# Cyclisation chemistry of 4H-1,2,6-thiadiazines

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3,5-Dichloro-4*H*-1,2,6-thiadiazin-4-one **1** condenses rapidly at room temperature with 1,2-diaminobenzene, 2-aminothiophenol and sodium 2-aminophenoxide to give, respectively, the purple thiadiazinoquinoxaline **4a**, red thiadiazinobenzothiazine **4b** and orange thiadiazinobenzoxazine **4c** in almost quantitative yield. The 10*H* tautomer **4a** is spectroscopically almost identical with the purple 10-methyl derivative **11** formed by condensation of **1** with *N*-methyl-1,2-diaminobenzene and by the methylation of **4a**. The chlorine substituent in these tricyclic thiadiazino compounds is readily displaced by nucleophiles, to give the 4-ethoxy **13** and 4-piperidino derivative **21**. The dicyanomethylene compound **2**, analogous to **1**, reacts in the same way as **1** with 2-aminothiophenol to give **4b** (87%), but its reaction with 1,2-diaminobenzene is more complex since, in addition to the analogous formation of **4a**, there is now the possibility of another cyclisation in the intermediate **16** which leads to the tetracyclic compound **14** and its substitution product **15**. This difference in reaction pathway between **1** and **2** is further illustrated by their condensation with 1,8-diaminonaphthalene: **1** is converted into **19** by simple displacement of chlorine, whilst **2** gives, almost quantitatively, the product **20** of cyclisation onto the neighbouring cyano group.

We have recently described some chemistry of the readily available 3,5-dichloro-4H-1,2,6-thiadiazin-4-one  $1^{1,2}$  and the related



new thiadiazine  $2^{2,3}$  directed towards the synthesis of their amino derivatives required as monomers for conjugated polymers incorporating the repeat unit 3. The chlorine atoms in 1 and 2 are readily displaced by nucleophiles such as thiophenols and amines.<sup>1,2</sup> We now describe the reactions of 1 and 2 with 1,4- and 1,5-bis-nucleophiles which provide a ready source of new, colourful polycyclic ring systems.

# **Results and discussion**

## Cyclisations with 3,5-dichloro-4H-1,2,6-thiadiazin-4-one 1

Thiadiazinone **1** reacted smoothly with ethanolic solutions of 1,2-diaminobenzene and 2-aminothiophenol at room temperature to give purple 4-chloro-10*H*-[1,2,6]thiadiazino[3,4-*b*]quinoxaline **4a** [ $\lambda_{max}$  548 nm (log  $\varepsilon$  3.58)], and the red 4-chloro[1,2,6]thiadiazino[3,4-*b*][1,4]benzothiazine **4b** [ $\lambda_{max}$  463 nm (log  $\varepsilon$  3.66)] respectively. The reactions were rapid and at relatively high concentrations (1 mmol of **1** and 2 mmol of the amine in *ca*. 10 ml EtOH) were complete within one hour; the new tricyclic products separated from the reaction mixture and recrystallisation gave analytically pure **4a** (96%) and **4b** (95%) in very high yields.

In view of the earlier work  $^{1,2}$  we propose that the first step is nucleophilic displacement of chlorine followed by cyclodehydration as shown in Scheme 1. This is supported by treatment of thiadiazinone 1 with the mono-Boc derivative  $5^4$  of 1,2-diaminobenzene, under the same conditions, to give the analogous first product 6 in good yield (76%); deprotection of



**6** with 3 M HCl in ethyl acetate<sup>5</sup> gave the cyclised product **4a** (72%) directly (Scheme 2). The ready cyclisation appears to



drive the reactions cleanly to completion since the analogous reaction of thiadiazinone **1** with 1,4-diaminobenzene, and its mono-Boc derivative,<sup>6</sup> gave the secondary amines **7a** (20%) and **7b** (38%) respectively in much lower yield. The Boc derivative **7b** was hydrolysed with HCl as before to give **7a** (93%).



Thiadiazinone 1 reacted slowly with 2-aminophenol (2 equiv. in boiling EtOH) to give the analogous secondary amine 8 (86%), where the amino group had preferentially displaced

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chlorine (Scheme 3). It is notable that even in boiling EtOH the uncyclised product **8** gave no sign of cyclodehydrating to give the thiadiazinobenzoxazine **9** with its higher energy S<sup>IV</sup> sulfurdiimide structure. However thiadiazinone **1** reacted rapidly and virtually quantitatively with the sodium salt of 2-aminophenol, in THF at room temperature in one hour, to give orange 4-chloro[1,2,6]thiadiazino[3,4-*b*][1,4]benzoxazine **4c** (99%) exactly analogous to **4a** and **b**.

The spectral data of the three tricyclic compounds 4 are in good agreement with the proposed structures with sulfur in the  $S^{II}$  oxidation state though, in principle, there is another regioisomer possible in each case with S<sup>IV</sup> sulfur, such as 9. In the formation of 4b and 4c the reagents 2-aminothiophenol and sodium 2-aminophenoxide would be expected to effect displacement of chlorine through the more nucleophilic sulfur and oxygen functions. However a further ambiguity arises in the 1,2-diaminobenzene reaction; by analogy with structures 4b and c, 4a is written with the amino hydrogen located at N-10 rather than N-1 or N-5, though delocalisation around the tricyclic system could possibly reduce the energy difference between these tautomers. Structure 4a was shown to be correct for the major tautomer (the only one observed) by comparison with the N-methylated derivative, 4-chloro-10-methyl-10H-[1,2,6]thiadiazino[3,4-b]quinoxaline 11 which was prepared in two ways. The first involved reacting thiadiazinone 1 with Nmethyl-1,2-diaminobenzene, where it was expected that the greater nucleophilicity of the secondary amine would result in formation of isomer 10 which would cyclise to the N-10 methylated derivative 11 (Scheme 4). This reaction gave a



monomethylated purple product (70%) whose spectral data supported structure **11**. No other isomeric product was observed, but a small amount (15%) of a yellow, highly fluorescent compound was obtained and identified as the tetracyclic

5,11-dimethyl-5H,11H-quinoxalino[2,3-b]quinoxaline **12** by comparison with the mp and spectral data in the literature.<sup>7</sup> The scope and mechanism of the unexpected and intriguing formation of **12** in this reaction is being investigated.

