1,2,3-Dithiazoles and new routes to 3,1-benzoxazin-4-ones, 3,1-benzothiazin-4-ones and *N*-arylcyanothioformamides

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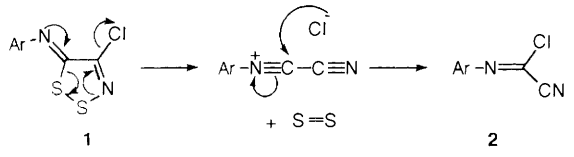
Treatment of methyl anthranilate with 4,5-dichloro-1,2,3-dithiazolium chloride **3** in dichloromethane at room temperature, followed by addition of pyridine, gave the imino derivative **7** (R = Me) as expected; anthranilic acid, however, gave 4-oxo-4*H*-3,1-benzoxazine-2-carbonitrile **5**. If triphenylphosphine was added to the reaction mixture instead of pyridine, methyl anthranilate gave methyl *N*-(cyanothioformyl)anthranilate **12** (X = *o*-CO_2Me) whilst anthranilic acid gave 4-oxo-4*H*-benzo-3,1-thiazine-2-carbonitrile **6**. These differences are explained mechanistically. When anthranilic acid was treated with the dithiazolium chloride **3** without the addition of pyridine, the delicate imino derivative **4** of the free carboxylic acid could be isolated (60%). This when heated in boiling toluene gave the benzoxazinone **5** quantitatively, and with triphenylphosphine at room temperature it gave the benzothiazinone **6** quantitatively. These reactions provide a good route to benzo substituted 2-cyanooxazinones and 2-cyanothiazinones from the corresponding anthranilic acids. With triphenylphosphine in dichloromethane at room temperature the imines **11** in general (*i.e.* without an *o*-CO_2H group) gave the corresponding *N*-arylcyanothioformamides **12** in very high yields, thus providing a good route to these compounds in two mild steps from the corresponding anilines.

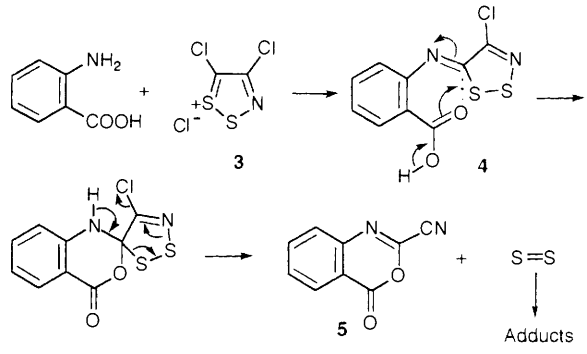
We have shown that the thermolysis (200–250 °C) of *N*-arylimino-1,2,3-dithiazoles **1** provides a new route to 2-cyanobenzothiazoles and to the cyano imidoyl chlorides **2**; formation of the latter is favoured by a *m*- or *p*-nitro group in the aryl ring.[1] This transformation requires the loss of both sulfur atoms from **1** and we assume that singlet diatomic sulfur, S_2, may indeed be formed as shown in Scheme 1. There is much



Scheme 1

interest in the generation and cycloaddition chemistry of S_2[2] and there is still a demand for a convenient precursor which would generate S_2 under mild, reagent-free conditions. We have therefore varied the structure of the aryl group in **1** in an attempt to maximise the generation of S_2, at a much lower temperature. High temperature decomposition (250 °C, 1 min) of the known imidodithiazoles[1] **1** (Ar = $C_6H_4NO_2$-4 and C_6H_4OMe-4) in anthracene was certainly of no avail, giving very low yields of 9-chloro- and 9,10-dichloro-anthracene as the only isolable products. Such high temperatures are incompatible with the useful generation and interception of S_2.

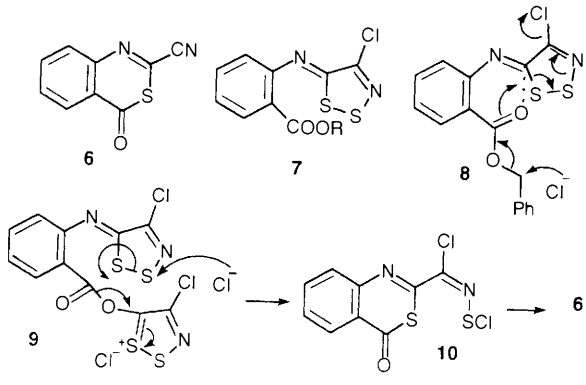
Our plan was to introduce a nucleophilic neighbouring group, such as CO_2H, into the *ortho* position of the aromatic ring, in the hope of effecting cyclisation followed by extrusion of S_2, in an aromatising reaction (Scheme 2). We first treated anthranilic acid with 4,5-dichoro-1,2,3-dithiazolium chloride **3**[3] (1 equiv.) in dichloromethane at room temperature, followed by pyridine (2 equiv.). The imine **4** was not observed but we did isolate the cyanobenzoxazinone **5** (46%) together with a very



Scheme 2

small amount (2%) of the unexpected cyanobenzothiazinone **6**.

