Chemistry of 4-dicyanomethylene-1,2,6-thiadiazines

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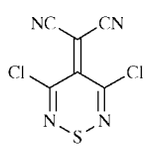
The chlorine atoms in 3,5-dichloro-4-dicyanomethylene-1,2,6-thiadiazine **1** are readily displaced by thiophenols in the presence of Hünig's base, the first at −78 °C and the second at 20 °C to give the orange mono- and bis-arylthio derivatives in high yield (Table 1). Similarly secondary amines give the red mono- and blue bis-amino compounds in high yield (Table 2); piperidine, for example, gives the former at −78 °C and the latter at −30 °C. A low limit of reactivity is reached with diisopropylamine which gives the mono derivative only, in low yield (30%). Reactions with ammonia and with primary amines are complex since the amines formed can cyclise onto the adjacent cyano group, aniline giving only a low yield of the pyrrolo[2,3-*c*][1,2,6]thiadiazine **8**. The 4-dicyanomethylene compound **1** is more reactive than the known 4-oxo analogue **2**, but can suffer the added complications of cyano group cyclisation and hydrolysis of dicyanomethylene to the keto group. 3,5-Dimorpholino-4-dicyanomethylene-1,2,6-thiadiazine **7c** is oxidized to the sulfoxide **9** with MCPBA or N_2O_4, and **9** reverts to **7c** with triphenylphosphine–tetrachloromethane, all in high yield. Thiadiazine **1** undergoes a complex reaction with DMSO at 20 °C to give the three furo[2,3-*c*]-[1,2,6]thiadiazines **10**, **11** and (tentatively) **12** which could all arise from the initial product **13** of displacement of chlorine by DMSO, by cyclisation and sulfoxide type rearrangements. Mechanisms are proposed for all new reactions.

We have recently described[1] the synthesis of 3,5-dichloro-4-dicyanomethylene-4*H*-1,2,6-thiadiazine† **1** by the addition of



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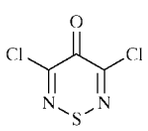

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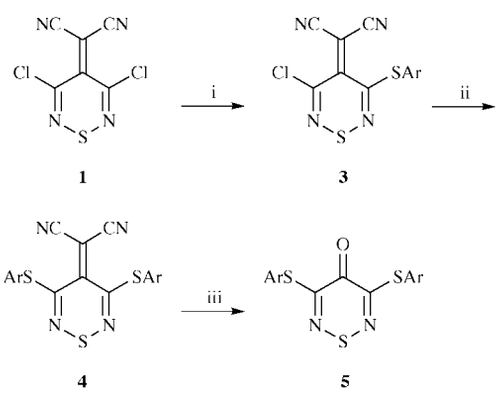
SCl_2 to TCNE, and compared **1** with the analogous 4-oxo compound **2**.[2] The most characteristic reaction of **2** is the displacement of its two chlorine atoms by a range of nucleophiles,[2] and we now describe the effect on such reactions of exchanging the 4-oxo group for the more powerfully electron-withdrawing and more reactive dicyanomethylene group.

Results and discussion

Reaction of 1 with thiophenols

The dichlorothiadiazine **1** reacts with thiophenols in the presence of a tertiary amine to afford mono- and di-substituted derivatives **3** and **4** in good to excellent yields (Table 1, Scheme 1). Mono-substitution could be achieved at −78 °C whilst the second chlorine was replaced smoothly at *ca.* 20 °C. A slight excess of thiophenol was required since a little disulfide was always formed by oxidation. In the absence of a tertiary amine no reaction was observed between the thiophenols and thiadiazine **1**; diisopropylethylamine (Hünig's base) was preferred because of its non nucleophilic nature, low viscosity and low density.

The solubility of the products was noticeably affected by the thiophenol substituents. The chloro derivatives **3c** and **4c** were poorly soluble in chloroform, DCM and benzene, whilst the bis(4-methoxyphenylthio) derivative **4d** was obtained as a foam from the usual recrystallisation solvents, 1,2-dichloroethane and cyclohexane. Attempted recrystallisation from aqueous ethanol gave 3,5-bis(4-methoxyphenylthio)-4*H*-1,2,6-thiadiazin-4-one **5** (Ar = 4-$MeOC_6H_4$) in good yield (78%). This showed the ready uncatalysed or self catalysed hydrolysis of the dicyanomethylene group; the same transformation was observed with DMSO.



Scheme 1 *Reagents and conditions*: (i) ArSH (1.1 equiv.), $EtNPr^i_2$ (1.1 equiv.), DCM, −78 °C, 1 h; (ii) ArSH (1.1 equiv.), $EtNPr^i_2$ (1.1 equiv.), C_6H_6, 20 °C, 1 h; (iii) EtOH, H_2O, 80 °C, 30 min, 78% (Ar = 4-$MeOC_6H_4$).

Reaction of 1 with amines

Since the reaction of thiadiazine **1** with ammonia and primary amines proved to be complex (see below) we next investigated its reactivity towards secondary amines. Both chlorine atoms were smoothly displaced to give the red mono-amino derivatives **6** and the blue bis-amino derivatives **7** (Table 2). Non-sterically hindered amines displaced both chlorines very readily; piperidine displaced the first chlorine at −78 °C and the second at −30 °C. Thus considerable care was required to

† Whilst common nomenclature has been used in the Discussion, a more formal (IUPAC) nomenclature is used throughout the Experimental section.

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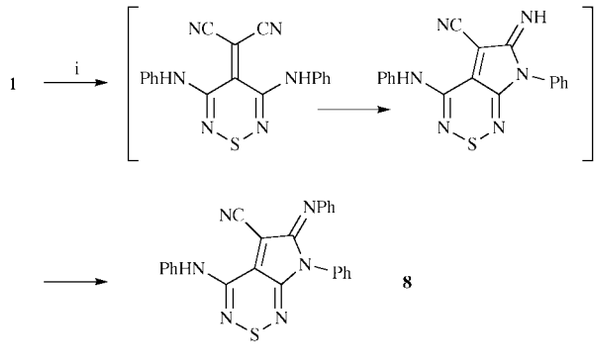
obtain the mono-amino derivatives with slow, monitored addition of exactly two equivalents of the amine, below 0 °C. Bulky amines gave lower yields of all the tertiary amines and required more severe conditions for complete reaction. A limit was reached with diisopropylamine where only the mono-amino derivative **6g** could be obtained, in a maximum yield of 30% with six equivalents of amine in refluxing DCM for three hours. Refluxing this derivative **6g** in neat diisopropylamine gave some indication (TLC) that the bis-amino product was being slowly formed, but it appeared to be unstable under the reaction conditions and could not be isolated.

The reaction of thiadiazine **1** with *N*-methylaniline required a relatively long time and an excess of amine for complete displacement of the second chlorine, but the yield of the bis-amine **7e** was high (87%). The slow reaction probably results more from deactivation by the phenyl group than from steric effects. Diphenylamine was so deactivated towards nucleophilic attack that thiadiazine **1** was recovered unchanged after several days treatment with it at reflux in DCM.

Attempts to displace both chlorine atoms of **1** with aniline or ammonia led to complex reaction mixtures. With aniline, only a deep red product was obtained in very low yield (5%) and was tentatively assigned the bicyclic structure, 4-anilino-5-cyano-7-phenyl-6-phenyliminopyrrolo[2,3-*c*][1,2,6]thiadiazine **8**, on spectroscopic grounds. This product could result from displacement of both chlorine atoms by aniline, cyclisation of one anilino group onto the neighbouring cyano group and exchange of the imino group so formed by aniline (Scheme 2). Similar cyclisations onto the nitrile carbon have been observed with other primary amines such as 1,2-diaminobenzene and 1,8-diaminonaphthalene.[3] Such cyclisation cannot occur, of course, in the reactions of secondary amines with **1** which are uncomplicated (Table 2). Treatment of **1** with ammonia gave no clean



Scheme 2 *Reagents and conditions*: (i) $PhNH_2$, (4 equiv.) DCM, 45 °C, 12 h.

products and we therefore attempted to synthesize the amino derivatives *via* a Gabriel synthesis.[4] The reaction of **1** with potassium phthalimide and 18-crown-6 in toluene was also complex but both the mono- and bis-phthalimido derivatives could be isolated in low yields (25 and 20% respectively). Attempts to control the reaction to give exclusively the mono- or bis-phthalimido thiadiazine were unsuccessful and their deprotection was therefore not pursued.

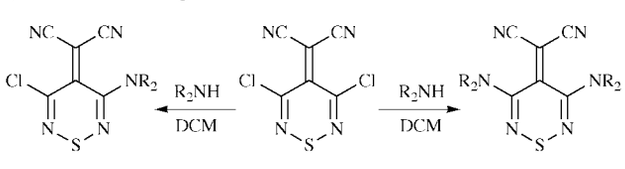
Comparison of the reactivity of thiadiazine 1 and thiadiazinone 2

From the above results, thiadiazine **1** is seen to react with thiophenols to displace both chlorine atoms readily at room temperature; the thiadiazinone **2** does the same,[2] in keeping with the strong nucleophilicity of the thiols. The bis(arylthio)-thiadiazines **4** undergo further reaction in aqueous ethanol to give the C-4 hydrolysed thiadiazinones. With amines, the reactivity of **1** and **2** depends greatly on the nucleophilicity of the amine. Sterically demanding amines such as diisopropylamine or deactivated amines such as *N*-methylaniline react much less readily, as expected. With reactive amines, thiadiazine **1** shows enhanced susceptibility towards displacement of the second chlorine over thiadiazinone **2**. Thus **1** reacts with *N*-methylaniline to give the mono- and bis-derivatives **6e** and **7e** at room temperature whereas **2** requires refluxing in neat *N*-methylaniline for the second displacement to occur.[2] The reactions of **2** are cleaner than those of **1** since there is little reactivity other than chlorine displacement. Where possible **1** can also suffer hydrolysis of the dicyanomethylene group or cyclisation onto a cyano group, resulting in more complex reactions.