The second route to compound **11** was methylation of **4a** with iodomethane in DMSO and aqueous sodium hydroxide at room temperature, in 95% yield. When EtOH was used in place of DMSO the sodium ethoxide generated displaced chloride to give 4-ethoxy-10-methyl-10*H*-[1,2,6]thiadiazino[3,4-*b*]quinoxaline **13** (59%) as the major product. The two *N*-methyl compounds **11** were identical.



A comparison of the spectral data, particularly the UV and <sup>13</sup>C NMR spectra, for compound **4a** and its methylated derivative **11** showed that they were almost identical, in agreement with the 10H structure **4a** being the tautomer isolated.

#### Cyclisations with 3,5-dichloro-4-dicyanomethylene-1,2,6-thiadiazine 2

An ethanolic solution of the dicyanomethylene compound 2 and 2-aminothiophenol gave the tricyclic thiadiazine 4b (87%), identical with the product from thiadiazinone 1, presumably by the same mechanism but with the expulsion of malononitrile upon cyclisation (Scheme 5). The reaction of 2 with 1,2-diaminobenzene was more complex however (Scheme 6,



Table 1). Two major products, thiadiazinoquinoxaline 4a and 4-chloro-5-cyano[1,2,6]thiadiazino[3',4':5,4]pyrrolo[1,2-a]benzimidazole 14, and a minor product 15 were isolated. Compound 4a was identical with that described above (Scheme 1). Attempts to improve the yields (Table 1) of 4a and 14 were unsuccessful, though we noted that an excess of 1,2-diaminobenzene reduced the yield of 14 whilst one equiv. actually improved the yield; this suggests that cyclisation onto the nitrile to yield 14 is acid catalysed.

Compound **14** was obtained as bright red needles (the kinetic polymorph from rapid crystallisation from 1,2-dichloroethane)

Table 1 Treatment of 3,5-dichloro-4-dicyanomethylene-1,2,6-thiadiazine 2 with 1,2-diaminobenzene in ethanol (5 ml) at 20 °C (see Scheme 6)

	Compound <b>2</b> / mmol	1,2-Diamino- benzene (equiv.)	Reaction time/h	Product yield (%)			
				2	4a ª	14	15
	0.24	1	48	22	36 <i><sup>b</sup></i>	34 <i><sup>b</sup></i>	Trace
	0.22	2	12		42	19	_
	0.26	3	36	_	23	Trace	_

<sup>a</sup> Yields calculated assuming 2 equiv. of amine required for the formation of 4a. <sup>b</sup> Yields take into account the recovered starting material 2.

or as deep red prisms (the thermodynamic polymorph from slow crystallisation from 1,2-dichloroethane), both with mp 254–256 °C. The bright red needles darkened in colour on heating above 145 °C. Microanalysis and HRMS gave the molecular formula as  $C_{12}H_4CIN_5S$ , indicating the loss of the elements of NH<sub>4</sub>Cl in its formation. The <sup>13</sup>C NMR spectra showed twelve separate resonances indicating an unsymmetrical molecule, and the signal at 112.3 ppm supported the presence of a cyanide indicated by IR stretching at 2230 cm<sup>-1</sup>; no amine stretching was observed. On this basis structure **14** was proposed and this was confirmed by X-ray crystallography.<sup>8</sup> An attempted independent synthesis of **14** from thiadiazinone **1** and 2-benzimidazolylacetonitrile gave only a trace (TLC) of the desired compound.

A probable route to the tetracyclic compound 14 is shown in Scheme 7. After displacement of chlorine by 1,2-diamino-



benzene to give the expected secondary amine 16 there are two possible cyclisation pathways. The primary amino group can attack the thiadiazine ring at C-4 to displace malononitrile to form 4a, exactly analogous to the cyclodehydration of Scheme 1. Alternatively the secondary amino group can cyclise onto the neighbouring nitrile carbon (*cf.* refs. 2 and 3) to give the iminopyrrole 17 which is intercepted in a second cyclisation with loss of ammonia; the two cyclisation steps could be acid catalysed. Finally the chlorine in 14 could be displaced by more 1,2-diaminobenzene to give the minor product 15; that this was the probable source of 15 was shown by its independent formation, as a major product (83%), from 14 and 4 equiv. of 1,2-diaminobenzene in hot ethanol.

Just as the secondary amino group in 16 cyclised onto the neighbouring nitrile to give 17, and hence 14, (Scheme 7) so, in principle, could the secondary amine in 15 cyclise similarly to give the symmetrical heptacyclic system 18, though this would presumably be more strained with its four contiguous 5-membered rings. Attempts to enforce this second cyclisation

by heating **15** in ethanol, in acetic acid and in polyphosphoric acid were unsuccessful.

### Cyclisations with 1,8-diaminonaphthalene

With these mechanisms in mind, we decided to treat the thiadiazines 1 and 2 with a bis-amine that could not form a 6-membered cyclic intermediate necessary for generation of the very stable products like 4a; we chose 1,8-diaminonaphthalene which would have to form a less favourable 7-membered ring when cyclising onto C-4 of the thiadiazine ring. Reaction of the thiadiazinone 1 with 1,8-diaminonaphthalene gave only the initial product 19 in moderate yield (46%), with no sign of cyclodehydration (Scheme 8). Since the analogous cyclisation



will also be disfavoured in the reaction of dicyanomethylenethiadiazine 2 with 1,8-diaminonaphthalene, it is reasonable to assume that the alternative cyclisation onto the cyano group (cf. Scheme 7) to give a product analogous to 14 would be favoured. Indeed, addition of 1,8-diaminonaphthalene to an ethanolic solution of 2 gave the green, pentacyclic 9-chloro-8-cyano-[1,2,6]thiadiazino[3',4':5,4]pyrrolo[1,2-a]perimidine **20**  $[\lambda_{max}]$ 662 nm (log  $\varepsilon$  3.77)] in up to 96% yield. This poorly soluble product separated from the reaction solution, and recrystallisation gave analytically pure material. Structure 20 is based on HRMS, microanalysis, IR and UV spectra and by analogy with the closely related product 14; in particular a doubly charged ion, M<sup>++</sup>, was observed in the HRMS, but low solubility prevented the collection of the NMR data. The conversion of 2 into 20 compared with that of 1 into 19, by 1,8-diaminonaphthalene, provides another example (cf. ref. 2) of the additional reactivity exhibited by the dicyanomethylene compound **2** over the simpler compound **1**.

