

Short Note

Benzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole)-4-carbonitrile

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Abstract: Electron-withdrawing heterocyclic units are found in most organic optoelectronic materials. Benzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole) is an interesting new heterocyclic system, the chemical properties of which are much less studied than other fused thiadiazoles. Cyano derivatives of electron-accepting heterocycles are known as potential components of photoluminescent materials. In this communication, benzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole)-4-carbonitrile was successfully obtained via the cyanation of 4-bromobenzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole) with copper(I) cyanide in DMF. The structure of the newly synthesized compound was established by means of elemental analysis, high-resolution mass spectrometry, ¹H and ¹³C NMR, and IR spectroscopy.

Keywords: sulfur–nitrogen heterocycles; benzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole); cyanation



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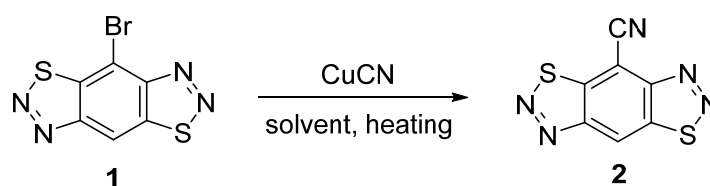
1. Introduction

Electron-accepting heterocycles play an important role in the design of organic chromophores due to their ability to reduce the band gap by promoting intramolecular charge transfer [1]. Strong electron-withdrawing building blocks containing thiadiazole rings containing low LUMO energy have attracted much attention [2–5] because they can be used in the development of various optoelectronic devices such as dye-sensitized solar cells, organic light-emitting diodes and organic field-effect transistors [6]. In recent years, we found that benzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole) possesses promising electron-accepting properties; its unsubstituted and bromo derivatives successfully participate in aromatic nucleophilic substitution, palladium-catalyzed cross-coupling, and direct C-H arylation [7,8]. The selective synthesis of 4-bromobenzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole) **1** [9] and the successful selective substitution of bromine or hydrogen atoms [10] made it possible to lay the foundation for the efficient synthesis of unsymmetrical derivatives of this heterocyclic system. Cyano derivatives of electron-accepting heterocycles, namely 2,1,3-benzothiadiazole, are shown to have interesting physical properties for the design of push–pull dyes [11], thermally activated delayed fluorescence sensitizers [12], mediators for electrocatalytic hydrogen evaluation on glassy carbon electrodes [13], and others. In continuation of our study of the reactivity of 4-bromobenzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole) **1**, we report its cyanation reaction to benzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole)-4-carbonitrile **2**.

2. Results and Discussion

The cyanation of bromo-benzo-bis-thiadiazoles has not been described in the literature. A search of the literature on the Reaxys and SciFinder databases for the cyanation of 4-bromo-2,1,3-benzothiadiazoles showed that the most common methods are heating at high temperature with copper(I) cyanide in DMF [14,15] or in NMP [16–18]. We have shown that bromide **1** reacted with copper (I) cyanide in both solvents under heating (Scheme 1). It turned out that the nature of the solvent, as well as the reaction temperature, significantly

affected the course of chemical transformation. The use of NMP as a solvent in the reaction with copper(I) cyanide led to the complete decomposition of the starting bromide **1** (Table 1, entries 1,2). The treatment of bromide **1** with CuCN in DMF at a temperature of 80 °C gave the cyanation product **2** in trace amounts due to its very slow formation (Table 1, entry 3). An increase in the reaction temperature led to an increase in the yield of the target product **2**; the highest yield was achieved at 140 °C (Table 1, entry 5). Other attempts to improve the yield of cyanide **2** were unsuccessful; a reaction with potassium cyanide in DMF or with zinc(II) cyanide in the presence of a tetrakis(triphenylphosphine)palladium catalyst (Pd(PPh₃)₄) in NMP [19] only led to a slow decomposition of the starting bromide **1** (Table 1, entries 6,7).



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

Table 1. Cyanation of 4-bromobenzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole) **1**.

Entry	Reagent	Solvent	Conditions	Yield, %	
				2	1
1	CuCN	NMP	100 °C, 24 h	0	0
2	CuCN	NMP	130 °C, 24 h	0	0
3	CuCN	DMF	80 °C, 24 h	4	70
4	CuCN	DMF	120 °C, 24 h	40	32
5	CuCN	DMF	140 °C, 24 h	65	0
6	KCN	DMF	120 °C, 24 h	0	82
7	Zn(CN) ₂	NMP	Pd(PPh ₃) ₄ , 120 °C, 24 h	0	60

The structure of benzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole)-4-carbonitrile **2** was confirmed by means of elemental analysis, high-resolution mass spectrometry, ¹H, ¹³C NMR, and IR spectroscopy. The presence of a cyano group in compound **2** was evidenced by the appearance of a band at 2233 cm⁻¹ in the IR spectrum and an intense signal in the ¹³C NMR spectrum ($\delta = 119.3$ ppm).

In conclusion, benzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole)-4-carbonitrile **2** was synthesized via the cyanation of 4-bromobenzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole) **1** with copper(I) cyanide in DMF. The compound obtained may serve as a precursor for the preparation of unsymmetrical 4,7-disubstituted benzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazoles) containing a cyano group as organic optoelectronic materials via palladium-catalyzed C–H direct arylation reactions with aryl and thienyl halogenides [10].

3. Materials and Methods

4-Bromobenzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole) **1** was prepared according to the published method [9]. 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 ¹H and ¹³C NMR spectra were determined with a Bruker AM-300 machine (Bruker AXS Handheld Inc., Kennewick, WA, USA) (at frequencies of 300 and 75 MHz) in CDCl₃ solution. The high-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization (ESI). The IR spectrum was measured with a Bruker “Alpha-T” instrument (Bruker Corporation, Billerica, Massachusetts, USA) in a KBr pellet.

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

CuCN (161 mg, 1.81 mmol) was added to a solution of 4-bromobenzo[1,2-*d*:4,5-*d'*]bis([1,2,3]thiadiazole) **1** (500 mg, 1.81 mmol) in anhydrous DMF (20 mL). The resulting mixture was degassed with argon in a sealed vial and then stirred at 140 °C for 24 h. On completion (monitored using TLC), water (80 mL) was added to the reaction mixture, and the organic layer was extracted with CH₂Cl₂ (3 × 70 mL), dried with MgSO₄ and then concentrated in vacuo. The residue was purified via column chromatography on silica gel (Silica gel Merck 60, eluent hexane–CH₂Cl₂, 1:1, *v/v*). Yield 257 mg (65%), red solid, *R*_f = 0.3 (hexane–CH₂Cl₂, 1:1, *v/v*). Mp = 186–187 °C. IR spectrum, ν , cm⁻¹: 3077 and 2923 (CH), 2233 (CN), 1337, 1289, 1235, 1212, 880, 846, 815, 678, 551, 523. ¹H NMR (ppm): δ 9.59 (s, 1H, CH). ¹³C NMR (ppm): δ 157.7, 157.1, 143.8, 140.3, 119.3 (CN), 113.8, 98.7. HRMS (ESI-TOF), *m/z*: calcd for C₇HN₅S₂Ag [M+Ag]⁺, 325.8719, found, 325.8726. Anal. calcd. for C₇HN₅S₂ (219.25): C, 38.35; H, 0.46; N, 31.94. Found: C, 38.20; H, 0.43; N, 31.82%.

Supplementary Materials: The following are available online: copies of ¹H, ¹³C NMR, IR, and HR mass spectra for compound **2**.

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Sample Availability: Samples of compound **2** are available from the authors.

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