

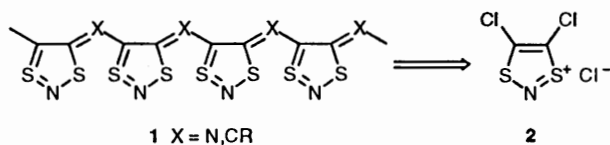
Organic Heterocyclothiazenes. Part 18.¹ 1,3,2-Dithiazolium Salts and 1,3,2-Dithiazolethiones

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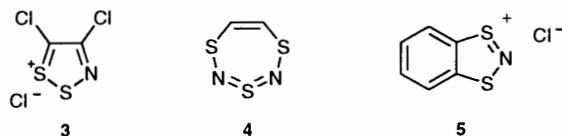
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1,3,2-Dithiazol-1-ium chloride **6** and 5-chloro-1,3,2-dithiazol-1-ium chloride **7** have been prepared by the reaction of trimethylsilyl azide with 1-chloroethane-1,2-bis(sulfonyl chloride) and 1,2-dichloroethane-1,2-bis(sulfonyl chloride) respectively. The corresponding neutral 1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione **8** and 5-chloro-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione **18** were unexpectedly obtained by treatment of these salts with base. Methylation and benzylation of the thione **8** provided the 5-methylthio-1,3,2-dithiazol-1-ium **9** and 4-benzylthio-1,3,2-dithiazol-1-ium **12** salts, which on treatment with base afforded 5-methylthio-**10** and 5-benzylthio-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione **13** respectively; further alkylation provided a route to symmetrical difunctionalised cations such as 4,5-dimethylthio-1,3,2-dithiazol-1-ium iodide **11**. Treatment of the dithiazolium chloride **7** with ammonia or aniline leads to 5-amino-**19** and 5-anilino-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione **20** respectively.

In a continuation of the study of heterocyclic compounds containing a high proportion of nitrogen and sulfur heteroatoms, we now discuss the chemistry of compounds containing the relatively rare 1,3,2-dithiazole ring system.²⁻⁴ One of the original aims of this work was to modify the structure of the conducting polymer, poly(sulfur nitride), (SN)_x to give more stable and useful conductors. Polymers of type **1** were thus considered of particular interest, and it was hoped that they could be prepared from 4,5-dichloro-1,3,2-dithiazol-1-ium chloride **2**.

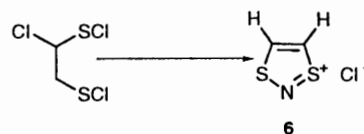


1,3,2-Dithiazol-1-ium Chloride 6.—Our study of these dithiazoles commenced with the preparation of the parent salt with a view to its conversion into the polymer precursor **2**, the 1,2,3-isomer **3** of which has been extensively studied.^{5,7} We had isolated the parent compound **6** as a by-product (40% crude) in the synthesis of the trithiadiazepine **4** by the reaction of 1-chloroethane-1,2-bis(sulfonyl chloride) with bis(trimethylsilyl)sulfur diimide where ring closure gave the 5- as well as the 7-membered ring.⁸ Wolmershäuser has shown that the reaction of benzene-1,2-bis(sulfonyl chloride) with trimethylsilyl azide affords 1,3,2-benzodithiazol-1-ium chloride **5** in quantitative yield.⁹



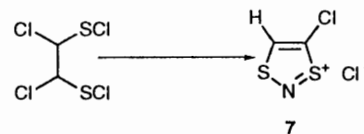
Analogously, the reaction of 1-chloroethane-1,2-bis(sulfonyl chloride)⁸ with trimethylsilyl azide (1 equiv.) in dichloromethane at room temperature gave the salt **6** (58%) as a colourless hygroscopic solid, whose spectral properties were similar to those reported earlier⁸ for the crude material. FAB mass spectral analysis showed a mass ion peak at 104 corresponding to the 1,3,2-dithiazol-1-ium cation and the ¹⁴N NMR spectrum showed a sharp resonance at δ 372 which

compares with the known 1,3,2-dithiazol-1-ium hexafluoroarsenate with a resonance at δ 375.³



5-Chloro-1,3,2-dithiazol-1-ium Chloride 7.—The need for functionality on the carbon atoms of the 1,3,2-dithiazole ring led us to investigate whether chlorine could be introduced either by treatment of more highly chlorinated sulfonyl chlorides with trimethylsilyl azide, or by chlorination of the salt **6**.