We saw above an example of the ready displacement of chlorine from 4-chlorothiadiazine 4a, during its methylation, to give the 4-ethoxy compound 13. We assumed that such reactivity would extend to the chloro derivatives of related compounds like 4b, c and 11. This was supported by the virtually quantitative displacement of chlorine in 4b by piperidine in refluxing DCM in one hour to give 21.

#### Conclusion

We have shown that a variety of highly coloured, stable polycyclic 1,2,6-thiadiazines can be readily prepared from the



monocyclic thiadiazines 1 and 2. By variation of the C-4 substituent and the heteroatom at position 10 of the tricyclic compounds 4 a wide range of potential new chromophores could be produced. Whilst the highly coloured compounds are not suitable for use as non-linear optical materials, simple oxidation of the sulfur to its dioxide would give compounds similar to the sulfone 22, the only other reported example of these ring systems, which has been investigated as an optical dye.<sup>9</sup>

#### Experimental

General experimental details have been described before.<sup>2,3</sup> Compounds **1** and **2** were prepared by the literature methods.<sup>1,3</sup> Additionally 250 MHz <sup>1</sup>H NMR and 62.9 MHz <sup>13</sup>C NMR were recorded on a Bruker WM250 machine.

## 4-Chloro-10H-[1,2,6]thiadiazino[3,4-b]quinoxaline 4a

Method 1. To a stirred solution of 3,5-dichloro-4H-1,2,6thiadiazin-4-one 1 (182 mg, 1.0 mmol) in EtOH (7 ml) at ca. 20 °C 1,2-diaminobenzene (216 mg, 2.0 mmol) was added in one portion. The mixture became purple and after 1 h a deep purple precipitate had formed. This was filtered off (215 mg, 91%) and the addition of a little water to the filtrate gave a second purple precipitate (12 mg, 5%). The precipitates (identical by TLC) were combined and crystallisation gave the title compound 4a (227 mg, 96%) as purple-red needles, mp 310 °C subl. (from EtOH) (Found: C, 45.7; H, 1.9; N, 23.8. Calc. for C<sub>9</sub>H<sub>5</sub>ClN<sub>4</sub>S: C, 45.8; H, 2.1; N, 23.7%); λ<sub>max</sub>(DCM)/nm 262 inf (inflection) (log ɛ 4.21), 267 (4.22), 283 (4.15), 291 inf (4.08), 326 (3.99), 341 inf (3.90), 366 (3.80), 385 (3.85), 407 (3.68), 485 inf (3.43), 522 (3.58), 548 (3.58), 595 inf (3.31); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 3228m (NH), 3188m, 3140m, 3072m and 3052m (Ar CH), 1608s, 1568w, 1514m, 1471s, 1415s, 1380s, 1275m, 1221m, 1117m, 957m, 925s, 879m, 803s, 768m, 743s, 721s, 620s, 604s;  $\delta_{\rm H}(400 \text{ MHz}; \text{DMSO-}d_6)$  10.18 (1H, s, NH), 6.90 (1H, ddd, J 1.6, 7.7, 7.7 Hz, Ar H), 6.87 (1H, dd, J 1.4, 6.4 Hz, Ar H), 6.66 (1H, ddd, J 1.4, 7.7, 7.7 Hz, Ar H), 6.37 (1H, dd, J 1.2, 7.8 Hz, Ar H); δ<sub>c</sub>(100 MHz; DMSO-d<sub>6</sub>) 150.0, 142.3, 139.7, 136.5, 135.9, 130.6 (Ar CH), 128.3 (Ar CH), 123.2 (Ar CH), 113.6 (Ar CH); m/z (EI) 236 (M<sup>+</sup>, 100%), 201 (M<sup>+</sup> - Cl, 32), 174 (M<sup>+</sup> - CHClN, 8), 168 (7), 162 (4), 154 (6), 149 (6), 143  $(M^+ - CCINS, 21), 131 (6), 118 (6), 102 (5), 90 (9), 76 (C_6H_4^+)$ 4), 69 (11) (Found: M<sup>+</sup>, 235.9922. C<sub>9</sub>H<sub>5</sub>ClN<sub>4</sub>S requires M, 235.9923).

**Method 2.** (i) To a stirred solution of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one **1** (22 mg, 0.12 mmol) in EtOH (2 ml) at *ca.* 20 °C 2-(*N*-*tert*-butoxycarbonylamino)aniline **5**<sup>4</sup> (50 mg, 0.24 mmol) was added in one portion. After 3 h the mixture was poured into ice–water and the yellow–orange precipitate was collected, washed (H<sub>2</sub>O), dried and recrystallisation gave the *3-[2-(N*-*tert*-butoxycarbonylamino)anilino]-5-chloro-4*H*-1,2,6-thiadiazin-4-one **6** (32 mg, 76%) as yellow crystals, mp >280 °C dec. (from EtOH);  $\lambda_{max}$ (EtOH)/nm 305 (log ε 4.11), 318 (4.12), 391 (3.64);  $v_{max}$ (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3425w and 3340w (NH), 3155w (Ar CH), 1712m, 1634m, 1596m, 1541s, 1480m, 1371m, 1181m, 1157s, 916s, 833m, 651s;  $\delta_{H}$ (250 MHz; CDCl<sub>3</sub>) 9.07 (1H, br, N*H*), 7.76 (1H, m, Ar *H*), 7.43 (1H, m, Ar *H*), 7.26–7.19 (2H, m, Ar *H*), 6.49 (1H, br, N*H*), 1.54 (9H, s, '*Bu*); *m/z* (EI) 354 (M<sup>+</sup>, 6%), 298 (M<sup>+</sup> – 'Bu, 17), 280 (26), 254 (21), 237 (36), 219

(18), 201 (7), 165 (15), 159 (17), 152 (8), 149 (8), 134 (14), 118 (7), 108 (14), 93 (CCINS<sup>+</sup>, 11), 78 (7), 57 ('Bu<sup>+</sup>, 100) (Found:  $M^+$ , 354.0550.  $C_{14}H_{15}CIN_4O_3S$  requires *M*, 354.0553). (ii) To a stirred solution of 3-[2-(*N*-tert-butoxycarbonylamino)anilino]-5-chloro-1,2,6-thiadiazin-4-one **6** (21 mg, 0.06 mmol) in ethyl acetate (1 ml) at *ca.* 20 °C, was added 3 M HCl. After 6 h the mixture was diluted with ethyl acetate (5 ml), treated with aqueous sodium bicarbonate and the organic layer was separated, dried and the volatiles were removed. Flash chromatography (Et<sub>2</sub>O) of the residue gave the title compound **4a** (10 mg, 72%) identical with that prepared above.

