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Reactions of 1,2,5-Thiadiazole-3,4-dicarbonitrile

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The known compound 1,2,5-thiadiazole-3,4-dicarbonitrile, **1a** preferentially forms mono addition compounds **3**, but also bis-addition compounds **4** with oxygen, nitrogen and sulfur nucleophiles. One preparation of **1a** produced bis[4-cyano-1,2,5-thiadiazol-3-ylmethyl(imino)]amine **2** as a minor product. The structure of compound **2**, the facile formation of triazine **5** and the monocyclic structures of **3** and **4** indicate extensive stereoelectronic interactions between vicinal substituents of 1,2,5-thiadiazole. A bicyclic diimino imide was not formed from **1a** in sulfur- or methoxide-catalysed reactions with ammonia in methanol.

The chemistry of 1,2,5-thiadiazoles was reviewed some years ago.[1] In several recent studies[2–5] the redox properties of their sulfur–nitrogen linkages have been reported. The interest in these heterocycles is also due to their reported biological activities, among these being antifungal, antibacterial, antiinflammatory and antidiabetic properties.[1]

With the objective of preparing a metal-free tetraazaporphyrin, conversion of the known compound 1,2,5-thiadiazole-3,4-dicarbonitrile, **1a**[6] into the diimino imide 4*H*-pyrrolo[3,4-*c*][1,2,5]thiadiazole-4,6(5*H*)-diimine was attempted. To our consternation this compound could not be obtained under conditions where phthalonitrile[7] and pyrazine-2,3-dicarbonitrile[8] form such diimino imides.

To investigate why this reaction was not possible, compound **1a** was reacted with a number of oxygen, nitrogen and sulfur nucleophiles in an attempt to obtain bicyclic addition compounds. To our knowledge no such investigation has been reported.

1,3-Diiminoisoindoline is formed from phthalonitrile by a sodium methoxide catalysed reaction with ammonia in methanol.[7] Since compound **1a** does not form a similar adduct, this might be due to steric strain or electronic interactions. For instance, Linstead noted[9] that anhydrides from pyrrole-*o*-dicarboxylic acids are unstable, and that their imides are unknown. Steric strain is indicated in 1,2,5-thiadiazole-3,4-dicarboxylic acid since a dimeric anhydride is reported,[6b] whereas the intramolecular anhydride is apparently unknown. The monoanion of the strongly acidic 1,2,5-thiadiazole-3,4-dicarboxylic acid is stable above pH 1 and the dianion above pH 2 in accordance with the electron-withdrawing 1,2,5-thiadiazole nucleus.[6b] On the other hand, the high values of log K_1/K_2 observed[10] for the unsaturated vicinal dicarboxylic acids furan-3,4-dicarboxylic acid, cyclopentene-1,2-dicarboxylic acid and maleic acid indicate strong intramolecular hydrogen bonds in their monoanions. Thus, a coplanar π-electron system, favoring such hydrogen bonding is indicated. The emerging picture of the stereoelectronic effects in different vicinally disubstituted (carboxy, nitrile) aromatics is thus complex, and further experiments were required to clarify the case of compound **1a**.

Results and discussion

The addition compounds obtained from **1a** are shown in Scheme 1.

Oxidation of **1a** with one equivalent of hydrogen peroxide in Me_2SO[11] gave compound **1b**, 4-cyano-1,2,5-thiadiazole-3-carboxamide, instead of a bicyclic imino imide. The presence of a cyano group in **1b** was confirmed by an IR absorption at 2258 cm^{-1} and a ^{13}C NMR signal at δ 112. Compound **1b** (16%) was also obtained in another reaction of **1a** with chlorosulfonic acid. The known[6a] diamide **1c** was similarly obtained from **1a** and two equivalents of hydrogen peroxide. The thioamide **1d** was obtained somewhat unexpectedly from **1a** and thioacetic acid. The expected acetyl isothioamide was perhaps hydrolysed under the reaction conditions used.