Treatment of 1,2-dichloromethane-1,2-bis(sulfonyl chloride)¹ with trimethylsilyl azide (1 equiv.) in dichloromethane at room temperature gave the salt **7** (31%) as a bright yellow solid. FAB mass spectral analysis showed peaks at 138 and 140 corresponding to the monochlorinated cation. However, yields of this reaction were variable and it soon became clear that a problem associated with this mode of synthesis was the nucleophilic nature of trimethylsilyl azide and its subsequent attack on the newly formed 5-chloro-1,3,2-dithiazol-1-ium chloride. The salt **7** in refluxing sulfuric acid gave a bright orange solid for which the FAB *m/z* spectrum showed mass ion peaks at 172, 174 and 176 corresponding to the cation **2**, but attempts at purification and further characterisation by reaction of this proved fruitless.



1,3,2-Dithiazolethiones.—Treatment of the salt **6** with various bases (triethylamine, Hünig's base, diisopropylamine, DBU) in dichloromethane or diethyl ether at room temperature gave the 1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione **8** in moderate yield (40–48%, two molecules of salt affording one molecule of thione). This black solid, with a pronounced metallic lustre, was identical with that which we had previously isolated in very low yield (5%) by the reaction of lithium acetylide with S₄N₃Cl in THF at –78 °C.⁴ An X-ray diffraction analysis of this compound has also been reported, though not details of its preparation.¹⁰

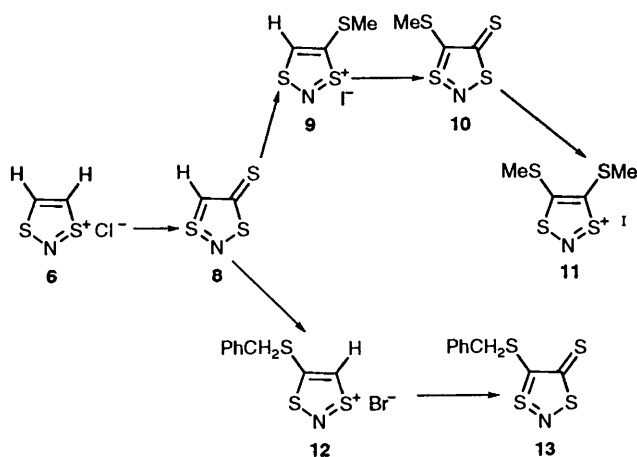
The mechanism of the conversion of **6** into **8** is unknown and requires further investigation, although the exocyclic sulfur of the thione **8** must come from another molecule of salt. Thus this provides a somewhat inefficient route to the thione **8** and we investigated whether external sources of sulfur would improve the yield of the thione. Addition of various sulfur sources (sulfur, sulfur dichloride, propylene sulfide) was found in this case to have little significant effect on the yield, though the use of weakly or non-nucleophilic bases such as triethylamine (48%) or Hunig's base (46%) led to cleaner reactions.

Alkylation of the thione **8** followed by treatment with base led to the formation of difunctionalised derivatives and provided a route to symmetrical cations. Treatment of the thione **8** with iodomethane under reflux gave 5-methylthio-1,3,2-dithiazol-1-ium iodide **9** as a yellow-brown solid. Addition of Hunig's base (3 equiv.) to a suspension of this salt in dichloromethane gave 5-methylthio-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione **10** in 24% yield.

Addition of salt **9** to Hunig's base and an excess of sulfur in dichloromethane afforded the thione **10** in 64% yield, now showing a significant improvement on addition of sulfur. On a larger scale this yield was not reproduced and the thione **10** was isolated in 46% yield, along with a trace amount of a deep-blue compound.

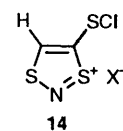
Treatment of the methylthio thione **10** with iodomethane gave the symmetrical salt, 4,5-dimethylthio-1,3,2-dithiazol-1-ium iodide **11** for which the FAB mass spectrum showed a strong peak at 196 corresponding to the cation.

