compound **4** in dichloromethane under similar conditions was 62%). To prepare the target bis(amino) derivative **1** we studied the Buchwald-Hartwig cross-coupling reaction of monoamine **4** with cyclopentaindole **3** in the presence of the palladium catalyst, tris(dibenzylideneacetone) dipalladium (0) ($Pd_2(dba)_3$), an XPhos ligand and *t*-BuOK as a base [11]. It was found that when the reaction mixture was refluxed in toluene for 48 h, complete disappearance of the starting compound **4** was observed with the formation of a bis-substituted product **1** with a high yield of 65% (Scheme 1). We have shown that the reaction of dibromide **2** with amine **3** (3 equiv) under the conditions of the Buchwald-Hartwig reaction led to complete decomposition of the starting product; it was not possible to isolate individual products from the reaction mixture.



Scheme 1. Synthesis of 4,7-bis(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)-[1,2,5]thiadiazolo[3,4-*c*]pyridine **1**.

The structure of 7-bromo-4-(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)-[1,2,5] thiadiazolo[3,4-*c*]pyridine **4** and 4,7-bis(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)-[1,2,5]thiadiazolo[3,4-*c*]pyridine **1** was confirmed by elemental analysis, high resolution mass-spectrometry, ^{1}H, ^{13}C NMR, IR and UV spectroscopy.

We measured the optical absorption spectra for compound **1** in THF, and compared it with the spectra of pyridazinothiadiazole-analogue **5** [7]. The spectra consisted of several spectral bands in the UV wavelength range and one wide band in the visible spectral region, which is explained by the process of intramolecular charge transfer (ICT). The spectra obtained for **1** and **5** in the UV region have an absorption maximum at a wavelength of 270 and 290 nm, respectively. The position of this short-wave maximum indicates that this band is associated with a π-π* electronic transition. For compound **1**, the maximum of the ICT bands is located in the shorter wavelength spectral region of 509 nm compared to the pyridazinothiadiazole analogue **5** (555 nm) [7]. However, compound **1** had an extremely low fluorescence intensity in the near-IR region of the spectrum (740 nm) compared to analogue **5**, probably due to the presence of non-radiative conversion in compound **1**.

In conclusion, 4,7-bis(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)-[1,2,5]thiadiazolo [3,4-*c*]pyridine **1** was successfully synthesized from 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine **2** by two synthetic procedures: aromatic nucleophilic substitution S_NAr and Buchwald-Hartwig cross-coupling reaction. The luminescent properties of bis(cyclopentaindole) derivative **1** were investigated.

3. Materials and Methods

4,7-Dibromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine **2** [12] and 1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole **3** [13] were prepared according to the published methods. 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). Melting points were determined on a Kofler hot-stage apparatus and are 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. J values are given in Hz. MS spectrum (EI, 70 eV) was obtained with a Finnigan MAT INCOS 50 instrument (Hazlet, NJ, USA). IR spectrum was measured with a Bruker "Alpha-T" instrument in KBr pellet. 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 Agilent cary 60 spectrophotometer (USA). Luminescence spectra were recorded using an Agilent Cary Eclipse (USA). Sample was placed in a 1 cm quartz cell at room temperature with a 5×10^{-5} mol/mL concentration.

Synthesis of 7-bromo-4-(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)-[1,2,5]thiadiazolo[3,4-*c*]pyridine **4** (Supplementary Materials).

1,2,3,3a,4,8b-Hexahydrocyclopenta[*b*]indole **3** (108 mg, 0.68 mmol) and 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine **2** (100 mg, 0.34 mmol) were dissolved in a vial with MeCN (10 mL) under a stream of nitrogen. The mixture was stirred for 12 h at 81 °C. On completion (monitored by TLC), the mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (3 × 35 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (Silica gel Merck 60, eluent hexane–CH_2Cl_2, 5:1, *v*/*v*). Yield 101 mg (80%), red solid, mp = 150–152 °C, R_f = 0.2 (Hexane:CH_2Cl_2, 5:1, *v*/*v*). IR spectrum, ν (cm^{-1}): 2924, 2862, 1518, 1482, 1457, 1394, 1298, 1263, 890, 749. ^1H NMR (ppm): δ 8.68 (d, *J* = 8.0, 1H), 8.31 (s, 1H), 7.30–7.24 (m, 2H), 7.10 (t, *J* = 7.1, 1H), 6.02 (t, *J* = 7.2, 1H), 4.04 (t, *J* = 7.1, 1H), 2.30–2.08 (m, 3H), 1.82–1.65 (m, 2H), 1.48–1.37 (m, 1H). ^{13}C NMR (ppm): δ 147.6, 145.5, 144.3, 143.9, 136.2, 127.4, 124.1, 123.9, 123.8, 117.8, 98.5, 67.6, 45.8, 36.9, 34.2, 23.9. MS (EI, 70eV), *m*/*z* (*I*, %): 375 ($[M + 1]^+$, 3), 374 ($[M]^+$, 8), 373 ($[M - 1]^+$, 2), 372 ($[M - 2]^+$, 6), 345 (8), 293 (11), 143 (18), 130 (100), 115 (17), 93 (80), 77 (25), 57 (20), 41 (20), 28 (10). HRMS (ESI-TOF), *m*/*z*: calcd for $C_{16}H_{14}{}^{79}BrN_4S$ $[M + H]^+$, 373.0117, found, 373.0112. Anal. calcd. for $C_{16}H_{13}BrN_4S$ (373.0117): C, 51.48; H, 3.51; N, 15.01. Found: C, 51.40; H, 3.52; N, 15.0%.

