Some chemistry of 4,5-dichloro-1,2,3-dithiazolium chloride and its derivatives

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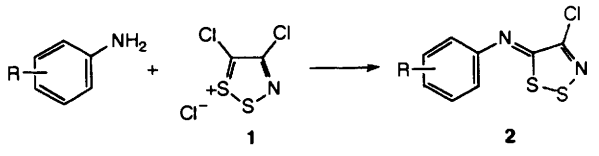
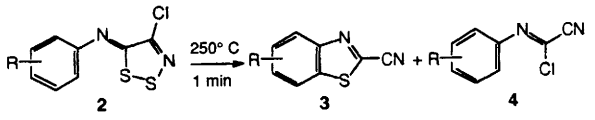
4,5-Dichloro-1,2,3-dithiazolium chloride **1** reacts with fluoroanilines (see Table 1) to give the iminodithiazoles **5** in very high yield. Thermolysis of the latter gave the corresponding 2-cyanobenzothiazoles **6** together, in some cases, with the cyanoimidoyl chlorides **7**. This reaction sequence provides modest yields of 2-cyanobenzothiazoles from the corresponding aniline, in two steps. Treatment of the iminodithiazoles with *m*-chloroperbenzoic acid in dichloromethane at or below room temperature opened the heterocyclic ring to give the *N*-arylcyanothioformamides (*e.g.* **8** ⟶ **10**), except for the *p*-nitrophenyl compound which gave *p*-nitrophenyl isothiocyanate **14** in high yield.

4,5-Dichloro-1,2,3-dithiazolium chloride **1**, which is readily prepared from chloroacetonitrile and disulfur dichloride, reacts rapidly with anilines in the presence of pyridine to give very stable, pale yellow to orange, *N*-arylimines **2**.[1,2]



1 **2**

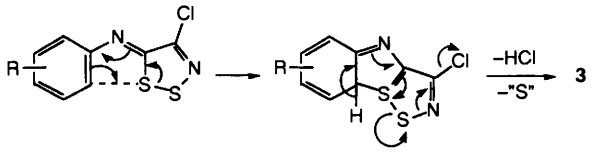
Previous work also showed that imino compounds **2** cyclised when vigorously heated to give sulfur, hydrogen chloride and 2-cyanobenzothiazoles **3**.[2] An electron-releasing group (R = *m*-OMe) favoured formation of the benzothiazole **3** whilst a strongly electron-withdrawing group (R = *m*- or *p*-NO_2) reduced the yield of **3** dramatically, in favour of the cyanoimidoyl chloride **4**, which became the major product.[2]



2 **3** **4**

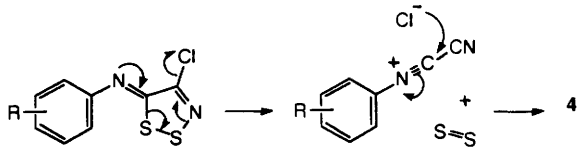
We have now explored further this new method for converting anilines into 2-cyanobenzothiazoles and cyanoimidoyl chlorides in two simple steps, with particular reference to fluoroanilines.

The benzothiazoles **3** could, presumably, be formed by an electrocyclisation and fragmentation process, as shown in Scheme 1. The sulfur atom is presumably not extruded as such



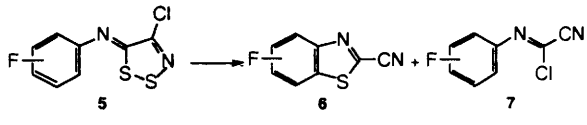
Scheme 1

but in some bimolecular process, possibly involving the nitrile sulfide. Imidoyl chloride formation involves the loss of both sulfur atoms and this could possibly occur by their direct loss as S_2 to form the nitrilium chloride shown (Scheme 2) which collapses to the observed product.