#### 4-Chloro[1,2,6]thiadiazino[3,4-b][1,4]benzothiazine 4b

Method 1. To a stirred solution of 3,5-dichloro-4H-1,2,6thiadiazin-4-one 1 (546 mg, 3 mmol) in EtOH (35 ml) at ca. 20 °C 2-aminothiophenol (640 µl, 6 mmol) was added in one portion. The mixture rapidly became red and after 1 h a red precipitate had formed. This was filtered off and crystallisation gave the *title compound* **4b** (645 mg, 85%) as orange-red needles, mp 149-152 °C (from EtOH) (Found: C, 42.6; H, 1.3; N, 16.5. Calc. for C<sub>9</sub>H<sub>4</sub>ClN<sub>3</sub>S<sub>2</sub>: C, 42.7; H, 1.6; N, 16.6%);  $\lambda_{max}(DCM)/$ nm 271 (log ɛ 4.33), 277 (4.33), 332 inf (3.87), 343 (3.93), 360 inf (3.84), 400 (3.80), 422 inf (3.74), 463 (3.66);  $v_{max}$ (Nujol)/cm<sup>-1</sup> 3045w (Ar CH), 1590s, 1569w, 1562w, 1546m, 1531m, 1515m, 1434m, 1300m, 1282s, 1274s, 1261s, 1227m, 1121m, 1086m, 1060s, 841m, 813m, 772s, 765s, 726m, 715m, 704s, 679m, 609s;  $\delta_{\rm H}(400 \text{ MHz}; \text{DMSO-}d_6)$  7.23–7.20 (1H, m, Ar H), 7.19–7.13 (2H, m, Ar H), 7.08–7.04 (1H, m, Ar H);  $\delta_{c}(100 \text{ MHz}; \text{DMSO-}$ d<sub>6</sub>) 153.5, 144.9, 138.9, 136.0, 131.2 (Ar CH), 130.01 (Ar CH), 128.6 (Ar CH), 126.7, 125.6 (Ar CH); m/z (EI) 253 (M<sup>+</sup>, 100%), 227 ( $M^+$  – CN, 7), 218 ( $M^+$  – Cl, 13), 192 ( $M^+$  – CClN, 20), 160 (M<sup>+</sup> – CCINS, 33), 151 (8), 134 (8), 113 (7), 108 (C<sub>6</sub>H<sub>4</sub>S<sup>+</sup>, 14), 93 (CCINS<sup>+</sup>, 8), 82 (5), 69 (25) (Found: M<sup>+</sup>, 252.9556.  $C_9H_4ClN_3S_2$  requires M, 252.9567). The addition of a little water to the filtrate gave a second red precipitate (76 mg) of slightly less pure product.

Method 2. To a stirred solution of (3,5-dichloro-4H-1,2,6-thiadiazin-4-ylidene)propanedinitrile 2 (48 mg, 0.21 mmol) in EtOH (5 ml) at *ca.* 20 °C 2-aminothiophenol (32 µl, 0.30 mmol) was added in one portion. After 2 h a red precipitate was produced, filtration and crystallisation of which gave the title compound 4b (33 mg, 87%) as orange-red needles, mp 149–152 °C (from EtOH), spectroscopically identical to the above specimen.

#### 4-Chloro[1,2,6]thiadiazino[3,4-b][1,4]benzoxazine 4c

To a solution of 2-aminophenol (981 mg, 9 mmol) in THF (60 ml) at ca. 20 °C, under nitrogen, excess of NaH (380 mg of 60% mineral suspension) was added. This solution (0.15 M, 8 ml, 1.20 mmol) was added slowly to a stirred solution of 3,5dichloro-4H-1,2,6-thiadiazin-4-one 1 (211 mg, 1.16 mmol) in THF (5 ml) at ca. 20 °C, under nitrogen. The mixture became orange and after 1 h no starting material remained (TLC). The mixture was diluted with DCM (30 ml) and washed with water  $(5 \times 10 \text{ ml})$ . The organic fraction was dried, filtered and the volatiles were removed. Crystallisation of the residue gave the title compound 4c (272 mg, 99%) as orange prisms, mp 158-163 °C (from EtOH) (Found: C, 45.3; H, 1.6; N, 17.6. C<sub>9</sub>H<sub>4</sub>-ClN<sub>3</sub>OS requires C, 45.6; H, 1.7; N, 17.7%); λ<sub>max</sub>(DCM)/nm 249 inf (log ɛ 4.04), 256 (4.08), 264 inf (4.00), 273 inf (3.77), 317 inf (3.78), 327 (3.83), 342 inf (3.77), 370 (3.66), 394 (3.65), 446 (3.85);  $v_{max}$ (Nujol)/cm<sup>-1</sup> 3105w and 3050w (Ar CH), 1615m, 1587w, 1547m, 1519m, 1456s, 1332s, 1308m, 1295m, 1283m, 1244m, 1207m, 1185m, 1107m, 969m, 903s, 877s, 802s, 767s, 750s, 720s, 617s;  $\delta_{\rm H}$ (400 MHz; DMSO- $d_6$ ) 7.24 (1H, dd, J 1.6, 7.6 Hz, Ar H), 7.18 (1H, ddd, J 1.65, 7.8, 7.7 Hz, Ar H), 7.04 (1H, ddd, J 1.3, 7.6, 7.6 Hz, Ar H), 6.88 (1H, dd, J 1.3, 8.1 Hz, Ar H);  $\delta_{\rm C}(100 \text{ MHz}; \text{DMSO-}d_6)$  151.0, 148.1, 145.8, 138.4,

133.9, 130.6 (Ar CH), 128.5 (Ar CH), 125.7 (Ar CH), 115.2 (Ar CH); m/z (EI) 237 (M<sup>+</sup>, 100%), 202 (M<sup>+</sup> - Cl, 5), 176 (M<sup>+</sup> - CClN, 9), 144 (M<sup>+</sup> - CClNS, 11), 118 (5), 93 (CClNS<sup>+</sup>, 11), 64 (6) (Found: M<sup>+</sup>, 236.9764. C<sub>9</sub>H<sub>4</sub>ClN<sub>3</sub>OS requires *M*, 236.9763).

