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Substitution at C-4 in 3,5-disubstituted 4*H*-1,2,6-thiadiazin-4-ones

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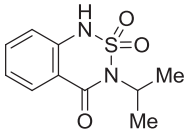
ABSTRACT

3,5-Diaryl-4*H*-1,2,6-thiadiazin-4-ones react with $NaBH_4$ to give the 3,5-diaryl-4*H*-1,2,6-thiadiazin-4-ols and with MeLi to give 4-methyl-3,5-diaryl-4*H*-1,2,6-thiadiazin-4-ols. The latter dehydrate with *p*-toluenesulfonic acid to give (3,5-diarylthiadiazin-4-ylidene)methanes. (3,5-Diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)methane **15** suffers mono bromination with NBS to give bromo(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)methane **17**. Dichloro- and dibromo(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene) methanes **18** and **19** are formed directly from the 3,5-diphenylthiadiazin-4-one **9** via the Appel reaction using Ph_3P and CCl_4 or CBr_4, respectively. 3,5-Diarylthiadiazin-4-ones treated with P_2S_5 give 3,5-diarylthiadiazine-4-thiones that react with tetracyanoethylene oxide to give the (thiadiazin-4-ylidene) malononitriles. Finally, the 3,5-diphenylthiadiazine-4-thione **20** reacts with ethyl diazoacetate to give ethyl 2-(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)acetate **26**. The above reactions show that a variety of substitutions at C-4 of 3,5-diaryl substituted 1,2,6-thiadiazin-4-ones can be achieved, which extends the potential applications of this heterocycle. All compounds are fully characterized and a brief comparison of their spectroscopic properties is given.

1. Introduction

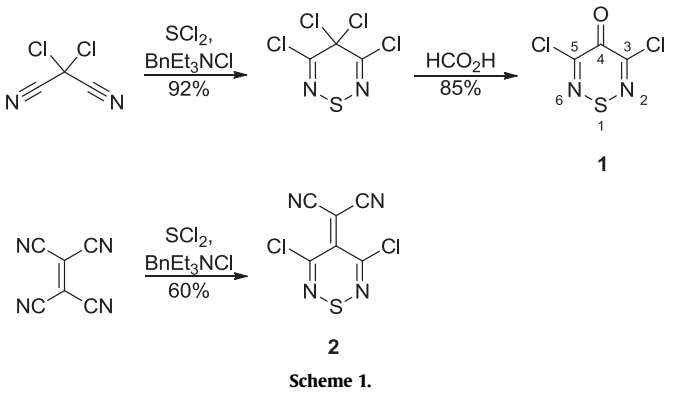
Various oxidised 1,2,6-thiadiazines such as the sulfoxides and, more importantly, the sulfones have received considerable attention in various areas of applied chemistry including the pharmaceutical,[1] agrochemical,[2] and materials[3] sectors. Commercially, an important 1,2,6-thiadiazine is bentazone [3-isopropyl-l*H*-2,l,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide], which is a selective herbicide of long-standing.[4] 1,2,6-Thiadiazines that are not oxidised on sulfur are rare.[5,6]



Bentazone

Two notable exceptions, 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**) and its dicyanomethylene analogue **2**, are potentially useful thiadiazine building blocks.[7–13] The former can be readily prepared from dichloromalononitrile and SCl_2, followed by hydrolysis with formic acid; in good overall yield (78%)[7] while the latter from tetracyanoethylene (TCNE) and SCl_2 (Scheme 1).[8,9]

While many 5-substituted derivatives of 3-chloro-4*H*-1,2,6-thiadiazin-4-ones have high fungicidal activity,[14–17] this usefulness has not prompted extensive studies and the known chemistry of the dichlorothiadiazines **1** and **2** remains limited. The chlorines in **1** and **2** can be successively displaced by a range of nucleophiles, the second requiring more vigorous conditions.[7,11,12,14] To the best of our knowledge there are no reports on the direct intermolecular condensation on the C-4 carbonyl of the dichlorothiadiazinone **1**. In our hands, attempts to directly convert the thiadiazinone **1** into the dicyanomethylene **2** using malononitrile failed. This could be owed (a) to the partially negative charge of the oxygen atom, which is stabilized by a positive charge on the sulfur atom in the resonance forms (Scheme 2) and (b) to the preference for displacement of the chlorine atoms at positions C-3 and C-5.



Scheme 1.

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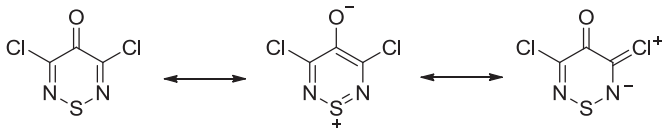
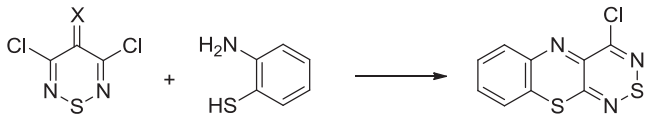


Scheme 2.

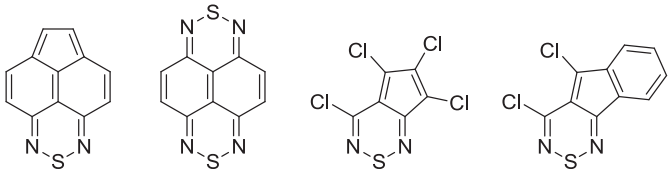
Nevertheless, both dichlorothiadiazine scaffolds **1** and **2** treated with bidentate bisnucleophiles initially suffer mono chloro substitution to give intermediates that readily undergo intramolecular cyclocondensation to give fused thiadiazines (e.g., the reaction with 2-aminobenzenethiol **3** to afford the thiazinothiadiazine **4**, Scheme 3).[11]



1 (X = O)
2 (X = $C(CN)_2$)

Scheme 3.

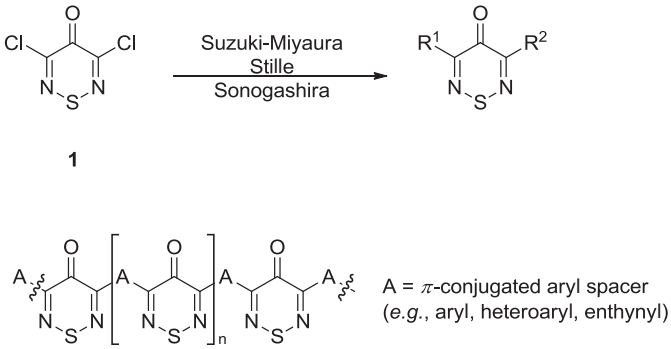
Fused 4*H*-1,2,6-thiadiazines such as acenaphtho[5,6-*cd*][1,2,6]thiadiazine (**5**),[18,19] and naphtho[1,8-*cd*:4,5-*c′d′*]bis([1,2,6]thiadiazine) (**6**),[20] have been studied as examples of 'extreme quinoids', that have ambiguous aromatic character. More recently Torroba et al., prepared cyclopenta[1,2,6]thiadiazines **7** and **8** starting from cyclic enaminonitriles,[21,22] some of which displayed unusual liquid crystalline properties or behaved as near infra-red dyes (Scheme 4).