Scheme 2

Apart from the inherent interest of fluorinated derivatives of compounds **3** and **4**, it was felt that fluoro substituents, being small and electron-withdrawing, would throw light on the factors controlling the alternative pathways of Schemes 1 and 2. The monofluoroanilines and 2,4- and 3,4-difluoroanilines all reacted cleanly with 4,5-dichloro-1,2,3-dithiazolium chloride **1** (1 equiv.) in dichloromethane at room temperature for 2 h, followed by addition of pyridine (2 equiv.), to give the appropriate iminodithiazole, **5a–e**, in very high yield (Table 1). These products when heated neat at 250 °C for 1 min gave black, messy reactions which were even more complex when conducted in a solvent. However all resulted in cyclisation to the corresponding 2-cyanobenzothiazole **6a–f**, usually in modest yield, whilst three (**5c, d, e**) also gave some imidoyl chloride, **7**. With **5e** both possible benzothiazoles (**6e** and **6f**) were formed together with a comparable amount of the imidoyl chloride **7e** (Table 1). In general, the fluorines appear not to be sufficiently electron-withdrawing for the imidoyl chlorides to become dominant, and this simple reaction sequence still provides an acceptable route to fluorinated 2-cyanobenzothiazoles.



5 **6** **7**

m-Chloroperbenzoic acid reactions

In view of the high temperature required for rearrangement of the iminodithiazoles **5** into benzothiazoles **6** and imidoyl chlorides **7**, we decided to attempt S-oxidation of the dithiazole ring in the expectation that the less aromatic system so formed would decompose at a lower temperature.

N-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-4-methoxyaniline **8**[2] was treated with *m*-chloroperbenzoic acid (1.1 equiv.) in dichloromethane at −20 °C and at room temperature; the

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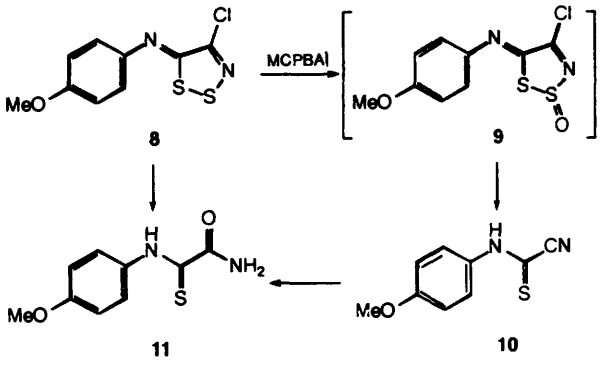
Table 1 Preparation and thermolysis of the iminodithiazoles **5**

Preparation			*Thermolysis*	
Starting amine	Product	Yield of product (%)	Products	Yield of products (%)
2-Fluoroaniline	**5a**	98	**6a**:**7a**	50:0
3-Fluoroaniline	**5b**	99	**6b**[a]:**7b**	34:0
4-Fluoroaniline	**5c**	92	**6c**:**7c**	34:10
2,4-Difluoroaniline	**5d**	90	**6d**:**7d**	11:2
3,4-Difluoroaniline	**5e**	91	**6e**[b]:**6f**[c]:**7e**	22:3:20

[a] 5-Fluorobenzothiazole-2-carbonitrile. [b] 5,6-Difluorobenzothiazole-2-carbonitrile. [c] 6,7-Difluorobenzothiazole-2-carbonitrile.



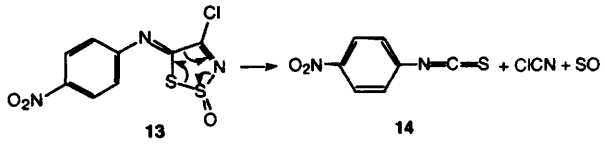
product isolated after chromatography proved to be *N*-(4-methoxyphenyl)cyanothioformamide **10**, in yields of 32 and 65% respectively. By analogy with the same oxidation of a similar iminodithiazole where the $S_{(2)}$-oxide was isolated,[3] we assume that the oxide **9** was formed but was readily hydrolysed on work-up to give the ring-opened product **10**. Similar oxidation of **8**, but with excess of *m*-chloroperbenzoic acid (3 equiv.) in refluxing dichloromethane gave the thioamide derivative **11** (72%), presumably by oxidative hydration of the cyano group in **10**. In a separate experiment, compound **10** was shown to be converted into **11** (80%) by treatment with *m*-chloroperbenzoic acid (2 equiv.) in refluxing dichloromethane. This efficient oxidative hydration of the cyano group of the cyanothioformamide **10**, without oxidation of the thioamide group, is worthy of further investigation.