Compound **2** (1%), was isolated from one preparation of **1a** where the removal of thionyl chloride was incomplete before extraction with sodium hydrogen carbonate and chloroform. Compounds **3a** (58%) and **4a** (25%) were formed from **1a** and ammonia in methanol with

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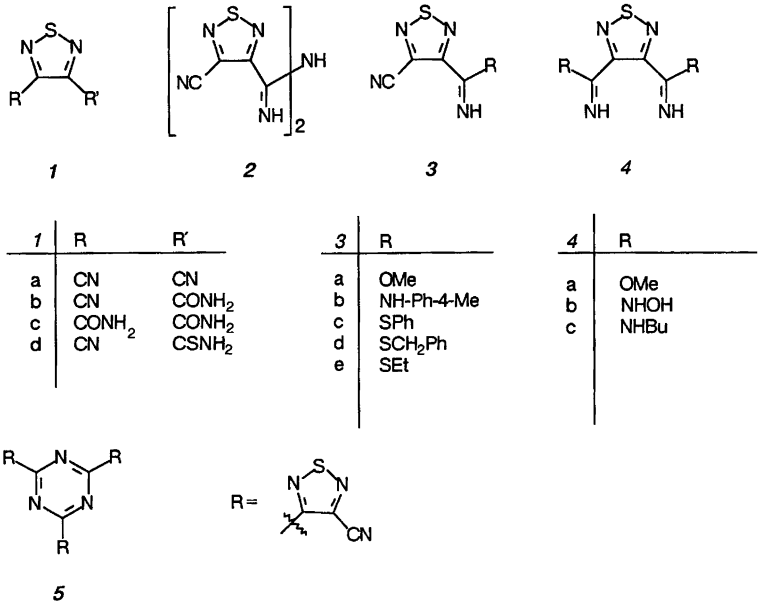

Scheme 1.

sodium methoxide as the catalyst. When sulfur was used as the catalyst,[12] only compound **4a** (42%) was isolated. Sulfur also was an efficient catalyst for the reaction of **1a** with 4-methylaniline; thus the yield of **3b** increased from 7% without sulfur, to 58% with sulfur added.

Compound **4c** (35%) was obtained from **1a** and butylamine in the presence of sulfur. However, the secondary amine bis(2-pyridyl)amine, **1a** and sulfur gave a solid which showed a depressed melting point with either reactant. This product had a strong IR absorption at 3337 cm^{-1} but dissociated to **1a** and the amine in chloroform solution. Consequently, neither NMR nor mass spectra could be obtained.

A reaction of **1a** with an excess of hydroxylamine gave **4b**. The reaction conditions were the same as those used by Linstead[13] to prepare the cyclic compound 2,5-dihydroxyimino-3,4-dimethylpyrrolidine from the acyclic DL-α,α′-dimethylsuccinonitrile.

The three thiols thiophenol, α-toluenethiol and ethanethiol add to only one cyano group when reacted with **1a**. The addition compound **3e** decomposed to some extent to the reactants when stored at ambient temperature. Chromatography on silica of crude **3e** separated a small amount (ca. 5%) of a compound which was considerably more polar. No molecular ion was obtained for this compound in the mass spectrum, but a MS fragment $C_6H_7N_4S_2$ and IR and NMR spectra indicated that water had been added.

The triazine **5** (83%) was formed when **1a** was heated in ethyleneglycol or with hydroquinone. These reaction conditions were used[14,15] to prepare phthalocyanines from diiminoisoindolines or phthalonitriles. It should be noted that the formation of triazines from other aromatic dinitriles requires far more drastic conditions than those used in this investigation. Phthalonitrile, for instance, trimerises in chlorosulfonic acid[16] or in the presence of other strong acids.[17]

Conclusions

The five-membered heterocyclic compound **1a** does not form a bicyclic diimino imide under reaction conditions previously used to prepare 1,3-diiminoisoindoline[7] from phthalonitrile and the bicyclic diimino imide[8] from the six-membered pyrazine-2,3-dicarbonitrile. The structures of compounds **3** and **4**, obtained from **1a** and oxygen, nitrogen and sulfur nucleophiles, show that no new cycle is formed. The preferred formation of monosubstituted compounds **3** instead of compounds **4** also indicates extensive stereoelectronic interactions between vicinal substituents of 1,2,5-thiadiazole. The formation of compound **2** and the ease with which compound **5** is formed, also support this conclusion.

The formation of compounds **2–5** indicated that a metal-ion template is probably required for the cyclotetramerisation of **1a**. This has subsequently been proved correct.[18]

Experimental

General. Mass spectra were obtained on an AEI MS-902 spectrometer at 70 eV (IP). IR spectra were obtained on a Nicolet 20-SXC FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Jeol EX400 NMR spectrometer, ^{13}C spectra were obtained at 100.40 MHz, ^1H spectra at 399.65 MHz. Tetramethylsilane (TMS) was used as the internal standard. Melting points were obtained on a Buchi 530 melting-point apparatus and are uncorrected. Merck Kieselgel 60F 254 was used for TLC

and Merck silica 63–200 μm was used for column chromatography.