#### 3-(4-Aminoanilino)-5-chloro-4H-1,2,6-thiadiazin-4-one 7a

**Method 1.** (i) To a stirred solution of 3,5-dichloro-4*H*-1,2,6thiadiazin-4-one 1 (419 mg, 2.29 mmol) in DCM (20 ml) at ca. 20 °C 4-(N-tert-butoxycarbonylamino)aniline<sup>6</sup> (478 mg, 2.29 mmol) was added in one portion and after 2 h pyridine (186  $\mu$ l, 2.30 mmol) was added. After a further 1 h the orange coloured mixture was adsorbed onto silica and flash chromatography (DCM) followed by recrystallisation gave the 3-[4-(N-tertbutoxycarbonylamino] anilino] -5-chloro-4H-1,2,6-thiadiazin-4one 7b (310 mg, 38%) as orange crystals, mp 184-185 °C (from EtOH);  $\lambda_{max}$ (EtOH)/nm 245 (log  $\varepsilon$  2.97), 319 (3.16), 336 (3.16);  $v_{\text{max}}$ (Nujol)/cm<sup>-1</sup> 3386m and 3300m (NH), 1728m, 1632m, 1596m, 1557m, 1525s, 1508s, 1318m, 1244m, 1229m, 1178m, 1159m, 889m, 837m;  $\delta_{\rm H}$ (250 MHz; CDCl<sub>3</sub>) 8.62 (1H, br, NH), 7.56 (2H, d, J 8.8 Hz, Ar H), 7.40 (2H, d, J 8.8 Hz, Ar H), 6.51 (1H, br, NH), 1.53 (9H, s, 'Bu);  $\delta_{\rm H}$ (62.9 MHz; CDCl<sub>3</sub>) 156.7, 152.7, 149.9, 141.8, 135.8, 132.0, 120.9, 119.4, 80.8 [C(CH<sub>3</sub>)<sub>3</sub>], 28.4 (CH<sub>3</sub>); m/z (EI) 354 (M<sup>+</sup>, 2%), 298 (M<sup>+</sup> - 'Bu, 3), 280 (12), 254 (24), 234 (3), 208 (5), 196 (38), 178 (13), 165 (4), 160 (11), 152 (43), 134 (32), 118 (5), 108 (50), 91 (5), 80 (16), 57 ('Bu, 88) (Found: M<sup>+</sup>, 354.0550. C<sub>14</sub>H<sub>15</sub>ClN<sub>4</sub>O<sub>3</sub>S requires M, 354.0553). (ii) To a stirred solution of 3-[4-(N-tert-butoxycarbonylamino)anilino]-5-chloro-4H-1,2,6-thiadiazin-4-one 7b (52 mg, 0.15 mmol) in ethyl acetate (5 ml) at ca. 20 °C, was added 3 M HCl. After consumption of the starting material (TLC) the volatiles were removed. Flash chromatography (Et<sub>2</sub>O) of the residue gave the *title compound* 7a (35 mg, 93%) as a red solid, mp 214–215 °C;  $\lambda_{max}$ (EtOH)/nm 240 (log  $\varepsilon$  3.74), 322 (3.92), 340 (3.92);  $v_{max}(Nujol)/cm^{-1}$  3462w, 3365w and 3304<br/>s (NH), 1616s, 1596s, 1568m, 1505w, 1175m;  $\delta_{\rm H}(270$ MHz; DMSO-d<sub>6</sub>) 7.33 (2H, d, J 8.6 Hz, Ar H), 6.54 (2H, d, J 8.6 Hz, Ar H), 5.04 (2H, br, NH<sub>2</sub>); m/z (EI) 254 (M<sup>+</sup>, 100%), 165 (24), 160 (7), 133 (64), 132 (9), 118 (22), 107 (38), 80 (13), 65 (7) (Found: M<sup>+</sup>, 254.00014. C<sub>9</sub>H<sub>7</sub>ClN<sub>4</sub>OS requires M, 254.0029).

Method 2. To a stirred solution of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one 1 (102 mg, 0.56 mmol) in EtOH (10 ml) at *ca.* 20 °C 1,4-diaminobenzene (30 mg, 0.28 mmol) was added in one portion and after 6 h pyridine (45  $\mu$ l, 0.56 mmol) was added. After 1 h the volatiles were removed and flash chromatography (Et<sub>2</sub>O) of the residue gave 3-(4-aminoanilino)-5-chloro-4*H*-1,2,6-thiadiazin-4-one 7a (14 mg, 20%) identical to that prepared above.

#### 3-Chloro-5-(2-hydroxyanilino)-4H-1,2,6-thiadiazin-4-one 8

To a stirred solution of 3,5-dichloro-4H-1,2,6-thiadiazin-4-one 1 (523 mg, 2.86 mmol) in EtOH (10 ml) at 20 °C 2-aminophenol (625 mg, 5.73 mmol) was added in one portion. The mixture was heated at reflux for 72 h and then cooled to ca. 20 °C. The volatiles were removed and flash chromatography (DCM-light petroleum, bp 60-80 °C) of the residue gave the title compound  $\boldsymbol{8}$  (626 mg, 86%) as orange crystals, mp 230–231 °C (from MeOH) (Found: C, 42.2; H, 2.2; N, 16.1. C<sub>9</sub>H<sub>6</sub>ClN<sub>3</sub>O<sub>2</sub>S requires C, 42.3; H, 2.4; N, 16.4%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 3400-3200br (Ar OH), 3346m (Ar NH), 3019w (Ar CH), 1607m, 1557w;  $\delta_{\rm H}$ (500 MHz; DMSO- $d_6$ ) 10.30 (1H, br, OH), 9.25 (1H, br, NH), 8.03 (1H, dd, J 1.4, 8.0 Hz, Ar H), 7.00-6.97 (1H, m, Ar H), 6.93 (1H, dd, J 1.5, 8.0 Hz, Ar H), 6.84 (1H, ddd, J 1.5, 7.8, 7.8 Hz, Ar H); δ<sub>c</sub>(126 MHz; DMSO-d<sub>6</sub>) 157.1, 149.6, 147.3, 140.4, 125.4, 124.7, 119.23, 119.20, 114.9; m/z (EI) 255 (M<sup>+</sup> 94%), 238 ( $M^+$  – OH, 11), 220 ( $M^+$  – Cl, 15), 173 (18), 166 (100), 146 (21), 134 (49), 120 (11), 93 (CCINS<sup>+</sup>, 22).

