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Short Note

5,5′-Bis[5-(9-decyl-9*H*-carbazol-3-yl)thien-2-yl]-4*H*,4′*H*-[3,3′-bi(1,2,6-thiadiazine)]-4,4′-dione

Andreas S. Kalogirou [1,*] and Panayiotis A. Koutentis [2]

[1] Department of Pharmacy, School of Sciences, European University Cyprus, 6 Diogenis Str., Engomi, P.O. Box 22006, 1516 Nicosia, Cyprus
[2] Department of Chemistry, University of Cyprus; P.O. Box 20537, 1678 Nicosia, Cyprus; koutenti@ucy.ac.cy
* Correspondence: A.Kalogirou@external.euc.ac.cy; Tel.: +35-722-892-804

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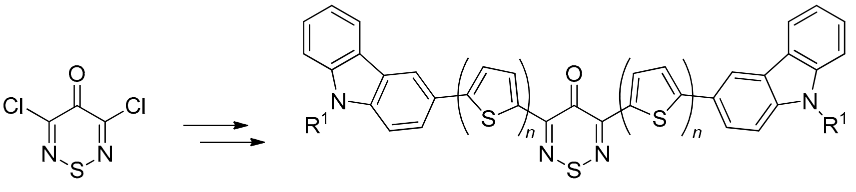
Abstract: Stille coupling of 5,5′-dichloro-4*H*,4′*H*-[3,3′-bi(1,2,6-thiadiazine)]-4,4′-dione (**8**) with 9-decyl-3-[5-(tributylstannyl)thien-2-yl]-9*H*-carbazole and $Pd(Ph_3P)_2Cl_2$ in PhMe, at ca. 110 °C, for 2 h, gave 5,5′-bis[5-(9-decyl-9*H*-carbazol-3-yl)thien-2-yl]-4*H*,4′*H*-[3,3′-bi(1,2,6-thiadiazine)]-4,4′-dione (**7**) in 51% yield. The latter is investigated as an oligomer donor for organic photovoltaics.

Keywords: heterocycle; 1,2,6-thiadiazine; oligomer; photovoltaics

1. Introduction

Non-oxidized 4*H*-1,2,6-thiadiazines are rare heterocycles. Nevertheless, interesting properties and applications of various analogues have appeared: selected 3-chloro-5-substituted-4*H*-1,2,6-thiadiazines display plant antifungal activity [1–5], whereas some fused analogues were studied as examples of "extreme quinoids" with ambiguous aromatic character [6], while others displayed liquid crystalline properties or behaved as near-infrared dyes [7,8]. Furthermore, selected 4*H*-1,2,6-thiadiazines were proposed as radical anion precursors for molecule-based magnetic and conducting materials [9], while π-conjugated polymers of 1,2,6-thiadiazines were proposed as potentially stable alternatives to the superconductor poly(sulfur nitride) $(SN)_x$ by both Woodward [10] and Rees [11–13]. 4*H*-1,2,6-Thiadiazines were also characterized by resonance Raman (RR), absorption (UV-vis) and photoluminescence (PL) spectroscopies to better understand their optical properties [14].