Table 1 The mono and bis(arylthio)-1,2,6-thiadiazines **3a**–**d** and **4a**–**d** (see Scheme 1)

Compound	Aryl	Yield (%)
3a	C_6H_5	76
4a	C_6H_5	92
3b	4-MeC_6H_4	69
4b	4-MeC_6H_4	93
3c	4-ClC_6H_4	96
4c	4-ClC_6H_4	85
3d	4-$MeOC_6H_4$	74
4d	4-$MeOC_6H_4$	98

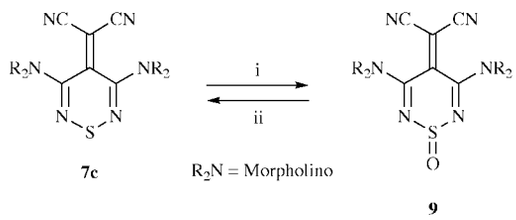
Table 2 The mono and bis(amino)-1,2,6-thiadiazines **6a**–**g** and **7a**–**f**



Compound	R_2NH	Equiv. of R_2NH	Time/h	Temp./°C	Yield (%)
6a	Pyrrolidine	2	1	−5 to 20	77
7a	Pyrrolidine	4	12	−5 to 45	84
6b	Piperidine	2	12	20 to 45	81
7b	Piperidine	5	24	20 to 45	78
6c	Morpholine	2	12	−5 to 45	83
7c	Morpholine	5	24	20 to 45	76
6d	Dibenzylamine	2	12	−5 to 45	74
7d	Dibenzylamine	5	24	20 to 45	81
6e	*N*-Methylaniline	2	12	−5 to 20	85
7e	*N*-Methylaniline	12	24	20 to 45	87
6f	Di-*n*-propylamine	2	1	−5 to 20	74
7f	Di-*n*-propylamine	4	12	−5 to 45	82
6g	Diisopropylamine	6	3	45	30

Oxidation of 4-dicyanomethylene-1,2,6-thiadiazines

1,2,6-Thiadiazine sulfoxides and, more importantly, the sulfones have received considerable attention in various areas of applied chemistry including the pharmaceutical,[5] agrochemical[6] and materials sectors.[7] However, the oxidation of 3,5-substituted-4*H*-1,2,6-thiadiazines has not been reported. The oxidation of thiadiazine **1** with MCPBA or with dinitrogen tetraoxide was unsuccessful; neither sulfoxide nor starting material could be recovered. We therefore turned to the oxidation of the more "electron rich" 3,5-dimorpholinothiadiazine **7c**; in spite of the risk of *N*-oxidation, **7c** was rapidly converted into the *S*-oxide **9** in high yield, by the same reagents (Scheme 3). Both



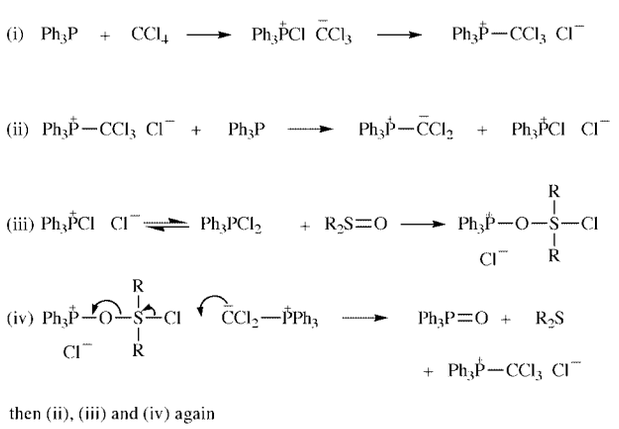
Scheme 3 *Reagents and conditions*: (i) MCPBA (1.6 equiv.), DCM, 20 °C, (85%) or N_2O_4 (g), DCM, 20 °C, (95%); (ii) Ph_3P (3.3 equiv.), CCl_4 (10 equiv.), DCM, 40 °C, 1 h (92%).

reactions were accompanied by a rapid colour change from deep violet [λ_{max} 543 nm (log ε 4.03)] to orange-red [λ_{max} 454 nm (log ε 3.24)]. In the reaction with dinitrogen tetraoxide care was required in the work up procedure; any attempt to perform an aqueous work up or to concentrate the reaction mixture led to complex mixtures. Since an excess of N_2O_4 gas was always used, careful monitoring (TLC) was also required; prolonged reaction times led to complex mixtures.

The product **9** was obtained as orange needles, mp > 300 °C. Both microanalysis and HRMS gave the formula $C_{14}H_{16}N_6O_3S$ and the location of the extra oxygen atom followed from the spectroscopic data. The IR spectrum showed strong stretching bands at 1129 and 1112 cm^{-1} supporting the presence of a sulfoxide, and the nitrile stretching at 2240 cm^{-1} was less intense and of higher frequency than that of the starting material **7c** (2207 cm^{-1}), indicative of less negative charge delocalised onto the dicyanomethylene group. This was supported by the ^{13}C NMR data which showed that the resonance of the central carbon of the dicyanomethylene group at 90.1 ppm was deshielded compared to that of **7c** (71.7 ppm). The ^{13}C NMR also showed that the molecule was symmetrical and that there was a significant barrier to rotation of the morpholino groups since four separate and well resolved carbon resonances at 66.1, 65.7, 48.4 and 45.6 ppm were observed, whereas in the starting material **7c** the morpholino groups showed only two resonances at 66.1 and 48.6 ppm. These observations were paralleled in the ^1H NMR spectra. The striking change in colour on oxidizing **7c** to the sulfoxide **9** may result from a much diminished delocalisation of electrons from the amino groups to the dicyanomethylene group in the latter. The sulfoxide was reduced back to thiadiazine **7c** (92%) with triphenylphosphine and tetrachloromethane;[8] triphenylphosphine oxide (94%) was also isolated and the reaction was accompanied by the expected colour change from orange-red to deep violet. Without tetrachloromethane there was no reaction, even on prolonged reflux with the phosphine in DCM, and the reducing agent is presumably a reactive species generated from the phosphine and tetrachloromethane; compare, for example, references 9 and 10. One possible sequence is suggested in Scheme 4.

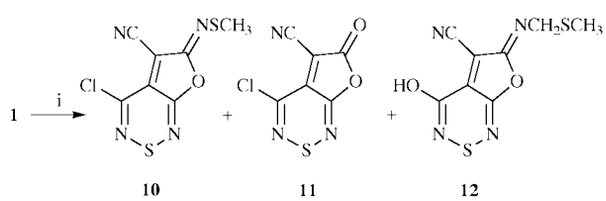
Reaction of thiadiazine 1 with DMSO

Thiadiazine **1** reacted with neat DMSO at room temperature to give a deep red mixture which, after aqueous work up and chromatography, gave three compounds characterized as



Scheme 4

4-chloro-5-cyano-6-methylthioimino-6*H*-furo[2,3-*c*][1,2,6]thiadiazine **10**, 4-chloro-5-cyano-6-oxo-6*H*-furo[2,3-*c*][1,2,6]thiadiazine **11** and, tentatively, 5-cyano-4-hydroxy-6-methylthiomethylimino-6*H*-furo[2,3-*c*][1,2,6]thiadiazine **12** (Scheme 5). Thiadiazine **1** (2 mmol) in DMSO (2 ml) after 3 h gave 7, 25 and 6% respectively and after 6 h gave 2, 29 and 9% respectively of the three products. It is possible that the imine **10** was slowly hydrolysed, or reacted further with DMSO, to give the lactone **11**, though both products were observed (TLC) to form equally rapidly at the start of the reaction.



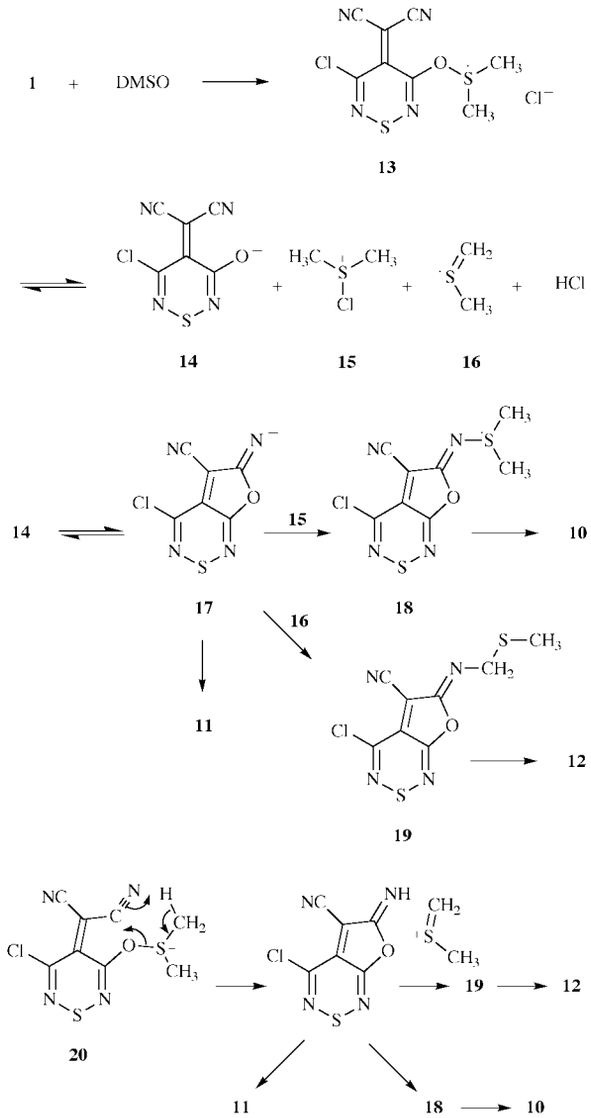
Scheme 5 *Reagents and conditions*: (i) DMSO, 20 °C, 3–6 h.