*1,2,5-Thiadiazole-3,4-dicarbonitrile (***1a***)*[6]. The following procedure is an adaptation of previously reported methods:[6] A mixture of (*Z*)-2,3-diamino-2-butenedinitrile (5 g, 46 mmol) and thionyl chloride (70 ml) was heated under reflux for 2.5 h. Excess thionyl chloride was removed under reduced pressure, the residue was dissolved in chloroform, and the organic phase was washed with 5% aqueous sodium hydrogen carbonate (4 × 20 ml). Drying over magnesium sulfate and removal of the solvent gave 6.2 g (98%) crude product which was chromatographed on silica (63 g). Chloroform eluted 5.1 g (80%), $R_f(CHCl_3) = 0.53$ of m.p. 47–50°C, lit.[6a] 48–49°C. IR (KBr): 2246, 1442, 1398, 1290, 1138, 847, 770 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 136.8, 108.9.

4-Cyano-1,2,5-thiadiazole-3-carboxamide, **1b** *and 1,2,5-thiadiazole-3,4-dicarboxamide,* **1c**. *General procedure.* Potassium carbonate (0.2 g for **1b**, 0.4 g for **1c**) was added to an ice-cold solution of **1a** (1.35 g, 10 mmol) in dimethyl sulfoxide (6 ml). 30% Aqueous hydrogen peroxide (1.1 ml, 10 mmol for **1b**, 2.2 ml for **1c**) was added dropwise over 10–20 min. The cold reaction mixture was stirred for 25 min and then poured onto ice (30 g), after which the precipitate was filtered off, washed with water and air-dried. **1b**: yield 0.88 g (57%), m.p. 148–150°C. MS [*m/z* (% rel. int.)]: 156 (12.7, *M* + 2), 155 (15.1, *M* + 1), 154 (72.8, *M*). Found 153.9948, calc. for $C_4H_2N_4OS$ 153.9949. IR (KBr): 3370, 3306, 3170, 2772, 2711, 2258, 1699 (s), 1620, 1460, 1341, 1117, 850, 778, 684 cm^{-1}. ^1H NMR [$(CD_3)_2CO$]: δ 7.45 (1 H), 7.90 (1 H). ^{13}C NMR [$(CD_3)_2CO$]: δ 159.69, 159.12, 149.65, 112.56. **1c**: yield after recrystallisation from H_2O 1.23 g (71%), m.p. 238–240°C, lit.[6a] m.p. 240°C. MS [*m/z* (% rel. int.)]: 174 (2.1, *M* + 2), 173 (2.8, *M* + 1), 172 (41.3, *M*), 129 (100, *M* – CONH). IR (KBr): 3479, 3200, 3031, 1700 (s), 1670 (s), 1590, 1544, 1433, 1382, 1289, 1115, 1071, 876, 818, 794, 771, 672 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ 7.88 (2 H), 8.27 (2 H). ^{13}C NMR [$(CD_3)_2SO$]: δ 161.9, 156.5.

Compound **1b** *from* **1a** *in chlorosulfonic acid.* Compound **1a** (0.9 g, 7 mmol) was added in one portion to ice-cold chlorosulfonic acid (3 ml). The ice-cold solution was stirred for 2 h after which it was left at ambient temperature for 48 h then poured onto ice (50 g). The aqueous solution was extracted with dichloromethane (2 × 30 ml), the combined organic extracts were washed with water (20 ml) and dried and the solvent was evaporated off. Crystallisation of the residue from acetone–diethyl ether gave 270 mg (16%) **1b** of m.p. 147–151°C. MS and IR spectra of the product were identical with those obtained of **1b** as described above.