We recently prepared a series of small molecule non-S-oxidized 4*H*-1,2,6-thiadiazin-4-ones **2**–**6** from 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**) and investigated them as efficient electron donors in solution-processed bulk heterojunction (BHJ) solar cells as substitutes to the widely used 2,1,3-benzothiadiazoles (Figure 1) [15]. The small molecule donors synthesized in combination with 3′phenyl-3′*H*-cyclopropa[8,25][5,6]fullerene-C70-D5*h*(6)-3′butanoic acid, methyl ester ($PC_{70}BM$) were used in BHJ solar cells with power conversion efficiencies (PCE) of ~3%, while in a latter work, 4*H*-1,2,6-thiadiazine containing polymers have shown PCEs of up to 3.8% [16]. The value of PCE in the earlier work was a combination of a good open circuit voltage (V_{oc}, up to 1.0 V), attributed to ideal HOMO energies of the oligomers (−5.58 to −5.30 eV), with moderate short circuit current (J_{sc}) and fill factor (FF) values (best obtained were 8.2 mA/cm^2 and 33%, respectively). This was attributed to the relatively high electron affinity (EA) energies of our donors (−3.52 to −3.41 eV), with the ideal LUMO required to be as low as −4.0 eV to achieve better PCEs in organic photovoltaics (OPVs) that use 3′*H*-cyclopropa[1,9][5,6]fullerene-C60-I*h*-3′-butanoic acid 3′-phenyl methyl ester (PCBM) as the acceptor [17]. An electrochemical study of selected 1,2,6-thiadiazines [18] showed that bithiadiazines have better EA values (−3.96 to −3.40 eV) than monothiadiazines, indicating that the optoelectronic properties of thiadiazine based functional materials can be chemically optimized. As such, a suitable bithiadiazine oligomer was synthesised for a study of the optoelectronic properties of this group of functional small molecules.



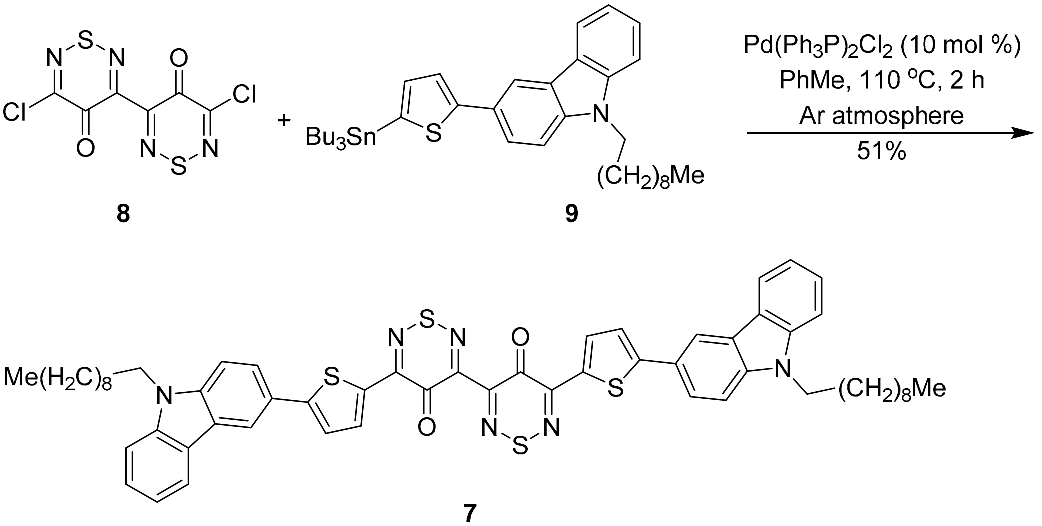
2 (n = 0; R^1 = 2-ethylhexyl)
3 (n = 1; R^1 = 2-ethylhexyl)
4 (n = 1; R^1 = *n*-decyl)
5 (n = 2; R^1 = 2-ethylhexyl)
6 (n = 2; R^1 = *n*-decyl)

Figure 1. 1,2,6-Thiadiazine containing oligomers studied as donors in bulk heterojunction (BHJ) organic photovoltaics (OPVs) [15].

2. Results and discussion

The targeted bithiadiazine oligomer was 5,5′-bis[5-(9-decyl-9*H*-carbazol-3-yl)thien-2-yl]-4*H*,4′*H*-[3,3′-bi(1,2,6-thiadiazine)]-4,4′-dione (**7**), which contained the thiophene-carbazole motif, which was suitable as a donor unit for the D-A-D functional small molecule. Oligomer **7** could be directly compared with the respective monothiadiazine oligomer **4** (Figure 1) which gave a PCE of ~2% [15]. Computational studies showed that compound **7** had a low band gap (~2.29 eV), with HOMO energies of −5.92 to −5.72 eV and LUMO energies of −2.98 to −3.57 eV (see SI) making the study of this oligomer intriguing.

