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Short Note

4,7-Bis(1,2,3,4,4a,9a-Hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine

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Abstract: New donor-acceptor-donor (D-A-D)-type structures are widely used to design effective organic light-emitting diodes (OLEDs). In this communication, 4,7-bis(1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine was obtained in a 65% yield by the treatment of 4,7-dichloro[1,2,5]oxadiazolo[3,4-*d*]pyridazine 1-oxide with 2,3,4,4a,9,9a-hexahydro-1*H*-carbazole. The structure of the newly synthesized compounds was established by means of an elemental analysis, ^{1}H, ^{13}C NMR, IR and UV spectroscopy, and HRMS and LR mass-spectrometry.

Keywords: dyes; S_NAr nucleophilic substitution; [1,2,5]oxadiazolo[3,4-*d*]pyridazines; 2,3,4,4a,9,9a-hexahydro-1*H*-carbazole

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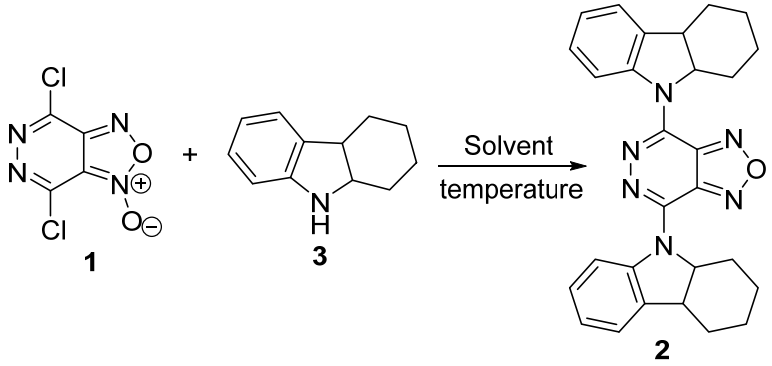
1. Introduction

4,7-Dihalogen-substituted 2,1,3-benzochalcogenadiazoles and [1,2,5]chalcogenadiazolo[3,4-*c*]pyridines (chalcogen = O, S, Se) are important precursors for the preparation of dye-sensitized solar cells (DSSCs) and organic light-emitting diodes (OLEDs) [1–3]. Recently, it was found that 4,7-dibromo[1,2,5]thiadiazolo[3,4-*d*]pyridazine—one of the strongest electron–acceptor systems—can also be an efficient intermediate for photovoltaic materials [4–6]. Selenium and oxygen analogs of chalcogenadiazolopyridazines may also have interesting photovoltaic properties. Our attempts to obtain 4,7-dibromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazine were not successful, and this compound turned out to be unstable for hydrolysis; as a result, only its hydroxy analog 7-bromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazin-4(5*H*)-one was isolated and characterized [7]. To the best of our knowledge, 4,7-dichloro[1,2,5]oxadiazolo[3,4-*d*]pyridazine 1-oxide **1** is the only known representative of dihalo[1,2,5]oxadiazolo[3,4-*d*]pyridazines [8]; its chemical properties, including nucleophilic S_NAr substitution and cross-coupling reactions, have not been previously studied. Herein, we report the synthesis of 4,7-bis(1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **2** by the reaction of 4,7-dichloro[1,2,5]oxadiazolo[3,4-*d*]pyridazine 1-oxide **1** with 2,3,4,4a,9,9a-hexahydro-1*H*-carbazole **3**.

2. Results and Discussion

The reaction of the nucleophilic substitution of chlorine atoms in the pyridazine ring of 4,7-dichloro[1,2,5]oxadiazolo[3,4-*d*]pyridazine 1-oxide **1** with 2,3,4,4a,9,9a-hexahydro-1*H*-carbazole **3** was investigated in order to obtain a bis-substitution product, which may be of interest as a donor-acceptor-donor (D-A-D)-type structure. It was shown that in this reaction, regardless of the solvent used, the formation of a compound **2** was observed; thus, together with the reaction of the nucleophilic substitution in the pyridazine ring, the oxygen atom is eliminated from the furoxan ring with the formation of 4,7-bis(1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **2** (Scheme 1). Refluxing 4,7-dichloro[1,2,5]oxadiazolo[3,4-*d*]pyridazine 1-oxide **1** with four

equivalents of 2,3,4,4a,9,9a-hexahydro-1*H*-carbazole **3** in CH_2Cl_2 at reflux for 6 h led to the formation of compound **2** in a low yield (Table 1, Entry 1). To increase the yield of compound **2**, we studied various solvents in this reaction. Heating the reaction mixtures to 81 °C in DMF or refluxing in MeCN with four equivalents of *N*-heterocyclic amine **3** resulted in bis-substitution product **2** in moderate yields. The reaction in MeCN required a reflux for 6 h, and a complete conversion in DMF was achieved at 81 °C in 3 h (Table 1, Entries 2, 3).