5 **6** **7** **8**

Scheme 4.

Recently, we have demonstrated that C–C coupling reactions can be applied to 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**) to form both symmetrical and non-symmetrical 1,2,6-thiadiazin-4-ones.[13,23] This development in the chemistry of the dichlorothiadiazinone **1** could potentially lead to the construction of novel π-conjugated oligomers and polymers (Scheme 5). π-Conjugated polymers of thiadiazines have been proposed by both Woodward[24] and Rees[8,10,11] as potentially stable alternatives to the superconductor poly(sulfur nitride) $(SN)_x$.



1

Scheme 5.

The optical/electrical properties of such oligomers or polymers could be moderated by manipulation of the thiadiazine C-4 position. Below we report our efforts to moderate the C-4 position of the model compound 3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-one (**9**) together with some related chemistry of 3,5-dithien-2-yl-4*H*-1,2,6-thiadiazin-4-one (**10**).

2. Results and discussion

2.1. Addition reactions

Both 3,5-diphenyl- and 3,5-dithien-2-yl-4*H*-1,2,6-thiadiazin-4-ones **9** and **10** were prepared in multigram quantities (up to 5 g) via Suzuki–Miyaura or Stille coupling reactions starting from 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**).[13] Our study on the chemistry of the C-4 position began with the formal addition of hydrogen and methane across the carbonyl. The mild reduction of the diphenylthiadiazinone **9** using $NaBH_4$ (2 equiv) in dry MeOH gave 3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ol (**11**) in 90% yield in only 5 min, however, owing to the poor solubility of the dithienylthiadiazinone **10** in MeOH the analogous reduction of the latter required a 1:1 mixture of MeOH and DCM (Table 1).

Table 1
Addition reactions of 3,5-diaryl-4*H*-1,2,6-thiadiazin-4-ones **9** and **10**

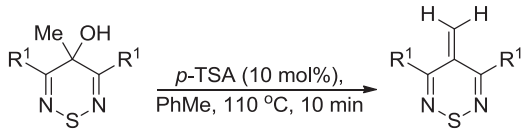
9 (R^1 = Ph)
10 (R^1 = Thien-2-yl)

11-14

R^1	Conditions	Time (min)	R^2	Yields (%)
Ph	$NaBH_4$ (2 equiv), MeOH, 50 °C	5	H	**11** (97)
Thien-2-yl	$NaBH_4$ (2 equiv), MeOH/DCM (1:1), 50 °C	15	H	**12** (98)
Ph	MeLi (4 equiv), THF, 0–10 °C	60	Me	**13** (90)
Thien-2-yl	MeLi (4 equiv), THF, 0–10 °C	60	Me	**14** (79)

Addition of methane could also be achieved by treating 3,5-diphenyl- and 3,5-dithien-2-ylthiadiazinones **9** and **10** with MeLi in dry THF at 0–10 °C, to give after 1 h 4-methyl-3,5-diphenyl- and 4-methyl-3,5-dithien-2-yl-4*H*-1,2,6-thiadiazin-4-ols **13** and **14** in high yields, respectively (Table 1).

Attempts to chlorodehydroxylate or prepare the triflate of 4-methyl-3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ol (**13**), using $SOCl_2$ or Tf_2O/Et_3N, respectively, gave only the dehydrated (3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)methane (**15**). In light of this facile dehydration the diphenyl- and dithienylthiadiazinols **13** and **14** were treated with catalytic *p*-TSA (10 mol %) in PhMe at ca. 110 °C for 10 min to afford the corresponding ylidenes **15** and **16** in high yields (Scheme 6).

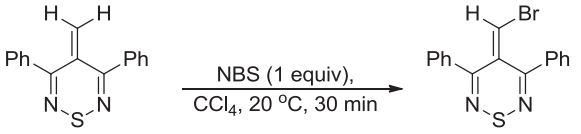


13 (R^1 = Ph)
14 (R^1 = thien-2-yl)

15 (R^1 = Ph, 90%)
16 (R^1 = thien-2-yl, 96%)

Scheme 6.

Interestingly, during the attempted chlorodehydroxylation of 4-methyl-3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ol (**13**) with neat $SOCl_2$ we observed traces of a compound that gave a molecular ion of *m*/*z* 298 Da with a chlorine isotope pattern tentatively corresponding to a chloro-dehydration. As such we investigated the possibility of further halogenating the (thiadiazinylidene)methanes. The attempted chlorination of the (diphenylthiadiazinylidene)methane **15** using $SOCl_2$ gave mixtures and was abandoned. Nevertheless, treating (3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)methane (**15**) with NBS (1 equiv) in CCl_4 at ca. 20 °C, gave bromo(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)methane (**17**) in 80% yield (Scheme 7). The analogous reactions with NCS and NIS at ca. 20 °C gave only recovered starting material while at ca. 70 °C the former gave again recovered starting material and the latter gave a complex reaction mixture (TLC) and no trace of the target compound. The analogous reaction of (dithienylthiadiazinylidene)methane **16** led to mainly unreacted starting material and baseline material.



15 **17** (80%)

Scheme 7.

Further attempts to bis halogenate by either treating the methylene **15** or the monobromoylidene **17** with additional NBS (2 and 3 equiv) in either CCl_4 or with Br_2 in AcOH led to complex mixtures but no trace of the dibrominated product (by TLC), as such this was not pursued further.

2.2. Preparation of dihalo(thiadiazin-4-ylidene)methanes

Fortunately, the dihalomethane thiadiazines **18** and **19** could be prepared via the Appel reaction.[25] Treating the diphenylthiadiazinone **9** with Ph_3P in CCl_4 or CBr_4 at elevated temperatures in a sealed tube and prolonged heating gave the desired dichloro(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)methane (**18**) and dibromo(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)methane (**19**), respectively. In the case of the CCl_4 reaction, heating at ca. 140 °C under microwave irradiation MW (250 W) (70 psi) was the best choice for small scale reactions (up to 0.75 mmol), giving a short reaction time (1 h) (95%) while with CBr_4, heating with microwave irradiation at ca. 140 °C MW (250 W) (68 psi) led to lower yields (70%) and the best yield was obtained when a sealed tube was used for 7 h at ca. 150 °C (91%) (Scheme 8).

9 **18** (Hal = Cl)
19 (Hal = Br)

Scheme 8. Reagents and conditions: Hal=Cl, Ph_3P (4 equiv), CCl_4, MW (250 W), 140 °C (70 PSI), 1 h, 95%; Hal=Br, Ph_3P (4 equiv), CBr_4 (2 equiv), PhH, MW (250 W), 140 °C (68 PSI), 1 h, 70% or sealed tube, 150 °C, 7 h, 91%.