4-Cyano-1,2,5-thiadiazole-3-carbothioamide, **1d**. *Method (i).* Thioacetic acid (0.53 g, 7 mmol) was added to a solution of **1a** (0.4 g, 3 mmol) in benzene (10 ml). The reaction mixture was stirred at ambient temperature for 2 h. The yellow precipitate was filtered off and washed with benzene. Yield 0.23 g (45%) of m.p. 140–141°C (decomp.). The filtrate was stirred for another 28 h, and a second crop [0.13 g, (25%), m.p. 140–141°C (decomp.)] was obtained. MS [*m/z* (% rel. int.)]: 172 (9.6, *M* + 2), 171 (7.2, *M* + 1), 170 (100, *M*). Found 169.9722, calc. for $C_4H_2N_4S_2$ 169.9721. IR (KBr): 3358, 3280, 3190, 2243 (w), 1624 (s), 1436, 1368, 1300, 1242, 1121, 930, 864, 842, 664, 601 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ 10.9 (1 H), 10.53 (1 H). ^{13}C NMR [$(CD_3)_2SO$]: δ 112.23 (CN), 134.01 (C-4), 160.3 (C-3), 185.50 (C = S).

Method (ii). A solution of **1a** (0.41 g, 3 mmol) and sodium sulfide nonahydrate (1.44 g, 6 mmol) in methanol (15 ml) was stirred at ambient temperature for 26 h. The solvent was removed under reduced pressure, the red liquid residue was dissolved in water (10 ml) and the solution was made acidic with 2 M hydrochloric acid and extracted with diethyl ether (3 × 20 ml). The combined organic phases were dried and concentrated to about 10 ml, whereupon a crystalline material separated. Yield: 0.17 g (33%) of m.p. 135–140°C (decomp.). This compound gave the same IR and ^1H NMR spectra as obtained for compound **1d** from method (i).

Bis[4-cyano-1,2,5-thiadiazol-3-yl(imino)methyl]amine, **2**, was prepared as described for the dinitrile **1a**, above, but on a fourfold scale. After removal of most of the thionyl chloride, the reaction mixture reacted exothermically with sodium hydrogen carbonate (5%, 100 ml). The crude product (10.9 g) obtained from the dried chloroform extract, was chromatographed on silica gel (110 g) with chloroform. The combined fractions of $R_f(CHCl_3) = 0.7$ yielded **1a** (9 g, 36%) while one fraction of $R_f(CHCl_3) = 0.09$ yielded **2** (390 mg, 1%), m.p. 151–259°C (slow decomp.). MS [*m/z* (% rel. int.)]: 291 (10, *M* + 2), 290 (14.5, *M* + 1), 289 (100, *M*). Found 288.955, calc. for $C_8H_3N_9S_2$ 288.9953. IR (KBr): 3325, 3283 (s), 2260, 2247 (w), 1620 (s), 1525, 1465, 1353, 1167, 1008, 848 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ 10.7 (1 H, amine), 10.1 (2 H, imines). ^{13}C NMR [$(CD_3)_2SO$]: δ 112.49 (CN), 133.05 (C-4), 158.14 (C-3), 159.03 (imines).

Methyl 4-cyano-1,2,5-thiadiazole-3-carboximidate, **3a**, *and dimethyl 1,2,5-thiadiazole-3,4-dicarboximidate,* **4a**. *Method (i).* Sodium methylate (0.6 mmol) in methanol (20 ml) was added to a solution of **1a** (1.36 g, 10 mmol) in methanol (50 ml). Gaseous ammonia was passed through the stirred solution for 20 min, stirring was continued at ambient temperature for 1 h, and the solvent was removed under reduced pressure at 50°C. Dichloromethane (40 ml) was added and some solid material (0.15 g) removed by filtration. The residue from the filtrate was dissolved in acetone (5 ml) and chromatographed on silica gel with acetone. The fractions with R_f(acetone) = 0.89 were combined and yielded **3a** 0.97 g (58%), m.p. 77–78°C. MS [*m/z* (% rel. int.)]: 169 (1.3, *M* + 1), 168 (11.4, *M*), 111 (100). Found 168.0108, calc. for $C_5H_4N_4OS$