Methyl anthranilate with the dithiazolium chloride **3** gave the expected imine **7** (R = Me) in good yield (72%). This was



thermally stable and did not cyclise under conditions used for the acid (Scheme 2) or in refluxing toluene. We therefore decided to make the corresponding benzyl ester **7** (R = CH_2Ph) which should be thermally more labile, especially in

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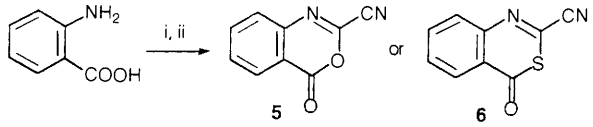
Table 1 Treatment of anthranilic acid with 4,5-dichloro-1,2,3-dithiazolium chloride **3**

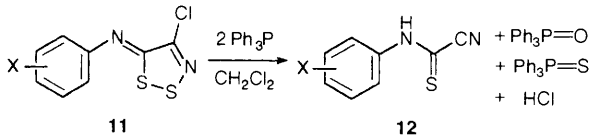


Conditions[a] (i) **3**, solvent, temp., time; (ii) added base, temp., time	Product	Yield(%) of product
(i) **3**, CH_2Cl_2, room temp., 2 h;[b] (ii) PPh_3 1 or 12 h	**6**	49
(i) **3**, CH_2Cl_2, −78 °C, 2 h; (ii) PPh_3 −78 °C, 2 h then room temp.[c]	**6**	52
(i) **3**, CH_2Cl_2, room temp., 2 h; (ii) pyridine, room temp., 2 h[d]	**5**	45
(i) **3**, CH_2Cl_2, room temp., 2 h; (ii) pyridine + PPh_3, room temp., 2 h	**6**	48
(i) **3**, CH_2Cl_2, room temp., 2 h; (ii) lutidine,[e] room temp., 2 h	**5**	18
(i) **3**, CH_2Cl_2, room temp., 2 h; (ii) TEA dropwise, room temp.	**5**	57
(i) **3**, CH_2Cl_2, room temp., 2 h; (ii) TEA + PPh_3, room temp., 2 h	—	—
(i) PPh_3, CH_2Cl_2, room temp., 1 h; (ii) **3**, room temp., 2 h	**6**	5
(i) **3**, CH_2Cl_2, room temp., 2 h; (ii) HB[f] room temp., 2 h	**5**	43
(i) **3**, CH_2Cl_2, room temp., 2 h; (ii) DBU[g,i] room temp., 2 h	**5**	70
(i) **3**, CH_2Cl_2, −78 °C or −30 °C or 0 °C or room temp., 2 h	—	—
(i) **3**, CH_2Cl_2, room temp., 2 h; (ii) PPh_3, room temp., 2 h[j]	**6**	69
(i) **3**, CH_2Cl_2, room temp., 2 h; (ii) pyridine, room temp., 2 h[j]	—	—
(i) PPh_3, CH_2Cl_2, −78 °C, 2 h; (ii) **3**, −78 °C, room temp.[j]	**6**	17

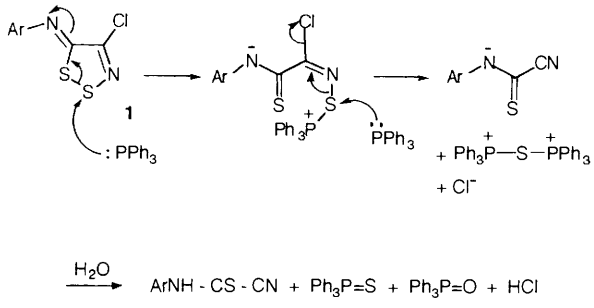
[a] Unless indicated otherwise the ratios are anthranilic acid (1 equiv.), **3** (1 equiv.), CH_2Cl_2 (10 ml), base (2 equiv.). [b] Same results after 12 or 20 h; when anthranilic acid was added slowly to a solution of **3** in DCM followed by addition of PPh_3, the yield of **5** became 60%. [c] If the reaction mixture was warmed to room temp. before addition of PPh_3, the yield became 51%. [d] When pyridine was added dropwise (1 h) the yield of **5** fell to 23%. [e] 1 or 2 Equiv. [f] HB: Hünig's base; 1 or 2 equiv. [g] 1 Equiv. added dropwise (1 or 3 h) or at one time; when DBU was added dropwise during 10 h the yields of **5** and **6** were respectively 47 and 11%. [h] When 1.5 or 2 equiv. of DBU were added in 1 h, the yield of **5** fell to 52 and 58%. [i] When a mixture of anthranilic acid and DBU in DCM was added dropwise to a solution of **3** in DCM the yields of **5** and **6** were 41 and 10% respectively. [j] Anthranilic acid (2 equiv.).

the presence of added chloride ions (*cf.* **8**). We attempted to make this ester by applying Weinreb's procedure[4] for activating carboxylic acids towards esterification with the dithiazolium chloride **3**, by treating anthranilic acid with **3** (2 equiv.) followed, after imine formation, by the addition of benzyl alcohol. In spite of using various reaction conditions, from −78 °C to room temperature, with pyridine or 2,6-dimethylpyridine as base, we did not obtain the ester but only minor amounts of the benzothiazinone **6** (9%). Possibly the activated derivative **9** of the imino anthranilic acid was formed but underwent an intramolecular reaction (arrows in **9**) rather than displacement by benzyl alcohol. This would give the intermediate **10** which could lose sulfur dichloride to give the observed cyanide **6**.[5] With this participation by sulfur in mind we added the strongly thiophilic nucleophile, triphenylphosphine, to the reaction mixture obtained from anthranilic acid and the dithiazolium salt **3**, and this did indeed give the benzothiazinone **6** in much better yield (49%). A mechanism for this transformation is proposed later, in the light of further evidence. First, we optimised the yield (to 69%) of the thiazinone **6** formed from anthranilic acid, the dithiazolium salt **3** and triphenylphosphine (see Table 1).