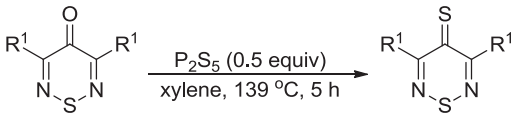
The dibromomethane **19** proved to be stable under several reducing conditions: H_2 over Pd/C in EtOH or $NaBH_4$ in MeOH, and In(0) in AcOH but the use of Zn in HCO_2H[26] led to decomposition of the starting material. Furthermore, the dichloromethane **18** and dibromomethane **19** were stable in the presence of nucleophiles, such as morpholine for 2 d at 100 °C, *o*-phenylenediamine in EtOH heated at reflux for 2 d and thiophenol in refluxing PhMe for 2 d. The limited reactivity of the dihalomethanes **18** and **19** could be attributed to steric effects, due to shielding from the phenyl groups.

2.3. Preparation of (thiadiazin-4-ylidene)malononitriles

Prior attempts to condense malononitrile and the dichlorothiadiazinone **1** to prepare the dicyanomethylene **2** had failed and this was tentatively owed to the high reactivity of the chlorine substituents at C-3 and C-5. With the 3,5-diphenyl- and 3,5-dithien-2-ylthiadiazinones **9** and **10** in hand the C-3 and C-5 positions were now blocked and the analogous condensation was reexamined. Treatment of either diphenyl- or dithienylthiadiazinones **9** and **10** with malononitrile in the presence of bases such as Et_3N, pyridine, *t*-BuLi or *n*-BuLi/diisopropylamine in THF or the use of Lewis acids $TiCl_4$ in PhH or ammonium acetate in Ac_2O, or simply refluxing the mixture in Ac_2O afforded only recovered starting thiadiazinones. Furthermore, the thiadiazinones **9** and **10** were unreactive towards a series of reagents like TCNE, tetracyanoethylene oxide (TCNEO), MeI, ethyl diazoacetate and the Wittig reagent (cyanomethyl)triphenylphosphonium chloride with NaH in THF. Nevertheless, the ylidenemalononitriles could be prepared from the more reactive thiones **20** and **21**.

2.4. Preparation of thiadiazine-4-thiones

Alternative routes to ylidenemalononitriles involve cycloaddition of TCNE or TCNEO to thiones[27–29] and fortunately, the thiadiazine-4-thiones could be readily prepared. The reaction of thiadiazinones **9** and **10** with of P_2S_5 (0.5 equiv) in xylenes heated at ca. 139 °C for 5 h gave the desired 3,5-diphenyl- and 3,5-dithien-2-yl-4*H*-1,2,6-thiadiazine-4-thiones **20** and **21** in 68% and 45% yields, respectively (1 g scales) (Scheme 9). Interestingly, the analogous reactions with Lawesson's reagent (0.5 equiv) in dry toluene or xylenes heated at ca. 110 °C and 139 °C, respectively, for 12 h led to complex mixtures containing mainly unreacted starting thiadiazinones (by TLC).



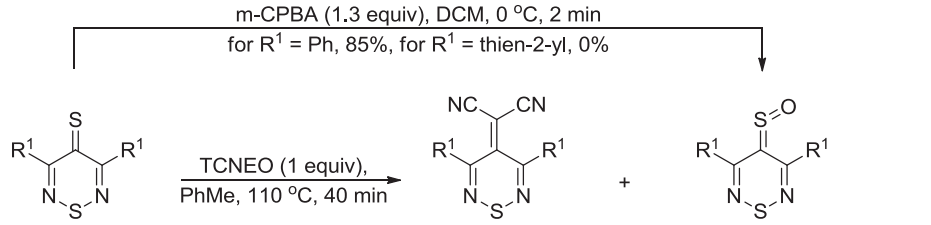
9, 10

20 (R^1 = Ph, 68%)
21 (R^1 = thien-2-yl, 45%)

Scheme 9.

2.5. Preparation of (thiadiazin-4-ylidene)malononitriles

3,5-Diphenyl-4*H*-1,2,6-thiadiazine-4-thione (**20**) treated with TCNE (1.2 equiv) in PhCl heated to ca. 132 °C for 12 h gave 2-(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)malononitrile (**22**) in a moderate 36% yield together with two purple coloured minor side products that could not be separated or characterized. The reaction of the dithienylthiadiazinethione **21** with TCNE, however, led to a complex reaction mixture and this was not altogether surprising since TCNE was known to react with thiophenes to give tricyanovinyl substituted thiophenes at C-2[30] and in rare cases Diels–Alder adducts can form.[31,32] In light of this we then reacted both diphenyl and dithienylthiadiazine-4-thiones **20** and **21** with TCNEO (1.2 equiv) in PhMe heated to ca. 110 °C for 40 min and obtained the desired ylidenemalononitriles **22** and **24** in 72% and 79% yields, respectively (Scheme 10). Interestingly, the reaction between



20 (R^1 = Ph)
21 (R^1 = Thien-2-yl)

22 (R^1 = Ph, 72%)
24 (R^1 = Thien-2-yl, 79%)

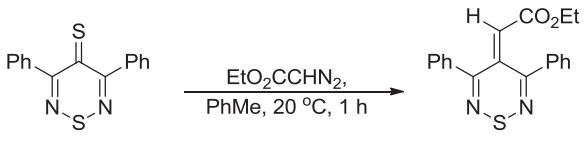
23 (R^1 = Ph,12%)
25 (R^1 = Thien-2-yl, 0%)

Scheme 10.

3,5-diphenyl-4*H*-1,2,6-thiadiazine-4-thione (**20**) and TCNEO also gave 3,5-diphenyl-4*H*-1,2,6-thiadiazine-4-thione oxide (**23**) as a minor side product in 12% yield (Scheme 10). The sulfine **23** could be prepared directly and in high yield (85%) by treating the diphenylthiadiazinethione **20** with *m*-CPBA (1.3 equiv) at ca. 0 °C for 2 min, however, the analogous reaction with the dithienylthiadiazine-4-thione **21** gave only decomposition (by TLC), and this was probably owed to the ability of *m*-CPBA to oxidise the electron rich thiophenes.[33]

The mechanistic rationale for the reactions between TCNE and TCNEO with thiones to give ylidenemalononitriles and also in the latter case the sulfine has been previously reported.[28,29] Briefly, both reagents cycloadd to the thione, TCNE via [2+2] and TCNEO via [2+3] cycloadditions. The adducts then fragment via retro-cycloaddition reactions, tentatively losing in the first case thiocarbonyl cyanide and in the second case carbonyl cyanide and elemental sulfur, leaving behind the desired ylidenemalononitriles. It has been postulated that sulfine **23** forms by direct attack of the thione onto the TCNEO oxygen leading to an effective oxygen transfer and generation of TCNE as a reaction side product.[29]

In light of this success we extended the [2+3] cycloaddition chemistry of the thiadiazinethiones by reacting both the diphenyl- and dithienylthiadiazinethiones **20** and **21** with ethyl diazoacetate (1.5 equiv) in PhMe at ca. 20 °C for 1 h and isolated ethyl 2-(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)acetate (**26**) in 97% yield from the former (Scheme 11) but failed to obtain a product from the dithienyl analogue, which gave a complex reaction mixture. Tentatively this could be attributed to the known reactivity of thiophenes with ethyl diazoacetate that can lead to competing cyclopropanation reactions.[34]



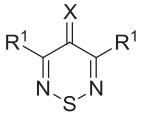
20 **26** (97%)

Scheme 11.