The 2-fluoro- **5a** and 4-fluoro-phenyl iminodithiazoles **5c** were similarly treated with *m*-chloroperbenzoic acid to give the corresponding cyanothioformamides in 59 and 37% yields, respectively. It was also shown, though by TLC evidence only, that all of the cyanothioformamides made in this work could be reconverted into the starting iminodithiazoles by treatment with sulfur dichloride in dichloromethane at room temperature[4] [eqn. (1)].

12a, b **5a, b**

a, Ar = 2-fluorophenyl; **b**, Ar = 4-fluorophenyl

Replacement of the methoxy group in **8** by a nitro group led to a very different, and unexpected, product on similar oxidation with *m*-chloroperbenzoic acid (1.1 equiv.) in dichloromethane at room temperature. *p*-Nitrophenyl isothiocyanate **14** was formed very cleanly (90%). Possibly the S-oxide **13** was formed, as before (*cf.* ref. 3), followed rapidly by fragmentation as shown.



Experimental

Mps were determined using a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer 1710 instrument. ^{1}H NMR spectra were recorded on a JEOL GSX 270 spectrometer. ^{13}C NMR spectra were recorded on a Bruker WM 250 operating at 63 MHz. *J* values in Hz. Mass spectra were recorded on a AE MS12 or a VG micromass 7070B mass spectrometer; M refers to the isotopomer with the most abundant isotopes (^{35}Cl and ^{32}S). Elemental microanalyses were carried out in the Department of Chemistry, Imperial College by the Organic Micro-Analytical Laboratory. Column chromatography was on silica gel (C60). Light petroleum refers to the fraction bp 40–60 °C.

N-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)aniline derivatives: general procedure

To a solution of the substituted aniline (2.33 mmol) in dichloromethane (10 cm^3) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (2.33 mmol). The mixture was stirred at room temperature for 2 h after which pyridine (4.66 mmol) was added to it to give a red solution. This was stirred for a further 2 h, filtered and the product isolated by flash column chromatography with light petroleum–diethyl ether (7:3) as eluent.

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-fluoroaniline 5a.** Treatment of 2-fluoroaniline (0.26 g, 2.33 mmol) with **1** (0.485 g, 2.33 mmol) and pyridine (0.387 cm^3, 4.66 mmol) in dichloromethane (10 cm^3), followed by column chromatography gave the *title compound* **5a** (0.567 g, 98%) as yellow needles, mp 69 °C (from light petroleum–dichloromethane) (Found: M$^+$, 245.9536. $C_8H_4ClFN_2S_2$ requires *M* 245.9488); ν_{max}(CCl$_4$)/cm^{-1} 1698, 1654, 1606, 1582, 1488, 1453, 1271, 1252, 1215, 1198 and 1164; δ_H(270 MHz, $CDCl_3$) 7.18–7.23 (4 H, m); *m*/*z* (240 °C) 246 (M$^+$, 38%), 185 (M$^+$ − S_2, 32), 147 (M$^+$ − [S_2, Cl], 11), 121 (M$^+$ − [S_2–N=C–Cl], 22) and 64 (S_2^+, 100).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-fluoroaniline 5b.** Treatment of 3-fluoroaniline (0.26 g, 2.33 mmol) with **1** (0.485 g, 2.33 mmol) and pyridine (0.387 cm^3, 4.66 mmol) in dichloromethane (10 cm^3), followed by column chromatography gave the *title compound* **5b** (0.570 g, 99%) as a yellow gum (Found: M$^+$, 245.9528. $C_8H_4ClFN_2S_2$ requires *M* 245.9488); ν_{max}(CCl$_4$)/cm^{-1} 1693, 1663, 1582, 1544, 1479, 1448, 1262 and 1166; δ_H(270 MHz, $CDCl_3$) 6.88–7.05 (1 H, m) and 7.37–7.46 (3 H, m); *m*/*z* (240 °C) 246 (M$^+$, 33%), 185 (M$^+$ − S_2, 31), 147 (M$^+$ − [S_2, Cl], 9), 121 (M$^+$ − [S_2–N=C–Cl], 17) and 64 (S_2^+, 100).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-4-fluoroaniline 5c.** Treatment of 4-fluoroaniline (0.26 g, 2.33 mmol) with **1** (0.485 g, 2.33 mmol) and pyridine (0.387 cm^3, 4.66 mmol) in dichloro-