To investigate the mechanism of this process we treated some other *N*-aryliminodithiazoles **11** [X = 3,4-$(OMe)_2$, 2-CO_2Me] with triphenylphosphine (2 equiv.) in (undried) dichloromethane at room temperature. In each case we obtained the readily isolated *N*-arylcyanothioformamide **12** in good yield, together with 1 equivalent each of triphenylphosphine oxide and triphenylphosphine sulfide. The reactions proceeded rapidly and cleanly and thus provide a good route to the cyanothioformanilides **12**, in two steps from the corresponding aniline.



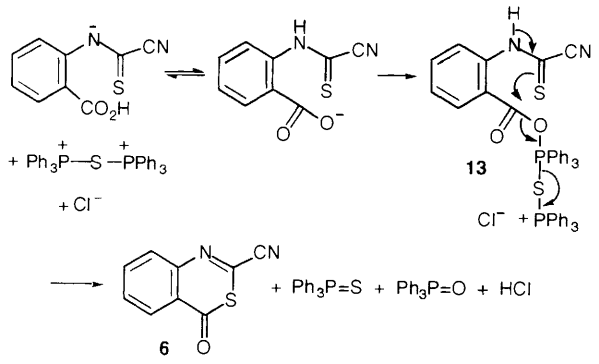
It is striking that the *o*-methoxycarbonyl compound **7** (R = Me) gave the corresponding cyanothioformamide (51%) with triphenylphosphine whilst the carboxylic acid **7** (R = H), generated *in situ* from anthranilic acid and the dithiazolium salt **3**, gave only the cyclised product **6** in similar yield. We explain this on the basis of the mechanisms shown in Schemes 3 and 4.



Scheme 3

Initial attack by phosphorus on S-2 of the 1,2,3-dithiazole **1** will open the ring with formation of the thioamide anion. Attack by a second triphenylphosphine on the same sulfur results in formation of the stabilised cyanothioformamide anion and Ph_3P^+-S-P^+Ph_3, hydrolysis of which during work-up would give the observed products (Scheme 3). In exactly the same way the imine bearing the carboxylic acid **7** (R = H) would give the ionic species, shown in Scheme 4, which could collapse to **13** in which the carboxylic acid is activated by the phosphonium salt; this then acts as a good leaving group to give all the observed products. The pathway of Scheme 4 is not, of course, available to the ester **7** (R = Me).

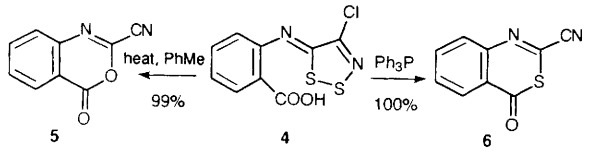
It would clearly be desirable to isolate and characterise the imino carboxylic acid **4** postulated above as an intermediate; this proved possible when, in the reaction between anthranilic



Scheme 4

acid and dithiazolium salt **3**, the subsequent addition of pyridine was omitted. Anthranilic acid was able to act as the required base and extra equivalents of it were beneficial. Thus, treatment of anthranilic acid (4 equiv.) with the dithiazolium salt **3** in dichloromethane at room temperature for 2 h gave the desired carboxylic acid **4** in 60% yield; the yields were 52 and 22%, respectively, with 3 and 5 equivalents of anthranilic acid. The acid **4** is a yellow solid, mp 128 °C with decomposition; it is slightly unstable to storage at room temperature, but it keeps well when dry at 4 °C in the dark under argon. On recrystallisation, and more rapidly on melting, some benzoxazinone **5** is always produced

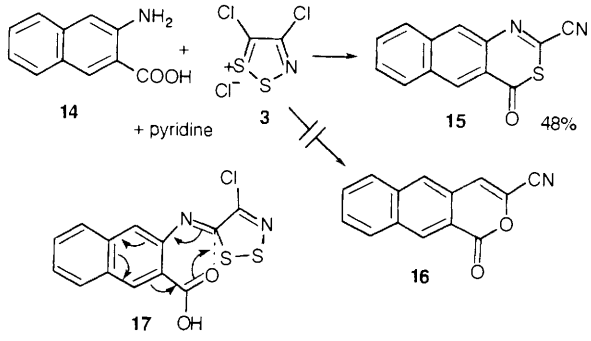
With the free acid **4** available we were now able to test its reaction with triphenylphosphine; indeed, with this reagent in dichloromethane at room temperature for 1 h, the benzothiazinone **6** was formed quantitatively, together with triphenylphosphine oxide and sulfide in 90–95% yield after chromatography. This provides strong support for the mechanisms proposed in Schemes 3 and 4, and enhances the synthetic value of this conversion of anthranilic acid into the benzothiazinone **6**. In contrast. treatment of the acid **4** with pyridine (2 equiv.) gave the alternative cyclisation product, the benzoxazinone **5**, in much lower yield (50%). However, simply heating the acid **4** in toluene gave the benzoxazinone **5** in virtually quantitative yield; **4** would thus appear to be a new attractive precursor for disulfur (see Scheme 2), and this will be reported on later.