2.6. Comparison of selected spectroscopic data of thiadiazinylidenes

With a range of 4*H*-1,2,6-thiadiazin-4-ylidenes in hand that varied at C-4, the absorption properties in the UV/vis absorption spectra could be compared. This comparison can yield qualitative information about optical band gaps that can be used in the design of oligomers or polymers needed for further materials studies. On comparing the 3,5-diphenylthiadiazines it was clear that the replacement of oxygen by either sulfur or carbon substituents shifted the longest wavelength absorption to the red (Table 2). On switching the C-4 oxygen for the more powerfully electron withdrawing $C(CN)_2$ red shifts of 97 and 157 nm were observed for the diphenyl and dithienylthiadiazinylidenes, respectively.

Table 2
Selected spectroscopic data for 3,5-disubstituted 4*H*-1,2,6-thiadiazines



Compound no.	R^1	X	λ_{max} (DCM)/nm (log ε)	^{13}C (ppm) $C(CN)_2$
9	Ph	O	348 (3.28)	—
18	Ph	CCl_2	358 (3.19)	—
19	Ph	CBr_2	361 (3.19)	—
15	Ph	CH_2	392 (2.84)	—
20	Ph	S	416 (3.37)	—
22	Ph	$C(CN)_2$	445 (3.07)	79.0 (in $CDCl_3$)
10	Thien-2-yl	O	327 (3.74)	—
16	Thien-2-yl	CH_2	395 (3.59)	—
21	Thien-2-yl	S	454 (3.15)	—
24	Thien-2-yl	$C(CN)_2$	484 (3.29)	78.6 (in $CDCl_3$)

The ^{13}C NMR data of ylidenemalononitriles **22** and **24** also indicated that a considerable negative charge was located on the central carbon of the malononitrile group [δ_C $C(CN)_2$ **22** (R^1=Ph) 79.0 ppm and **24** (R^1=thien-2-yl) 78.6 ppm] indicating the presence of a considerable push–pull effect,[35] the 'push' originating presumably from the electron rich arenes at C-3 and C-5 and also from the thiadiazine ring sulfur. The above data tentatively support that electron transfer occurred from the 3,5-diaryl substituents to the thiadiazine ring and that modifications at the C-4 positions strongly affect the properties of these 3,5-diarylthiadiazinylidenes.

3. Conclusions

The modification of 3,5-diphenyl and 3,5-dithien-2-yl-4*H*-1,2,6-thiadiazin-4-ones **9** and **10** at the C-4 position using $NaBH_4$ or MeLi has successfully afforded 4*H*-thiadiazin-4-ols. Furthermore, various 4*H*-ylidenemethanes could be prepared either via the dehydration of 4-methylthiadiazin-4-ols or via the Appel reaction of thiadiazinones with Ph_3P and CX_4 (X=Br or Cl), or via cycloaddition—retrocycloaddition reactions of the readily prepared thiadiazinethiones and TCNEO. Spectroscopic studies indicate that modifying the C-4 position can dramatically alter the longest wavelength absorption in the visible spectra and this information can be of use for the design of π-extended oligomers and polymers.

4. Experimental

4.1. General procedures

THF was distilled over sodium in the presence of benzophenone and Et_2O was distilled over CaH_2. Reactions were protected by $CaCl_2$ drying tubes. Anhydrous Na_2SO_4 was used for drying organic extracts and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm).[36] Melting points were determined using a PolyTherm-A, Wagner & Munz, Koefler-Hotstage Microscope apparatus. Decomposition points (decomp.) and mp >250 °C were determined using a TA Instruments DSC Q1000 with samples hermetically sealed in aluminium pans under an argon atmosphere, using heating rates of 5 °C/min. Solvents used for recrystallization are indicated after the melting point. A CEM Discover Microwave Reactor was used for microwave experiments. UV spectra were obtained using a Perkin–Elmer Lambda-25 UV/vis spectrophotometer and inflections are identified by the abbreviation 'inf'. IR spectra were recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer with Pike *Miracle* Ge ATR accessory 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). Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Low resolution (EI) mass spectra were recorded on a Shimadzu Q2010 GCMS with direct inlet probe. 3,5-Diphenyl-4*H*-1,2,6-thiadiazin-4-one **9** and 3,5-di-(thien-2-yl)-4*H*-1,2,6-thiadiazin-4-one **10**,[13] TCNE[37] and TCNEO[38] were prepared according to literature procedures.

4.2. 3,5-Diphenyl-4*H*-1,2,6-thiadiazin-4-ol (11)

To a stirred suspension of 3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-one (**9**) (100 mg, 0.376 mmol) in MeOH (4 mL) at ca. 20 °C, was added $NaBH_4$ (28.4 mg, 0.75 mmol) and the mixture was placed to a preheated oil bath at ca. 50 °C until no starting material remained (TLC). The mixture was then diluted (DCM), washed (H_2O) and dried (Na_2SO_4) to give the *title compound* **11** (98 mg, 97%) as yellow flakes; mp 75–77 °C (from pentane); R_f 0.60 (DCM). Found: C, 67.03; H, 4.62; N, 10.32. $C_{15}H_{12}N_2OS$ requires C, 67.14; H, 4.51; N, 10.44%; λ_{max} (DCM)/nm 240 inf (306), 246 (3.07), 277 inf (2.91), 348 (3.03); ν_{max}/cm^{-1} 3356w, 3310w, 3260w (OH), 3059w (Ar CH), 1703w, 1493w, 1445s, 1385m, 1360s, 1265s, 1234w, 1200m, 1182w, 1157w, 1070s, 1040w, 1020s, 969s, 932m, 910w, 847m; δ_H (500 MHz; $CDCl_3$) 7.99–7.97 (5H, m, Ph *H*), 7.47–7.46 (5H, m, Ph *H*), 6.07 (1H, s, C*H*OH); δ_C (125 MHz; $CDCl_3$) 150.3 (s), 136.6 (s), 130.6 (d), 128.8 (d), 126.8 (d), 52.4 (d, *C*HOH); *m*/*z* (EI) 268 (M^+, 7%), 267 (M^+-1, 7), 252 (21), 251 (6), 221 (100), 220 (43), 149 (25), 137 (11), 135 (9), 121 (7), 116 (14), 103 (36), 77 (36), 51 (18).

