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Short Note

3-Chloro-5-(3-*n*-hexylthien-2-yl)-4*H*-1,2,6-thiadiazin-4-one

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Abstract: Stille coupling of 5-chloro-4-oxo-4*H*-1,2,6-thiadiazin-3-yl trifluoromethanesulfonate (**7**) with tributyl(3-*n*-hexylthien-2-yl)stannane and $Pd(Ph_3P)_2Cl_2$ in PhMe at ca. 20 °C, for 24 h gave 3-chloro-5-(3-*n*-hexylthien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**9**) with a 60% yield. The latter is a potentially useful building block for the synthesis of oligomeric and polymeric donors for organic photovoltaics.

Keywords: Stille; heterocycle; 1,2,6-thiadiazine; hexylthiophene; unsymmetrical

1. Introduction

Non-oxidized 4*H*-1,2,6-thiadiazines are a rare class of heterocycles. However, recent interest in their properties and applications has fueled the development of their chemistry: many 3-chloro-5-substituted-4*H*-1,2,6-thiadiazines show plant antifungal activity [1–5], whereas several fused analogues were studied as examples of "extreme quinoids" with ambiguous aromatic character [6], and others display liquid crystalline properties or behave as near-infrared dyes [7,8]. Moreover, selected 4*H*-1,2,6-thiadiazines were proposed as radical anion precursors for molecule-based magnetic and conducting materials [9], while both Woodward [10] and Rees [11–13] proposed π-conjugated polymers of 1,2,6-thiadiazines as potentially stable alternatives to the superconductor poly(sulfur nitride) $(SN)_x$. Recently, 4*H*-1,2,6-thiadiazines were characterized by resonance Raman (RR), absorption (UV–vis), and photoluminescence (PL) spectroscopies to better understand their optical properties [14], while an electrochemical study of selected 1,2,6-thiadiazines [15] revealed that they might have useful electronic properties.

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) [16]. The small-molecule donors synthesized in combination with $PC_{70}BM$ were used in BHJ solar cells with Power Conversion Efficiencies (PCE) of ~2.8%, while in a later work, 4*H*-1,2,6-thiadiazine-containing polymers showed PCEs of up to 3.8% [17].

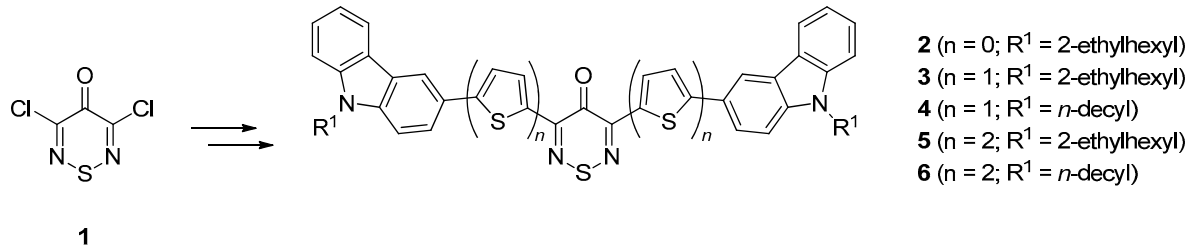
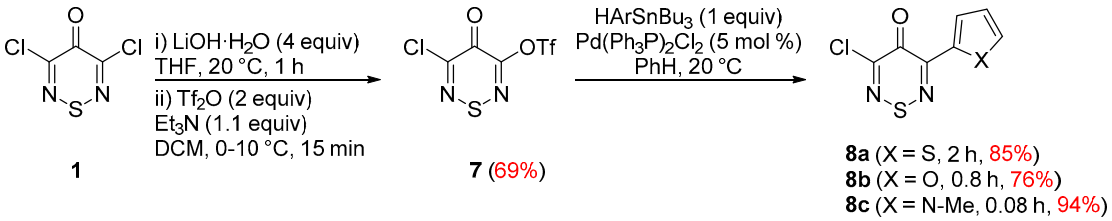


Figure 1. Examples of 1,2,6-Thiadiazine-containing oligomers studied as donors in bulk heterojunction (BHJ) organic photovoltaics (OPVs) [16].

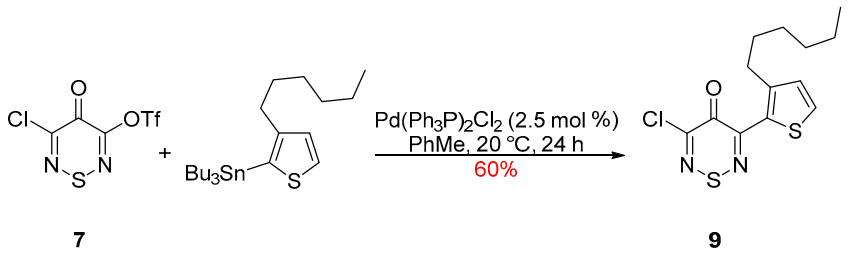
The common feature of the two previous efforts to prepare thiadiazine-containing light-harvesting donors, either oligomers or polymers, is that they both have a symmetric motif of donor–acceptor alternating units (D–A–D). Interestingly, asymmetrical donor molecules can lead to improved performance due to a larger electron transition dipole moment [18]. As such, to synthesize unsymmetrical donor molecules (D–A–D′), we required access to an unsymmetrical thiadiazine monomer. Use of the readily available dichlorothiadiazinone **1** was not possible as attempts to monoarylate this scaffold using aryltributylstannanes (1 equiv) even in mild conditions gave mixtures of starting material with mono- and bis-arylated products [19]. Nevertheless, dichlorothiadiazinone **1** can be converted in two steps to 5-chloro-4-oxo-4*H*-1,2,6-thiadiazin-3-yl trifluoromethanesulfonate (**7**) that can undergo chemoselective Stille couplings to afford mono hetaryls **8a**–**c** (Scheme 1) [19].