We briefly explored the extension of these anthranilic acid reactions to substituted derivatives. 4-Chloro- and 4,5-dimethoxy- anthranilic acid and 3-amino-2-naphthoic acid **14** with the dithiazolium salt **3** without additional base, as described above, all gave the corresponding imino carboxylic acid in 85, 53, and 72% yield, respectively; the dimethoxy compound was noticeably less stable than the others. When heated in toluene the chloro and dimethoxy compounds gave the corresponding benzoxazinone (30 and 95%, respectively) and, with triphenylphosphine, the corresponding benzothiazinone (42 and 49% respectively). The benzothiazinones could be made more simply and in better yield in a one-pot procedure, without isolation of the imino carboxylic acid.

The synthesis, chemistry and biological activity of 3,1-benzoxazin-4-ones and 3,1-benzothiazin-4-ones have been moderately well studied.[6] They continue to be of interest, for example as potent alternate substrate inhibitors of human leukocyte elastase.[7] Both ring systems have been made from anthranilic acids, by acylation or thioacylation followed by cyclodehydration.[8] Functional substituents in the 2-position are rather less common and 2-cyano groups are rare, though 2-cyano-3,1-benzoxazin-4-one itself was recently synthesised by the reaction of *o*-isocyanatobenzoyl chloride with cyanotrimethylsilane.[9] Cyano-3,1-benzothiazin-4-ones have not hitherto been reported.

Somewhat surprisingly the imino naphthoic acid derivative, when heated in toluene or on treatment with pyridine at room temperature, gave complex mixtures and with triphenylphosphine the corresponding naphthothiazinone **15** was formed in only 24% yield. Furthermore, when 3-amino-2-naphthoic acid **14** was treated with the dithiazolium salt **3** and pyridine in the standard way it gave the thiazinone **15** (48%) with none of the usual oxazinone **16**. These results suggest that the first step in



the formation of the oxazinone from the imine (*cf.* Scheme 2) is an electrocyclic process (or one with a significant electrocyclic component). This process (arrows in **17**) would then have a very high activation energy, as with all electrocyclic reactions involving the naphthalene 2,3-bond, and thiazinone formation (as in Schemes 3 and 4) would supervene.

Finally, we confirmed the utility of the two-step process for the conversion of anilines into cyanothioformanilides **12**, *via* the imines **11**, with three other examples. We treated 3,4-dimethoxyaniline, 2-cyano-4,5-dimethoxyaniline and methyl 2-amino-4,5-dimethoxybenzoate with the dithiazolium chloride **3** in dichloromethane at room temperature in the standard way to give the imines **11** [X = 3,4-$(MeO)_2$; 2-CN-4,5-$(MeO)_2$; 2-CO_2Me-4,5-$(MeO)_2$] in 47, 76 and 78% yield, respectively. With triphenylphosphine (2 equiv.) in moist dichloromethane at room temperature for 3 h, these gave the corresponding cyanothioformanilides **12** in 98, 76 and 93%, respectively.

Experimental

Mps were determined using a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer 1710 or Perkin-Elmer Paragon 1000PC instruments. ^{1}H NMR spectra were recorded on JEOL GSX 270 or Bruker AM300WB spectrometers. ^{13}C NMR spectra were recorded on a Bruker WM 250 operating at 63 MHz; *J* values are given in Hz. Mass spectra were recorded on a VG micromass 7070E or a VG Autospec 'Q' 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)anthranilic acid derivatives 1

General procedure. To a solution of the anthranilic or naphthoic acid derivative in dichloromethane was added 4,5-

dichloro-1,2,3-dithiazolium chloride **3**. The mixture was stirred at room temperature for 2 h after which the crude product was purified by flash column chromatography.

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)anthranilic acid 4.** Treatment of anthranilic acid (1.37 g, 10 mmol) with the dithiazolium salt **3** (0.520 g, 2.5 mmol) and then column chromatography (dichloromethane) gave the *title compound* **4** (0.40 g, 60%) as a yellow powder, mp 128 °C (Found: C, 39.65; H, 2.05; N, 10.15. $C_9H_5ClN_2O_2S_2$ requires C, 39.65; H, 1.85; N, 10.3%); $\nu_{max}(CCl_4)/cm^{-1}$ 1685 (CO), 1588, 1571, 1540, 1500, 1472, 1455, 1434, 1294 and 1266; δ_H(270 MHz, $CDCl_3$) 7.47–7.52 (1 H, m), 7.71–7.52 (2 H, m) and 8.47 (1 H, m); *m/z* 272 (M^+, 13%), 256 (M^+ − O, 47), 239 (M^+ − [O, OH]), 172 (M^+ − [O, OH, Cl, S], 81), 164 (M^+ − [O, OH, S–N=C − Cl], 100) and 90 (M^+ − [COOH, $CCNS_2Cl$], 37).

3-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylideneamino)-2-naphthoic acid 17. Treatment of 3-amino-2-naphthoic acid (0.738 g, 4 mmol) with the dithiazolium salt **3** (0.208 g, 1 mmol), in dichloromethane–tetrahydrofuran (1:1) and then column chromatography (dichloromethane) gave the *title compound* (0.232 g, 72%) as orange needles, mp 150 °C (Found: C, 48.55; H, 2.25; N, 8.45. $C_{13}H_7ClN_2O_2S_2$ requires C, 48.35; H, 2.2; N, 8.7%); $\nu_{max}(CCl_4)/cm^{-1}$ 2306, 1742 (CO), 1625, 1587, 1548, 1494, 1445, 1417, 1266 and 1208; δ_H(270 MHz, $CDCl_3$) 7.61–7.70 (2 H, m), 7.91 (2 H, m), 8.00 (1 H, d, *J* 4.63), 8.08 (1 H, s) and 9.03 (1 H, s); *m/z* 322 (M^+, 12%), 289 (M^+ − [O, OH], 3), 256 (M^+ − [O, OH, S], 28), 222 (M^+ − [O, OH, S, Cl], 100), 196 (M^+ − [O, OH, S–N=C − Cl], 51) and 140 (M^+ − [COOH, $CCNS_2Cl$], 35).