4.3. 3,5-Dithien-2-yl-4*H*-1,2,6-thiadiazin-4-ol (12)

Following the procedure described for the preparation of compound **11**, treatment of 3,5-dithien-2-yl-4*H*-1,2,6-thiadiazin-4-one (**10**) (105 mg, 0.376 mmol) in MeOH/DCM (1:1, 4 mL) gave the *title compound* **12** (103 mg, 98%) as yellow needles; mp 110–112 °C (from cyclohexane); R_f 0.50 (DCM). Found: C, 47.20; H, 2.79; N, 9.87. $C_{11}H_8N_2OS_3$ requires C, 47.12; H, 2.88; N, 9.99%; λ_{max} (DCM)/nm 269 (log ε 3.23), 285 inf (3.10), 381 (3.33), 389 (3.32), 406 inf (3.19); ν_{max}/cm^{-1} 3480w, 3292brw (OH), 3088w (Ar CH), 1533m, 1425s, 1373w, 1352w, 1287w, 1250w, 1246m, 1088w, 1063m, 1022w, 999s, 926m, 916m, 907w, 856m, 847s, 795w; δ_H (500 MHz; $CDCl_3$) 7.63 (2H, d, *J* 3.5, thienyl *H*), 7.50 (2H, d, *J* 5.0, thienyl *H*), 7.12 (2H, dd, *J* 4.5, 4.5, thienyl *H*-4), 5.91 (1H, s, C*H*OH); δ_C (125 MHz; $CDCl_3$) 146.1 (s), 142.9 (s), 130.6 (d), 127.9 (d), 126.4 (d), 54.0 (d); *m*/*z* (EI) 280 (M^+, 25%), 263 (6), 233 (2), 171 (8), 142 (35), 127 (4), 115 (6), 112 (6), 110 (100), 97 (5), 84 (17), 71 (8), 64 (11), 58 (11), 49 (12).

4.4. 4-Methyl-3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ol (13)

To a stirred solution of 3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-one (**9**) (100 mg, 0.376 mmol) in THF (4 mL) at ca. 0 °C protected from moisture with a $CaCl_2$ drying tube, was added MeLi (0.33 mL, 1.50 mmol) and the mixture was left to warm to ca. 10 °C until no starting material remained (TLC). The mixture was then diluted (DCM), washed (H_2O), dried (Na_2SO_4) and adsorbed onto silica. Chromatography (hexane/DCM, 1:1) gave the *title compound* **13** (95.6 mg, 90%) as pale yellow needles; mp (DSC) onset 122.9 °C, peak 123.3 °C (from cyclohexane); R_f 0.33 (hexane/DCM, 1:1). Found: C, 68.16; H, 5.11; N, 9.83. $C_{16}H_{14}N_2OS$ requires C, 68.06; H, 5.00; N, 9.92%; λ_{max} (DCM)/nm 235 (log ε 3.23), 248 inf (3.14), 284 (3.01), 340 (3.03); ν_{max}/cm^{-1} 3333brw (OH), 3055w (Ar CH), 2992w, 1491w, 1439m, 1369m, 1273m, 1179m, 1155w, 1078w, 1057m, 1032w, 1001w, 982w, 947w, 926w, 841w, 818m, 768s, 762s; δ_H (500 MHz; $CDCl_3$) 7.82 (4H, d, *J* 7.5, Ph *H*), 7.42–7.37 (6H, m, Ph *H*), 2.43 (1H, s, O*H*), 1.66 (3H, s, CH_3); δ_C (125 MHz; $CDCl_3$) 155.8 (s), 135.1 (s), 130.1 (d), 129.6 (d), 128.1 (d), 68.4 (s), 19.0 (*C*H_3); *m*/*z* (EI) 282 (M^+, 7%), 267 (2), 263 (2), 239 (5), 179 (31), 160 (4), 146 (7), 136 (100), 109 (9), 104 (27), 85 (4), 77 (20), 71 (6), 57 (8), 51 (9).

4.5. 4-Methyl-3,5-dithien-2-yl-4*H*-1,2,6-thiadiazin-4-ol (14)

Following the procedure described for compound **13** treatment of 3,5-dithien-2-yl-4*H*-1,2,6-thiadiazin-4-one (**10**) (105 mg, 0.376 mmol) gave the *title compound* **14** (103 mg, 98%) as yellow plates; mp 32–34 °C; R_f 0.33 (hexane/DCM, 1:1). Found: C, 49.07; H, 3.39; N, 9.66. $C_{12}H_{10}N_2OS_3$ requires C, 48.95; H, 3.42; N, 9.51%; λ_{max} (DCM)/nm 277 (log ε 4.23), 354 (3.90), 429 (3.95); ν_{max}/cm^{-1} 3433brw (OH), 3100w and 3076w (Ar CH), 2976w, 1697w, 1647w, 1541m, 1520w, 1418s, 1356m, 1267m, 1229m, 1211w, 1169m, 1078w, 1047s, 976w, 949w, 905w, 851s, 812w, 779w; δ_H (500 MHz; $CDCl_3$) 7.87 (2H, d, *J* 4.0, thienyl *H*), 7.42 (2H, d, *J* 5.0, thienyl *H*), 7.05 (2H, dd, *J* 4.5, 4.5, thienyl *H*-4), 3.04 (1H, s, CO*H*CH_3), 1.62 (3H, s, CH_3); δ_C (125 MHz; $CDCl_3$) 150.4 (s), 139.5 (s), 130.4 (d), 130.1 (d), 127.7 (d), 66.8 (s), 19.9 (*C*H_3); *m*/*z* (EI) 294 (M^+, 49%), 279 (15), 251 (7), 185 (23), 170 (4), 142 (100), 116 (9), 109 (24), 84 (12), 71 (7), 58 (7).

4.6. (3,5-Diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)methane (15)

To a stirred solution of 4-methyl-3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ol (**13**) (50.0 mg, 0.177 mmol) in PhMe (2 mL) at ca. 20 °C was added *p*-TSA (3.4 mg, 0.018 mmol) and the mixture was heated at ca. 110 °C (preheated oil bath) until no starting material remained (TLC). The reaction mixture was then allowed to cool to ca. 20 °C, diluted (DCM) and adsorbed onto silica. Chromatography (hexane/DCM, 7:3) gave the *title compound* **15** (42.8 mg, 90%) as yellow plates; mp 67–68 °C (from cyclohexane); R_f 0.70 (hexane/DCM, 1:1). Found: C, 72.74; H, 4.67; N, 10.69. $C_{16}H_{12}N_2S$ requires C, 72.70; H, 4.58; N, 10.60%; λ_{max} (DCM)/nm 247 (log ε 3.42), 333 (3.09), 392 (2.84); ν_{max}/cm^{-1} 3053w (Ar CH), 2955w, 2924w, 2853w, 1593w, 1576w, 1531m, 1489m, 1472w, 1441m, 1396w, 1352s, 1277m, 1175m, 1076m, 1028w, 999w, 989m, 968w, 918s, 851w, 841w, 831w, 781s; δ_H (500 MHz; $CDCl_3$) 7.82–7.81 (4H, m, Ph *H*), 7.45–7.43 (6H, m, Ph *H*), 5.59 (2H, s, CH_2); δ_C (125 MHz; $CDCl_3$) 158.2 (s), 137.2 (s), 130.2 (d), 128.6 (d), 128.5 (s), 127.5 (d), 117.3 (=*C*H_2); *m*/*z* (EI) 264

(M^+, 84%), 263 (100), 185 (4), 160 (67), 134 (6), 115 (42), 109 (5), 103 (11), 89 (14), 77 (18), 63 (10), 58 (9), 51 (14).