With the Pd coupling chemistry (Stille) of halothiadiazines already investigated [15,19], we selected 5,5′-dichloro-4*H*,4′*H*-[3,3′-bi(1,2,6-thiadiazine)]-4,4′-dione (**8**) as the suitable starting material for preparing a bithiadiazine-containing oligomer. Bithiadiazine **8** can be readily prepared from dichlorothiadiazine **1** in four steps with an overall yield of 47% [20]. Moreover, the required tributylstannyl reagent 9-decyl-3-[5-(tributylstannyl)thien-2-yl]-9*H*-carbazole (**9**) was known and had been effectively used in prior work to prepare monothiadiazine oligomers [15]. The Stille coupling reaction proceeded smoothly to give the expected bithiadiazine (**7**) (Scheme 1).



Scheme 1. Synthesis of 5,5′-bis[5-(9-decyl-9*H*-carbazol-3-yl)thien-2-yl]-4*H*,4′*H*-[3,3′-bi(1,2,6-thiadiazine)]-4,4′-dione (**7**).

The ultraviolet-visible (UV-vis) absorption spectrum of bithiadiazinone **7** was measured in solution (CH_2Cl_2) and gave a lowest energy absorption peak at λ_{max} at 472 nm with an onset value of 571 nm corresponding to an optical band gap (E_g^{opt}) of 2.17 eV (Table 1). The small band gap of this oligomer as well as the broad absorption between 300 and 600 nm, similar to monothiadiazine **4** (see SI), which overlapped with the absorption regime of $PC_{70}BM$ (350–500 nm) [21], shows that the oligomer was suitable as a donor for bulk heterojunction solar cells.

Oligomer **7** was also analysed using cyclic voltammetry (CV) that revealed one reversible reduction and two reversible oxidations (see SI). The oligomer showed an electrochemical HOMO value of −5.69 eV, a LUMO value of −3.66 eV and an electrochemical band gap (E_g^{echem}) of 2.03 eV (Table 1). Both the LUMO and band gap energies were favorably lower than those of the respective monothiadiazinone small molecules previously studied [15].

Table 1. Cyclic votammetry (CV) and UV-vis data of 5,5′-bis[5-(9-decyl-9*H*-carbazol-3-yl)thien-2-yl]-4*H*,4′*H*-[3,3′-bi-(1,2,6-thiadiazine)]-4,4′-dione (**7**). All the values correspond to peak onsets.

E_{ox} (V)	E_{HOMO} (eV)	E_{red} (V)	E_{LUMO} (eV)	E_g^{echem} (eV)	λ_{max} (nm)	E^{opt} (eV)
0.59	−5.69	−1.44	−3.66	2.03	571	2.17

Despite the good optoelectronic characteristics of the compound, initial OPV studies showed that even though the compound had a good V_{oc} (~1 V), the corresponding J_{sc}, FF and PCE values were very low indicating that it was unsuitable as a donor for OPVs. The failure of this can be attributed to poor morphology of the layering as well as a lack of a favorable HOMO/HOMO offset between donor and acceptor, which leads to an unfavorable hole transfer.

3. Materials and Methods

The reaction mixture was monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254}, Darmstadt, Germany). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used, using Merck Silica Gel 60 (less than 0.063 mm). 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. ^1H and ^{13}C-NMR spectra were recorded on a Bruker Avance 500 machine (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. APT NMR studies identified carbon multiplicities, which are indicated by (s), (d), (t) and (q) notations. The MALDI-TOF mass spectrum (+ve mode) was recorded on a Bruker Autoflex III Smartbeam instrument (Bruker). The elemental analysis was run by the London Metropolitan University Elemental Analysis Service. 5,5′-Dichloro-4*H*,4′*H*-[3,3′-bi(1,2,6-thiadiazine)]-4,4′-dione (**8**) was prepared according to the literature [20].