Compound **10** was obtained as deep red plates that were thermally very stable, mp > 280 °C. Two strong UV absorption bands, [λ_{max} 488 nm (log ε 4.20) and 359 (4.21)], supported the presence of the 1,2,6-thiadiazine ring system. Microanalysis and HRMS gave the molecular formula $C_7H_3ClN_4OS_2$. LRMS showed strong losses of 15 and 46 Da from the parent ion, *m*/*z* 258 (100%) to give 243 (29) and 212 (37) respectively. HRMS assigned these losses to CH_3 and CH_2S and LSMS confirmed that these two ions *m*/*z* 243 and 212 were direct fragments from the parent ion. Furthermore the low mass ion of *m*/*z* 47 (28) was identified as $(CH_3S)^+$ by HRMS and strongly supported the presence of a methylthio group. A very weak ion at *m*/*z* 197 (2) was seen during the LSMS and tentatively supported the connectivity of the methylthio group to a nitrogen atom, CH_3SN. ^1H NMR revealed a single resonance (2.84 ppm) which was assigned to that of the methylthio group. ^{13}C NMR showed seven separate carbon resonances indicating an unsymmetrical molecule. The carbon resonance at 110.5 ppm was assigned to the nitrile group and this was supported by a moderate nitrile stretching band at 2233 cm^{-1} in the IR spectrum, whilst the high field carbon resonance at 24.4 ppm was assigned to the methylthio group. Based on the spectroscopic data the methylthioimine structure **10** was assigned to this red compound. However, this structure was very similar to that of lactone **11**, mp 109–113 °C, and yet the melting point of the imine **10** (> 280 °C) was much higher. X-Ray diffraction studies[11] on single crystals of the imine confirmed structure **10** and showed that within the planar molecular sheets there are strong attractive interactions between the nitrile nitrogens of one molecule and the CH_3SN sulfur of another (*ca.* 3.0 Å); presumably this interaction, which cannot be present in the lactone **11**, is responsible for the large difference in their melting points.

Compound **11** was obtained as bright yellow needles, mp 109–113 °C, which dissolved readily in DCM. The survival of the 1,2,6-thiadiazine ring was supported by two UV absorption bands at λ_{max} 431 nm (log ε 4.27) and 407 (4.45). Microanalysis and HRMS gave the molecular formula $C_6ClN_3O_2S$. LRMS showed a strong loss of 28 Da (CO) from the parent ion *m*/*z* 213 (100%) to give 185 (23); HRMS supported this assignment of CO which suggested the presence of a carbonyl function. IR spectroscopy showed strong carbonyl stretching at 1816 cm^{-1}, typical for lactones, and strong nitrile stretching at 2230 cm^{-1}. ^{13}C NMR spectroscopy showed six separate carbon resonances indicating an unsymmetrical molecule; and one of the carbon resonances could clearly be assigned to the nitrile at 110.5 ppm.

Compound **12** was obtained as a dark precipitate, mp > 280 °C, upon dilution of the reaction mixture with water. Microanalysis and HRMS gave the molecular formula $C_8H_6N_4O_2S_2$. Owing to the highly insoluble nature of compound **12** no NMR data were obtained. IR spectroscopy identified strong nitrile stretching at 2213 cm^{-1}, and a broad band at 3300 cm^{-1} indicating the presence of an OH or an NH group; no strong evidence of carbonyl stretching bands was observed. HRMS showed a weak parent ion *m*/*z* 254 (7%) which readily lost 15 and 46 Da to give the ions 239 (11) and 208 (14) which corresponded to losses of CH_3 and CH_2S respectively. The spectroscopic data were insufficient to confirm a structure for this compound, but the 3-hydroxy compound **12**, or its keto tautomer, were tentatively assigned as the most likely. Attempts to acetylate the precipitate to improve its solubility were unsuccessful.

The formation of the three products isolated **10**, **11** and **12** is, we believe, unprecedented, but a rational mechanistic scheme is proposed (Scheme 6) based on the diverse chemistry of sulfoxides.[12] DMSO is considered to act as a nucleophile, displacing a chlorine in **1** to give the salt **13**. This could cleave to give the 3-oxido anion **14** which is well set up to cyclise onto the neighbouring cyano group. The resulting bicyclic species **17** could then undergo the remaining transformations summarized in Scheme 6. It is also possible that cyclisation could occur in the first intermediate **13**, accompanying the O–S bond cleavage in a concerted manner, as shown in **20**.



Scheme 6

Experimental †

All reactions were carried out under a dry nitrogen atmosphere. Anhydrous magnesium sulfate was used for drying organic extracts and volatiles were removed under reduced pressure. Ether refers to diethyl ether and light petroleum refers to the fraction bp 60–80 °C. Low temperature reactions were performed using ice–salt water baths (−5 °C) or solid CO_2–acetone baths (−78 °C).

All reactions and column eluents were monitored by TLC using commercial aluminium backed thin-layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 350 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using Sorbsil C60 M40 silica.

Melting points were determined using a Reichert Kofler hot-stage apparatus. Solvents used for recrystallisation are indicated after the melting point. UV spectra were obtained using a Perkin-Elmer Lambda II spectrometer and inflections are identified by the abbreviation "inf". IR spectra were recorded on a Perkin-Elmer 1710FT spectrometer and strong, medium and weak peaks are represented by s, m and w respectively. ^1H NMR spectra were recorded on JEOL GSX 270 (at 270 MHz), Bruker AM300WB (at 300 MHz) and Bruker AM500 (at 500 MHz) machines. ^{13}C NMR spectra were recorded on JEOL GSX 270 (at 68 MHz), Bruker AM300WB (at 76 MHz) and Bruker RX-400 (at 100 MHz) machines. Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Mass spectra were recorded on a VG micromass 7070E or a VG Autospec "Q" mass spectrometer. Microanalyses were performed on a Perkin-Elmer 2400 CHN Analyser.

Reaction of (3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile 1 with thiophenols

Monoarylthiothiadiazines 3. (See Scheme 1 and Table 1) Typical procedure: to a stirred suspension of (3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile **1** (207 mg, 0.9 mmol) in DCM (3 ml) at −78 °C, under nitrogen, thiophenol (105 µl, 1.02 mmol) was added followed by the slow addition of Hünig's base (174 µl, 1 mmol) at −78 °C. After 1 h no starting thiadiazine remained (TLC). Chromatography (light petroleum–DCM, 1:1) gave *(3-chloro-5-phenylthio-4H-1,2,6-thiadiazin-4-ylidene)propanedinitrile* **3a** (208 mg, 76%) as orange crystals, mp 138–140 °C (from cyclohexane) (Found: C, 47.7; H, 1.7; N, 18.2. $C_{12}H_5ClN_4S_2$ requires C, 47.4; H, 1.6; N, 18.4%); λ_{max}(DCM)/nm 264 (log ε 3.95), 338 (4.00), 447 (4.20); ν_{max}(Nujol)/cm^{-1} 3077w and 3052w (Ar CH), 2217s (CN), 1576w, 1519s, 1455s, 1282s, 1267s, 1146s, 1075s, 1023m, 999m, 812s, 762s, 753s, 702m, 690m, 628m; δ_H(270 MHz; $CDCl_3$) 7.67–7.49 (5H, m, Ar *H*); δ_C(68 MHz; $CDCl_3$) 153.37, 137.44, 136.43 (Ar *C*-2), 134.64, 131.75 (Ar *C*-4), 130.61 (Ar *C*-3), 126.22 (Ar *C*-1), 113.75 (*C*N), 113.14 (*C*N), 78.64 [*C*$(CN)_2$]; *m*/*z* (EI) 304 (M^+, 58%), 277 (M^+ − CHN, 17), 269 (M^+ − Cl,

14), 246 (50), 242 (29), 237 ($M^+ - ClS$, 20), 210 (35), 185 (13), 135 ($C_7H_5NS^+$, 6), 123 (35), 109 ($C_6H_5S^+$, 100), 77 ($C_6H_5^+$, 35), 69 (24), 65 (62).

Similar treatment of **1** with the appropriate thiophenol gave the following compounds:

[3-Chloro-5-(4-methylphenylthio)-4H-1,2,6-thiadiazin-4-ylidene]propanedinitrile ***3b.*** Orange crystals (69%), mp 175–178 °C (from cyclohexane) (Found: C, 49.0; H, 2.2; N, 17.5. $C_{13}H_7ClN_4S_2$ requires C, 49.1; H, 2.2; N, 17.6%); λ_{max}(DCM)/nm 231 (log ε 4.10), 262 (3.86), 341 (3.94), 450 (4.13); ν_{max}(Nujol)/cm^{-1} 3045w (Ar CH), 2217s (CN), 1596w, 1525s, 1494m, 1456s, 1286s, 1270s, 1149s, 1088m, 1075s, 812s, 756s, 700s, 633m, 600s; δ_H(270 MHz; $CDCl_3$) 7.47 (2H, d, *J* 8.4 Hz, Ar *H*-2), 7.36 (2H, d, *J* 7.9 Hz, Ar *H*-3), 2.50 (3H, s, CH_3); δ_C(68 MHz; $CDCl_3$) 153.89, 142.46 (Ar *C*-4), 137.54, 136.38 (Ar *C*-2), 134.53, 131.51 (Ar *C*-3), 122.64 (Ar *C*-1), 113.81 (*C*N), 113.20 (*C*N), 78.62 [*C*$(CN)_2$], 22.21 (*C*H_3); *m*/*z* (EI) 318 (M^+, 7%), 303 ($M^+ - CH_3$, 0.5), 292 ($M^+ - CN$, 2), 283 ($M^+ - Cl$, 2), 257 ($M^+ - CClN$, 56), 242 (34), 224 (9), 123 ($C_7H_7S^+$, 49), 108 ($C_6H_4S^+$, 11), 91 ($C_7H_7^+$, 100), 77 ($C_6H_5^+$, 50), 69 (23), 65 (34).