4.7. (3,5-Dithien-2-yl-4*H*-1,2,6-thiadiazin-4-ylidene)methane (16)

Following the procedure described for compound **15** treatment of 4-methyl-3,5-dithien-2-yl-4*H*-1,2,6-thiadiazin-4-ol (**14**) (53 mg, 0.18 mmol) gave the *title compound* **16** (47.7 mg, 96%) as orange plates; mp 66–67 °C (from pentane, fridge); R_f 0.70 (hexane/DCM, 1:1). Found: C, 52.22; H, 2.83; N, 10.07. $C_{12}H_8N_2S_3$ requires C, 52.14; H, 2.92; N, 10.14%; λ_{max} (DCM)/nm 254 inf (log ε 3.44), 273 (3.61), 299 inf (3.39), 382 (3.57), 395 (3.59); ν_{max}/cm^{-1} 3100w and 3075w (Ar CH), 1591w, 1520m, 1504w, 1425s, 1352w, 1337w, 1271w, 1231m, 1055m, 955m, 943w, 926m, 920m, 905w, 851s; δ_H (500 MHz; $CDCl_3$) 7.65 (2H, dd, *J* 3.4, 1.3, thienyl *H*), 7.46 (2H, dd, *J* 5.3, 1.2, thienyl *H*), 7.07 (2H, dd, *J* 5.0, 4.0, thienyl *H*-4), 5.96 (2H, s, CH_2); δ_C (125 MHz; $CDCl_3$) 149.6 (s), 141.4 (s), 130.3 (d), 128.4 (s), 127.4 (d), 127.3 (d), 114.8 (*C*H_2); *m*/*z* (EI) 276 (M^+, 100%), 243 (6), 231 (4), 192 (5), 167 (13), 140 (8), 121 (19), 109 (9), 97 (7), 77 (14), 69 (7), 58 (9).

4.8. Bromo(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene) methane (17)

To a stirred solution of (3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene)methane (**13**) (50.0 mg, 0.189 mmol) in CCl_4 (2 mL) at ca. 20 °C, was added NBS (33.8 mg, 0.19 mmol) and stirred until no starting material remained. The reaction mixture was then adsorbed onto silica and chromatography (hexane/DCM, 7:3) gave the *title compound* **17** (52 mg, 80%) as yellow plates; mp 98–99 °C (from pentane, fridge); R_f 0.74 (hexane/DCM, 7:3). Found: C, 55.96; H, 3.19; N, 8.23. $C_{16}H_{11}BrN_2S$ requires C, 55.99; H, 3.23; N, 8.16%; λ_{max}(DCM)/nm 246 (log ε 3.51), 350 (3.24), 381 inf (3.08), 397 (3.04); ν_{max}/cm^{-1} 3055w (Ar CH), 1574w, 1506w, 1491w, 1443w, 1341m, 1308w, 1281w, 1238w, 1173w, 1161w, 1074w, 1028w, 1007w, 995w, 974w, 922w, 841m, 802w, 793w, 716s; δ_H (500 MHz; $CDCl_3$) 7.98–7.96 (2H, m, Ph *H*), 7.85 (2H, dd, *J* 7.5, 1.3, Ph *H*), 7.48–7.46 (6H, m, Ph *H*), 6.85 (1H, s); δ_C (125 MHz; $CDCl_3$) (1 quaternary missing) 153.2 (s), 152.0 (s), 135.7 (s), 130.8 (d), 130.1 (d), 130.1 (s), 129.0 (d), 128.7 (d), 127.8 (d), 127.4 (d), 110.4 (d, *C*HBr); *m*/*z* (EI) 344 (M^++2, 11%), 342 (M^+, 11), 263 (778), 185 (6), 160 (100), 133 (11), 131 (17), 116 (17), 114 (21), 109 (13), 89 (9), 77 (18), 65 (6), 51 (12).

4.9. Dichloro(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene) methane (18)

3,5-Diphenyl-4*H*-1,2,6-thiadiazin-4-one (**9**) (100 mg, 0.365 mmol), Ph_3P (394 mg, 1.50 mmol) and CCl_4 (1 mL) were placed in a MW reactor (250 W) and heated to ca. 140 °C (70 psi) for 1 h. The reaction mixture was then allowed to cool to ca. 20 °C, diluted (DCM) and adsorbed onto silica. Chromatography (hexane/DCM, 7:3) gave the *title compound* **18** (119 mg, 95%) as yellow plates; mp 154–156 °C (from pentane); R_f 0.75 (hexane/DCM, 7:3). Found: C, 57.75; H, 2.96; N, 8.32. $C_{16}H_{10}Cl_2N_2S$ requires C, 57.67; H, 3.02; N, 8.41%; λ_{max}(DCM)/nm 247 (log ε 3.41), 257 inf (3.37), 358 (3.19); ν_{max}/cm^{-1} 3059w (Ar CH), 1574w, 1506w, 1489w, 1443m, 1317m, 1296m, 1246w, 1177w, 1138w, 1076w, 1026w, 928s, 914w, 878s, 843w, 781s, 768s; δ_H (500 MHz; $CDCl_3$) 7.93 (4H, d, *J* 7.5, Ph *H*), 7.50–7.43 (6H, m, Ph *H*); δ_C (125 MHz; $CDCl_3$) 148.1 (s), 134.8 (s), 130.4 (d), 128.9 (d), 127.4 (d), 126.2 (s), 121.2 (s); *m*/*z* (EI) 336 (M^++4, 4%), 334 (M^++2, 17), 332 (M^+, 26), 299 (13), 297 (36), 294 (33), 262 (27), 215 (6), 196 (35), 194 (100), 185 (36), 183 (56), 159 (11), 152 (6), 148 (20), 139 (9), 130 (18), 121 (6), 113 (23), 109 (9), 103 (6), 77 (22), 63 (12), 51 (18).