Analogously, the thione **8** with benzyl bromide gave 4-benzylthio-1,3,2-dithiazol-1-ium bromide **12** as a bright yellow solid for which the FAB mass spectrum showed the appropriate strong peak at 226, and addition of Hunig's base gave the corresponding thione **13** (24%). Treatment of the salt **12** with Hunig's base and an excess of sulfur in dichloromethane by inverse addition afforded **13** in much higher yield (70%).



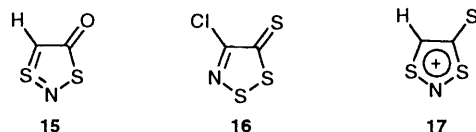
Conversion of the thiocarbonyl group of **8** into a gem dichloro group would be equivalent to formation of the salt **7**; treatment of the thione **8** in chlorinated solvents with various chlorinating agents (chlorine, phosphorus pentachloride, sulfuryl chloride) led to destruction of its purple colour and formation of a yellow precipitate thought to be salts of the sulfenyl chloride **14**, which were unstable and readily reverted to the thione on attempted isolation. More forcing chlorination conditions (elevated temperature, large excess of chlorinating agents) caused decomposition to black tars.

The use of lead tetraacetate in the conversion of dithiazole-thiones into the corresponding keto derivatives has previously been described.⁴ Treatment of the thione **8** in dichloromethane at -20°C with lead tetraacetate gave an unstable yellow com-



pound thought to be 1- $\lambda^4\delta^2$,3,2-dithiazol-4-one **15**, for which spectral analysis shows a strong mass ion peak and fragmentation peaks at 73 (loss of NS) and 45 (CHS).

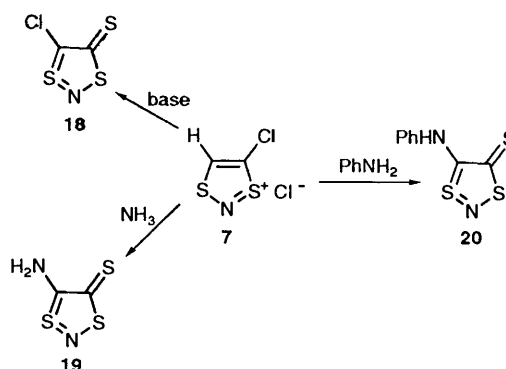
The use of Wittig and aza-Wittig reagents and diazo compounds in reactions with the thione **8** proved disappointing; the decreased reactivity of compound **8** towards these reagents compared with the analogous 4-chloro-1,2,3-dithiazole-5-thione **16**,⁷ may result from a greater contribution of the mesoionic form **17**.



Treatment of the salt **7** with Hunig's base (2 equiv.) in dichloromethane gave 5-chloro-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione **18** (30%) as a black solid which was unstable and readily decomposed to insoluble material. The thione **18** exhibited a purple colour in dichloromethane solution; this can be compared with the isomeric chlorothione **16** which is deep maroon in the solid state but has an intense yellow colour in dichloromethane.⁶ The UV spectrum of compound **18** showed a long wavelength absorption at 559 nm compared to that of the 1,2,3-isomer **16** at 429 nm. The mass spectra of both isomers showed strong mass ion peaks, but distinctly different fragmentation patterns, the 1,3,2-isomer showing a large fragmentation peak for loss of NS, and the 1,2,3-isomer showing large fragmentation peaks for loss of CS₂ and ClCS (loss of CS₂).

Treatment of the salt **7** with dry ammonia in THF gave 5-amino-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione **19** in low yield (11%) as a dark red oil. The reaction proceeded *via* the thione **18** which was observed by TLC; treatment of the chlorothione **18** in THF with ammonia gave the same amino thione **19** in 55% yield. This reaction is analogous to that of the parent salt **6**, but in addition to attack at the reactive hydrogen, nucleophilic displacement of the chlorine atom occurs. The amino thione **19** appeared to be an attractive starting material for preparation of the target polymer **1** (X = N); heating it in refluxing ethanol led to some decomposition but no self condensation products.