Scheme 1. Synthesis of 3-chloro-5-hetaryl-4*H*-1,2,6-thiadiazin-4-ones **8a**,**b**,**c**.

2. Results and Discussion

During studies on the use of thienylthiadiazines for the construction of unsymmetrical D–A–D's, we prepared several monochloro monothienyl analogues such as **8a** and its 4-*n*-dodecylthien-2-yl analogue [20]. The presence of suitable alkyl side chains on the thienyl moieties helps to improve the solubility and can influence the solid-state morphology of the D–A–D's. As such, accessing analogues with different alkyl side chains was important for the evolution of our ongoing studies. In light of this, we prepared 3-chloro-5-(3-*n*-hexylthien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**9**) as a new soluble monomer that possesses an alkyl side chain at the C-3 thienyl position and a reactive 3-chlorine that can be displaced in a subsequent Stille coupling (Scheme 2). Furthermore, the thiophene C-5 position can be the site of further coupling reactions, either directly via a C–H arylation or in two steps by bromination with *N*-bromosuccinimide (NBS) followed by a Stille coupling.



Scheme 2. Synthesis of 3-chloro-5-(3-*n*-hexylthien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**9**).

The synthesis of thienylthiadiazinone **9** was achieved by modifying the previous methods [19,20]: Stille coupling of 3-chloro-5-triflate thiadiazinone **7** with tributyl(3-*n*-hexylthien-2-yl)stannane (1 equiv) and $Pd(Ph_3P)_2Cl_2$ (2.5 mol%), in PhMe at ca. 20 °C gave the desired product **9** with a 60% yield (Scheme 2). The lower catalyst loading (2.5 versus 5 mol%) helped suppress the formation of unwanted bithienylthiadiazine. The yield of thienylthiadiazinone **9** was slightly lower than that of the previously prepared monothienylthiadiazine **8a** (Scheme 1), probably due to steric factors, as the thienyl C-3 *n*-hexyl group was next to the coupling site. We consider thienylthiadiazinone **9** to be a useful scaffold that will enhance the use of thiadiazines in the synthesis of functional materials for applications in electronics.

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 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. ^{1}H 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. Attached proton test (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. The compound 5-chloro-4-oxo-4*H*-1,2,6-thiadiazin-3-yl trifluoromethanesulfonate (**7**) was prepared according to the literature [19].

3-Chloro-5-(3-n-hexylthien-2-yl)-4H-1,2,6-thiadiazin-4-one (**9**)

To a stirred mixture of 5-chloro-4-oxo-4*H*-1,2,6-thiadiazin-3-yl trifluoromethanesulfonate (**7**) (59.3 mg, 0.200 mmol) in PhMe (2 mL) at ca. 20 °C, tributyl(3-*n*-hexylthien-2-yl)stannane (91.4 mg, 0.200 mmol) and $Pd(Ph_3P)_2Cl_2$ (7.0 mg, 0.005 mmol) were added. The solution was then stirred at this temperature until no starting material remained (TLC, 24 h). The reaction mixture was then adsorbed onto silica and chromatographed (*n*-hexane/DCM, 60:40) to give the *title compound* **9** (38.1 mg, 60%) as yellow needles, mp 47–48 °C (from MeCN, 0 °C); R_f 0.67 (*n*-hexane/DCM, 60:40); (found: C, 49.68; H, 4.85; N, 8.81. $C_{13}H_{15}ClN_2OS_2$ required C, 49.59; H, 4.80; N, 8.90%); λ_{max}(DCM)/nm 256 inf (log ε 3.73), 288 (4.00), 371 (4.35); ν_{max}/cm^{-1} 2951w, 2926w, 2868w and 2851w (C-H), 1632s, 1501w, 1439m, 1395s, 1373w, 1358w, 1339w, 1289w, 1271w, 1238w, 1175m, 1090w, 1015m, 939w, 856m, 843w, 822m, 793m, 752s; δ_H(500 MHz; $CDCl_3$) 7.59 (1H, d, *J* 5.1, Ar C*H*), 7.06 (1H, d, *J* 5.1, Ar C*H*), 3.04 (2H, dd, *J* 7.7, 7.7, CH_2), 1.65–1.59 (2H, m, CH_2), 1.41–1.28 (6H, m, CH_2), 0.90 (3H, t, *J* 6.7, CH_3); δ_C(125 MHz; $CDCl_3$) 159.9 (s), 154.0 (s), 151.1 (s), 150.5 (s), 132.7 (d), 130.5 (d), 126.1 (s), 31.7 (t), 31.3 (t), 29.8 (t), 29.3 (t), 22.6 (t), 14.1 (q); *m/z* (MALDI-TOF) 316 (M^+ + 2, 46%), 314 (M^+, 65), 243 (83), 225 (21).

Supplementary Materials: The following are available online: mol file, ^{1}H and ^{13}C-NMR spectra.

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

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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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