4.10. Dibromo(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene) methane (19)

3,5-Diphenyl-4*H*-1,2,6-thiadiazin-4-one (**9**) (100 mg, 0.365 mmol), Ph_3P (394 mg, 1.50 mmol), CBr_4 (249 mg, 0.751 mmol) and dry PhH (1 mL) were placed in a sealed tube and heated to 150 °C for 7 h until no starting material remained (TLC). After the reaction was finished, the reaction mixture was diluted with DCM and adsorbed onto silica. Chromatography (hexane/DCM, 7:3) gave the *title compound* **19** (144 mg, 91%) as yellow plates; mp (DSC) onset 151.7 °C, peak 153.5 °C (from pentane); R_f 0.75 (hexane/DCM, 7:3). Found: C, 45.58; H, 2.42; N, 6.61. $C_{16}H_{10}Br_2N_2S$ requires C, 45.52; H, 2.39; N, 6.64%; λ_{max} (DCM)/nm 245 (log ε 3.33), 261 (3.38), 361 (3.19); ν_{max}/cm^{-1} 3057w (Ar CH), 1557w, 1508w, 1487w, 1441m, 1315s, 1294m, 1277w, 1175m, 1134m, 1076w, 1032w, 1024w, 1009w, 997w, 920w, 862s, 856m, 779s, 766s; δ_H (500 MHz; $CDCl_3$) 7.96 (4H, d, *J* 7.5, Ph *H*), 7.50–7.42 (6H, m, Ph *H*); δ_C (125 MHz; $CDCl_3$) 149.1 (s), 134.3 (s), 133.6 (s), 130.4 (d), 128.9 (d), 127.6 (d), 91.9 (s); *m*/*z* (EI) 424 (M^++4, 7%), 422 (M^++2, 17), 420 (M^+, 7), 343 (7), 341 (7), 262 (100), 216 (6), 159 (17), 131 (13), 113 (18), 109 (10), 77 (15), 63 (8), 51 (16).

4.11. 3,5-Diphenyl-4*H*-1,2,6-thiadiazine-4-thione (20)

To a stirred solution of 3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-one (**9**) (100 mg, 0.375 mmol) in xylene (4 mL) was added P_2S_5 (83.5 mg, 0.188 mmol) and the reaction mixture was heated at ca. 139 °C until no starting material remained (TLC). The reaction mixture was then allowed to cool to ca. 20 °C, filtered through a pad of silica gel and washed with hexane (30 mL) to remove xylene and then elution with hexane/DCM (7:3) gave the *title compound* **20** (72 mg, 68%) as yellow needles; mp 109–110 °C (from pentane/DCM, at ca. 0 °C); R_f 0.65 (hexane/DCM, 7:3). Found: C, 63.82; H, 3.50; N, 9.95. $C_{15}H_{10}N_2S_2$ requires C, 63.80; H, 3.57; N, 9.92%; λ_{max} (DCM)/nm 235 inf (log ε 3.43), 253 (3.57), 416 (3.37); ν_{max}/cm^{-1} 3030w (Ar CH), 1578w, 1466w, 1435w, 1425w, 1329m, 1319m, 1290w, 1271w, 1177w, 1152s, 1072w, 1030w, 1001w, 910w, 824m, 773m; δ_H (500 MHz; $CDCl_3$) 7.84 (4H, d, *J* 7.5, Ph *H*), 7.46–7.42 (6H, m, Ph *H*); δ_C (125 MHz; $CDCl_3$) 191.6 (s, *C*=S), 169.0 (s), 137.7 (s), 130.6 (d), 128.3 (d), 127.9 (d); *m*/*z* (EI) 282 (M^+, 52%), 281 (M^+–1, 100), 204 (4), 179 (8), 141 (5), 135 (13), 121 (22), 103 (41), 89 (15), 77 (19), 76 (19), 63 (6), 51 (12).

4.12. 3,5-Dithien-2-yl-4*H*-1,2,6-thiadiazine-4-thione (21)

Following the procedure described for compound **20** treatment of 3,5-dithien-2-yl-4*H*-1,2,6-thiadiazin-4-one (**10**) (104 mg, 0.375 mmol) gave the *title compound* **21** (50 mg, 45%) as bright green needles; mp 134–136 °C (from cyclohexane); R_f 0.75 (hexane/DCM, 7:3). Found: C, 44.92; H, 2.00; N, 9.45. $C_{11}H_6N_2S_4$ requires C, 44.87; H, 2.05; N, 9.51%; λ_{max} (DCM)/nm 296 (log ε 3.35), 454 (3.15); ν_{max}/cm^{-1} 3088w (Ar CH), 1491w, 1412s, 1391w, 1350s, 1306s, 1260m, 1223w, 1211w, 1161s, 1136w, 1113w, 1078w, 1071w, 1057w, 947w, 914w, 874w, 851m, 839w, 802s; δ_H (500 MHz; $CDCl_3$) 8.29 (2H, dd, *J* 4.0, 1.0, thienyl *H*), 7.56 (2H, dd, *J* 5.0, 1.5, thienyl *H*), 7.15 (2H, dd, *J* 4.5, 4.0, thienyl *H*); δ_C (125 MHz; $CDCl_3$) 181.7 (s, *C*=S), 160.3 (s), 139.1 (s), 133.6 (d), 132.7 (d), 126.9 (d); *m*/*z* (EI) 294 (M^+, 100%), 293 (93), 261 (5), 210 (4), 185 (12), 147 (7), 141 (26), 139 (25), 127 (12), 115 (14), 109 (80), 95 (24), 71 (16), 69 (18), 58 (14).

4.13. 2-(3,5-Diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene) malononitrile (22)

To a stirred solution of 3,5-diphenyl-4*H*-1,2,6-thiadiazine-4-thione (**20**) (100 mg, 0.355 mmol) in PhCl (2 mL) was added TCNE (54.6 mg, 0.426 mmol) and the reaction mixture was heated at ca.

132 °C until no starting material remained (TLC). The reaction mixture was then allowed to cool to ca. 20 °C, diluted (DCM) and adsorbed onto silica. Chromatography (hexane/DCM, 1:1) gave the *title compound* **22** (35.6 mg, 79%) as yellow needles; mp (DSC) onset 213.2 °C, peak 214.5 °C (from pentane/DCM, 0 °C); R_f 0.40 (hexane/DCM, 1:1). Found: C, 68.86; H, 3.15; N, 17.73. $C_{18}H_{10}N_4S$ requires C, 68.77; H, 3.21; N, 17.82%; λ_{max} (DCM)/nm 261 (log ε 3.31), 381 (2.91), 445 (3.07); ν_{max}/cm^{-1} 3046w (Ar CH), 2218m (C≡N), 1512s, 1491w, 1477s, 1439s, 1343s, 1277m, 1177w, 1159w, 1103w, 1078w, 1028w, 999w, 966w, 939w, 920w, 837w, 818s, 797m, 775m; δ_H (500 MHz; $CDCl_3$) 7.87 (4H, br s, Ph *H*), 7.59 (6H, br s, Ph *H*); δ_C (125 MHz; $CDCl_3$) 150.4 (s), 142.7 (s), 134.7 (s), 132.1 (d), 129.5 (d), 127.8 (d), 111.8 (s, *C*≡N), 79.0 [s, *C*(C≡N)$_2$]; *m*/*z* (EI) 314 (M$^+$, 23%), 288 (5), 210 (9), 177 (16), 167 (15), 149 (100), 138 (9), 125 (7), 121 (10), 113 (14), 111 (14), 105 (10), 99 (12), 97 (17), 93 (10), 84 (41), 77 (12), 71 (41), 57 (56), 51 (21). Further elution (DCM) gave a mixture of two purple compounds, which could not be separated or characterized.

