Short Note

7,7’-(4,4-Bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene-2,6-diyl)bis(4-bromobenzo[c][1,2,5]thiadiazole)

Nikita S. Gudim 1, Ekaterina A. Knyazeva 1,2 and Oleg A. Rakitin 1,2,*

1 N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prospekt, 119991 Moscow, Russia; nikitosgudim@gmail.com (N.S.G.); katerina_knyazev@mail.ru (E.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: 2,6-Bis(benzo[c][1,2,5]thiadiazol-4-yl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophenes are of interest for the synthesis of molecules which can be employed in optoelectronic devices. In this communication, 7,7’-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene-2,6-diyl)bis(4-bromobenzo[c][1,2,5]thiadiazole) was obtained by direct C–H cross-coupling of 4,7-dibromobenzo[c][1,2,5]thiadiazole with 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene in the presence of palladium(II) acetate and potassium pivalate. The structure of newly synthesized compound was established by means of elemental analysis, high-resolution mass spectrometry, 1H, 13C NMR, IR and UV spectroscopy.

Keywords: π-conjugated molecules; direct C–H arylation; 4,7-dibromobenzo[c][1,2,5]thiadiazole; 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene

1. Introduction

π-Conjugated molecules have been often used in organic optoelectronic devices such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), organic solar cells (OSCs) and others [1,2]. Numerous combinations of donor, acceptor and π-spacer elements are employed to achieve the desired properties of the optoelectronic material by increasing polarizability and tuning the energy band gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [3–5]. One of the interesting molecular intermediates 2,6-bis(benzo[c][1,2,5]thiadiazol-4-yl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophenes, which contain electron deficient moiety, for example benzo[c][1,2,5]thiadiazole, linked through a π-conjugated bridge, i.e., 4H-cyclopenta[2,1-b:3,4-b’]dithiophene, has been frequently used for the synthesis various polymer and oligomer materials [6–13].

From a synthetic point of view, the formation of 2,6-bis(benzo[c][1,2,5]thiadiazol-4-yl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophenes requires the formation of C–C bonds, as a rule, using cross-coupling reactions. In all the reactions described, the cross-coupling by Stille [6–9] and, less often, by Suzuki [10,11] was employed. Yields may vary from 30% to 98%. On the other hand, it is known that direct arylation can occur via the C–H bond without the need for organometallic intermediates. This method was proposed several decades ago by Ohta et al. [14] with the example of direct arylation of thiophenes with aryl halides. Recently, direct C–H arylation has been developed as a method for synthesis conjugated materials for use in organic electronics from simple building blocks [15–18]. This method offers shorter and cheaper reaction paths for intermediates and the final synthesis of materials, and also leads to less toxic waste compared to classical cross-coupling protocols. Herein, we report the synthesis of 7,7’-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene-2,6-diyl)bis(4-bromobenzo[c][1,2,5]thiadiazole) by direct C–H cross-coupling of 4,7-dibromobenzo[c][1,2,5]thiadiazole with 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene.
2. Results and Discussion

We studied the Pd-catalyzed direct C–H arylation reaction of 4,7-dibromobenzo[c][1,2,5]thiadiazole 1 with 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene 2 and the most frequently used bases in this type of reactions—potassium and cesium pivalates (generated in situ from the corresponding carbonates and pivalic acid) and potassium acetate (Scheme 1, Table 1). The search for optimal conditions was carried out by varying the bases, solvents, and the reaction temperature. It was found that the reaction between 4,7-dibromobenzo[c][1,2,5]thiadiazole 1 and 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene 2 in the presence of palladium(II)acetate and potassium pivalate begins at temperatures above 60 °C; at a temperature of 40 °C, the starting compounds remain in the reaction mass (Table 1, Entry 1). When the reaction was carried out under heating (at 80 °C or higher) in DMF or DMAc, product 3 was isolated in a yield of 23–27% (Table 1, Entries 2–4). It has been shown that increasing the temperature or replacing potassium pivalate with cesium pivalate does not improve the yields of the target product. We assume that the low yields are the result of the oligomerization of product 3 and 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene 2.

Scheme 1. Synthesis of 7,7′-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene-2,6-diyl]bis(4-bromobenzo[c][1,2,5]thiadiazole) 3.