[3-Chloro-5-(4-chlorophenylthio)-4H-1,2,6-thiadiazin-4-ylidene]propanedinitrile ***3c.*** Orange crystals (96%), mp 190 °C (from 1,2-dichloroethane–cyclohexane) (Found: C, 42.5; H, 1.3; N, 16.3. $C_{12}H_4Cl_2N_4S_2$ requires C, 42.6; H, 1.2; N, 16.6%); λ_{max}(DCM)/nm 233 (log ε 4.24), 262 (3.94), 339 (3.97), 445 (4.18); ν_{max}(Nujol)/cm^{-1} 3085w and 3053w (Ar CH), 2221s (CN), 1574m, 1525s, 1456s, 1392m, 1285s, 1270s, 1150s, 1093s, 1081s, 1073s, 1012s, 838m, 823s, 807s, 758s, 746s, 700s, 630s; δ_H(270 MHz; $CDCl_3$) 7.45 (4H, s, Ar *H*); δ_C(68 MHz; $CDCl_3$) 152.85, 138.63 (Ar *C*-4), 137.86 (Ar *C*-2), 137.50, 134.88, 131.06 (Ar *C*-3), 124.63 (Ar *C*-1), 113.72 (*C*N), 113.03 (*C*N), 78.58 [*C*$(CN)_2$]; *m*/*z* (EI) 338 (M^+, 7%), 277 ($M^+ - CClN$, 82), 242 ($M^+ - CCl_2N$, 71), 157 (13), 143 ($C_6H_4ClS^+$, 53), 108 ($C_6H_4S^+$, 100), 99 (23), 76 ($C_6H_4^+$, 31), 69 (19), 63 (20).

[3-Chloro-5-(4-methoxyphenylthio)-4H-1,2,6-thiadiazin-4-ylidene]propanedinitrile ***3d.*** Orange crystals (74%), mp 110–111 °C (from cyclohexane) (Found: C, 46.8; H, 2.1; N, 16.6. $C_{13}H_7ClN_4OS_2$ requires C, 46.7; H, 2.1; N, 16.8%); λ_{max}(DCM)/nm 244 (log ε 4.27), 266 inf (4.00), 337 (3.94), 450 (4.15); ν_{max}(Nujol)/cm^{-1} 3088w (Ar CH), 2213s (CN), 1589s, 1569m, 1505s, 1495s, 1445s, 1409m, 1289s, 1270s, 1255s, 1178s, 1145s, 1107m, 1072s, 1026s, 831s, 813s, 798m, 752s, 707s, 640m; δ_H(270 MHz; $CDCl_3$) 7.41 (2H, d, *J* 8.9 Hz, Ar *H*-2), 6.97 (2H, d, *J* 8.9 Hz, Ar *H*-3), 3.84 (3H, s, CH_3O); δ_C(68 MHz; $CDCl_3$) 162.57 (Ar *C*-4), 154.44, 138.15 (Ar *C*-2), 137.50, 134.50, 116.38 (Ar *C*-1), 116.26 (Ar *C*-3), 113.84 (*C*N), 113.23 (*C*N), 78.42 [*C*$(CN)_2$], 56.19 (*C*H_3O); *m*/*z* (EI) 334 (M^+, 14%), 319 ($M^+ - CH_3$, 0.5), 308 ($M^+ - CN$, 1), 303 ($M^+ - CH_3O$, 0.5), 299 ($M^+ - Cl$, 0.5), 273 ($M^+ - CClN$, 54), 258 (23), 230 (10), 139 ($C_7H_7OS^+$, 100), 124 ($C_6H_4OS^+$, 17), 96 (34), 76 ($C_6H_4^+$, 12), 70 (27), 63 (15).

Bis(arylthio)thiadiazines 4. Typical procedure: to a stirred suspension of (3-chloro-5-phenylthio-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile **3a** (91 mg, 0.30 mmol) in benzene (2 ml) at 20 °C, under nitrogen, thiophenol (37 µl, 0.36 mmol) was added followed by the slow addition of Hünig's base (63 µl, 0.36 mmol) at 20 °C. After 1 h no starting material remained (TLC) and chromatograpy (light petroleum–DCM, 1 : 3) gave *[3,5-bis(phenylthio)-4H-1,2,6-thiadiazin-4-ylidene]propanedinitrile* **4a** (104 mg, 92%) as red-orange plates, mp 177–178 °C (from cyclohexane) (Found: C, 57.0; H, 2.7; N, 14.8. $C_{18}H_{10}N_4S_3$ requires C, 57.1; H, 2.65; N, 14.8%); λ_{max}(DCM)/nm 264 (log ε 4.12), 343 (4.10), 477 (4.12); ν_{max}(Nujol)/cm^{-1} 3059w (Ar CH), 2206s and 2195m (CN), 1578w, 1489s, 1476s, 1465s, 1442s, 1417s, 1287s, 1177m, 1146s, 1086m, 1070s, 1024m, 1002m, 826s, 742s, 704s, 689s, 666m, 634s, 602s; δ_H(270 MHz; $CDCl_3$) 7.57–7.42 (10H, m, Ar *H*); δ_C(68 MHz; $CDCl_3$) 147.67, 138.63, 136.41 (Ar *C*-2), 131.37 (Ar *C*-4), 130.45 (Ar *C*-3), 127.01 (Ar *C*-1), 113.98 (*C*N), 76.77 [*C*$(CN)_2$]; *m*/*z* (EI) 378 (M^+, 15%), 320 ($M^+ - CNS$, 4), 287 (2), 242 (26), 218 (24), 210 (8), 185 (13), 154 (4), 141 (23), 135 ($C_7H_5NS^+$, 4), 128 (13), 123 (18), 109 ($C_6H_5S^+$, 100), 77 ($C_6H_5^+$, 40), 65 (51).

Similar treatment of the monoarylthiothiadiazines **3** with the appropriate thiophenol gave the following compounds:

[3,5-Bis(4-methylphenylthio)-4H-1,2,6-thiadiazin-4-ylidene]-propanedinitrile ***4b.*** Red-orange needles (93%), mp 154–155 °C (from cyclohexane) (Found: C, 59.0; H, 3.7; N, 13.65. $C_{20}H_{14}N_4S_3$ requires C, 59.1; H, 3.45; N, 13.8%); λ_{max}(DCM)/nm 230 (log ε 4.43), 266 (4.12), 345 (4.14), 480 (4.10); ν_{max}(Nujol)/cm^{-1} 3080w (Ar CH), 2209s and 2198m (CN), 1595w, 1494s, 1428s, 1398m, 1286s, 1179m, 1144m, 1069m, 1017m, 818s, 809s, 741s, 706s; δ_H(270 MHz; $CDCl_3$) 7.49 (4H, d, *J* 8.2 Hz, Ar *H*-2), 7.34 (4H, d, *J* 7.9 Hz, Ar *H*-3), 2.48 (6H, s, CH_3); δ_C(68 MHz; $CDCl_3$) 148.01, 141.87 (Ar *C*-4), 138.67, 136.32 (Ar *C*-2), 131.25 (Ar *C*-3), 123.40 (Ar *C*-1), 114.04 (*C*N), 76.50 [*C*$(CN)_2$], 22.13 (*C*H_3); *m*/*z* (EI) 406 (M^+, 64%), 348 ($M^+ - CNS$, 18), 315 ($M^+ - C_7H_7$, 18), 256 (16), 224 ($M^+ - C_8H_8NS_2$, 15), 199 (12), 137 (37), 123 ($C_7H_7S^+$, 67), 91 ($C_7H_7^+$, 100), 79 (39), 77 ($C_6H_5^+$, 36), 65 (19).

[3,5-Bis(4-chlorophenylthio)-4H-1,2,6-thiadiazin-4-ylidene]-propanedinitrile ***4c.*** Orange crystals (85%), mp 176–176.5 °C (from 1,2-dichloroethane–cyclohexane) (Found: C, 48.1; H, 1.5; N, 12.3. $C_{18}H_8Cl_2N_4S_3$ requires C, 48.4; H, 1.8; N, 12.6%); λ_{max}(DCM)/nm 232 (log ε 4.45), 266 (4.10), 344 (4.09), 473 (4.09); ν_{max}(Nujol)/cm^{-1} 3080w (Ar CH), 2186s (CN), 1573m, 1418s, 1392m, 1297s, 1281m, 1266m, 1139m, 1121m, 1089s, 1062s, 1016s, 833s, 823s, 734s, 703m, 650s; δ_H(270 MHz; $CDCl_3$) 7.47 (4H, d, *J* 8.9 Hz, Ar *H*), 7.42 (4H, d, *J* 8.4 Hz, Ar *H*); δ_C(68 MHz; $CDCl_3$) 147.43, 138.41 (Ar *C*-4), 138.25, 137.85 (Ar *C*-2), 130.88 (Ar *C*-3), 125.26 (Ar *C*-1), 113.87 (*C*N), 77.81 [*C*$(CN)_2$]; *m*/*z* (EI) 446 (M^+, 10%), 411 ($M^+ - Cl$, 1), 355 (2), 277 ($M^+ - C_7H_4ClNS$, 18), 242 (14), 175 (13), 157 (24), 143 ($C_6H_4ClS^+$, 100), 123 (23), 111 ($C_6H_4Cl^+$, 12), 108 ($C_6H_4S^+$, 99), 99 (25), 76 ($C_6H_4^+$, 36), 69 (23), 63 (21).

