

Short Note

# 5,5'-Bis[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]-4,4'-diphenyl-2,2'-bithiazole

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**Abstract:** Stille coupling between 5,5'-dibromo-4,4'-diphenyl-2,2'-bithiazole and 9-(2-ethylhexyl)-3-(tributylstannyl)-9*H*-carbazole in the presence of Pd(Ph<sub>3</sub>P)<sub>2</sub>Cl<sub>2</sub> in toluene, heated at reflux for 2 h, gave 5,5'-bis[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]-4,4'-diphenyl-2,2'-bithiazole in 85% yield.

**Keywords:** bithiazole; carbazole; Stille coupling

## 1. Introduction

Thiazoles (Figure 1) are well-studied heterocycles that are present in nature and show numerous applications in medicinal chemistry, already reviewed [1–3]. A well-known example of a natural thiazole is vitamin B1 (Thiamine) [4], while examples of thiazole-containing drugs are the antiviral ritonavir [5] and the H<sub>2</sub>-receptor antagonist famotidine [6]. Thiazole dimers are also important: 2,4'-bithiazoles appear in natural products such as the anticancer agents bleomycins [7], while 2,2'-bithiazoles have been studied as electron acceptors with potential applications in materials sciences [8,9].



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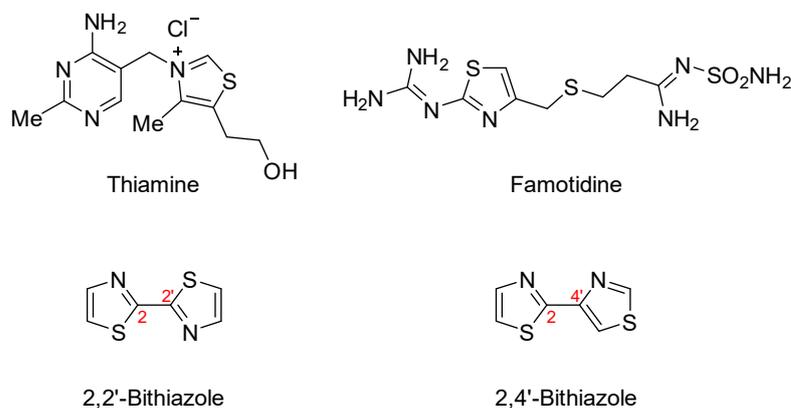
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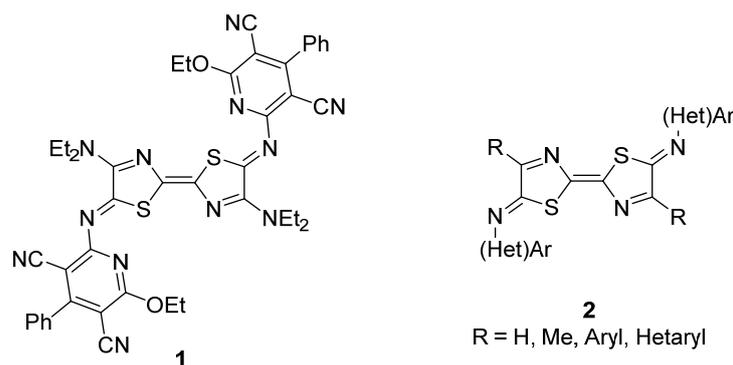
**Figure 1.** Thiamine, famotidine and the parent structures of 2,2'- and 2,4'-bithiazoles.

Our pursuit of 2,2'-bithiazoles began in 2015 when we identified quinoidal 2,2'-bithiazole **1** as a side product during our investigation into the chemistry of 1,2,3-dithiazoles [10]. Subsequently, our group devised a high-yielding synthetic route towards (2*E*,5*Z*,5'*Z*)-5,5'-diarylimino quinoidal 2,2'-bithiazoles **2** (Figure 2) [11].

During the above studies, we had also embarked on preparing donor–acceptor–donor (D–A–D) molecules for solution-processed bulk heterojunction (BHJ) solar cells. In this regard, we investigated small molecules and polymers containing non-S-oxidized 4*H*-1,2,6-thiadiazin-4-ones, which we combined with PC<sub>70</sub>BM to yield BHJ solar cells with Power Conversion Efficiencies (PCEs) of ~3% for the former and up to 3.8% for the latter [12,13].