168.0106. IR (KBr): 3309, 3012, 2960, 2242, 1650 (s), 1474, 1331, 1137, 1076, 954, 846, 797 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.09 (3 H), 8.78 (1 H). ^{13}C NMR ($CDCl_3$): δ 54.39 (CH_3), 111.25 (CN), 132.39 (C-4), 155.06 (C-3), 158.80 (imidate). The subsequent fractions with R_f(acetone) = 0.74 were combined and yielded **4a**, 0.50 g (25%), m.p. 47–50°C. MS [*m/z* (% rel. int.)]: 201 (0.6, *M* + 1), 200 (1.1, *M*), 199 (5.2, *M* − 1), 185 (22.4, *M* − CH_3), 169 (100, *M* − OCH_3). Found 200.0366, calc. for $C_6H_8N_4O_2S$ 200.0368. *M* − 1, found 199.0292, calc. for $C_6H_7N_4O_2S$ 199.0290. *M* − CH_3, found 185.0133, calc. for $C_5H_5N_4O_2S$ 185.0133. *M* − OCH_3, found 169.0182, calc. for $C_5H_5N_4OS$ 169.0184. IR (KBr): 3254, 3219, 2983, 2949, 1649 (s), 1490, 1456, 1432, 1402, 1336, 1304, 1196, 1151, 1096, 1064, 939, 840, 805, 715 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.98 (6 H), 8.32 (2 H). ^{13}C NMR ($CDCl_3$): δ 54.10 (CH_3), 152.41 (C-3, C-4), 161.78 (imidates).

Method (ii). Sulfur (0.1 g, 3 mmol) was added to a solution of **1a** (0.4 g, 3 mmol) in methanol (10 ml). Gaseous ammonia was passed through the stirred reaction mixture for 15 min and stirring was continued for 17 h at 30–35°C. The suspension was filtered, and the filtrate evaporated to yield 0.47 g of a semi-solid residue. The crude product was heated with diethyl ether (20 ml), and a small amount of undissolved material was removed by filtration. The filtrate was concentrated to a small volume, hexane (1 ml) was added and white crystals 0.25 g (42%) of **4a** m.p. 42–48°C were obtained. MS and IR spectra were the same as for **4a** obtained by method (i).

4-Cyano-1,2,5-thiadiazole-3-[N'-(4-tolyl)carboxamidine], **3b**. Compound **1a** (0.4 g, 3 mmol), 4-tolylamine (0.6 g, 6 mmol) and sulfur (0.1 g, 3 mmol) in methanol (15 ml) were stirred at ambient temperature for 20 h. The solvent was removed under reduced pressure, diethyl ether (20 ml) was added, and undissolved material was removed by filtration. The filtrate was washed with water, dried and evaporated to yield 0.43 g (58%) m.p. 175–179°C (decomp.). MS [*m/z* (% rel. int.)]: 245 (5.4, *M* + 2), 244 (17.4, *M* + 1), 243 (100, *M*), 242 (89.3, *M* − 1). Found 243.0580, calc. for $C_{11}H_9N_5S$ 243.0579. IR (KBr): 3447, 3353, 3177, 2921, 2239, 1657 (s), 1596, 1504, 1483, 1317, 1239, 1109, 843, 788, 584, 558 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ 6.78 (1 H, s), 6.89 (2 H, d, *J* 7.8 Hz), 7.17 (2 H, d, *J* 8.3 Hz), 9.35 (1 H, s). ^{13}C NMR [$(CD_3)_2SO$]: δ 20.45 (CH_3), 112.64 (CN), 121.34 (Ph), 129.61 (Ph), 131.84 (Ph), 133.17 (C-4), 145.24 (C-3), 145.96 (Ph), 159.34 (imine).