4-Oxo-4*H*-3,1-benzoxazine-2-carbonitrile derivatives (*e.g.* 5)

General procedure. A solution of the *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-anthranilic or -naphthoic acid derivative in toluene (5 cm^3) was heated at reflux for 2 h after which the solvent was removed by evaporation and the crude product purified by flash chromatography to give the title compounds.

4-Oxo-4*H*-3,1-benzoxazine-2-carbonitrile 5. The imine **4** (0.025 g, 0.095 mmol) was heated in toluene after which column chromatography (light petroleum–dichloromethane, 6:4) gave the title compound **5** (0.016 g, 99%) as needles, mp 125 °C (lit.,[9] mp 125–126 °C) (from light petroleum–dichloromethane) (Found: C, 62.8; H, 2.15; N, 16.3. Calc. for $C_9H_4N_2O_2$: C, 62.8; H, 2.3; N, 16.3%); $\nu_{max}(CCl_4)/cm^{-1}$ 2250 (CN) 1791, 1772 (CO), 1625, 1601, 1475, 1467, 1422, 1266 and 1203; δ_H(270 MHz, $CDCl_3$) 7.70–7.78 (2 H, m), 7.92–7.99 (1 H, m) and 8.29 (1 H, dd, *J* 6.58, 7.81); δ_C(63 MHz, $CDCl_3$) 110.08, 118.72, 128.37, 129.29, 131.73, 134.66, 137.44, 144.36 and 155.83; *m/z* 172 (M^+, 88%), 146 (M^+ − CN, 100), 144 (M^+ − CO, 12) and 90 (M^+ − [COOC(CN)], 40).

4-Oxo-4*H*-3,1-benzothiazine-2-carbonitrile derivatives (*e.g.* 6)

General procedure. A solution of the *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)anthranilic acid derivative and PPh_3 (2 equiv.) in dichloromethane (5 cm^3) was stirred at room temperature for 30 min after which it was filtered and the product purified by flash column chromatography to give the title compounds.

4-Oxo-4*H*-3,1-benzothiazine-2-carbonitrile 6. Treatment of the imine **4** (0.272 g, 1 mmol) with PPh_3 (0.525 g, 2 mmol) followed by column chromatography (light petroleum–dichloromethane, 8:2) gave the *title compound* **6** (0.186 g, 100%) as needles, mp 122 °C (from light petroleum–dichloromethane) (Found: C, 57.45; H, 2.1; N, 14.7. $C_9H_4N_2OS$ requires C, 57.4; H, 2.15; N, 14.9%); $\nu_{max}(CCl_4)/cm^{-1}$ 2225 (CN), 1679 (CO), 1597, 1570, 1546, 1469, 1451, 1422, 1319, 1266 and 1213; δ_H(270 MHz, $CDCl_3$) 7.72–7.78 (1 H, m), 7.96 (2 H, d, *J* 3.42) and 8.30 (1 H, d, *J* 7.81); δ_C(63 MHz, $CDCl_3$) 114.09, 122.24, 125.80, 133.41, 133.49, 137.42, 137.75, 147.85 and 180.05; *m/z* 189 (M^+ + 1, 13), 188 (M^+, 100%), 187 (M^+ − 1, 34), 162 (M^+ − CN, 34), 161 (M^+ − 1, CN, 9), 160 (M^+ − CO, 80), 159 (M^+ − 1, CO, 6) and 134 (M^+ − [CO, CN], 25).

4-Oxo-4*H*-3,1-naphthothiazine-2-carbonitrile 15. Treatment of 3-amino-2-naphthoic acid (0.187 g, 1 mmol) with dithiazolium salt **3** (0.208 g, 1 mmol) and PPh_3 (0.525 g, 2 mmol) followed by column chromatography (light petroleum–dichloromethane, 5:5) gave the *title compound* (0.109 g, 48%) as pale yellow needles, mp 216 °C (from light petroleum–dichloromethane) (Found: C, 65.65; H, 2.65; N, 11.5. $C_{13}H_6N_2OS$ requires C, 65.5; H, 2.5; N, 11.75%); $\nu_{max}(CCl_4)/cm^{-1}$ 2225 (CN), 1697 (CO), 1676, 1619, 1544, 1445, 1423, 1357, 1336 and 1266; δ_H(270 MHz, $CDCl_3$) 7.71–7.81 (2 H, m), 8.11 (2 H, t, *J* 7.81), 8.46 (1 H, s) and 8.87 (1 H, s); δ_C(63 MHz, $CDCl_3$) 113.64, 116.69, 119.26, 128.10, 129.36, 129.81, 130.60, 130.89, 133.26, 133.51, 133.96, 136.78 and 142.53; *m/z* (200 °C), 238 (M^+, 100%), 210 (M^+ − CO, 68), 136 (M^+ − [CO, S, CN], 21) and 140 (M^+ − [CO, S, CCN], 42).