Treatment of the salt **7** with aniline in dichloromethane at room temperature afforded the analogous 5-anilino-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione **20** (66%) as bronze crystals with a metallic lustre which had an intense crimson colour in dichloromethane solution. Structure **20** was confirmed by X-ray crystallographic analysis.¹¹



Experimental

For general points see earlier parts of the series. Light petroleum refers to the fraction b.p. 40–60 °C unless otherwise stated. ^{14}N NMR experiments gave N chemical shifts relative to anhydrous liquid ammonia at 0 °C (δ 0), positive values corresponding to downfield shifts. Nitromethane (δ 380.2) was used as an external reference. In reactions involving the formation of thiones, yields are calculated on the basis of two molecules of salt giving one molecule of thione, unless an additional sulfur source was present.

1,3,2-Dithiazol-1-ium Chloride 6.—Trimethylsilyl azide (0.85 cm³, 6.40 mmol) in dichloroethane (5 cm³) was added dropwise to a solution of 1-chloromethane-1,2-bis(sulphenyl chloride)⁸ (1.17 g, 5.91 mmol) in dichloromethane (50 cm³) under N₂ at 25 °C; gas evolution was observed and a cream coloured precipitate formed. The mixture was stirred under N₂ for 1 h. The solid was filtered off, washed (CH₂Cl₂) and dried to afford the *title compound 6* (479 mg, 58%) as a colourless hygroscopic solid⁸ m.p. > 230 °C (decomp.) [Found: M⁺, 103.9629. C₂H₂NS₂ (FAB) requires M, 103.9629; ν_{max} (Nujol)/cm⁻¹ 3093s, 1389s, 1228w, 1019w, 852w, 823w and 770m; λ_{max} (EtOH)/nm (log ϵ) 296 (4.13) and 291 (4.11); δ_{H} (250 MHz; D₂O) 11.24; δ_{N} (18.06 MHz, D₂O)/[$\nu_{1/2}$ (Hz)] 372 (130); m/z (FAB, glycerol) 104 (M⁺).

5-Chloro-1,3,2-dithiazol-1-ium Chloride 7.—Trimethylsilyl azide (0.265 cm³, 2.00 mmol) in dichloromethane (2 cm³) was added dropwise to a solution of 1,2-dichloroethane-1,2-bis(sulphenyl chloride)¹ (0.460 g, 1.98 mmol) in dichloromethane (20 cm³) under N₂ at 25 °C; gas evolution was observed and a yellow precipitate formed. The mixture was stirred under N₂ for 1.5 h. The solid was filtered off, washed (CH₂Cl₂) and dried to afford the *title compound 7* (107 mg, 31%) as a yellow solid which decomposed on heating (> 85 °C) [Found: M⁺, 137.9239. C₂HCINS₂ (FAB) requires M, 137.9239; ν_{max} (Nujol)/cm⁻¹ 3143s, 1408m, 1177m, 998w, 943w, 877w, 839w, 772m, 688w, 558w and 513w; λ_{max} (EtOH)/nm (log ϵ) 296 (4.13) and 291 (4.11); m/z (FAB, glycerol) 138, 140 (M⁺).

1- $\lambda^4\delta^2$,3,2-Dithiazole-4-thione 8.—1,3,2-Dithiazol-1-ium chloride **6** (156 mg, 1.12 mmol) in dichloromethane (10 cm³), under N₂ and protected from light, was treated with triethylamine (315 mm³, 2.26 mmol); white fumes were observed and the mixture turned purple. Dry flash column chromatography (30–50% CH₂Cl₂–light petroleum) followed by flash column chromatography (30–50% CH₂Cl₂–light petroleum) gave the *title compound 8* (36 mg, 48%) as black lustrous crystals; m.p. 140 °C (lit.,⁴ 140 °C) [Found: M⁺, 134.9284. C₂HNS₃ requires M, 134.9271; ν_{max} (CHCl₃)/cm⁻¹ 1293 (C=S), 1266s, 1146w, 978m, 707w and 667w; λ_{max} (EtOH)/nm (log ϵ) 549 (3.21) 277 (4.03) and 224 (4.42); δ_{H} (250 MHz; CDCl₃) 9.01; δ_{C} (62.9 MHz, CDCl₃) 160.3 and 212.9 (C=S); δ_{N} (18.06 MHz; CDCl₃)/[$\nu_{1/2}$ (Hz)] 314 (160); m/z (100 °C) 135 (M⁺, 100%), 89 (M⁺ – NS, 86), 88 (9), 78 (9), 46 (NS, 14) and 45 (CHS⁺, 62).