General procedure for the preparations of phenyl 4-cyano-1,2,5-thiadiazole-3-carbothioimidate, **3c**, *benzyl 4-cyano-1,2,5-thiadiazole-3-carbothioimidate,* **3d** *and ethyl 4-cyano-1,2,5-thiadiazole-3-carbothioimidate,* **3e**. A solution of **1a** (0.4 g, 3 mmol) and the thiol (3 mmol) in methanol (10 ml) was stirred for 24 h. Solid precipitates of **3c** or **3d** formed and were removed by filtration. The filtrates were concentrated and yielded additional amounts of **3c** or **3d**, or the total yield of **3e** upon addition of hexane. Compound **3e** was chromatographed on silica gel with chloroform. **3c**, Yield 0.55 g (75%), m.p. 102–103°C (decomp.). MS [*m/z* (% rel. int.)]: 247 (0.6, *M* + 1), 246 (1.2, *M*), 245 (5.6, *M* − 1). Found 244.9958, calc. for $C_{10}H_5N_4S_2$ (*M* − 1) 244.9956. IR (KBr): 3247, 3058, 2246, 1598, 1477, 1452, 1440, 1407, 1294, 1246, 1139, 875, 827, 753 cm^{-1}. ^1H NMR [$(CD_3)_2CO$]: δ 7.63 (5 H, m), 10.31 (1 H, s). ^{13}C NMR [$(CD_3)_2CO$]: δ 112.87 (CN), 126.33 (Ph), 131.71 (Ph), 131.13 (Ph), 133.36 (C-4), 137.34 (Ph), 160.37 (imine), 162.14 (C-3). **3d**, Yield 0.64 g (82%), m.p. 92–93°C (decomp.), MS [*m/z* (% rel. int.)]: 262 (4.1, *M* + 2), 261 (6.7, *M* + 1), 260 (39.7, *M*). Found 260.0195, calc. for $C_{11}H_8N_4S_2$ 260.0190. IR (KBr): 3288, 3062, 3026, 2928, 2245, 1575, 1494, 1454, 1403, 1297, 1219, 1110, 897, 870, 834, 753, 707, 692, 515 cm^{-1}. ^1H NMR [$(CD_3)_2CO$]: δ 4.40 (2 H, s), 7.43 (4 H, m), 11.34 (1 H, s). ^{13}C NMR [$(CD_3)_2CO$]: δ 33.94 (CH_2), 113.04 (CN), 128.57 (Ph), 129.37 (Ph), 129.68 (Ph), 129.79 (Ph), 136.24 (C-4), 161.20 (imine), 161.56 (C-3). **3e**, Yield 0.53 g (89%), m.p. 88–90°C (decomp.) R_f($CHCl_3$) = 0.3. MS [*m/z* (% rel. int.)]: 200 (2.7, *M* + 2), 199 (3.0, *M* + 1), 198 (30.0, *M*). Found 198.0036, calc. for $C_6H_6N_4S_2$ 198.0034. IR (KBr): 3286, 2978, 2964, 2929, 2245, 1654, 1582, 1454, 1398, 1226, 1138, 1119, 889, 850, 835, 566 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.44 (t, 3 H, *J* 7.8 Hz), 2.95 (br, 2 H), 10.47 (br, 1 H). ^{13}C NMR ($CDCl_3$): δ 12.91 (CH_3), 23.33 (CH_2), 111.96 (CN), 132.40 (C-4), 160.42 (imine), 162.45 (C-3). A second compound was eluted after compound **3e**. Yield 0.02 g, m.p. 181–184°C (decomp.) R_f($CHCl_3$) = 0.0. MS [*m/z* (% rel. int.)]: 201 (8.0), 200 (10.6), 199 (81.3), 198 (15.6). Found 199.0114, calc. for $C_6H_7N_4S_2$ 199.0112. IR (KBr): 3350, 3316, 2970, 2925, 2781, 1679 (s), 1587 (s), 1452, 1375, 1322, 1269, 1126, 984, 906, 847, 754, 668, 578 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ 1.13 (3 H, t, *J* 7.3 Hz), 2.70 (2 H, q, *J* 7.3 Hz), 7.52 (1 H, s). ^{13}C NMR [$(CD_3)_2SO$]: δ 76.04, 153.95, 160.93, 177.50.

1,2,5-Thiadiazole-3,4-bis[N'-hydroxycarboxamidine], **4b**. A mixture of **1a** (0.4 g, 3 mmol), hydroxylamine hydrochloride (0.46 g, 6.6 mmol) and sodium carbonate (0.23 g, 2.2 mmol) in ethanol (8 ml) and water (6 ml) was heated with stirring at 90°C for 22 h. The solvents were removed under reduced pressure and the solid residue was stirred with pyridine (15 ml) and filtered. The pyridine was removed from the filtrate, and 0.25 g (41%) of **4b** m.p. 210–215°C (decomp.) was obtained. MS [*m/z* (% rel. int.)]: 204 (4.1, *M* + 2), 203 (6.6, *M* + 1), 202 (81.6, *M*), 155 (100). Found 202.0271, calc. for $C_4H_6N_6O_2S$ 202.0273. IR (KBr): 3417, 3292–3136 (s, br), 2833, 1679 (s), 1578, 1412, 1262, 1088, 1052, 877, 822 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ 3.5–4.2 (br), 7.27–8.54 (m, br), 9.68–9.90 (m), 11.05 (s). ^{13}C NMR [$(CD_3)_2SO$]: δ 149.07 (C-3, C-4), 149.85 (imines).