# 4-Chloro-10-methyl-10*H*-[1,2,6]thiadiazino[3,4-*b*]quinoxaline 11

Method 1. To a stirred solution of 3,5-dichloro-4H-1,2,6thiadiazin-4-one 1 (91 mg, 0.50 mmol) in EtOH (5 ml) at 0 °C N-methyl-1,2-diaminobenzene (115 µl, 1.01 mmol) was added in one portion. The mixture became brown and was allowed to warm to ca. 20 °C. After 5 h a black precipitate was formed, filtration of which gave the *title compound* **11** (83 mg, 70%) as purple needles, mp 207-216 °C (from EtOH) (Found: C, 48.15; H, 2.7; N, 22.25. C<sub>10</sub>H<sub>7</sub>ClN<sub>4</sub>S requires C, 48.0; H, 2.8; N, 22.4%);  $\lambda_{max}$ (DCM)/nm 269 (log  $\varepsilon$  4.21), 280 inf (4.15), 291 inf (4.07), 322 (4.01), 335 inf (3.91), 367 (3.77), 386 (3.84), 407 (3.67), 496 inf (3.36), 530 inf (3.50), 556 (3.51), 606 inf (3.21);  $v_{max}$ (Nujol)/cm<sup>-1</sup> 3068w and 3019w (Ar CH), 1607w, 1586m, 1559w, 1516s, 1497m, 1336m, 1118m, 1050m, 1039m, 854m, 813m, 763m, 748s, 715m, 607s;  $\delta_{\rm H}$ (400 MHz; DMSO- $d_6$ ) 7.07 (1H, ddd, J 1.5, 7.6, 7.7 Hz, Ar H), 6.99 (1H, dd, J 1.5, 7.8 Hz, Àr H), 6.81 (1H, ddd, J 1.2, 7.6, 7.7 Hz, Ar H), 6.71 (1H, dd, J 1.1, 8.2 Hz, Ar H), 2.84 (3H, s,  $CH_3N$ );  $\delta_C(100 \text{ MHz}; \text{DMSO-}$ d<sub>6</sub>) 149.2, 142.9, 139.1, 137.4, 135.8, 130.8 (Ar CH), 128.9 (Ar CH), 123.7 (Ar CH), 113.2 (Ar CH), 28.9 (CH<sub>3</sub>N); m/z (EI) 250  $(M^{+}, 100\%), 235 (M^{+} - CH_{3}, 36), 184 (13), 174 (M^{+} - C_{2}H_{3}-$ ClN, 14), 162 (12), 142 ( $M^+ - C_2H_3$ ClNS, 14), 129 (8), 113 (8), 102 (10), 90 (8), 77 (9), 70 (8) (Found: M<sup>+</sup>, 250.0077.  $C_{10}H_7ClN_4S$  requires M, 250.0080). Addition of a little water to the filtrate gave 5,11-dimethyl-5H,11H-quinoxalino[2,3-b]quinoxaline 12 (20 mg, 15%) as a yellow-green precipitate, mp 235–242 °C (lit.,<sup>7</sup> 242 °C); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 1679w, 1633w, 1600m, 1579s, 1549s, 1417m, 1343m, 1313m, 1300m, 1245m, 1111m, 743s; m/z (EI) 262 (M<sup>+</sup>, 100%), 247 (M<sup>+</sup> - CH<sub>3</sub>, 80), 232  $[M^+ - 2(CH_3), 17]$ , 131  $(M^{++}, 15)$ , 124 (4), 102 (6), 90 (4), 77 (5).

Method 2. To a stirred solution of 4-chloro-10H-[1,2,6]thiadiazino[3,4-b]quinoxaline 4a (50 mg, 0.21 mmol) in DMSO (15 ml) at ca. 20 °C saturated aqueous NaOH (0.5 ml) was added. The mixture became green and iodomethane (0.5 ml) was added in one portion and the solution gradually became purple. After 6 h the mixture was diluted with DCM (50 ml), extracted with water  $(5 \times 20 \text{ ml})$  and the organic fraction was dried, filtered and the volatiles were removed. Crystallisation of the residue gave the title compound 11 (50 mg, 95%) as purple needles, mp 207-216 °C (from EtOH), identical to that described above. If EtOH was used as solvent instead of DMSO then the same procedure gave 4-ethoxy-10-methyl-10H-[1,2,6]thiadiazino[3,4-b]quinoxaline 13 (32 mg, 59%) as purple needles, mp 210–220 °C (from EtOH);  $\lambda_{max}$ (Nujol)/cm<sup>-1</sup> 3140w and 3074w (Ar CH), 1626m, 1603s, 1585m, 1554s, 1505s, 1466s, 1407m, 1379s, 1363s, 1340s, 1314m, 1271m, 1194s, 1160m, 1118m, 1039s, 1037m, 925m, 913m, 751s, 721m, 635m; m/z (EI) 260 (M<sup>+</sup>, 100%), 232 (M<sup>+</sup> -  $C_2H_4$ , 75), 217 (M<sup>+</sup> -  $C_2H_3O$ , 25), 203 (15), 189 (18), 170 (9), 162 (14), 143 (21), 129 (8), 113 (6), 102 (8), 90 (C<sub>6</sub>H<sub>4</sub>N<sup>+</sup>, 9), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 5), 63 (4) (Found: M<sup>+</sup>, 260.0734. C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>OS requires *M*, 260.0731).