Scheme 1. Synthesis of 4,7-bis(1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **2**.

Table 1. Reaction of 4,7-dichloro-[1,2,5]oxadiazolo[3,4-*d*]pyridazine 1-oxide **1** with 2,3,4,4a,9,9a-hexahydro-1*H*-carbazole **3**.

Entry	Solvent	Temperature, °C	Time, h	Yield, of 2%
1	CH_2Cl_2	41	6	15
2	MeCN	81	6	65
3	DMF	81	3	60

The structure of 4,7-bis(1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **2** was confirmed by means of an elemental analysis, ^{1}H, ^{13}C NMR, IR and UV spectroscopy, and HRMS and LR mass-spectrometry. According to the mass spectra, elemental analysis, and ^{1}H and ^{13}C NMR data, this is the product of the addition of two hexahydrocarbazole molecules and the elimination of two HCl and oxygen, which is also confirmed by the identity of the two *N*-heterocyclic amine fragments and the symmetry of the oxadiazolopyridazine ring. The deoxygenation of 1,2,5-oxadiazole *N*-oxide to the furazan ring was somewhat unexpected, since it is known that this process usually requires the presence of sufficiently strong reducing agents such as triphenylphosphine or zinc [9]. The photophysical properties of D-A-D dye **2** are being investigated.

3. Materials and Methods

4,7-Dichloro-[1,2,5]oxadiazolo[3,4-*d*]pyridazine 1-oxide **1** [8] and 2,3,4,4a,9,9a-hexahydro-1*H*-carbazole **3** [10] 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. ^{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 a $CDCl_3$ solution, with TMS as the standard. J values are given in Hz. The MS spectrum (EI, 70 eV) was obtained with a Finnigan MAT INCOS 50 instrument (Hazlet, NJ, USA). The IR spectrum was measured with a Bruker "Alpha-T" instrument (Santa Barbara, CA 93117, USA) in a 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 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 a 4.8×10^{-5} mol/mL concentration in CH_2Cl_2.

Synthesis of 4,7-bis(1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **2** (Supplementary Materials).

2,3,4,4a,9,9a-Hexahydro-1*H*-carbazole **3** (167 mg, 0.97 mmol) was added with stirring to a solution of 4,7-dichloro-[1,2,5]oxadiazolo[3,4-*d*]pyridazine 1-oxide **1** (100 mg, 0.48 mmol) in dry MeCN (15 mL). The mixture was stirred at reflux for 6 h. Then, the mixture was poured into water (25 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent hexane–CH_2Cl_2, 2:1, *v*/*v*). Yield 144 mg (65%), violet solid, R_f = 0.3 (hexane–CH_2Cl_2, 2:1, *v*/*v*). Mp = 144–146 °C. IR spectrum, ν, cm^{-1}: 2929 and 2855 (C–H), 1482, 1454, 1424, 1271, 1214, 1164, 1094, 1020, 971, 927, 886, 847, 752, 689, 576. ^{1}H NMR (ppm): δ 8.55 (d, *J* = 8.0, 2H), 7.33 (t, *J* = 8.0, 2H), 7.27 (d, *J* = 7.3, 2H), 7.11 (t, *J* = 7.3, 2H), 5.42–5.35 (m, 2H), 3.72–3.66 (m, 2H), 2.43 (d, *J* = 14.5, 2H), 2.13–1.91 (m, 4H), 1.71–1.62 (m, 4H), 1.41–1.31 (m, 6H). ^{13}C NMR (ppm): δ 143.0, 141.2, 141.0, 134.6, 127.5, 123.3, 122.5, 118.2, 63.7, 40.2, 27.7, 24.3, 22.6, 21.0. HRMS (ESI-TOF), *m*/*z*: calcd for $C_{28}H_{29}N_6O_2$ $[M + H]^+$, 465.2397, found, 465.2395. MS (EI, 70eV), *m*/*z* (*I*, %): 464 ($[M]^+$, 27), 447 (12), 170 (30), 155 (31), 143 (56), 130 (100), 115 (58), 41 (62). UV-Vis spectra (in CH_2Cl_2), λmax: 289 nm (ε = 17,097 M^{-1} cm^{-1}), 554 nm (ε = 7954 M^{-1} cm^{-1}). Anal. calcd. for $C_{28}H_{28}N_6O_2$ (464.5618): C, 72.39; H, 6.08; N, 18.09. Found: C, 72.48; H, 6.23; N, 18.32%.

Supplementary Materials: The following are available online: copies of ^{1}H, ^{13}C NMR, IR, HMRS, UV-Vis and mass-spectra for the compound **2**.

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

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