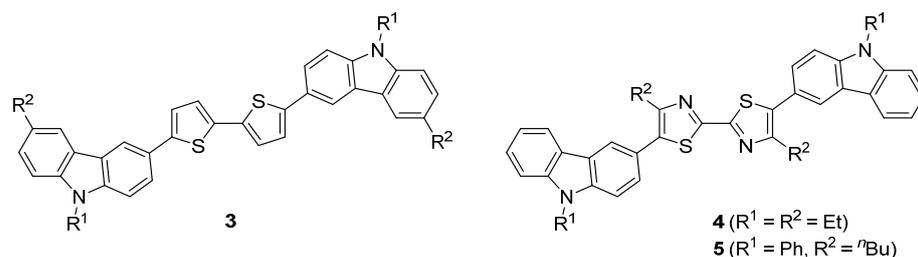


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**Figure 2.** Structures of quinoidal (2*E*,5*Z*,5'*Z*)-2,2'-bithiazoles **1** and **2**.

Interestingly, carbazole-bound 2,2'-bithienyls **3** [14–17] have been used in various optoelectronic applications, such as photoelectric conversion agents for imaging [14], organic field-effect transistors [15] and organic light-emitting diodes [16], and they have been combined to BODIPY units as potential hole transport materials for perovskite solar cells [17]. As such, to enhance the PCE of the solar cells under our investigation, we chose to explore the use of analogous 2,2'-bithiazole derivatives as non-fullerene acceptors. To the best of our knowledge, there are no reports of the use of 2,2'-bithiazole-carbazoles in OPV devices: a Reaxys search revealed only two analogous 2,2'-bithiazole-carbazoles **4** and **5** (Figure 3) that appear on PubChem (ID 102230564 and 122233114, respectively) without any reported experimental data.



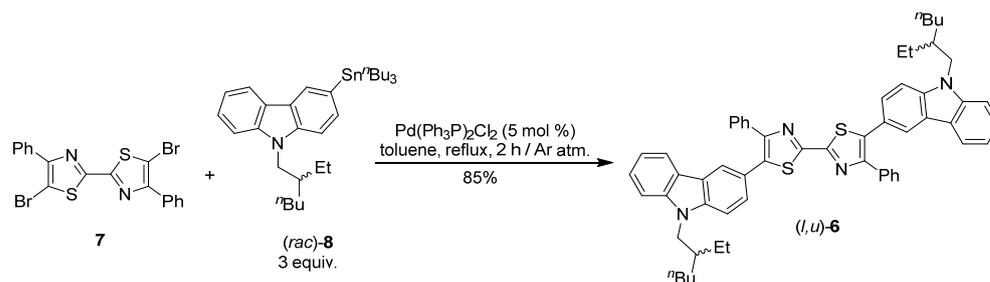
**Figure 3.** General structures of carbazole-bound 2,2'-bithienyls **3** and PubChem-reported carbazole-bound 2,2'-bithiazoles **4** and **5**.

Herein, we report the synthesis of a new 2,2'-bithiazole bearing carbazole substituents. As demonstrated in our previous study [12], these substituents were found to expand the  $\pi$ - $\pi$  conjugation, thereby facilitating charge transfer.

## 2. Results and Discussion

The target, 5,5'-bis[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]-4,4'-diphenyl-2,2'-bithiazole (**6**), was synthesized via our adapted Stille coupling protocol developed for halothiadiazines [12]. The starting material, bithiazole **7**, was readily obtained in two steps with an overall yield of 58%, starting from 2-bromoacetophenone and rubeanic acid [11,18]. Additionally, the tributylstannyl reagent, 9-(2-ethylhexyl)-3-(tributylstannyl)-9*H*-carbazole (**8**), had been previously used effectively by us to prepare thiadiazine oligomers [12]. The Stille coupling proceeded smoothly to give the expected bithiazole **6** in 85% yield (Scheme 1).