methane (10 cm^3), followed by column chromatography gave the *title compound* **5c** (0.553 g, 92%) as yellow needles, mp 53 °C (from light petroleum–dichloromethane) (Found: M^+, 245.9536. $C_8H_4ClFN_2S_2$ requires *M* 245.9488); $\nu_{max}(CCl_4)/cm^{-1}$ 1694, 1664, 1606, 1588, 1498, 1464, 1289, 1232, 1210, 1161 and 1164; δ_H(270 MHz, $CDCl_3$) 7.11–7.25 (4 H, m); *m/z* (220 °C) 246 (M^+, 40%), 185 ($M^+ - S_2$, 33), 147 ($M^+ - [S_2, Cl]$, 15), 121 ($M^+ - [S_2–N=C–Cl]$, 45) and 64 (S_2^+, 100).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,4-difluoroaniline 5d.** Treatment of 2,4-difluoroaniline (0.30 g, 2.33 mmol) with **1** (0.485 g, 2.33 mmol) and pyridine (0.387 cm^3, 4.66 mmol) in dichloromethane (10 cm^3), followed by column chromatography gave the *title compound* **5d** (0.554 g, 90%) as yellow needles, mp 92 °C (from light petroleum–dichloromethane) (Found: C, 36.3; H, 1.1; N, 10.5. $C_8H_3ClF_2N_2S_2$ requires C, 36.3; H, 1.1; N, 10.6%); $\nu_{max}(CCl_4)/cm^{-1}$ 1591, 1552, 1506, 1265 and 1210; δ_H(270 MHz, $CDCl_3$) 6.93–7.01 (2 H, m) and 7.15–7.24 (1 H, m); *m/z* 264 (M^+, 24%), 203 ($M^+ - [Cl, CN]$, 21), 171 ($M^+ - [Cl, CN, S]$, 38), 139 ($M^+ - [Cl, CN, S_2]$, 27), 125 ($ClCNS_2^+$, 7) 113 ($M^+ - [Cl, CN, S_2, O]$, 24) and 64 (S_2^+, 100).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3,4-difluoroaniline 5e.** Treatment of 3,4-difluoroaniline (0.30 g, 2.33 mmol) with **1** (0.485 g, 2.33 mmol) and pyridine (0.387 cm^3, 4.66 mmol), followed by column chromatography gave the *title compound* **5e** (0.530 g, 91%) as yellow needles, mp 55 °C (from light petroleum–dichloromethane) (Found: C, 36.1; H, 1.0; N, 10.5. $C_8H_3ClF_2N_2S_2$ requires C, 36.3; H, 1.1; N, 10.6); $\nu_{max}(CCl_4)/cm^{-1}$ 1591, 1552, 1506, 1425, 1294, 1265 and 1210; δ_H(270 MHz, $CDCl_3$) 6.96–7.30 (3 H, m); *m/z* 264 (M^+, 30%), 203 ($M^+ - [Cl, CN]$, 20), 171 ($M^+ - [Cl, CN, S]$, 23), 139 ($M^+ - [Cl, CN, S_2]$, 17), 125 ($ClCNS_2^+$, 10), 113 ($M^+ - [Cl, CN, S_2, O]$, 34) and 64 (S_2^+, 100).

Benzothiazole-2-carbonitrile derivatives: general procedure

N-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)anilines were heated under nitrogen at 250 °C for 1 min. The product was isolated by flash column chromatography. Light petroleum–diethyl ether eluted sulfur and then the following products.