[3,5-Bis(4-methoxyphenylthio)-4H-1,2,6-thiadiazin-4-ylidene]propanedinitrile ***4d.*** Red-orange foam (98%); ν_{max}(film)/cm^{-1} 3092w (Ar CH), 2213m (CN), 1591s, 1573s, 1494s, 1461s, 1435s, 1295s, 1251s, 1174s, 1144s, 1107m, 1066m, 1029s, 1007m, 830s, 810m, 799s, 740s, 702s, 666m, 642s; δ_H(300 MHz; $CDCl_3$) 7.46 (4H, d, *J* 8.9 Hz, Ar *H*-2), 6.98 (4H, d, *J* 8.9 Hz, Ar *H*-3), 3.86 (6H, s, CH_3O); δ_C(76 MHz; $CDCl_3$) 161.66 (Ar *C*-4), 147.82, 138.11, 137.53 (Ar *C*-2), 116.58 (Ar *C*-1), 115.39 (Ar *C*-3), 113.43 (*C*N), 75.76 [*C*$(CN)_2$], 55.47 (*C*H_3O); *m*/*z* (EI) 438 (M^+, 42%), 390 (9), 347 (3), 272 (4), 235 (7), 215 (3), 171 (7), 153 (23), 139 ($C_7H_7OS^+$, 100), 124 ($C_6H_4OS^+$, 16), 96 (16), 70 (5) (Found: M^+, 438.0292. $C_{20}H_{14}N_4O_2S_3$ requires *M*, 438.0292). Attempted crystallisation of the title compound from aqueous ethanol gave a precipitate of *3,5-bis(4-methoxyphenylthio)-4H-1,2,6-thiadiazin-4-one* **5** (78%) as orange needles, mp 150–154 °C (from EtOH) (Found: C, 51.9; H, 3.2; N, 7.0. $C_{17}H_{14}N_2O_3S_3$ requires C, 52.3; H, 3.6; N, 7.2%); ν_{max}(Nujol)/cm^{-1} 3007w (Ar CH), 1626s (C=O), 1593s, 1576w, 1494s, 1467s, 1439m, 1297s, 1250s, 1177m, 1068m, 1034m, 1024m, 821s, 747s; δ_H(270 MHz; $CDCl_3$) 7.40 (4H, d, *J* 8.7 Hz, Ar *H*-2), 6.96 (4H, d, *J* 8.9 Hz, Ar *H*-3), 3.84 (6H, s, CH_3O); δ_C(68 MHz; $CDCl_3$) 161.78, 160.94, 160.13, 137.91 (Ar *C*-2), 117.69 (Ar *C*-1), 115.88 (Ar *C*-3), 56.10 (*C*H_3O); *m*/*z* (EI) 390 (M^+, 97%), 251 ($M^+ - C_7H_7OS$, 10), 197 ($C_8H_7NOS_2^+$, 7), 165 ($C_8H_7NOS^+$, 8), 139 ($C_7H_7OS^+$, 100), 121 (17), 103 (16), 96 (20), 77 ($C_6H_5^+$, 20).

Reaction of (3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)-propanedinitrile 1 with secondary amines

Monoaminothiadiazines 6. (See Table 2) Typical procedure: to a stirred solution of (3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile **1** (230 mg, 1 mmol) at −5 °C, pyrrolidine (167 µl, 2 mmol) was added slowly. The mixture became deep red and was allowed to warm to *ca.* 20 °C. Chromato-

graphy (light petroleum–DCM, 1:3) gave *(3-chloro-5-pyrrolidino-4H-1,2,6-thiadiazin-4-ylidene)propanedinitrile* **6a** (204 mg, 77%) as red crystals, mp 143–144 °C (from cyclohexane) (Found: C, 45.6; H, 2.8; N, 26.2. $C_{10}H_8ClN_5S$ requires C, 45.3; H, 3.0; N, 26.4%); λ_{max}(DCM)/nm 248 (log ε 3.87), 330 (3.96), 520 (4.07); ν_{max}(Nujol)/cm^{-1} 2214s (CN), 1526s, 1495s, 1475s, 1455s, 1390m, 1378m, 1344m, 1332m, 1275m, 1249m, 1152m, 936m, 815s, 720s, 661m, 629m, 615m; δ_H(270 MHz; $CDCl_3$) 3.71–3.48 (4H, br s, CH_2N), 2.09–2.03 (4H, br s, CH_2); δ_C(68 MHz; $CDCl_3$) 145.70, 136.02, 131.85, 114.51 (*C*N), 113.30 (*C*N), 75.17 [*C*(CN)$_2$], 50.63 (*C*H$_2$N), 26.03 (*C*H$_2$); *m/z* (EI) 265 (M$^+$, 39%), 238 (M$^+$ − CHN, 12), 225 (M$^+$ − C_3H_4, 6), 210 (M$^+$ − C_4H_7, 21), 203 (M$^+$ − CHClN, 53), 185 (15), 176 (M$^+$ − C_4H_6Cl, 32), 169 (9), 161 (M$^+$ − C_4H_7ClN, 31), 149 (M$^+$ − C_5H_7ClN, 33), 144 (13), 134 (8), 129 ($C_5H_9N_2S^+$, 6), 108 ($C_4N_2S^+$, 9), 95 ($C_5H_7N_2^+$, 36), 70 ($C_4H_8N^+$, 100), 68 (35), 46 (NS^+, 35).

Similar treatment of **1** with the appropriate amine gave the following compounds:

(3-Chloro-5-piperidino-4H-1,2,6-thiadiazin-4-ylidene)-propanedinitrile ***6b***. Red crystals (81%), mp 134–135 °C (from cyclohexane) (Found: C, 47.3; H, 3.8; N, 24.9. $C_{11}H_{10}ClN_5S$ requires C, 47.3; H, 3.6; N, 25.1%); λ_{max}(DCM)/nm 252 (log ε 3.92), 333 (4.03), 510 (4.00); ν_{max}(Nujol)/cm^{-1} 2212s (CN), 1500s (C=C), 1484s, 1440s, 1388s, 1367s, 1354s, 1326m, 1295s, 1277s, 1258s, 1243s, 1215s, 1166m, 1150s, 1132s, 1115m, 1075m, 1050s, 1029s, 989m, 935s, 913s, 864s, 857m, 833s, 824s, 803m, 762s, 738s, 636s, 626s, 604s; δ_H(270 MHz; $CDCl_3$) 3.50–3.36 (4H, br d, CH_2N), 1.79–1.75 (6H, br s, CH_2); δ_C(68 MHz; $CDCl_3$) 148.25, 135.17, 134.38, 113.91 (*C*N), 113.30 (*C*N), 75.41 [*C*(CN)$_2$], 49.93 (*C*H$_2$N), 25.49 (*C*H$_2$), 24.59 (*C*H$_2$); *m/z* (EI) 279 (M$^+$, 73%), 253 (M$^+$ − CN, 15), 244 (M$^+$ − Cl, 4), 239 (M$^+$ − C_3H_4, 27), 225 (M$^+$ − C_4H_6, 19), 217 (26), 169 (M$^+$ − $C_6H_{10}N_2$, 23), 134 (M$^+$ − $C_6H_{10}ClN_2$, 11), 109 ($C_6H_9N_2^+$, 24), 84 ($C_5H_{10}N^+$, 91).

(3-Chloro-5-morpholino-4H-1,2,6-thiadiazin-4-ylidene)-propanedinitrile ***6c***. Red crystals (83%), mp 169–171 °C (from cyclohexane) (Found: C, 42.9; H, 2.7; N, 24.7. $C_{10}H_8ClN_5OS$ requires C, 42.7; H, 2.85; N, 24.9%); λ_{max}(DCM)/nm 251 (log ε 3.88), 332 (3.99), 490 (4.04); ν_{max}(Nujol)/cm^{-1} 2216s (CN), 1510s (C=C), 1484s, 1459s, 1447s, 1396s, 1378m, 1362m, 1332m, 1312m, 1286s, 1265s, 1233s, 1149m, 1115s, 1063m, 999m, 937m, 929s, 868s, 821s, 772m, 736s, 645s, 632m, 606m; δ_H(270 MHz; $CDCl_3$) 3.96–3.89 (4H, br s, CH_2O), 3.55–3.51 (2H, br s, CH_2N), 3.29–3.26 (2H, br s, CH_2N); δ_C(68 MHz; $CDCl_3$) 148.56, 135.31, 134.61, 114.09 (*C*N), 113.05 (*C*N), 76.39 [*C*(CN)$_2$], 66.10 (*C*H$_2$O), 48.94 (*C*H$_2$N); *m/z* (EI) 281 (M$^+$, 79%), 255 (M$^+$ − CN, 8), 246 (M$^+$ − Cl, 4), 224 (M$^+$ − C_3H_5O, 30), 220 (16), 216 (14), 211 (21), 205 (8), 196 (M$^+$ − C_4H_7NO, 41), 169 (M$^+$ − $C_5H_8N_2O$, 51), 162 (46), 135 (25), 129 (14), 116 (9), 111 ($C_5H_7N_2O^+$, 16), 108 ($C_4N_2S^+$, 17), 86 ($C_4H_8NO^+$, 33), 56 ($C_3H_4O^+$, 100).

(3-Chloro-5-dibenzylamino-4H-1,2,6-thiadiazin-4-ylidene)-propanedinitrile ***6d***. Red needles (74%), mp 166–167 °C (from cyclohexane) (Found: C, 61.4; H, 3.6; N, 17.7. $C_{20}H_{14}ClN_5S$ requires C, 61.4; H, 3.6; N, 17.9%); λ_{max}(DCM)/nm 252 (log ε 3.96), 333 (3.95), 502 (4.03); ν_{max}(Nujol)/cm^{-1} 3085w, 3058w and 3028w (Ar CH), 2212s (CN), 1603w and 1585w (C=N) or (C=C), 1498s, 1481s, 1455s, 1429s, 1391m, 1353s, 1329m, 1148m, 1131m, 1054m, 934m, 831m, 812m, 802m, 761m, 737s, 702m, 696m, 638m, 603m; δ_H(270 MHz; $CDCl_3$) 7.39–7.31 (6H, m, Ar *H*), 7.16–7.12 (4H, m, Ar *H*), 4.67–4.63 (2H, br s, CH_2N), 4.54–4.52 (2H, br s, CH_2N); δ_C(68 MHz; $CDCl_3$) 147.35, 135.87, 135.42, 134.36, 129.80 (Ar *C*H), 129.42 (Ar *C*H), 129.17 (Ar *C*H), 114.04 (*C*N), 113.03 (*C*N), 76.66 [*C*(CN)$_2$], 54.76 (*C*H$_2$N); *m/z* (EI) 391 (M$^+$, 0.5%), 330 (M$^+$ − CClN, 1), 300 (M$^+$ − C_7H_7, 1.5), 274 (M$^+$ − C_8H_7N, 0.5), 91 ($C_7H_7^+$, 100).

