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Short Note

(*E*)-7-(4-(Diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile

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Abstract: Donor-acceptor-donor (D-A-A) structures with 2,1,3-benzothiadiazole as an internal acceptor and the 4(7)-cyanogroup as anchor acceptor have been investigated for various photovoltaic applications such as dye-sensitized solar cells (DSSCs) and organic light emitting diodes (OLEDs). They are usually obtained by cyanation of 4(7)-bromo-2,1,3-benzothiadiazoles. In this communication, the reaction of (*E*)-4-(2-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)vinyl)-*N*,*N*-diphenylaniline with cyanating agents was studied and it was shown that the best yield of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile was achieved by heating with zinc cyanide in NMP at 120 °C in the presence of tetrakis(triphenylphosphine)palladium (0). The structure of newly synthesized compound was established by means of an elemental analysis, high resolution mass-spectrometry, ^{1}H, ^{13}C-NMR, IR, UV spectroscopy and mass-spectrometry.

Keywords: (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile; pyridine; zinc cyanide; cyanation

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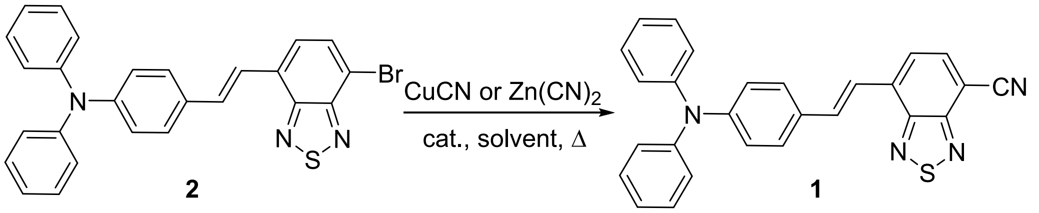
1. Introduction

2,1,3-Benzothiadiazoles represent a very important class of heterocyclic compounds and are often included into a wide variety of biologically active compounds and various photovoltaic devices [1–4]. Cyano derivatives of 2,1,3-benzothiadiazoles are less known, but are promising precursors for these applications. As follows from a search in the Reaxys database, more than 50 representatives of 4(7)-substituted benzothiadiazoles have been described that are of interest for electrocatalytic hydrogen production [5], applications in donor−acceptor oligomeric semiconductors [6], in push−pull fluorophores for turn-on fluorescence [7], in organic dyes with a donor-acceptor-donor (D-A-A) configuration for dye-sensitized solar cells (DSSCs) [8] and as emitters for high performances deep-red/near-infrared organic light emitting diodes (OLEDs) [9]. Herein, we report the synthesis of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile by the cyanation of (*E*)-4-(2-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)vinyl)-*N*,*N*-diphenylaniline.

2. Results and Discussion

To obtain the target (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile **1**, we studied several methods for introducing a cyano group into the molecule of monobromo derivative **2**, the synthesis of which was carried out according to the procedure described in the literature [10]. The study of the substitution reaction of the bromine atom in the benzene ring for the cyano group was carried out with copper and zinc cyanides under various conditions. We demonstrated that the nature of the reagents, solvents and the temperature of the reaction significantly affected the course of chemical transformation (Scheme 1, Table 1). It was found that bromide **2** reacted with copper cyanide when heated in dipolar aprotic DMF. TLC showed that complete conversion of compound **2** was observed when the reaction mixture was heated to 120 °C for 28 h. The yield of the target product was 40% (Table 1, Entry 2). However, the replacement of copper cyanide with zinc cyanide in the presence of tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) in *N*-methylpyrrolidone (NMP) increased the yield of target product **1** to 87% (Entry 4).



Scheme 1. Synthesis of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile **1**.

Table 1. Reaction of (*E*)-4-(2-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)vinyl)-*N*,*N*-diphenylaniline **2** with metal cyanides.

Entry	Reagent	Catalyst.	Solvent	Temperature, °C	Time, h	Yield, of 1%
1	CuCN	-	DMF	80	24	15
2	CuCN	-	DMF	120	28	40
3	$Zn(CN)_2$	$Pd(PPh_3)_4$	NMP	80	16	20
4	$Zn(CN)_2$	$Pd(PPh_3)_4$	NMP	120	24	87

The structure of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile **1** was confirmed by means of elemental analysis, high resolution mass-spectrometry, ^{1}H, ^{13}C-NMR, IR and UV spectroscopy, and mass-spectrometry. HRMS and elemental analysis supports the molecular formula of compound **1**. The ^{1}H-NMR spectrum of **1** showed characteristic C-H signals of the benzene ring and one resolved C-H doublet of the ethylene fragment (8.02 ppm). Evidence for the *E*-isomer was the presence of a large spin–spin constant of 16.3 Hz between the protons of the ethylene fragment as was proved for the starting bromo derivative **2** [11]. The IR spectrum of compound **1** contains a signal characteristic of the cyano group 2219 cm^{-1}.