Methyl *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)anthranilate 7 (R = Me). Treatment of methyl anthranilate (0.302 g, 2 mmol) with the dithiazolium salt **3** (0.416 g, 2 mmol) and then pyridine (0.36 cm^3, 4 mmol) gave the *title compound* (0.406 g, 71%) as an orange oil; $\nu_{max}(CCl_4)/cm^{-1}$ 1723 (CO), 1606, 1572, 1480, 1436, 1300 and 1266; δ_H(270 MHz, $CDCl_3$) 3.83 (3 H, s, OCH_3), 7.00 (1 H, d, *J* 7.93), 7.27 (1 H, t, *J* 7.69), 7.58 (1 H, t, *J* 7.44) and 8.02 (1 H, dd, *J* 1.77, 7.93); *m/z* 286 (M^+, 17%) and 187 (M^+ − [Cl, S_2], 100).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-4,5-dimethoxyanthranilic acid 11 [X = 4,5-(OMe)$_2$-2-CO$_2$H].** Treatment of 4,5-dimethoxyanthranilic acid (1.13 g, 5.77 mmol) with the dithiazolium salt **3** (0.3 g, 1.44 mmol) followed by column chromatography (dichloromethane) gave the *title compound* (0.250 g, 53%) as orange needles, mp 132 °C; $\nu_{max}(CCl_4)/cm^{-1}$ 1759 (CO), 1597, 1514, 1503, 1423 and 1266; δ_H(270 MHz, $CDCl_3$) 4.00 (3 H, s, OMe), 4.01 (3 H, s, OMe), 7.23 (1 H, s) and 7.93 (1 H, s). On mass spectral fragmentation this compound gave the spectrum for its thermolysis product, 6,7-dimethoxy-4-oxo-4*H*-3,1-benzoxazine-2-carbonitrile (see next experiment) and S_8.

6,7-Dimethoxy-4-oxo-4*H*-3,1-benzoxazine-2-carbonitrile. The acid **11** [X = 4,5-(OMe)$_2$-2-CO$_2$H] (0.055 g, 0.165 mmol) was heated in toluene after which column chromatography (light petroleum–dichloromethane, 5:5) gave the *title compound* (0.038 g, 95%) as pale yellow needles, mp 175 °C (from light petroleum–dichloromethane) (Found: *m/z* 232.0500. $C_{11}H_8N_2O_4$ requires M^+, 232.0484); $\nu_{max}(CCl_4)/cm^{-1}$ 2245 (CN), 1777 (CO), 1599, 1514, 1423, 1381, 1305 and 1266; δ_H(270 MHz, $CDCl_3$) 4.02 (3 H, s, OMe), 4.04 (3 H, s, OMe), 7.12 (1 H, s) and 7.56 (1 H, s); *m/z* 232 (M^+, 100%), 217 (M^+ − CH_3, 49), 200 (M^+ − CN, 22), 162 (M^+ − [COO, CN], 12), 150 (M^+ − [COOC(CN)], 8), 135 (M^+ − [COOC(CN), CH_3], 11) and 120 (M^+ − [COOC(CN), $(CH_3)_2$], 5).

6,7-Dimethoxy-4-oxo-4*H*-3,1-benzothiazine-2-carbonitrile. The acid **11** [X = 4,5-(OMe)-2-CO$_2$H] (0.1 g, 0.30 mmol) was treated with PPh_3 (0.160 g, 0.60 mmol) after which column chromatography (light petroleum–dichloromethane, 6:4) gave the *title compound* (0.036 g, 49%) as pale yellow needles, mp 194 °C (from light petroleum–dichloromethane) (Found: *m/z* 248.0211. $C_{11}H_8N_2O_3S$ requires M^+, 248.0255); $\nu_{max}(CCl_4)/cm^{-1}$ 2235 (CN), 1663 (CO), 1600, 1567, 1510, 1451, 1439, 1409, 1380, 1284 and 1266; δ_H(270 MHz, $CDCl_3$) 4.04 (3 H, s, OMe), 4.06 (3 H, s, OMe), 7.35 (1 H, s) and 7.66 (1 H, s); *m/z* 248 (M^+, 100%), 232 (M^+ − O, 14), 222 (M^+ − CN, 13) and 220 (M^+ − CO, 30).

4-Chloro-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)anthranilic acid 11 (X = 5-Cl-2-CO$_2$H). 4-Chloroanthranilic acid (0.280 g, 1.64 mmol) was treated with the dithiazolium salt **3** (0.085 g, 0.41 mmol) after which column chromatography (light

petroleum–dichloromethane, 7:3) gave the *title compound* (0.107 g, 85%) as yellow needles, mp 153 °C (from light petroleum–dichloromethane); $\nu_{max}(CCl_4)/cm^{-1}$ 1463, 1378 and 1207; δ_H(270 MHz, $CDCl_3$) 7.43 (1 H, dd, *J* 1.95, 8.54), 7.68 (1 H, d, *J* 1.71) and 8.38 (1 H, d, *J* 8.54); *m/z* 306 (M^+, 65%), 273 (M^+ – [OOH], 32), 206 (M^+ – [OOH, Cl, S], 66), 180 (M^+ – [OOH, S–N=C–Cl], 100) and 124 (M^+ – [COOH, $CCNS_2Cl$], 32).