[3-Chloro-5-(N-methylanilino)-4H-1,2,6-thiadiazin-4-ylidene]propanedinitrile ***6e***. Red crystals (85%), mp 126–127 °C (from cyclohexane) (Found: C, 52.05; H, 2.7; N, 23.1. $C_{13}H_8ClN_5S$ requires C, 51.8; H, 2.7; N, 23.3%); λ_{max}(DCM)/nm 267 (log ε 4.04), 348 (4.10), 505 (3.96); ν_{max}(Nujol)/cm^{-1} 3065w (Ar CH), 2225s (CN), 1596m and 1586m (C=N) or (C=C), 1521s, 1489s, 1465s, 1411s, 1379s, 1317m, 1294s, 1156m, 1134s, 1084s, 1049s, 1026m, 919m, 838w, 812s, 776s, 758m, 724s, 702s, 621s, 601s; δ_H(270 MHz; $CDCl_3$) 7.46–7.11 (5H, m, Ar *H*), 3.49 (3H, s, CH_3N); δ_C(100 MHz; CD_2Cl_2) 145.25, 143.99, 138.15, 133.78, 129.72 (Ar *C*H), 127.34 (Ar *C*H), 123.97 (Ar *C*H), 113.06 (*C*N), 112.50 (*C*N), 77.26 [*C*(CN)$_2$], 40.77 (*C*H$_3$N); *m/z* (EI) 301 (M$^+$, 30%), 275 (M$^+$ − CN, 10), 266 (M$^+$ − Cl, 25), 239 (M$^+$ − CHClN, 47), 234 (21), 105 ($C_7H_7N^+$, 35), 91 ($C_6H_5N^+$, 13), 77 ($C_6H_5^+$, 100).

[3-Chloro-5-(di-n-propylamino)-4H-1,2,6-thiadiazin-4-ylidene]propanedinitrile ***6f***. Red crystals (74%), mp 70–71.5 °C (from EtOH–water) (Found: C, 49.1; H, 4.55; N, 23.5. $C_{12}H_{14}ClN_5S$ requires C, 48.8; H, 4.75; N, 23.7%); λ_{max}(DCM)/nm 252 (log ε 3.82), 335 (3.96), 522 (4.00); ν_{max}(Nujol)/cm^{-1} 2209s (CN), 1520s, 1484s, 1462s, 1445s, 1430s, 1367s, 1326s, 1311s, 1296s, 1286s, 1239s, 1195s, 1163m, 1140s, 1107s, 1091s, 1042m, 1020m, 946s, 911m, 858m, 824s, 805s, 754m, 746m, 734s, 627m, 606s; δ_H(270 MHz; $CDCl_3$) 3.68–3.60 (2H, br s, CH_2N), 3.29–3.23 (2H, br s, CH_2N), 1.66–1.57 (4H, m, CH_2), 0.87 (6H, t, *J* 7.3 Hz, CH_3); δ_C(68 MHz; $CDCl_3$) 146.67, 136.21, 132.78, 113.70 (*C*N), 113.09 (*C*N), 76.03 [*C*(CN)$_2$], 52.67 (*C*H$_2$N), 21.52 (*C*H$_2$), 12.24 (*C*H$_3$); *m/z* (EI) 295 (M$^+$, 14%), 266 (M$^+$ − C_2H_5, 27), 252 (M$^+$ − C_3H_7, 3), 224 (26), 211 (5), 205 (M$^+$ − C_3H_5ClN, 11), 197 (8), 188 (6), 163 (16), 134 (3), 129 (3), 100 ($C_6H_{14}N^+$, 3), 70 (6), 58 ($C_3H_8N^+$, 10), 43 ($C_3H_7^+$, 100).

(3-Chloro-5-diisopropylamino-4H-1,2,6-thiadiazin-4-ylidene)-propanedinitrile ***6g***. Lustrous metallic red crystals (30%), mp 123–125 °C (from cyclohexane) (Found: C, 49.1; H, 4.5; N, 23.5. $C_{12}H_{14}ClN_5S$ requires C, 48.8; H, 4.75; N, 23.7%); λ_{max}(DCM)/nm 252 (log ε 3.83), 337 (3.96), 526 (4.00); ν_{max}(Nujol)/cm^{-1} 2218s (CN), 1526s (C=C), 1494s, 1446s, 1406m, 1372s, 1359s, 1317m, 1258s, 1197m, 1170m, 1148s, 1126s, 1048s, 926s, 871m, 820m, 806s, 710s, 633s, 617m, 601m; δ_H(270 MHz; $CDCl_3$) 3.98–3.91 (1H, br, C*H*N), 1.78–1.36 (6H, br, CH_3); δ_C(68 MHz; $CDCl_3$) 144.24, 137.18, 131.02, 113.31 (*C*N), 112.87 (*C*N), 76.55 [*C*(CN)$_2$], 51.38 (*C*HN), 21.81 (*C*H$_3$); *m/z* (EI) 295 (M$^+$, 6%), 280 (M$^+$ − CH_3, 1), 253 (M$^+$ − C_3H_6, 8), 238 (M$^+$ − C_4H_9, 24), 211 (M$^+$ − C_6H_{12}, 23), 177 (M$^+$ − C_5H_9ClN, 36), 58 ($C_3H_8N^+$, 9), 43 ($C_3H_7^+$, 100).

Bisaminothiadiazines 7. (See Table 2) Typical procedure: to a stirred solution of (3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)-propanedinitrile **1** (230 mg, 1 mmol) at −5 °C, pyrrolidine (334 μl, 4 mmol) was added slowly. The mixture became red then blue and was allowed to warm to *ca.* 20 °C. After 12 h only the product was present (TLC) and chromatography (light petroleum–DCM, 1:3) gave *(3,5-dipyrrolidino-4H-1,2,6-thiadiazin-4-ylidene)propanedinitrile* **7a** (252 mg, 84%) as blue crystals, mp 190 °C (subl.) (from cyclohexane) (Found: C, 56.2; H, 5.1; N, 27.7. $C_{14}H_{16}N_6S$ requires C, 56.0; H, 5.3; N, 28.0%); λ_{max}(DCM)/nm 229 (log ε 4.28), 323 (4.15), 591 (4.03); ν_{max}(Nujol)/cm^{-1} 2215s (CN), 1538s, 1500s, 1456s, 1397s, 1378m, 1343s, 1324s, 1299m, 1251m, 1224m, 1188m, 1175m, 1152m, 1108m, 918m, 860m, 837m, 805m, 734s, 681s, 626m, 615m, 595s; δ_H(270 MHz; $CDCl_3$) 3.67–3.32 (8H, br s, CH_2N), 2.00 (8H, br s, CH_2); δ_C(68 MHz; $CDCl_3$) 146.76, 133.03, 115.44 (*C*N), 70.75 [*C*(CN)$_2$], 49.80 (br s, *C*H$_2$N), 25.92 (*C*H$_2$); *m/z* (EI) 300 (M$^+$, 48%), 274 (M$^+$ − CN, 9), 203 (M$^+$ − $C_5H_9N_2$, 8), 200 (16), 161 (2), 149 (2), 129 (4), 116 (3), 103 (6), 95 (6), 70 ($C_4H_8N^+$, 100), 68 (24).

Similar treatment of **1** with the appropriate amine gave the following compounds:

(3,5-Dipiperidino-4H-1,2,6-thiadiazin-4-ylidene)propanedinitrile ***7b***. Blue crystals (78%), mp 149–150 °C (from cyclohexane) (Found: C, 58.8; H, 5.9; N, 25.4. $C_{16}H_{20}N_6S$ requires C, 58.5; H, 6.1; N, 25.6%); λ_{max}(DCM)/nm 236 (log ε 4.20), 331

(4.10), 567 (3.94); ν_{max}(Nujol)/cm^{-1} 2213s (CN), 1515s (C=C), 1499s, 1474s, 1455s, 1439s, 1397m, 1377m, 1365m, 1352m, 1316m, 1267m, 1220m, 1115m, 1020m, 801m, 731s, 629m; δ_H(270 MHz; $CDCl_3$) 3.51–3.48 (4H, br, CH_2N), 3.13–3.10 (4H, br, CH_2N), 1.79–1.65 (12H, br d, CH_2); δ_C(68 MHz; $CDCl_3$) 150.30, 132.78, 115.10 (*C*N), 70.93 [*C*(CN)$_2$], 49.57 (*C*H$_2$N), 25.34 (*C*H$_2$), 24.95 (*C*H$_2$); *m*/*z* (EI) 328 (M^+, 93%), 302 ($M^+ - CN$, 12), 274 ($M^+ - C_4H_6$, 4), 259 ($M^+ - C_5H_9$, 5), 252 (4), 245 ($M^+ - C_5H_9N$, 5), 217 ($M^+ - C_6H_{11}N_2$, 10), 214 (12), 129 (8), 116 (6), 109 ($C_6H_9N_2^+$, 3), 84 ($C_5H_{10}N^+$, 100), 69 ($C_5H_9^+$, 12).

(3,5-Dimorpholino-4H-1,2,6-thiadiazin-4-ylidene)propanedinitrile ***7c***. Blue crystals (76%), mp 190 °C (subl.) (from cyclohexane) (Found: C, 50.7; H, 4.6; N, 25.0. $C_{14}H_{16}N_6O_2S$ requires C, 50.6; H, 4.8; N, 25.3%); λ_{max}(DCM)/nm 229 (log ε 4.21), 329 (4.10), 543 (4.03); ν_{max}(Nujol)/cm^{-1} 2207s (CN), 1509s (C=C), 1471s, 1444s, 1433s, 1395s, 1379s, 1368m, 1351s, 1331m, 1307m, 1286m, 1265s, 1252s, 1200m, 1171m, 1115s, 1067m, 1056m, 1015m, 1006m, 991m, 906m, 866m, 852m, 804m, 744s, 675m, 667m, 650m, 631m, 618m, 594m; δ_H(270 MHz; $CDCl_3$) 3.90 (8H, br s, CH_2O), 3.53–3.38 (4H, br s, CH_2N), 3.19–3.06 (4H, br s, CH_2N); δ_C(68 MHz; $CDCl_3$) 150.09, 130.82, 114.90 (*C*N), 71.69 [*C*(CN)$_2$], 66.14 (*C*H$_2$O), 48.60 (*C*H$_2$N); *m*/*z* (EI) 332 (M^+, 100%), 306 ($M^+ - CN$, 1), 275 ($M^+ - C_3H_5O$, 3), 247 ($M^+ - C_4H_7NO$, 4), 214 ($M^+ - C_4H_8NOS$, 15), 189 (7), 161 (5), 157 (5), 135 (5), 129 (11), 116 (5), 108 (2), 104 (4), 86 ($C_4H_8NO^+$, 68), 56 ($C_3H_4O^+$, 46).