The electronic absorption and luminescence spectra of compound **1** were measured in DCM. The absorption spectrum consisted of one prominent absorption maxima in the UV region, associated with the π-π* transition of the conjugated system (λ_{max} = 327 nm), and one broad band in the visible range, which is attributed to intramolecular charge transfer (ICT) between the donor and acceptor parts (λ_{max} = 501 nm). (See Supplementary Materials Figure S6). The luminescence spectra of the compound **1** showed bright near infrared (NIR) fluorescence (λ_{em} = 729 nm) (See Supplementary Materials Figure S7) and the large Stokes shift of 228 nm, which may lead to a decrease in the fluorescence quenching of the compound **1** in the solid state [12].

In conclusion, it was shown that cyanation (*E*)-4-(2-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)vinyl)-*N*,*N*-diphenylaniline **2** with zinc cyanide in the presence of ($Pd(PPh_3)_4$) in NMP gave cyanoderivative **1**, which can be considered as a possible near-infrared emitter that can be used in NIR OLEDs design and other possible applications as an IR luminophors.

3. Materials and Methods

(*E*)-4-(2-(7-Bromobenzo[*c*][1,2,5]thiadiazol-4-yl)vinyl)-*N*,*N*-diphenylaniline **1** was prepared according to the published method [10]. The solvents and reagents were purchased from commercial sources and used as received. An elemental analysis was performed using a 2400 Elemental Analyzer (Perkin ElmerInc., 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 DMSO-d_6 solution. IR spectrum was measured with a Bruker "Alpha-T" instrument (Santa Barbara, CA 93117, USA) 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 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 5×10^{-5} mol/mL concentration in acetone. Solution UV–visible absorption spectra was recorded using an Agilent Cary 60 spectrophotometer (United States). Solution luminescence spectra was recorded using an Agilent Cary Eclipse (United States).

Synthesis of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile **1** (Supplementary Materials).

$Zn(CN)_2$ (29 mg, 0.24 mmol) and $Pd(PPh_3)_4$ (20 mg, 15% mmol) were added to a solution of (*E*)-4-(2-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)vinyl)-*N*,*N*-diphenylaniline **2** (60 mg, 0.12 mmol) in anhydrous NMP (5 mL). The resulting mixture was degassed with argon in a sealed vial and then stirred at 120 °C for 28 h. Upon completion (TLC monitoring), water (30 mL) was added to the reaction mixture and the organic layer was extracted with CH_2Cl_2 (3 × 35 mL), dried over $MgSO_4$ and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent hexane–CH_2Cl_2, 2:1, *v*/*v*). Yield 45 mg (87%), red solid, $R_f = 0.1$ (hexane–CH_2Cl_2, 2:1, *v*/*v*). Mp = 207–209 °C. IR spectrum, ν, cm^{-1}: 2960, 2926 and 2854 (all C-H), 2219 (CN), 1586, 1531, 1491, 1267, 1081, 979, 842, 753, 700. ^{1}H-NMR (ppm): δ 8.02 (d, *J* = 16.3 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.52–7.46 (m, 3H), 7.30–7.22 (m, 4H), 7.15–7.02 (m, 8H). ^{13}C-NMR (ppm): δ 153.8, 152.6, 149.1, 147.1, 137.4, 136.5, 136.1, 129.0, 129.5, 128.5, 125.2, 124.2, 123.8, 122.4, 120.9, 116.0, 102.4. HRMS (ESI-TOF), *m/z*: calcd for $C_{27}H_{18}N_4S$ $[M]^+$, 430.1247, found, 430.1244. MS (EI, 70eV), *m*/*z* (I, %): 432 ($[M + 2]^+$, 5), 431 ($[M + 1]^+$, 30), 430 ($[M]^+$, 100), 429 (($[M\text{-}1]^+$, 2), 167 (4), 77 (3), 51 (2). UV-Vis spectra (in CH_2Cl_2), λ_{max}: 327 nm (ε 32487 M^{-1} cm^{-1}), 501 nm (ε = 27557 M^{-1} cm^{-1}). Anal. calcd. for $C_{27}H_{18}N_4S$ (430.1247): C, 75.33; H, 4.21; N, 13.01. Found: C, 75.31; H, 4.20; N, 12.99%.

Supplementary Materials: The following are available online: copies of ^{1}H, ^{13}C-NMR, IR, HMRS, mass-spectrometry, and UV-Vis and luminescence spectra for the compound **1**. Figure S1. ^{1}H-NMR spectrum of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile **1**. Figure S2. ^{13}C-NMR spectrum of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile **1**. Figure S3. IR spectrum of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile **1**. Figure S4. HRMS spectrum of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile **1**. Figure S5. Mass-spectrum of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile **1**. Figure S6. UV-spectrum of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile **1**. Figure S7. Luminescence-spectrum of (*E*)-7-(4-(diphenylamino)styryl)benzo[*c*][1,2,5]thiadiazole-4-carbonitrile **1**.

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