#### 4-Chloro-5-cyano[1,2,6]thiadiazino[3',4':5,4]pyrrolo[1,2-a]benzimidazole 14

Method 1 (see Table 1). To a stirred solution of (3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)propanedinitrile 2 (51 mg, 0.22 mmol) in EtOH (5 ml) at *ca.* 20 °C 1,2-diaminobenzene (47.5 mg, 0.44 mmol) was added in one portion. After 12 h no starting material remained (TLC). The mixture was adsorbed onto silica and chromatography (DCM) gave 4-chloro-10*H*-[1,2,6]thiadiazino[3,4-*b*]quinoxaline 4a (22 mg, 42%) as a purple solid, mp >310 °C (from EtOH), identical to that described above. Further elution (DCM) gave the *title compound* 14 (12 mg, 19%) as bright red needles or dark red prisms, mp 254–256 °C (from 1,2-dichloroethane) (Found: C, 50.3; H, 1.5; N, 24.35. C<sub>12</sub>H<sub>4</sub>ClN<sub>5</sub>S requires C, 50.5; H, 1.4; N,

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24.6%); λ<sub>max</sub>(DCM)/nm 235 (log ε 3.77), 267 (4.29), 285 inf (4.37), 289 (4.38), 295 inf (4.35), 343 inf (3.90), 356 (4.03), 423 (3.85), 450 inf (3.98), 475 (4.04), 503 inf (3.98), 539 inf (3.61); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 3085w (Ar CH), 2230s (CN), 1618m, 1559s, 1531s, 1480m, 1451s, 1436s, 1413s, 1299m, 1218m, 1161s, 1131m, 941s, 825s, 792s, 766s, 750s, 737m, 646m, 623s;  $\delta_{\rm H}(400$ MHz; DMSO-d<sub>6</sub>) 8.09-8.05 (1H, m, Ar H), 7.97-7.93 (1H, m, Ar H), 7.60–7.54 (2H, m, Ar H);  $\delta_{\rm C}(100 \text{ MHz}; \text{DMSO-}d_6)$ 152.8, 148.5, 142.8, 142.0, 128.1, 126.0 (Ar CH), 125.53 (Ar CH), 125.47, 121.0 (Ar CH), 112.5 (Ar CH), 112.3 (CN), 88.0 [=C(CN)]; m/z (EI) 285 (M<sup>+</sup>, 100%), 250 (M<sup>+</sup> - Cl, 15), 239  $(M^+ - NS, 3), 219 (14), 146 (6), 142 (6), 122 (9), 102 (9), 90$ (C<sub>6</sub>H<sub>4</sub>N<sup>+</sup>, 11), 76 (C<sub>6</sub>H<sub>4</sub><sup>+</sup>, 9), 63 (11), 57 (5) (Found: M<sup>+</sup>, 284.9878.  $C_{12}H_4ClN_5S$  requires M, 284.9876). Further elution (DCM-ether, 1:1) gave 4-(2-aminoanilino)-5-cyano[1,2,6]thiadiazino[3',4':5,4]pyrrolo[1,2-a]benzimidazole 15 (1 mg, 1%) as a red solid, mp >300 °C (from 1,2-dichloroethane) (Found: C, 60.5; H, 3.15; N, 27.55. C<sub>18</sub>H<sub>11</sub>N<sub>7</sub>S requires C, 60.5; H, 3.1; N, 27.45%); λ<sub>max</sub>(DCM)/nm 262 (log ε 4.68), 280 (4.66), 301 inf (4.48), 353 inf (4.31), 495 inf (4.39), 525 (4.40), 563 inf (4.17); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 3393w and 3316w (NH and NH<sub>2</sub>), 3085w (Ar CH), 2215m (CN), 1621m, 1601m, 1555s, 1508s, 1455s, 1445s, 1414s, 1192m, 1170m, 832m, 756m, 741m, 668m, 600s;  $\delta_{\rm H}$ (400 MHz; DCM- $d_2$ ) 8.08–8.04 (1H, m, Ar H), 7.91– 7.87 (1H, m, Ar H), 7.70 (1H, br s, NH), 7.52-7.45 (3H, m, Ar H), 7.19 (1H, ddd, J 1.4, 7.7, 7.7 Hz, Ar H), 6.93 (1H, dd, J 1.3, 8.0 Hz, Ar H), 6.88 (1H, ddd, J 1.2, 7.6, 7.6 Hz, Ar H), 3.89 (2H, br s, NH<sub>2</sub>); δ<sub>C</sub>(100 MHz; DMSO-d<sub>6</sub>) 152.8, 149.5, 148.5, 143.6, 141.0, 128.2, 127.3 (Ar CH), 126.4 (Ar CH), 124.9 (Ar CH), 124.1 (Ar CH), 121.7, 120.3 (Ar CH), 118.3, 116.0 (Ar CH), 115.7 (Ar CH), 114.0 (CN), 112.1 (Ar CH), 82.8  $[=C(CN)]; \delta_{C}(100 \text{ MHz}; DMSO-d_{6} \text{ DEPT } 135) 127.3 (Ar CH),$ 126.4 (Ar CH), 124.9 (Ar CH), 124.1 (Ar CH), 120.3 (Ar CH), 116.0 (Ar CH), 115.7 (Ar CH), 112.1 (Ar CH); m/z (EI) 357  $(M^{+},\ 100\%),\ 341\ (M^{+}-NH_{2},\ 49),\ 311\ (M^{+}-NS,\ 56),\ 284\ (M^{+}-CHN_{2}S,\ 49),\ 178.5\ (M^{++},\ 12),\ 162\ (4),\ 107\ (5),\ 91\ (4),\ 80$ (5), 69 (28) (Found:  $M^+$ , 357.0819.  $C_{18}H_{11}N_7S$  requires M, 357.0797).

Method 2. To a stirred solution of 3,5-dichloro-4H-1,2,6-thiadiazin-4-one 1 (91 mg, 0.50 mmol) in EtOH (5 ml) at *ca*. 20 °C 2-benzimidazolylacetonitrile (78.5 mg, 0.50 mmol) was added in one portion. The mixture was refluxed at 80 °C for 12 h and only a trace of the title compound 14 was observed by TLC comparison with an authentic sample under several solvent systems.

## 4-(2-Aminoanilino)-5-cyano[1,2,6]thiadiazino[3',4':5,4]pyrrolo[1,2-*a*]benzimidazole 15

To a stirred suspension of 4-chloro-5-cyano[1,2,6]thiadiazino-[3',4':5,4]pyrrolo[1,2-*a*]benzimidazole **14** (23 mg, 0.08 mmol) in EtOH (3 ml) 1,2-diaminobenzene (37 mg, 0.34 mmol) was added. The mixture was refluxed for 8 h, allowed to cool to *ca*. 20 °C and filtered to give a deep red precipitate, crystallisation of which gave the title compound **15** (24 mg, 83%) as deep red prisms, mp >300 °C (from 1,2-dichloroethane), identical to that described above.