The UV-vis spectrum of bithiazole **6** in DCM exhibited a lowest energy absorption band at  $\lambda_{\text{max}}$  at 405 nm ( $\log \epsilon$  3.30) with an onset value of 472 nm corresponding to an optical band gap ( $E_{\text{g}}^{\text{opt}}$ ) of 2.63 eV (Table 1). The bithiazole was also analyzed using cyclic voltammetry (CV) that revealed one reversible reduction and one irreversible oxidation (see Supplementary Materials). The dimer **6** showed an electrochemical HOMO value of  $-5.84$  eV, a LUMO value of  $-3.68$  eV and an electrochemical band gap ( $E_{\text{g}}^{\text{chem}}$ ) of 2.16 eV (Table 1). These values are close to the respective HOMO and LUMO values of PCBM, a commonly used fullerene acceptor molecule, of  $-6.2$  eV and  $-3.95$  eV [19].



**Scheme 1.** Synthesis of (*l,u*)-5,5'-bis[9-(2-ethylhexyl)-9H-carbazol-3-yl]-4,4'-diphenyl-2,2'-bithiazole, (*l,u*)-6.

**Table 1.** UV-vis and CV of 5,5'-bis[9-(2-ethylhexyl)-9H-carbazol-3-yl]-4,4'-diphenyl-2,2'-bithiazole (6). All the values correspond to peak onsets.

$E_{\text{ox}}$ (V)	$\lambda_{\text{max}}$ (nm)	$E_{\text{g}}^{\text{opt}}$ (eV)	$E_{\text{HOMO}}$ (eV)	$E_{\text{red}}$ (V)	$E_{\text{LUMO}}$ (eV)	$E_{\text{g}}^{\text{echem}}$ (eV)
0.74	472	2.63	−5.84	−1.42	−3.68	2.16

Bithiazole 6 showed good optical absorption coverage with P3HT; however, initial OPV device studies using the title molecule in combination with P3HT in BHJ solar cells were unsuccessful owing to fabrication issues and were not pursued further. Potentially, bithiazole 6 could find similar optoelectronic D-A-D applications to the bithienyls mentioned above.

### 3. Materials and Methods

The reaction mixture was monitored by TLC using commercial glass-backed thin-layer chromatography (TLC) plates (Merck Kieselgel 60 F<sub>254</sub>). The plates were observed under UV light at 254 and 365 nm. The melting point was determined using a PolyTherm-A, Wagner & Munz, Kofler—Hotstage Microscope apparatus (Wagner & Munz, Munich, Germany). The solvent used for recrystallization is indicated after the melting point. The UV-vis spectrum was obtained using a Perkin-Elmer Lambda-25 UV/vis spectrophotometer (Perkin-Elmer, Waltham, MA, USA) and inflections are identified by the abbreviation “inf”. The IR spectrum was recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer (Shimadzu, Kyoto, Japan) with Pike Miracle Ge ATR accessory (Pike Miracle, Madison, WI, USA), and strong, medium and weak peaks are represented by s, m and w, respectively. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 500 instrument (at 500 and 125 MHz, respectively) (Bruker, Billerica, MA, USA). Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Coupling values *J* are given in Hz. Attached proton test (APT) NMR studies were used for the assignment of the <sup>13</sup>C peaks as CH<sub>3</sub>, CH<sub>2</sub>, CH and C<sub>q</sub> (quaternary). The MALDI-TOF mass spectrum (+ve mode) was recorded on a Bruker Autoflex III Smartbeam instrument (Bruker). Cyclic voltammetry (CV) measurements were performed on a Princeton Applied Research 263A potentiostat/galvanostat apparatus (Princeton Applied Research, Oak Ridge, TN, USA). The elemental analysis was run by the London Metropolitan University Elemental Analysis Service on a Perkin Elmer 2400 Elemental analyzer (Perkin Elmer, Waltham, MA, USA). 5,5'-Dibromo-4,4'-diphenyl-2,2'-bithiazole (7) [11] and 9-(2-ethylhexyl)-3-(tributylstannyl)-9H-carbazole (8) [12] were prepared according to the literature procedures.