1,2,5 - Thiadiazole - 3,4 - bis[N' - butylcarboxamidine], **4c**. Compound **4c** was prepared from **1a**, butylamine and sulfur as described for compound **3b**. Yield 0.30 g (35%)

after recrystallisation from acetone–diethyl ether, m.p. 76–78 °C. MS [*m/z* (% rel. int.)]: 284 (1.6, *M* + 2), 283 (3.2, *M* + 1), 282 (17.4, *M*), 210 (100, *M* – $C_4H_{10}N$). Found 282.1628, calc. for $C_{12}H_{22}N_6S$ 282.1628. *M* – $C_4H_{10}N$ found 210.0814, calc. for $C_8H_{12}N_5S$ 210.0813. IR (KBr): 3463, 3437, 3313, 3263, 3111, 2955, 2930, 2868, 2683, 1655 (s), 1607 (s), 1430, 1377, 1194, 1094, 885, 817, 530 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.97 (6 H, t, *J* 7.3 Hz), 1.46 (4 H, q, *J* 7.3 Hz), 1.70 (4 H, q, *J* 7.3 Hz), 3.33 (4 H, t, *J* 7.3 Hz). ^1H NMR [$(CD_3)_2SO$]: δ 0.91 (6 H, t, *J* 7.3), 1.37 (4 H, q, *J* 7.3), 1.57 (4 H, q, *J* 7.3), 2.09 (2 H, s), 3.24 (H_2O + 2 H, m), 7.88 (2 H, s). ^{13}C NMR ($CDCl_3$): δ 13.90, 20.65, 31.44, 43.16, 153.29, 155.06.

Reaction of **1a** *with bis(2-pyridyl)amine.* A mixture of **1a** (0.41 g, 3 mmol) and sulfur (0.1 g, 3 mmol) in ethanol (10 ml) was stirred at ambient temperature for 26 h. TLC of the reaction mixture showed $R_f(CHCl_3) = 0.93$ (sulfur), 0.6 (**1a**). Bis(2-pyridyl)amine (0.51 g, 3 mmol) was added and stirring was continued for 19 h. The solid material (0.09 g) was removed by filtration. Evaporation of the filtrate gave a solid which was triturated with hexane (15 ml), and filtered to give 0.74 g, m.p. 81–83 °C. $R_f(CHCl_3) = 0.0$. The solid compound was heated with hexane (15 ml) and filtered to give undissolved material: 0.56 g m.p. 83–84 °C. The filtrate was concentrated to give a further 0.15 g m.p. 83–84 °C. Bis(2-pyridyl)amine: m.p. 95 °C, mixed m.p. 70–75 °C. MS [*m/z* (% rel. int.)]: 172 (7.7), 171 (64.7), 170 (100), 136 (18). IR (KBr): 3337 (s), 3020, 1605, 1590, 1529, 1440, 1346, 773 cm^{-1}.

2,4,6-Tris(4-cyano-1,2,5-thiadiazol-3-yl)-1,3,5-triazine, **5**. *Method (i).* A solution of **1a** (0.4 g, 3 mmol) in 1.2-ethanediol (10 ml) was heated with stirring at 100 °C for 15 h. The reaction mixture, with some white precipitate, was poured onto ice (50 g), and filtered and the filter was washed with acetone. Yield 0.34 g (83%), m.p. > 290 °C. MS [*m/z* (% rel. int.)]: 410 (12.5, *M* + 2), 409 (17.0, *M* + 1), 408 (86.3, *M*), 382 (38.6, *M* – CN), 136 (100, **1a**). Found 407.9526, calc. for $C_{12}N_{12}S_3$ 407.9531. *M* – CN, found 381.9498, calc. for $C_{11}N_{11}S_3$ 381.9500. IR (KBr): 2248 (w), 1532 (vs), 1472 (s), 1318, 1281, 1126, 835, 811, 712, 560 cm^{-1}. ^{13}C NMR [$(CD_3)_2SO$]: δ 112.05 (CN), 134.71, 157.68, 165.53.

Method (ii). 1,4-Hydroquinone (0.22 g, 2 mmol) and **1a** (0.27 g, 2 mmol) were ground together in a mortar, transferred to a small flask and heated with stirring at 165–170 °C for 15 h. The dark, glassy product was ground in a mortar, heated under reflux with ethanol (20 ml) and filtered. The dark solid was triturated with acetone (10 ml) and diethyl ether (10 ml) to yield 0.23 g (85%) of **5**, m.p. > 280 °C. The IR spectrum was the same as for compound **5** obtained by method (i).

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