[3,5-Bis(dibenzylamino)-4H-1,2,6-thiadiazin-4-ylidene]propanedinitrile ***7d***. Blue crystals (81%), mp 190–191 °C (from cyclohexane) (Found: C, 73.8; H, 5.3; N, 15.1. $C_{34}H_{28}N_6S$ requires C, 73.9; H, 5.1; N, 15.2%); λ_{max}(DCM)/nm 236 (log ε 4.23), 338 (4.12), 565 (3.99); ν_{max}(Nujol)/cm^{-1} 3168w, 3106w, 3087m, 3060m and 3030m (Ar CH), 2210s (CN), 1604w and 1587w (C=N) or (C=C), 1509s, 1495s, 1477s, 1462s, 1452s, 1434s, 1397s, 1363s, 1326s, 1296m, 1237s, 1187s, 1149m, 1115m, 1077s, 1030m, 965m, 942m, 860s, 838s, 822m, 750s, 738s, 651m, 633m, 604s; δ_H(270 MHz; $CDCl_3$) 7.23–7.19 (12H, m, Ar *H*), 7.05 (8H, m, Ar *H*), 4.67–4.62 (4H, br d, CH_2N), 4.37–4.31 (4H, br d, CH_2N); δ_C(68 MHz; $CDCl_3$) 150.82, 136.28, 131.56, 129.08 (Ar *C*H), 129.35 (Ar *C*H), 128.56 (Ar *C*H), 115.42 (*C*N), 71.94 [*C*(CN)$_2$], 54.11 (*C*H$_2$N); *m*/*z* (EI) 552 (M^+, 3%), 461 ($M^+ - C_7H_7$, 3), 369 ($M^+ - C_{14}H_{15}$, 2), 196 (3), 154 (10), 127 (11), 91 ($C_7H_7^+$, 100).

[3,5-Bis(N-methylanilino)-4H-1,2,6-thiadiazin-4-ylidene]propanedinitrile ***7e***. Blue crystals (87%), mp 176–177 °C (from cyclohexane) (Found: C, 64.4; H, 4.35; N, 22.4. $C_{20}H_{16}N_6S$ requires C, 64.5; H, 4.3; N, 22.6%); λ_{max}(DCM)/nm 257 (log ε 4.16), 268 (4.17), 360 (4.04), 554 (3.90); ν_{max}(Nujol)/cm^{-1} 3100w, 3060w and 3017m (Ar CH), 2209s (CN), 1595s and 1585m (C=N) or (C=C), 1505s (C=C), 1478s, 1451s, 1412s, 1402s, 1380s, 1353s, 1330m, 1310m, 1293m, 1267m, 1212s, 1174m, 1148m, 1135s, 1120m, 1102s, 1047s, 1022m, 892m, 843m, 787m, 766s, 745s, 700s, 659m, 633s, 620m; δ_H(270 MHz; $CDCl_3$) 7.33–7.14 (10H, m, Ar *H*), 3.35 (6H, s, CH_3N); δ_C(68 MHz; $CDCl_3$) 149.64, 145.07, 139.03, 130.07 (Ar *C*H), 127.10 (Ar *C*H), 124.71 (Ar *C*H), 114.85 (*C*N), 73.77 [*C*(CN)$_2$], 41.17 (*C*H$_3$N); *m*/*z* (EI) 372 (M^+, 74%), 265 ($M^+ - C_7H_9N$, 7), 234 ($M^+ - C_7H_8NS$, 23), 106 ($C_7H_8N^+$, 7), 91 ($C_6H_5N^+$, 18), 77 ($C_6H_5^+$, 100).

[3,5-Bis(di-n-propylamino)-4H-1,2,6-thiadiazin-4-ylidene]propanedinitrile ***7f***. Blue crystals (82%), mp 84–87 °C (from EtOH–water) (Found: C, 59.9; H, 7.8; N, 23.0. $C_{18}H_{28}N_6S$ requires C, 60.0; H, 7.8; N, 23.3%); λ_{max}(DCM)/nm 236 (log ε 4.21), 333 (4.13), 586 (3.99); ν_{max}(Nujol)/cm^{-1} 2204s (CN), 1489s, 1451s, 1431s, 1395s, 1383s, 1367s, 1354s, 1342s, 1325m, 1306m, 1272m, 1249m, 1215m, 1189m, 1156s, 1076s, 901m, 862m, 835m, 748s, 634m, 616m; δ_H(270 MHz; $CDCl_3$) 3.59–3.50 (4H, br s, CH_2N), 3.16–3.11 (4H, br s, CH_2N), 1.75–1.46 (8H, br m, CH_2), 1.05–0.86 (12H, t, *J* 7.3 Hz, CH_3); δ_C(68 MHz; $CDCl_3$) 149.37, 133.68, 115.10 (*C*N), 71.18 [*C*(CN)$_2$], 52.26 (br s, *C*H$_2$N), 21.44 (*C*H$_2$), 12.25 (*C*H$_3$); *m*/*z* (EI) 360 (M^+, 86%), 331 ($M^+ - C_2H_5$, 40), 317 ($M^+ - C_3H_7$, 51), 289 (5), 275 ($M^+ - C_6H_{13}$, 12), 262 ($M^+ - C_6H_{12}N$, 33), 205 (18), 149 (15), 100 ($C_6H_{14}N^+$, 100), 70 (19), 58 ($C_3H_8N^+$, 33), 43 ($C_3H_7^+$, 94).

N-(4-Anilino-5-cyano-7-phenyl-6*H*-pyrrolo[2,3-*c*][1,2,6]-thiadiazin-6-ylidene)aniline 8

To a stirred solution of (3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile **1** (115 mg, 0.5 mmol) in DCM (15 ml) at *ca.* 20 °C, aniline (169 μl, 2 mmol) was added. The mixture was complex (TLC). Refluxing at 50 °C for 12 h gave a deep red product, and on cooling to *ca.* 20 °C the volatiles were removed. Chromatography (DCM) gave the *title compound* **8** (11 mg, 5%) as red needles, mp 220–225 °C (from EtOH); δ_H(270 MHz; $CDCl_3$) 8.03–6.97 (15H, m, Ar *H*), 5.70–5.60 (1H, br, N*H*); δ_H(270 MHz; $CDCl_3$, D_2O exchanged) 8.03–6.97 (15H, m, Ar *H*); δ_C(68 MHz; $CDCl_3$) 150.73, 150.71, 149.28, 145.13, 138.06, 133.54, 130.14 (Ar *C*H), 130.00 (Ar *C*H), 129.74 (Ar *C*H), 129.62 (Ar *C*H), 128.61 (Ar *C*H), 125.70 (Ar *C*H), 125.59 (Ar *C*H), 125.52 (Ar *C*H), 122.65 (Ar *C*H), 121.44, 119.16, 115.62 (*C*N); *m*/*z* (EI) 420 (M^+, 100%), 404 ($M^+ - H_2N$, 10), 374 ($M^+ - NS$, 7), 343 ($M^+ - C_6H_5$, 6), 317 ($M^+ - C_7H_5N$, 4), 301 (7), 267 (6), 236 (3), 210 (M^{++}, 7), 194 (5), 162 (11), 132 (3), 113 (7), 103 ($C_7H_5N^+$, 5), 77 ($C_6H_5^+$, 34) (Found: M^+, 420.1155. $C_{24}H_{16}N_6S$ requires *M*, 420.1157).

(3-Chloro-5-phthalimido-4*H*-1,2,6-thiadiazin-4-ylidene)-propanedinitrile and (3,5-diphthalimido-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile

To a stirred solution of (3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile **1** (125 mg, 0.54 mmol) in toluene (3 ml) at *ca.* 20 °C was added potassium phthalimide (200 mg, 1.08 mmol) and 18-crown-6 (143 mg, 0.54 mmol). The mixture became brown and TLC indicated several new products. The mixture was heated to 80 °C for 2 h and allowed to cool to *ca.* 20 °C. Chromatography (light petroleum–DCM, 1:1) gave *(3-chloro-5-phthalimido-4H-1,2,6-thiadiazin-4-ylidene)propanedinitrile* (46 mg, 25%) as yellow prisms, mp > 190 °C (dec.) (from 1,2-dichloroethane) (Found: C, 49.3; H, 1.3; N, 20.6. $C_{14}H_4ClN_5O_2S$ requires C, 49.3; H, 1.2; N, 20.5%); λ_{max}(DCM)/nm 229 (log ε 4.37), 234 inf (4.33), 246 inf (4.18), 302 (3.33), 406 (4.31); ν_{max}(Nujol)/cm^{-1} 3105w and 3070w (Ar CH), 2220s (CN), 1797s and 1735s (C=O), 1611w, 1520s (C=C), 1481s, 1471s, 1372s, 1303s, 1220s, 1179m, 1153s, 1096m, 1066s, 909s, 882s, 810s, 788s, 739s, 723s, 713s, 647s, 629m; δ_H(270 MHz; $CDCl_3$) 8.05–7.99 (2H, m, Ar *H*), 7.91–7.86 (2H, m, Ar *H*); δ_C(68 MHz; $CDCl_3$) 164.39 (C=O), 144.49, 138.20, 136.70, 136.53 (Ar *C*H), 131.81, 125.98 (Ar *C*H), 113.02 (*C*N), 112.67 (*C*N), 79.17 [*C*(CN)$_2$]; *m*/*z* (EI) 341 (M^+, 7%), 315 ($M^+ - CN$, 3), 306 ($M^+ - Cl$, 3), 280 ($M^+ - CClN$, 59), 236 (24), 178 (10), 160 (12), 147 (6), 128 (7), 104 ($C_7H_4O^+$, 100), 76 ($C_6H_4^+$, 100), 50 (62), 46 (NS^+, 18).