5,5′-Bis[5-(9-decyl-9H-carbazol-3-yl)thien-2-yl]-4H,4′H-[3,3′-bi(1,2,6-thiadiazine)]-4,4′-dione (**7**)

To a stirred mixture of 5,5′-dichloro-4*H*,4′*H*-[3,3′-bi(1,2,6-thiadiazine)]-4,4′-dione (**8**) (29.5 mg, 0.100 mmol) in PhMe (1 mL) at ca. 20 °C was added 9-decyl-3-[5-(tributylstannyl)thien-2-yl]-9*H*-carbazole (204 mg, 0.300 mmol) and $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol). 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), dried (Na_2SO_4), adsorbed onto silica and chromatographed (*n*-hexane/CH_2Cl_2, 50:50) to give the title compound **7** (51 mg, 51%) as red needles, m.p. 165–167 °C (from 1,2-dichloroethane/MeCN); R_f 0.31 (*n*-hexane/CH_2Cl_2, 50:50); (found: C, 69.45; H, 5.93; N, 8.49. $C_{58}H_{60}N_6O_2S_4$ requires C, 69.56; H, 6.04; N, 8.39%); λ_{max}

(CH_2Cl_2)/nm 243 (log ε 5.08), 298 (4.94), 349 (4.66), 472 (4.93); ν_{max}/cm^{-1} 2953w, 2924m and 2853w (C-H), 1628m, 1608m, 1601m, 1468m, 1422s, 1387m, 1352w, 1329m, 1283m, 1273m, 1236m, 1153m, 1123w, 1096m, 1078w, 934m, 898m, 872w, 824m, 795m, 783m, 770w, 743m; δ_H (500 MHz; $CDCl_3$) 8.43 (2H, d, *J* 1.5, Ar C*H*), 8.33 (2H, d, *J* 4.0, Ar CH), 8.12 (2H, d, *J* 7.8, Ar C*H*), 7.81 (2H, dd, *J* 8.5, 1.6, Ar C*H*), 7.48 (2H, dd, *J* 7.7, 7.7, Ar C*H*), 7.44 (2H, d, *J* 4.0, Ar CH), 7.40 (4H, dd, *J* 8.0, 4.7, Ar CH), 7.27–7.24 (2H, m, Ar CH), 4.29 (4H, t, *J* 7.2, CH_2), 1.90–1.84 (4H, m, CH_2), 1.41–1.23 (28H, m, CH_2), 0.87 (6H, t, *J* 6.8, CH_3); δ_C (125 MHz; $CDCl_3$) 161.4 (s), 157.2 (s), 155.7 (s), 155.2 (s), 141.0 (s), 140.8 (s), 135.2 (d), 133.8 (s), 126.2 (d), 124.5 (s), 124.2 (d), 123.4 (s), 123.2 (d), 122.7 (s), 120.6 (d), 119.4 (d), 118.3 (d), 109.2 (d), 109.0 (d), 43.3 (t), 31.8 (t), 29.50 (t), 29.47 (t), 29.4 (t), 29.2 (t), 29.0 (t), 27.3 (t), 22.6 (t), 14.1 (q); *m*/*z* (MALDI-TOF) 1002 (M^+ + 2, 25%), 1001 (M^+ + 1, 46), 1000 (M^+, 72), 873 (57), 589 (79), 526 (100).

Supplementary Materials: The following are available online http://www.mdpi.com/xxx/s1, Figure S1: Cyclic voltammogram of bithiadiazinone **7**, Figure S2: UV-vis absorption spectrum of bithiadiazinone **7**, Figure S3: UV-vis absorption spectra of compounds **7** (bithiadiazinone) and **4** (monothiadiazinone) in CH_2Cl_2, Table S1: Computational ground state energy values of bithiadiazinone **7**, Table S2: Main excited states of bithiadiazinone **7**, Table S3: Computational ground and excited state energy values of bithiadiazinone **7**, Figure S4: Molecular orbitals for the singlet ground state of bithiadiazinone **7**, 2D MDL molfile, ^{1}H and ^{13}C-NMR spectra of bithiadiazinone **7**.

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Author Contributions: A.S.K. designed and performed the experiments, analyzed the data and wrote the paper; P.A.K. conceived the experiments.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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