# 3-(8-Aminonaphthalen-1-ylamino)-5-chloro-1,2,6-thiadiazin-4-one 19

To a stirred solution of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4one **1** (184 mg, 1.01 mmol) in DCM (10 ml) at 20 °C 1,8diaminonaphthalene (317 mg, 2.01 mmol) was added in one portion. The mixture was heated at reflux for 18 h and then cooled to *ca.* 20 °C. The volatiles were removed and flash chromatography (DCM–light petroleum) of the residue gave the *title compound* **19** (134 mg, 46%) as brick-red needles, mp 219– 220 °C decomp. (from ethyl acetate) (Found: C, 51.1; H, 2.9; N, 18.0.  $C_{13}H_9CIN_4OS$  requires C, 51.2; H, 3.0; N, 18.4%);  $v_{\rm max}({\rm CHCl_3})/{\rm cm^{-1}}$  3357w and 3280m (Ar NH), 1631m (C=O), 1602m, 1555m, 1516m, 753m;  $\delta_{\rm H}(500~{\rm MHz};{\rm DMSO-}d_6)$  11.02–10.93 (1H, br, N*H*), 7.98–6.90 (6H, m, Ar *H*), 6.70–6.55 (2H, br, N*H*);  $\delta_{\rm C}(126~{\rm MHz};{\rm DMSO-}d_6)$  157.4, 146.0, 136.0, 135.0, 126.72, 126.66, 126.4, 125.6, 125.2, 123.1, 121.9, 116.5, 114.8; m/z (EI) 304 (M<sup>+</sup>, 27%), 286 (49), 221 (43), 215 (51), 193 (25), 168 (44), 166 (100), 155 (28), 140 (36), 139 (27), 130 (23), 115 (24), 93 (CCINS<sup>+</sup>, 22).

# 9-Chloro-8-cyano[1,2,6]thiadiazino[3',4':5,4]pyrrolo[1,2-a]perimidine 20

To a stirred solution of (3,5-dichloro-4H-1,2,6-thiadiazin-4ylidene)propanedinitrile 2 (57.5 mg, 0.25 mmol) in EtOH (4 ml) at ca. 20 °C 1,8-diaminonaphthalene (39.5 mg, 0.25 mmol) was added in one portion. After 12 h at ca. 20 °C filtration gave a black precipitate which on crystallisation gave the title compound 20 (68 mg, 81%) as deep green needles, mp >300 °C (from glacial acetic acid) (Found: C, 57.1; H, 2.1; N, 20.7.  $C_{16}H_6ClN_5S$  requires C, 57.3; H, 1.8; N, 20.9%);  $\lambda_{max}(DCM)/nm$ 274 (log ε 4.84), 326 (4.00), 387 (4.35), 406 (4.37), 431 (3.94), 457 inf (3.86), 491 inf (3.60), 568 inf (3.60), 609 (3.75), 662 (3.77), 722 (3.54);  $v_{max}$ (Nujol)/cm<sup>-1</sup> 3103w and 3062w (Ar CH), 2231m (CN), 1653w, 1623s, 1583s, 1570s, 1527s, 1494s, 1455s, 1417s, 1387s, 1235s, 1221m, 1184m, 1166s, 1132s, 1124m, 1058m, 1005m, 904s, 827s, 801m, 793m, 770s, 708s, 663m, 622s; *m/z* (EI) 335 (M<sup>+</sup>, 100%), 299 (M<sup>+</sup> - HCl, 29), 267 (6), 212 (5), 167.5 (M<sup>++</sup>, 8), 162 (12), 151 (10), 140 (7), 113 (8), 91 (4), 69 (55) (Found: M<sup>+</sup>, 335.0027. C<sub>16</sub>H<sub>6</sub>ClN<sub>5</sub>S requires M, 335.0032). The use of two equivalents of 1,8diaminonaphthalene, under similar conditions, gave the title compound 20 in 96% yield.

# 4-Piperidino[1,2,6]thiadiazino[3,4-*b*][1,4]benzothiazine 21

To a solution of 4-chloro[1,2,6]thiadiazino[3,4-b][1,4]benzothiazine 4b (126.5 mg, 0.50 mmol) in DCM (5 ml) at ca. 20 °C piperidine (99 µl, 1 mmol) was added in one portion. The mixture was refluxed for 1 h after which time TLC indicated a new product and no starting material. The mixture was diluted with DCM (20 ml), washed with water  $(3 \times 5 \text{ ml})$  and the organic fraction was dried, filtered and the volatiles were removed. Crystallisation of the residue gave the *title compound* 21 (149 mg, 99%) as red prisms, mp 101-103 °C (from EtOH-water);  $\lambda_{max}(DCM)/nm 240 (\log \varepsilon 4.24), 269 (3.93), 389 inf (4.14), 382$ (3.82), 492 (3.90);  $v_{max}$ (Nujol)/cm<sup>-1</sup> 3030w (Ar CH), 1588m, 1558m, 1515s, 1505s, 1461s, 1435s, 1417m, 1370s, 1351m, 1299s, 1285s, 1275s, 1257m, 1237m, 1227m, 1203m, 1133m, 1125m, 1036m, 1026m, 968m, 955m, 916s, 883m, 855m, 815s, 804m, 790m, 760s, 739m, 721s, 625s, 601s;  $\delta_{\rm H}$ (300 MHz; DCM- $d_2$ ) 7.25-7.21 (1H, m, Ar H), 7.15-7.09 (2H, m, Ar H), 6.92-6.89 (1H, m, Ar H), 3.57 [4H, br s, 2(CH<sub>2</sub>N)], 1.69 [6H, br s,  $3(CH_2)$ ];  $\delta_C(76$  MHz; DCM- $d_2$ ) 149.3 (C=N), 144.4 (C=N), 139.9 (C=N), 135.7, 130.2 (Ar CH), 129.7, 128.2 (Ar CH), 127.5 (Ar CH), 125.4 (Ar CH), 48.0 (CH<sub>2</sub>N), 25.7 (CH<sub>2</sub>CH<sub>2</sub>N), 24.8 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); *m*/*z* (EI) 302 (M<sup>+</sup>, 41%), 267 (4), 236 (3), 220 (6), 186 (3), 161 (26), 134 (2), 108 (6), 84 (C5H10N<sup>+</sup>, 100) (Found: M<sup>+</sup>, 302.0650. C14H14N4S2 requires *M*, 302.0660).

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