5-Methylthio-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione 10.—(i) 1,3,2-Dithiazole-4-thione **8** (96 mg, 0.710 mmol) was stirred with iodomethane (2 cm³) while protected from light until all the thione had been consumed, to give 4-methylthio-1,3,2-dithiazolium iodide **9** as a yellow–brown solid. Excess of iodomethane was removed by evaporation. A suspension of the salt **9** in dichloromethane (10 cm³) was treated with triethylamine (297 mm³, 2.13 mmol); white fumes and a purple colour were observed and the mixture was stirred for 1 h protected from light. Extensive dry flash column chromatography (20–80% CH₂Cl₂–light petroleum) gave the *title compound 10* (15 mg, 24%) as black lustrous crystals; m.p. 103–104 °C (decomp.)

(Found: M⁺, 180.9155. C₃H₃NS₄ requires M, 180.9148); ν_{max} (CHCl₃)/cm⁻¹ 1471m, 1382m, 1241s, 1090m, 988m and 917s; λ_{max} (EtOH)/nm (log ϵ) 546 (2.80), 262 (3.77) and 223 (4.02); δ_{H} (250 MHz; CDCl₃) 2.72; δ_{C} (62.9 MHz; CDCl₃) 204.6 (C=S), 182.9 and 19.0 (S–CH₃); δ_{N} (18.06 MHz; CDCl₃)/[$\nu_{1/2}$ (Hz)] 276 (295); m/z (140 °C) (181 M⁺, 100%), 135 (M⁺ – NS, 32), 88 (34), 78 (11), 76 (14), 46 (9), 45 (10) and 44 (8).

(ii) The thione **8** (1.105 g, 7.51 mmol) was stirred with iodomethane (5 cm³) while protected from light until all the thione had been consumed. This gave 5-methylthio-1,3,2-dithiazol-1-ium iodide **9** as a yellow–brown solid upon removal of the excess of iodomethane. The salt **9** was added to a mixture of Hunig's base (2.65 cm³, 15.2 mmol) and sulfur (1.32 g, 5.16 mmol) in dichloromethane (100 cm³); white fumes and a purple colour were observed. The reaction mixture was stirred for 1.5 h protected from light. Extensive dry flash column chromatography (20–80% CH₂Cl₂–light petroleum) gave the *title compound 10* (0.624 g, 46%) identical with that prepared previously, and a trace of a blue compound, m/z (170 °C) 234 (M⁺, 98%), 219 (M⁺ – CH₃, 100), 204 (M⁺ – 2CH₃, 39), 173 (13), 94 (57) and 78 (25).

4,5-Dimethylthio-1,3,2-dithiazol-1-ium Iodide 11.—The thione **10** (29 mg, 0.162 mmol) was dissolved in iodomethane (2 cm³) and refluxed under N₂ for 4 h; removal of excess of iodomethane gave the *title compound 11* (52 mg, 99%) as a red–purple solid, m.p. 138–140 °C [Found: M⁺, 195.9383. C₄H₆NS₄ (FAB) requires M, 195.9383; ν_{max} (Nujol)/cm⁻¹ 1421m, 1324m, 1296s, 1093s, 1006w, 959w, 763w, 733w and 697w; m/z (FAB, MNBA) 196.

5-Benzylthio-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione 13.—(i) Compound **8** (96 mg, 0.710 mmol) was stirred with benzyl bromide (2 cm³) whilst protected from light until all the thione had been consumed. This gave 4-benzylthio-1,3,2-dithiazol-1-ium bromide **12** as a yellow–brown solid [m/z (FAB, MNBA) 226], after excess of benzyl bromide had been removed (CH₂Cl₂ wash). A suspension of the salt in dichloromethane (10 cm³) was treated with triethylamine (0.297 cm³, 2.13 mmol); white fumes and a purple colour were observed. The reaction was stirred for 1 h protected from light. Extensive dry flash column chromatography (20–80% CH₂Cl₂–light petroleum) gave the *title compound 13* (22 mg, 24%) as black lustrous crystals; m.p. 140–141.5 °C (Found: M⁺, 256.9465. C₉H₇NS₄ requires M, 256.9461; ν_{max} (CHCl₃)/cm⁻¹ 1382m, 1234m, 1084m and 917s; λ_{max} (EtOH)/nm (log ϵ) 546 (3.32), 304 (3.95) and 224 (4.41); δ_{H} (250 MHz; CDCl₃) 7.33–7.28 (5 H, m, Ph-H) and 4.03 (2 H, s, CH₂); δ_{C} (62.9 MHz; CDCl₃) 206.5 (C=S), 177.0, 134.0, 129.2, 129.1, 128.7 and 39.1; m/z (140 °C) 257 (M⁺, 34%), 91 (Bn, 100) and 65 (13).