Table 1. Reaction of 4,7-dibromobenzo[c][1,2,5]thiadiazole 1 with 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene 2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Base</th>
<th>T, °C</th>
<th>Time, h</th>
<th>Yield of 3, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMF</td>
<td>K₂CO₃/PivOH</td>
<td>40</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>DMF</td>
<td>K₂CO₃/PivOH</td>
<td>80</td>
<td>4</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>DMAc</td>
<td>AcOK</td>
<td>155</td>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>DMAc</td>
<td>Cs₂CO₃/PivOH</td>
<td>155</td>
<td>4</td>
<td>23</td>
</tr>
</tbody>
</table>

The structure of 7,7′-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene-2,6-diyl]bis(4-bromobenzo[c][1,2,5]thiadiazole) 3 was confirmed by means of elemental analysis, high-resolution mass spectrometry, ¹H, ¹³C NMR, IR and UV spectroscopy.

3. Materials and Methods

4,7-Dibromobenzo[c][1,2,5]thiadiazole 1 [19] and 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene 2 [20] 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 Elmer Inc., Waltham, MA, USA). The melting point was determined on a Kofler hot-stage apparatus and is uncorrected. ¹H and ¹³C 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 CDCl₃ solution with TMS as the standard. J values are given in Hz. The IR spectrum was measured using a Bruker “Alpha-T” instrument in KBr pellet. The high-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization (Supplementary Materials). The solution’s UV-visible absorption spectra were recorded using an OKB Spektr SF-2000 UV/Vis/NIR spectrophotometer controlled with SF-2000 software. The sample was measured in a 1 cm quartz cell at room temperature with 4.8 × 10⁻³ mol/mL concentration in CH₂Cl₂.
Synthesis of 7,7′-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene-2,6-diyl) bis(4-bromobenzenc[c][1,2,5]thiadiazole 3 (Supplementary Materials).

A mixture of 4,7-dibromobenzenc[c][1,2,5]thiadiazole 1 (880 mg, 3.02 mmol), pivalic acid (520 mg, 4.33 mmol) and potassium carbonate (800 mg, 5.79 mmol) in dry DMF (20 mL) was degassed by argon for 20 min, and Pd(OAc)$_2$ (50 mg, 0.23 mmol) was added. The mixture was stirred at room temperature for 10 min and then the solution of 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene 2 (580 mg, 1.44 mmol) in DMF (7 mL) was dropwise added during 0.5 h. Reaction mixture was heated to 80 °C for 4 h. On completion, the mixture was poured into water and extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic phases were washed with water (5 × 25 mL), dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (silica gel Merck 60, eluent-petroleum ether). Yield 322 mg (27%), purple solid with mp = 46–47 °C, R$_f$ = 0.71 (petroleum ether–ethyl acetate, 10:1, v/v). IR spectrum, ν, cm$^{-1}$: 3499, 3438, 2954, 2921 and 2853 (C–H), 1631, 1575, 1498, 1395, 1227, 1183, 823. $^1$H NMR (ppm, CDCl$_3$): δ 8.10 (t, J = 4.6, 2H, the ratio was 1:2:1 due to racemic 2-ethylhexyl groups [21,22]), 7.84 (d, J = 7.8, 2H), 7.70 (d, J = 7.8, 2H), 2.10–1.99 (m, 4H), 1.07–0.93 (m, 18H), 0.68–0.61 (m, 12H). $^{13}$C NMR (ppm): δ 159.5, 153.9, 151.6, 139.4, 132.4, 128.0, 124.2, 123.6, 123.4, 111.4, 54.4, 43.2, 35.4, 34.3, 28.6, 27.6, 22.8, 14.0, 10.8. HRMS (ESI-TOF), m/z: calcd for C$_{37}$H$_{60}$Br$_2$N$_4$S$_4$ [M + H]$^+$, 828.0473, found, 828.0478. UV-Vis (CH$_2$Cl$_2$, $\lambda_{\text{max}}$, nm/logε): 364/3.75, 539/4.01. Anal. calcd for C$_{37}$H$_{60}$Br$_2$N$_4$S$_4$ (828.0473): C, 53.62; H, 4.83; N, 6.76. Found: C, 53.89; H, 4.97; N, 6.86%.

Supplementary Materials: The following are available online: copies of $^1$H, $^{13}$C NMR, IR and UV-Vis spectra for the compound 3.

Author Contributions: Analysis of experimental results and NMR data, E.A.K.; synthetic experiments and resources, N.S.G.; conceptualization, writing—review and editing supervision and project administration, O.A.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Education and Science of the Russian Federation, grant number FENU-2020-0019 (2020073GZ).

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.

References