4.14. 2-(3,5-Diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene) malononitrile (22) and 3,5-diphenyl-4*H*-1,2,6-thiadiazine-4-thione oxide (23)

To a stirred solution of 3,5-diphenyl-4*H*-1,2,6-thiadiazine-4-thione (**20**) (100 mg, 0.355 mmol) in PhMe (2 mL) was added TCNEO (61.3 mg, 0.426 mmol) and the reaction mixture was heated at ca. 110 °C until no starting material remained (TLC). The reaction mixture was then allowed to cool to ca. 20 °C, diluted (DCM) and adsorbed onto silica. Chromatography (hexane/DCM, 1:1) gave the *title compound* **22** (88 mg, 79%) as yellow needles; mp (DSC) onset 213.2 °C, peak 214.5 °C (from pentane/DCM, 0 °C), identical to that described above. Further elution (hexane/DCM, 1:1) gave the *title compound* **23** (13.2 mg, 12%) as red flakes; mp 124–125.5 °C (from pentane/EtOH, at ca. 0 °C); R_f 0.50 (hexane/DCM, 1:1). Found: C, 60.33; H, 3.29; N, 9.31. $C_{15}H_{10}N_2OS_2$ requires C, 60.38; H, 3.38; N, 9.39%; λ_{max}(DCM)/nm 251 (log ε 3.18), 284 (3.02), 426 (2.90); ν_{max}/cm^{-1} 3059w (Ar CH), 1483w, 1437w, 1321m, 1302w, 1269w, 1165w, 1142w, 1082s, 1074m, 1030w, 999w, 986w, 922w, 841w, 793m, 770m; δ_H (500 MHz; $CDCl_3$) 7.95 (2H, d, *J* 7.0, Ph *H*), 7.77–7.75 (2H, m, Ph *H*), 7.56–7.47 (6H, m, Ph *H*); δ_C (125 MHz; $CDCl_3$) 166.0 (s), 153.5 (s), 153.45 (s), 136.2 (s), 135.1 (s), 132.0 (d), 131.1 (d), 129.3 (d), 128.4 (d), 128.0 (d), 127.3 (d); *m*/*z* (EI) 298 (M$^+$, 100%), 281 (75), 269 (15), 265 (15), 249 (8), 220 (11), 205 (7), 190 (11), 175 (21), 167 (8), 149 (13), 146 (10), 135 (15), 121 (31), 103 (38), 89 (10), 77 (49), 63 (11), 51 (29).

4.15. 2-(3,5-Dithien-2-yl-4*H*-1,2,6-thiadiazin-4-ylidene) malononitrile (24)

Following the procedure described for compound **22** treatment of 3,5-dithien-2-yl-4*H*-1,2,6-thiadiazine-4-thione (**21**) (105 mg, 0.355 mmol) gave the *title compound* **24** (91.5 mg, 79%) as red needles; mp 217–220 °C (from cyclohexane); R_f 0.25 (hexane/DCM, 7:3). Found: C, 51.42; H, 1.83; N, 17.09. $C_{14}H_6N_4S_3$ requires C, 51.51; H, 1.85; N, 17.16%; λ_{max}(DCM)/nm 259 inf (log ε 3.45), 281 (3.63), 422 (3.41), 484 (3.29); ν_{max}/cm^{-1} 3111w and 3094w (Ar CH), 2218m (C≡N), 1520m, 1505s, 1452m, 1439m, 1418s, 1348m, 1337w, 1287w, 1248w, 1225w, 1109w, 1057w, 907w, 858m, 851m, 828w, 816m; δ_H (500 MHz; $CDCl_3$) 7.66 (2H, d, *J* 5.0, thienyl *H*), 7.58 (2H, d, *J* 3.5, thienyl *H*), 7.19 (2H, dd, *J* 4.3, 4.3, thienyl *H*-4); δ_C (125 MHz; $CDCl_3$) 142.7 (s), 142.0 (s), 138.0 (s), 133.0 (d), 129.7 (d), 128.0 (d), 111.8 (*C*≡N), 78.6 (s); *m*/*z* (EI) 326 (M$^+$, 100%), 293 (44), 277 (4), 249 (4), 217 (7), 171 (60), 149 (12), 144 (12), 127 (12), 115 (8), 109 (46), 97 (8), 82 (11), 69 (29), 58 (23).

4.16. Ethyl 2-(3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-ylidene) acetate (26)

To a stirred solution of 3,5-diphenyl-4*H*-1,2,6-thiadiazine-4-thione (**21**) (100 mg, 0.355 mmol) in PhMe (4 mL) at ca. 20 °C was added ethyl diazoacetate (56 μL, 0.533 mmol) and the reaction mixture was stirred at this temperature until no starting material remained (TLC). The reaction mixture was then diluted with DCM (20 mL) and adsorbed onto silica. Chromatography (hexane/DCM, 1:1) gave the *title compound* **26** as yellow plates; mp (DSC) onset 82.0 °C, peak 84.0 °C (from pentane, at ca. 0 °C); R_f 0.41 (hexane/DCM, 1:1). Found: C, 67.73; H, 4.85; N, 8.28. $C_{19}H_{16}N_2O_2S$ requires C, 67.84; H, 4.79; N, 8.33%; λ_{max}(DCM)/nm 242 (log ε 3.61), 253 inf (3.58), 276 inf (3.40), 380 (3.39), 385 inf (3.36); ν_{max}/cm^{-1} 3059w (Ar CH), 2982w, 2938w, 2901w, 1703s (C=O), 1599w, 1512w, 1489w, 1472w, 1439m, 1395w, 1368w, 1354m, 1315w, 1267s, 1180w, 1153w, 1123w, 1078w, 1036m, 1007w, 966w, 930w, 876m, 833w, 806w, 776m; δ_H (500 MHz; $CDCl_3$) 7.96 (2H, d, *J* 5.0, Ph *H*), 7.89 (2H, d, *J* 7.0, Ph *H*), 7.48 (3H, br s, Ph *H*), 7.42–7.40 (3H, m, Ph *H*), 3.72 (2H, q, *J* 7.0, C*H*$_2$), 0.93 (3H, t, *J* 7.0, C*H*$_3$); δ_C (125 MHz; $CDCl_3$) 165.3 (s), 152.3 (s), 152.2 (s), 137.8 (s), 135.5 (s), 132.1 (s), 130.7 (d), 130.0 (d), 129.0 (d), 128.7 (d), 128.0 (d), 126.0 (d), 116.6 (d, *C*HCO$_2$Et), 60.8 (*C*H$_2$), 13.7 (*C*H$_3$); *m*/*z* (EI) 336 (M$^+$, 21%), 307 (9), 291 (6), 262 (100), 216 (3), 204 (2), 185 (9), 160 (55), 133 (8), 121 (5), 116 (13), 109 (10), 103 (7), 89 (8), 77 (19), 65 (7), 51 (8).

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