7-Chloro-4-oxo-4*H*-3,1-benzoxazine-2-carbonitrile. The acid **11** (X = 5-Cl-2-CO_2H) (0.1 g, 0.367 mmol) was heated in toluene after which column chromatography (light petroleum–dichloromethane, 6:4) gave the *title compound* (0.020 g, 30%) as colourless needles, mp 101 °C (from light petroleum–dichloromethane) (Found: *m/z* 205.9888. $C_9H_3ClN_2O_2$ requires M^+, 205.9883); $\nu_{max}(CCl_4)/cm^{-1}$ 2245 (CN), 1789 (CO), 1623, 1599, 1422, 1266 and 1243; δ_H(270 MHz, $CDCl_3$) 7.68 (1 H, dd, *J* 2.08, 8.42), 7.75 (1 H, d, *J* 1.96) and 8.20 (1 H, d, *J* 8.55); *m/z* 206 (M^+, 87%), 180 (M^+ – CN, 100) and 124 (M^+ – [COOC(CN)], 23).

7-Chloro-4-oxo-4*H*-3,1-benzothiazine-2-carbonitrile. The acid **11** (X = 5-Cl-2-CO_2H) (0.1 g, 0.367 mmol) was treated with PPh_3 (0.170 g, 0.734 mmol) after which column chromatography (light petroleum–dichloromethane, 8:2) gave the *title compound* (0.030 g, 42%) as colourless needles, mp 108 °C (from light petroleum–dichloromethane) (Found: *m/z* 221.9656. $C_9H_3ClN_2OS$ requires M^+, 221.9654); $\nu_{max}(CCl_4)/cm^{-1}$ 2235 (CN), 1683 (CO), 1592, 1532, 1422, 1311 and 1266; δ_H(270 MHz, $CDCl_3$) 7.70 (1 H, dd, *J* 2.20, 8.55), 7.96 (1 H, d, *J* 1.96) and 8.24 (1 H, d, *J* 8.54); *m/z* 222 (M^+, 100%), 196 (M^+ – CN, 68), 194 (M^+ – CO, 86), 187 (M^+ – Cl, 34) and 168 (M^+ – [CO, CN], 10).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3,4-dimethoxyaniline 11 [X = 3,4-(MeO)$_2$].** 4-Aminoveratrole (0.153 g, 1 mmol) was treated with the dithiazolium salt **3** (0.208 g, 1 mmol) and then pyridine (0.18 cm^3, 2 mmol) after which column chromatography (hexane–dichloromethane, 6:4) gave the *title compound* (0.136 g, 47%) as orange needles, mp 112 °C (from hexane–dichloromethane) (Found: *m/z* 287.9789. $C_{10}H_9ClN_2O_2S_2$ requires M^+, 287.9793); ν_{max}(KBr)/cm^{-1} 1776, 1560, 1508, 1465, 1419, 1332, 1268 and 1239; δ_H(300 MHz, $CDCl_3$) 3.91 (6 H, 2 × OMe), 6.86 (1 H, s) and 6.97 (2 H, s); *m/z* 288 (M^+, 100%), 273 (M^+ – CH_3, 49), 257 (M^+ – [CN, CH_3], 50), 195 (M^+ – [CN, Cl, S], 30), 180 (M^+ – [CN, Cl, S, CH_3]), 163 (M^+ – [CN, Cl, S_2]) and 148 (M^+ – [CN, Cl, S_2, CH_3]).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-4,5-dimethoxyanthranilonitrile 11 [X = 2-CN-4,5-(MeO)$_2$].** 2-Amino-4,5-dimethoxybenzonitrile (0.178 g, 1 mmol) was treated with dithiazolium salt **3** (0.208 g, 1 mmol) and then pyridine (0.18 cm^3, 2 mmol) after which column chromatography (dichloromethane) gave the *title compound* (0.238 g, 76%) as yellow needles, mp 164–166 °C (from hexane–dichloromethane) (Found: *m/z* 312.9745. $C_{11}H_8ClN_3O_2S_2$ requires M^+, 312.9746); ν_{max}(KBr)/cm^{-1} 2224 (CN), 1592, 1550, 1516, 1498, 1463, 1446, 1394, 1349, 1282, 1222 and 1204; δ_H(300 MHz, $CDCl_3$) 3.93 (6 H, 2 × OMe), 6.79 (1 H, s) and 7.13 (1 H, s); *m/z* 313 (M^+, 66%), 298 (M^+ – CH_3, 16), 220 (M^+ – [CN, Cl, S], 43), 205 (M^+ – [CN, Cl, S, CH_3], 25), 188 (M^+ – [CN, Cl, S_2], 100) and 173 (M^+ – [CN, Cl, S_2, CH_3], 19).

Methyl *N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-4,5-dimethoxyanthranilate 11 [X = 2-CO_2Me-4,5-(MeO)$_2$]. Methyl 2-amino-4,5-dimethoxybenzoate (0.422 g, 2 mmol) was treated the dithiazolium salt **3** (0.416 g, 2 mmol) and then pyridine (0.36 cm^3, 4 mmol) after which column chromatography (dichloromethane) gave the *title compound* (0.539 g, 78%) as yellow needles, mp 122 °C (from hexane–dichloromethane) (Found: *m/z* 345.9840. $C_{12}H_{11}ClN_2O_4S_2$ requires M^+, 345.9848); ν_{max}(KBr)/cm^{-1} 1713 (CO), 1599, 1560, 1508, 1464, 1438, 1383, 1356, 1255 and 1211; δ_H(300 MHz, $CDCl_3$) 3.82 (3 H, s, OMe), 3.91 (3 H, s, OMe), 3.94 (3 H, s, CO_2Me), 6.50 (1 H, s) and 7.55 (1 H, s); *m/z* 346 (M^+, 28%), 247 (M^+ – [CN, Cl, S_2], 100), 232 (M^+ – [Cl, S_2, CH_3], 12) and 222 (M^+ – [Cl, S_2, CN], 11).