Further elution (light petroleum–DCM, 1:1) gave *(3,5-diphthalimido-4H-1,2,6-thiadiazin-4-ylidene)propanedinitrile* (49 mg, 20%) as yellow prisms, mp 275 °C (dec.) (from 1,2-dichloroethane) (Found: C, 58.3; H, 2.05; N, 18.6. $C_{22}H_8N_6O_4S$ requires C, 58.4; H, 1.8; N, 18.6%); λ_{max}(DCM)/nm 229 (log ε 4.63), 235 inf (4.59), 246 inf (4.47), 297 (3.76), 306 (3.74), 408 (4.29); ν_{max}(Nujol)/cm^{-1} 3095w and 3043w (Ar CH), 2218s (CN), 1790s and 1741s (C=O), 1608m, 1515s (C=C), 1485s, 1467s, 1353s, 1304s, 1235m, 1205m, 1177m, 1155m, 1133m, 1101m, 1079s, 1063s, 984m, 969s, 885s, 851m, 807m, 787m, 740s, 712s, 668m, 628s; δ_H(270 MHz; DMSO-d_6) 8.17–8.14 (4H, m, Ar *H*), 8.06–8.03 (4H, m, Ar *H*); *m*/*z* (EI) 452 (M^+, 26%), 426 ($M^+ - CN$, 3), 410 ($M^+ - CNO$, 3), 280 (21), 274 (5), 252 (2), 236 (5), 178 (4), 160 (2), 147 (25), 130 (21), 104 ($C_7H_4O^+$, 93), 76 ($C_6H_4^+$, 100).

A final elution (light petroleum–acetone, 3:1) gave an unknown purple solid (16 mg, 10%), mp 140–150 °C (from 1,2-

dichloroethane–pentane) (Found: C, 47.0; H, 6.3; N, 11.5%) ν_{max}(Nujol)/cm^{-1} 2163s (CN), 1626w, 1604m, 1511w, 1467s, 1377m, 1349s, 1284m, 1248m, 1233m, 1133m, 1106s, 962s, 838m, 722w; *m*/*z* (FAB) 303 (M^+ or MH^+, 100%).

(3,5-Dimorpholino-1-oxo-4*H*-1,2,6-thiadiazin-4-ylidene)-propanedinitrile 9

Method 1. To a stirred solution of (3,5-dimorpholino-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile **7c** (90 mg, 0.27 mmol) in DCM (15 ml) was introduced gaseous N_2O_4. The deep purple mixture rapidly became orange and the passage of N_2O_4 was stopped. TLC indicated no starting thiadiazine but showed a new orange product. Chromatography (ethyl acetate) gave the *title compound* **9** (89 mg, 95%) as orange needles, mp > 300 °C (from THF) (Found: C, 48.5; H, 4.75; N, 24.2. $C_{14}H_{16}N_6O_3S$ requires C, 48.3; H, 4.6; N, 24.1%); λ_{max}(DCM)/nm 261 (log ε 4.25), 315 (3.02), 454 (3.24); ν_{max}(Nujol)/cm^{-1} 2240w (CN), 1577s, 1533s, 1455s, 1363m, 1302m, 1276s, 1256m, 1215m, 1129s, 1112s, 1068m, 1053m, 1003m, 903m, 861m, 851m, 806m, 777s, 757s, 643s; δ_H(270 MHz; DMSO-d_6) 3.86–3.66 [10H, m, 4(CH_2O)+1(CH_2N)], 3.59–3.48 (2H, m, CH_2N), 3.40–3.17 [4H, m, 2(CH_2N)]; δ_C(68 MHz; DMSO-d_6) 152.32, 144.97, 111.50 (*C*N), 90.05 [*C*(CN)$_2$], 66.06 (*C*H$_2$O), 65.71 (*C*H$_2$O), 48.37 (*C*H$_2$N), 45.56 (*C*H$_2$N); *m*/*z* (EI) 348 (M^+, 3%), 332 ($M^+ - O$, 30), 300 ($M^+ - OS$, 4), 243 (3), 214 (5), 189 (3), 162 (6), 135 (4), 129 (6), 112 ($C_5H_8N_2O^+$, 16), 103 (5), 86 ($C_4H_8NO^+$, 39), 77 (7), 70 (9), 55 (75), 42 (83).

Method 2. To a stirred solution of (3,5-dimorpholino-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile **7c** (10 mg, 0.03 mmol) in DCM (5 ml) at 20 °C, MCPBA (1.1 equiv.) was added in one portion. After 10 min the mixture still contained starting material (TLC); however, the introduction of a further portion of MCPBA (0.5 equiv.) resulted in the complete consumption of the starting material within 30 min. Chromatography (ethyl acetate) gave the title compound **9** (8.9 mg, 85%) as orange needles, identical to that described above.

Reaction of sulfoxide 9 with triphenylphosphine–tetrachloromethane

To a stirred solution of (3,5-dimorpholino-1-oxo-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile **9** (8.4 mg, 0.024 mmol) in DCM (5 ml) at 20 °C, triphenylphosphine (7 mg, 0.027 mmol) and tetrachloromethane (0.2 ml) were added. The mixture was taken to reflux (*ca.* 45 °C) and after 2 h no triphenylphosphine remained (TLC); however, both the reduced product and starting sulfoxide were present. The addition of more triphenylphosphine (3.2 mg, 0.012 mmol), after 30 min warming, resulted in the complete consumption of the starting material. Chromatography (DCM–ether, 1:1) gave (3,5-dimorpholino-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile **7c** (7.3 mg, 92%) as a purple solid, identical to that described above. Further elution (ethyl acetate) gave triphenylphosphine oxide (6.3 mg, 94%), identical to an authentic sample. The experiment was repeated with the exclusion of tetrachloromethane and on reflux (*ca.* 45 °C) no reaction was observed until a little tetrachloromethane was added.

Reaction of (3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)-propanedinitrile 1 with DMSO

(See Scheme 5) A solution of (3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile **1** (483 mg, 2.1 mmol) in DMSO (2 ml) was stirred for 3 h. The mixture became red and TLC indicated the presence of several new products. Dilution of the mixture with water (20 ml) gave a dark grey precipitate and filtration of this gave *5-cyano-4-hydroxy-6-methylthiomethylimino-6H-furo[2,3-c][1,2,6]thiadiazine* **12** (32 mg, 6%) as a green-brown precipitate, mp > 280 °C (Found: C, 37.3; H, 2.4; N, 20.7. $C_8H_6N_4O_2S_2$ requires C, 37.8; H, 2.4; N, 22.0%); ν_{max}(Nujol)/cm^{-1} 3300br (OH), 2213s (CN), 1607s, 1576s, 1523m, 1500s, 1427m, 1318s, 1225s, 1198m, 1100w, 1048m, 1009m, 991m, 917m, 860s, 768s, 760s, 705m, 638m; *m*/*z* (EI) 254 (M^+, 7%), 239 ($M^+ - CH_3$, 11), 221 ($M^+ - HS$, 7), 208 ($M^+ - NS$ or CH_2S, 14), 194 (11), 177 (19) (Found: M^+, 253.9939. $C_8H_6N_4O_2S_2$ requires *M*, 253.9932); LSMS (EI, *B*/*E* of *m*/*z* 254) 239 ($M^+ - CH_3$, 100%), 223 (34), 208 (36), 194 (13), 177 (4), 169 (7). The filtrate was extracted with DCM (5 × 5 ml) and the combined DCM fractions were dried, filtered and the volatiles were removed. Chromatography (DCM) of the residue gave *4-chloro-5-cyano-6-methylthioimino-6H-furo[2,3-c][1,2,6]-thiadiazine* **10** (27 mg, 5%) as deep red plates, mp > 280 °C (from 1,2-dichloroethane–cyclohexane) (Found: C, 32.5; H, 1.1; N, 21.5. $C_7H_3ClN_4OS_2$ requires C, 32.6; H, 1.2; N, 21.7%); λ_{max}(DCM)/nm 257 (log ε 3.88), 359 (4.21), 488 (4.20); ν_{max}(Nujol)/cm^{-1} 2233m (CN), 1636w, 1577s, 1473s, 1376s, 1291m, 1181m, 995s, 919s, 810m, 799m, 761m, 724m, 667m, 608m; δ_H(500 MHz; CD_2Cl_2) 2.84 (3H, s, CH_3S); δ_C(100 MHz; CD_2Cl_2) 158.21 (*C*=NSMe), 144.69, 141.44, 124.51, 110.46 (*C*N), 96.16 [=*C*(CN)], 24.39 (*C*H$_3$S); *m*/*z* (EI) 258 (M^+, 100%), 243 ($M^+ - CH_3$, 29), 212 ($M^+ - CH_2S$, 37), 185 ($M^+ - C_2H_3NS$, 6), 47 (CH_3S^+, 28), 46 (NS^+, 16) (Found: M^+, 257.9435. $C_7H_3ClN_4OS_2$ requires *M*, 257.9437); LSMS (EI, *B*/*E* of *m*/*z* 258) 243 ($M^+ - CH_3$, 100%), 212 ($M^+ - CH_2S$, 95), 195 ($M^+ - CH_3NS$, 2), 185 ($M^+ - C_2H_3NS$, 6), 177 (4), 169 (7). Further elution (DCM) gave *4-chloro-5-cyano-6-oxo-6H-furo-[2,3-c][1,2,6]thiadiazine* **11** (112 mg, 25%) as yellow needles, mp 109–113° C (from cyclohexane) (Found: C, 33.8; N, 19.5. $C_6ClN_3O_2S$ requires C, 33.8; N, 19.7%); λ_{max}(DCM)/nm 323 inf (log ε 3.38), 398 inf (4.41), 407 (4.45), 431 (4.27); ν_{max}(Nujol)/cm^{-1} 2230s (CN), 1816s (C=O), 1634w, 1595s, 1568s, 1523w, 1452s, 1385s, 1354m, 1317m, 1304s, 1160s, 1035m, 950m, 939m, 921s, 816m, 771m, 722s, 708m, 638s; δ_C(68 MHz; $CDCl_3$) 159.58 (*C*=O), 156.05, 143.67, 130.68, 110.51 (*C*N), 88.81 [=*C*(CN)]; *m*/*z* (EI) 213 (M^+, 100%), 185 ($M^+ - CO$, 23), 167 ($M^+ - NS$, 19), 157 [$M^+ - 2(CO)$, 7], 139 ($M^+ - CNOS$, 9), 132 (14), 96 (8), 74 ($CNOS^+$, 22) (Found: M^+, 212.9405. $C_6ClN_3O_2S$ requires *M*, 212.9400).

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