4-Fluorobenzothiazole-2-carbonitrile 6a. Thermolysis of **5a** (0.1 g, 0.406 mmol) and purification by column chromatography with light petroleum–diethyl ether (6:4) as eluent afforded the *title compound* **6a** (0.036 g, 50%) as pale yellow needles, mp 114 °C (from light petroleum–dichloromethane) (Found: M^+, 178.0008. $C_8H_3FN_2S$ requires M, 178.0001); $\nu_{max}(CCl_4)/cm^{-1}$ 2235 (CN), 1624, 1599, 1562, 1474, 1445, 1325, 1310, 1276 and 1253; δ_H(270 MHz, $CDCl_3$) 7.35 (1 H, ddd, *J* 0.98, 7.99, 9.02), 7.62 (1 H, dd, *J* 4.64, 8.15) and 7.76 (1 H, d, *J* 8.30); *m/z* (220 °C) 178 (M^+, 100) and 126 ($M^+ - [N=C–CN]$, 20).

5-Fluorobenzothiazole-2-carbonitrile 6b. Thermolysis of **5b** (0.1 g, 0.406 mmol) and purification by column chromatography with light petroleum–diethyl ether (6:4) as eluent afforded the *title compound* **6b** (0.024 g, 34%) as pale yellow needles, mp 110 °C (from light petroleum–dichloromethane) (Found: M^+, 178.0013. $C_8H_3FN_2S$ requires *M*, 178.0001); $\nu_{max}(CCl_4)/cm^{-1}$ 2233 (CN), 1611, 1585, 1559, 1472, 1320, 1247 and 1204; δ_H(270 MHz, $CDCl_3$) 7.42 (1 H, dt, *J* 2.44, 8.55) and 7.82–7.97 (2 H, m); *m/z* (220 °C) 178 (M^+, 100) and 126 ($M^+ - [N=C–CN]$, 40).

6-Fluorobenzothiazole-2-carbonitrile 6c. Thermolysis of **5c** (0.1 g, 0.406 mmol) and purification by column chromatography with light petroleum–diethyl ether (8:2) as eluent afforded the *title compound* **6c** (0.024 g, 34%) as pale yellow needles, mp 112 °C (from light petroleum–dichloromethane) (Found: M^+, 178.0008. $C_8H_3FN_2S$ requires M, 178.0001); $\nu_{max}(CCl_4)/cm^{-1}$ 2233 (CN), 1624, 1599, 1562, 1473, 1445, 1412, 1325, 1310, 1276 and 1253; δ_H(270 MHz, $CDCl_3$) 7.41 (1 H, dt, *J* 2.69, 8.89), 7.66 (1 H, dd, *J* 2.57, 7.68) and 8.20 (1 H, q, *J* 4.50); *m/z* (220 °C) 178 (M^+, 100) and 126 ($M^+ - [N=C–CN]$, 35) and *N*-chlorocyanomethylidene-4-fluoroaniline **7c** (0.008 g, 10%) as a colourless oil; $\nu_{max}(CCl_4)/cm^{-1}$ 2241, 1578, 1510, 1430 and 1294; δ_H(270 MHz, $CDCl_3$) 7.12–7.18 (2 H, m) and 7.25–7.32 (2 H, m).

4,6-Difluorobenzothiazole-2-carbonitrile 6d. Thermolysis of **5d** (0.1 g, 0.406 mmol) followed by column chromatography with light petroleum–diethyl ether (8:2) as eluent afforded the *title compound* **6d** (0.012 g, 11%) as pale yellow needles, mp 154 °C (from light petroleum–dichloromethane); $\nu_{max}(CCl_4)/cm^{-1}$ 2238 (CN), 1580, 1498, 1445, 1422, 1298 and 1266; δ_H(270 MHz, $CDCl_3$) 7.20 (1 H, dt, *J* 2.32, 6.94) and 7.49 (1 H, dd, *J* 1.22, 7.34); *m/z* (240 °C) 196 (M^+, 100) and 144 ($M^+ - [N=C–CN]$, 26) and *N*-chlorocyanomethylidene-2,4-difluoroaniline **7d** as a colourless oil (0.004 g, 2%); $\nu_{max}(CCl_4)/cm^{-1}$ 2243, 1647, 1606, 1578, 1510, 1429, 1294, 1259 and 1210; *m/z* (220 °C) 200 (M^+, 26), 165 (M^+ – Cl, 77) and 113 ($M^+ - [N=C–CN, Cl]$, 100).