Methyl *N*-(cyanothioformyl)anthranilate 12 (X = *o*-CO_2Me). Treatment of the imine **11** (X = *o*-CO_2Me) (0.576 g, 2 mmol) with PPh_3 (1.050 g, 4 mmol) in dichloromethane (15 cm^3) at room temperature for 3 h, followed by column chromatography (light petroleum–diethyl ether, 8:2), gave the cyclised derivative **6** (5%) and the *title compound* (0.226 g, 51%) as orange needles, mp 118 °C (from light petroleum–dichloromethane) (Found: C, 54.65; H, 3.55; N, 12.6. $C_{10}H_8N_2O_2S$ requires C, 54.5; H, 3.65; N, 12.7%); $\nu_{max}(CCl_4)/cm^{-1}$ 2225 (CN), 1697 (CO), 1591, 1531, 1453, 1439, 1381, 1315, 1297, 1280 and 1266; δ_H(270 MHz, $CDCl_3$) 4.01 (3 H, s, OCH_3), 7.36 (1 H, m), 7.65 (1 H, m), 8.17 (1 H, m) and 9.37 (1 H, m); *m/z* 220 (M^+, 6%), 193 (M^+ – CN, 66) and 162 (M^+ – [CN, S], 100).

3,4-Dimethoxy-*N*-(cyanothioformyl)aniline 12 [X = 3,4-(OMe)$_2$]. The imine **11** [X = 3,4-(OMe)$_2$] (0.1 g, 0.347 mmol) was treated with PPh_3 (0.182 g, 0.693 mmol) in dichloromethane (5 cm^3) at room temperature for 1 h, after which column chromatography (hexane–dichloromethane, 5:5) gave the *title compound* (0.075 g, 98%) as orange needles, mp 120–122 °C (from hexane–dichloromethane) (Found: *m/z* 222.0462. $C_{10}H_{10}N_2O_2S$ requires M^+, 222.0463); $\nu_{max}(CCl_4)/cm^{-1}$ 2229 (CN), 1595, 1555, 1513, 1442, 1402, 1344, 1273 and 1246; δ_H(300 MHz, $CDCl_3$) 3.88 (3 H, s, OMe), 3.94 (3 H, s, OMe), 6.82–6.91 (1 H, m), 7.16 (1 H, m), 7.53 (1 H, m) and 9.42 (1 H, s, NH); *m/z* 222 (M^+, 20%), 195 (M^+ – [CN, H], 100), 180 (M^+ – [CN, H, CH_3], 51), 152 (M^+ – [CSCN], 26), 137 (M^+ – [CSCN, CH_3], 10) and 122 (M^+ – [CSCN, 2 CH_3], 8).

***N*-(Cyanothioformyl)-4,5-dimethoxyanthranilonitrile 12 [X = 2-CN-4,5-(MeO)$_2$].** The imine **11** [*X* = 2-CN-4,5-(MeO)$_2$] (0.2 g, 0.64 mmol) was treated with PPh_3 (0.335 g, 1.28 mmol) in dichloromethane (10 cm^3) at room temperature for 2 h after which the mixture was cooled in an ice-bath. The resulting precipitate was filtered off and washed with dichloromethane to provide the *title compound* (0.120 g, 76%) as a pale yellow powder, mp 120–122 °C; $\nu_{max}(CCl_4)/cm^{-1}$ 2240 (CN), 1607, 1565, 1540, 1518, 1475, 1441, 1381, 1325, 1265, 1238 and 1211; δ_H(300 MHz, [$^2H_6$]-DMSO) 3.81 (3 H, s, OMe), 3.84 (3 H, s, OMe), 7.26 (1 H, m) and 7.50 (1 H, s).

Methyl 4,5-dimethoxy-*N*-(cyanothioformyl)anthranilate 12 [X = 2-CO_2Me-4,5-(MeO)$_2$]. The imine **11** [X = 2-CO_2Me-4,5-(MeO)$_2$] (0.1 g, 0.288 mmol) was treated with PPh_3 (0.151 g, 0.57 mmol) in dichloromethane (5 cm^3) at room temperature for 1 h after which column chromatography (dichloromethane), gave the *title compound* (0.075 g, 93%) as yellow needles, mp 178–180 °C (light petroleum–dichloromethane) (Found: *m/z* 280.0516. $C_{12}H_{12}N_2O_4S$ requires M^+, 280.0517); ν_{max}(KBr)/cm^{-1} 2235 (CN), 1765 (CO), 1681, 1613, 1531, 1504, 1464, 1434, 1392, 1358, 1281 and 1223; δ_H(300 MHz, $CDCl_3$) 3.81 (6 H, 2 × OMe), 3.99 (3 H, s, COOMe), 7.56 (2 H, m) and 9.30 (1 H, s); *m/z* 280 (M^+, 6%), 253 (M^+ – [CN, H], 100), 238 (M^+ – [CN, CH_3], 37), 222 (M^+ – [CN, S, CH_3], 36) and 210 (M^+ – [CSCN, CH_3], 6).

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