#### 5,5'-Bis [9-(2-ethylhexyl)-9H-carbazol-3-yl]-4,4'-diphenyl-2,2'-bithiazole (6)

To a stirred mixture of 5,5'-dibromo-4,4'-diphenyl-2,2'-bithiazole (7) (15.0 mg, 0.031 mmol) in anhyd. toluene (1 mL) at, ca., 20 °C, 9-(2-ethylhexyl)-3-(tributylstannyl)-9H-carbazole (8) (52.9 mg, 0.093 mmol) and Pd(Ph<sub>3</sub>P)<sub>2</sub>Cl<sub>2</sub> (1.1 mg, 0.0016 mmol) were added. The solution was then deaerated by bubbling Ar gas into the reaction mixture for 10 min

and then the mixture was heated at reflux under Ar, until no starting material remained (TLC, 2 h). On cooling to, ca., 20 °C, *t*-BuOMe (10 mL) was added and the mixture was washed with saturated KF (aq) to remove organotin residues, dried (Na<sub>2</sub>SO<sub>4</sub>), adsorbed onto silica and chromatographed (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, 60:40 *v/v*) to give the *title compound 6* (23 mg, 85%) as orange needles, mp 75–77 °C (from MeCN); R<sub>f</sub> 0.40 (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, 60:40 *v/v*); (found: C, 79.42; H, 6.55; N, 6.50. C<sub>58</sub>H<sub>58</sub>N<sub>4</sub>S<sub>2</sub> requires C, 79.59; H, 6.68; N, 6.40%); λ<sub>max</sub> (CH<sub>2</sub>Cl<sub>2</sub>)/nm 241 (log ε 3.78), 265 inf (3.54), 298 inf (3.43), 363 inf (3.15), 383 inf (3.25), 405 (3.30); ν<sub>max</sub>/cm<sup>-1</sup> 2955w, 2926m and 2855w (C-H), 1734m, 1684m, 1653m, 1647w, 1624w, 1599m, 1558m, 1506m, 1491m, 1462s, 1443m, 1414w, 1379w, 1348m, 1331m, 1319w, 1275m, 1256w, 1219m, 1204m, 1153m, 1125w, 936m, 914w, 887w, 851w, 802s, 768s, 746s, 729s; δ<sub>H</sub> (500 MHz; CDCl<sub>3</sub>) 8.20 (2H, d, <sup>4</sup>J<sub>H-H</sub> 1.4, Ar CH), 8.02 (2H, d, <sup>3</sup>J<sub>H-H</sub> 7.7, Ar CH), 7.69–7.67 (4H, m, Ar CH), 7.50–7.47 (4H, m, Ar CH), 7.42 (2H, d, <sup>3</sup>J<sub>H-H</sub> 8.1, Ar CH), 7.35 (2H, d, <sup>3</sup>J<sub>H-H</sub> 8.6, Ar CH), 7.32–7.29 (6H, m, Ar CH), 7.24 (2H, dd, <sup>3</sup>J<sub>H-H</sub> 7.2, 7.2, Ar CH), 4.19–4.17 (4H, m, CH<sub>2</sub>), 2.12–2.04 (2H, m, CH), 1.46–1.24 (16H, m, CH<sub>2</sub>), 0.95 (6H, t, <sup>3</sup>J<sub>H-H</sub> 7.4, CH<sub>3</sub>), 0.88 (6H, t, <sup>3</sup>J<sub>H-H</sub> 7.2, CH<sub>3</sub>); δ<sub>C</sub> (125 MHz; CDCl<sub>3</sub>) 158.5 (Cq), 150.1 (Cq), 141.3 (Cq), 140.8 (Cq), 136.6 (Cq), 134.9 (Cq), 129.1 (CH), 127.8 (CH), 127.3 (CH), 126.1 (CH), 123.1 (Cq), 122.5 (Cq), 121.5 (Cq), 120.4 (CH), 119.2 (CH), 109.3 (CH), 109.2 (CH), 47.6 (CH<sub>2</sub>), 39.4 (CH), 31.0 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 24.4 (CH<sub>2</sub>), 23.0 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>), 10.9 (CH<sub>3</sub>); *m/z* (MALDI-TOF) 875 (MH<sup>+</sup>, 21%), 776 (MH<sup>+</sup>-C<sub>7</sub>H<sub>15</sub>, 100).

**Supplementary Materials:** The following supporting information can be downloaded online: molfile, Figure S1: Cyclic voltammogram of bithiazole **6**; Figure S2: UV-vis absorption spectrum of bithiazole **6**, <sup>1</sup>H, <sup>13</sup>C NMR and mass spectra.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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