5,6-Difluorobenzothiazole-2-carbonitrile 6e. Thermolysis of **5e** (0.1 g, 0.406 mmol) and purification by column chromatography with light petroleum–diethyl ether (8:2) as eluent afforded the *title compound* **6e** (0.048 g, 22%) as pale yellow needles, mp 124 °C (from light petroleum–dichloromethane) (Found: M^+, 195.9929. $C_8H_2F_2N_2S$ requires *M*, 195.9906); $\nu_{max}(CCl_4)/cm^{-1}$ 2237 (CN), 1570, 1489, 1454, 1422, 1299, 1266 and 1212; δ_H(270 MHz, $CDCl_3$) 7.35–7.81 (1 H, m) and 8.01–8.05 (1 H, m); *m/z* (220 °C) 196 (M^+, 100) and 144 ($M^+ - [N=C–CN]$, 33), 6,7-difluorobenzothiazole-2-carbonitrile **6f** (0.005 g, 3%) as a pale yellow solid, mp 86 °C (from light petroleum–dichloromethane) (Found: M^+, 195.9922. $C_8H_2F_2N_2S$ requires *M*, 195.9906); $\nu_{max}(CCl_4)/cm^{-1}$ 2237 (CN), 1579, 1500, 1426, 1291 and 1266; δ_H(270 MHz, $CDCl_3$) 6.94–7.01 (1 H, m) and 7.18–7.27 (1 H, m); *m/z* (220 °C) 196 (M^+, 100), 144 ($M^+ - [N=C–CN]$, 48), and *N*-chlorocyanomethylidene-3,4-difluoroaniline **7e** (0.045 g, 20%) as a colourless oil; $\nu_{max}(CCl_4)/cm^{-1}$ 2243, 1647, 1606, 1578, 1510, 1429, 1294, 1259 and 1213; δ_H(270 MHz, $CDCl_3$) 6.94–7.02 (1 H, m), 7.13–7.27 (1 H, m) and 7.47–7.52 (1 H, m); *m/z* (220 °C) 200 (M^+, 26), 165 (M^+ – Cl, 77) and 113 ($M^+ - [N=C–CN, Cl]$, 100).

***N*-(4-Methoxyphenyl)cyanothioformamide 10.** To a cooled (0 °C) solution of the iminodithiazole **8** (0.1 g, 0.39 mmol) in dichloromethane (10 cm^3) was added *m*-chloroperbenzoic acid (0.075 g, 0.43 mmol). The mixture was stirred at 0 °C for 3 h then warmed to room temperature for 15 h. Purification by column chromatography with light petroleum–diethyl ether (7:3) as eluent afforded the *title compound* **10** as an orange solid (0.06 g, 81%), mp 112 °C (from light petroleum–dichloromethane) (Found: M^+, 192.0378. $C_9H_8N_2OS$ requires M, 192.0357); $\nu_{max}(CCl_4)/cm^{-1}$ 2229 (CN), 1608, 1510, 1462, 1441, 1427, 1305 and 1255; δ_H(270 MHz, $CDCl_3$) 3.85 (3 H, s, OCH_3) 6.88–7.01 (2 H, m), 7.31 (1 H, t, *J* 7.40), 7.73 (1 H, d, *J* 7.40) and 9.40 (1 H, s, NH); *m/z* 192 (M^+, 21%), 165 ($M^+ - [CN, H]$, 100), 150 ($M^+ - [CN, H, Me]$, 70) and 122 ($M^+ - [S=C–CN]$, 51).

***N*-Carbamoylthiocarbonyl-4-methoxyaniline 11.** To a solution of the iminodithiazole **8** (0.1 g, 0.39 mmol) in dichloromethane (10 cm^3) was added *m*-chloroperbenzoic acid (0.2 g, 1.16 mmol). The mixture was stirred at reflux for 15 h after which purification by column chromatography with light petroleum–diethyl ether (8:2) as eluent afforded the *title compound* **11** as a yellow solid (0.042 g, 72%), mp 186 °C (from light petroleum–dichloromethane) (Found: M^+, 210.0481. $C_9H_{10}N_2O_2S$ requires M, 210.0462); $\nu_{max}(CCl_4)/cm^{-1}$ 1623, 1601, 1588, 1517, 1446, 1395, 1343, 1312 and 1277; δ_H(270 MHz, $CDCl_3$) 3.95 (3 H, s, OCH_3), 7.13 (2 H, d, *J* 9.04), 7.19 (1 H, s, NH), 8.21 (2 H, d, *J* 9.04) and 8.28 (2 H, s, NH_2); *m/z* 210 (M^+, 98%), 166 ($M^+ - [CONH_2]$, 100), 135 ($M^+ - [CONH_2, OMe]$, 9) and 118 ($M^+ - [CONH_2, S]$, 4).