Synthesis of 4,7-bis(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)-[1,2,5]thiadiazolo[3,4-*c*]pyridine **1** (Supplementary Materials).

7-Bromo-4-(2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl)-[1,2,5]thiadiazolo[3,4-*c*] pyridine **4** (100 mg, 0.26 mmol), $Pd_2(dba)_3$ (23 mg, 0.026 mmol), XPhos (24 mg, 0.052 mmol) and *t*-BuOK (32 mg, 0.28 mmol) were dissolved in a vial with toluene (10 mL) under a stream of nitrogen. After 10 min, 1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole **3** (54 mg, 0.26 mmol) was added using a syringe. The temperature of the oil bath was increased to 120 °C, and stirring was continued for 48 h. This reaction was stopped by pouring it into ice water. Then, the solution was extracted with CH_2Cl_2 (3 × 35 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (Silica gel Merck 60, eluent hexane–CH_2Cl_2, 5:1, *v*/*v*). Yield 76 mg (65%), violet solid, mp = 130–132 °C, R_f = 0.3 (CH_2Cl_2, 5:1, *v*/*v*). IR spectrum, ν (cm^{-1}): 2925, 2854, 1603, 1486, 1456, 1260, 1099, 1023, 802, 736, 529. ^1H NMR (ppm): δ 8.66 (dd, *J* = 8.4, 3.4, 1H), 8.23 (s, 1H), 7.26–7.20 (m, 2H), 7.11 (d, *J* = 7.3, 1H), 7.02 (t, *J* = 7.4, 1H), 6.93 (t, *J* = 7.2, 1H), 6.66 (t, *J* = 7.3, 1H), 6.39 (t, *J* = 8.2, 1H), 6.06 (t, *J* = 7.3, 1H), 5.18–5.011 (m, 1H), 4.01 (t, *J* = 8.2, 1H), 3.96–3.90 (m, 1H), 2.29–1.99 (m, 4H), 1.92–1.78 (m, 6H), 1.45–1.35 (m, 2H). ^{13}C NMR (ppm): δ 150.1, 146.3, 145.1, 144.9, 141.1, 136.0, 133.9, 129.9, 127.4, 127.2, 124.7, 124.1, 123.2, 122.5, 118.1, 117.0, 107.1, 69.4, 67.5, 46.1, 45.8, 37.0, 35.5, 34.4, 33.7, 24.3, 23.9. MS (EI, 70eV), *m*/*z* (*I*, %): 453 ($[M + 2]^+$, 6), 452 ($[M + 1]^+$, 30), 451 ($[M]^+$, 100), 422 (12), 265 (8), 197 (35), 130 (70), 115 (32), 77 (25), 41 (33). HRMS (ESI-TOF), *m*/*z*: calcd for $C_{27}H_{26}N_5S$ $[M + H]^+$, 452.1903, found, 452.1922. Anal. calcd. for $C_{27}H_{25}N_5S$ (452.1903): C, 71.81; H, 5.58; N, 15.51. Found: C, 71.79; H, 5.55; N, 15.47%. UV-Vis spectra (in THF), λmax: 271 nm (ε = 14757 M^{-1} cm^{-1}), 509 nm (ε = 4646 M^{-1} cm^{-1}). Luminescence spectra: in THF λmax: 740 nm.

Supplementary Materials: The following are available online: copies of ^{1}H, ^{13}C NMR, IR, UV-Vis, luminescence, and mass-spectra for compounds **1** and **4**.

Author Contributions: Conceptualization, T.N.C.; methodology, O.A.R.; software, T.N.C.; validation, O.A.R.; formal analysis, investigation, T.N.C.; resources, O.A.R.; data curation, O.A.R.; writing—original draft preparation, T.N.C.; writing—review and editing, T.N.C.; 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 received no external funding.

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.

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