N-(Fluorophenyl)cyanothioformamides: general procedure
To a cooled (0 °C) solution of the iminodithiazoles **5a** and **5c** (0.1 g, 0.405 mmol) in dichloromethane (10 cm^3) was added *m*-chloroperbenzoic acid (0.07 g, 0.405 mmol). The mixture was stirred at 0 °C for 30 min then allowed to warm to room temperature over 15 h. Column chromatography with light petroleum–diethyl ether (6:4) as eluent afforded the following compounds.

***N*-(2-Fluorophenyl)cyanothioformamide 12a.** An orange solid (0.043 g, 59%), mp 81 °C (from light petroleum–dichloromethane) (Found: C, 53.0; H, 2.9; N, 15.5. $C_8H_5FN_2S$ requires C, 53.3; H, 2.8; N, 15.5); $\nu_{max}(CCl_4)/cm^{-1}$ 2306 (CN), 1710, 1599, 1521, 1505, 1487, 1461, 1422, 1383, 1266 and 1110; δ_H(270 MHz, $CDCl_3$) 7.18–7.45 (2 H, m), 7.67 (1 H, t, *J* 8.19), 8.50 (1 H, t, *J* 8.19) and 9.34 (1 H, s, NH); *m/z* (200 °C) 180 (M^+, 6%), 153 (M^+ − [CN, H], 100) and 95 (M^+ − [HN–C(S)–CN], 31).

***N*-(4-Fluorophenyl)cyanothioformamide 12b.** An orange solid (0.027 g, 37%), mp 97 °C (from light petroleum–dichloromethane) (Found: C, 53.0; H, 2.9; N, 15.6. $C_8H_5FN_2S$ requires C, 53.3; H, 2.8; N, 15.5); $\nu_{max}(CCl_4)/cm^{-1}$ 2306 (CN), 1606, 1510, 1422, 1386 and 1113; δ_H(270 MHz, $CDCl_3$) 7.11–7.21 (2 H, m), 7.31–7.41 (1 H, m), 7.84–7.99 (1 H, m) and 9.36 (1 H, s, NH); *m/z* (200 °C) 180 (M^+, 6%), 153 (M^+ − [CN, H], 100) and 95 (M^+ − [HN–C(S)–CN], 65).

4-Nitrophenyl isothiocyanate 14
To a cooled (0 °C) solution of *N*-(4-chloro-5*H*-1,2,3-dithiazole-5-ylidene-4-nitroaniline[2] (0.1 g, 0.37 mmol) in dichloromethane (10 cm^3) was added *m*-chloroperbenzoic acid (0.069 g, 0.4 mmol). The mixture was stirred at 0 °C for 30 min then allowed to warm to room temperature over 15 h. Purification by column chromatography with light petroleum–diethyl ether (6:4) as eluent afforded the title compound **14** (0.064 g, 90%) as an orange solid, mp 118 °C (from light petroleum–dichloromethane) (lit.,[5] mp 112–113 °C); $\nu_{max}(CCl_4)/cm^{-1}$ 1618, 1596, 1559, 1519, 1422, 1342 and 1266; δ_H(270 MHz, $CDCl_3$) 8.07 (2 H, d, *J* 4.93) and 8.33 (2 H, d, *J* 4.75); *m/z* 180 (M^+, 94%), 164 (M^+ − O, 24), 150 (M^+ − NO, 27), 134 (M^+ − NO_2, 62), 107 (M^+ − [NCS, O], 15), 90 (M^+ − [NCS, O_2], 60) and 76 (M^+ − [NCS, NO_2], 12).

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