(ii) The thione **8** (39 mg, 0.285 mmol) was stirred with benzyl bromide (0.5 cm³) in dichloromethane (1 cm³) whilst protected from light until all the thione had been consumed. This gave the salt **12** as a yellow solid on removal of the excess benzyl bromide. This salt was added to a mixture of Hunig's base (0.100 cm³, 0.574 mmol) and sulfur (329 mg, 1.3 mmol) in dichloromethane (15 cm³); white fumes and purple colour were observed. The reaction was stirred for 16 h protected from light. Extensive dry flash chromatography (20–80% CH₂Cl₂–light petroleum) gave the *title thione 13* (51 mg, 70%) identical with that prepared previously.

1- $\lambda^4\delta^2$,3,2-Dithiazol-4-one 15.—Compound **8** (99 mg, 0.732 mmol) in dichloromethane (5 cm³) at –20 °C was added dropwise to lead tetraacetate (0.473 g, 1.07 mmol) in dichloromethane at –20 °C and protected from light. The purple colour of the thione disappeared to give a brown suspension. Dry flash column chromatography (25% CH₂Cl₂–

light petroleum) gave the *title compound 15* (69 mg, 79%) as an unstable golden-yellow oil (Found: M^+ , 118.9500. $C_2H_7NOS_2$ requires M , 118.9500); δ_C (62.9 MHz; $CDCl_3$) 200.2 and 136.6; m/z (160 °C) (M^+ , 100%), 86 (24), 78 (5), 73 (M^+ - NS, 9), 71 (7), 69 (5), 59 (M^+ - COS, 4), 57 (10) and 46 (20).

5-Chloro-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione 18.—Hunig's base (186 mm³, 107 mmol) was added to a suspension of the salt 7 (93 mg, 0.533 mmol) in dichloromethane (10 cm³) under N_2 and protected from light. The reaction was stirred for 4 h. Dry flash column chromatography (20–50% CH_2Cl_2 –light petroleum) gave the *title compound 18* (15 mg, 30%) as a black solid which decomposed on heating; $\nu_{max}(CHCl_3)/cm^{-1}$ 1266m(C=S), 1210s, 677w, 667w, 526m and 508m; $\lambda_{max}(EtOH)/nm$ 559, 296 and 286; m/z (100 °C) 171/169 (M^+ , 46/100%), 125/123 (M^+ - NS, 38/91), 91 (6), 88 (38), 81 (32), 79 (86), 78 (14), 76 (12), 64 (5), 56 (8), 46 (NS, 18), 44 (24) and 32 (10).

5-Amino-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione 19.—(i) Ammonia gas was passed through a suspension of the salt 7 (260 mg, 1.49 mmol) in THF (70 cm³) protected from light; initially a purple suspension was formed (TLC showed this to be compound 18) which on consumption of the purple compound gave a red reaction mixture. Dry flash column chromatography (Et_2O) gave the *title compound 19* (12 mg, 11%) as a red unstable oil (Found: M^+ , 149.9376. $C_2H_2N_2S_3$ requires M , 149.9380); $\nu_{max}(CHCl_3)/cm^{-1}$ 3478m, 3358m, 1611m, 1594m, 1469w, 1397s, 1293s, 1171w, 1131w, 978w and 843w; $\lambda_{max}(EtOH)/nm$ 500, 285 and 230; m/z (180 °C) 150 (M^+ , 100%), 104 (M^+ - NS, 31), 89 (7), 88 (7), 78 (9), 77 (15), 76 (12), 71 (13), 70 (30), 69 (10), 60 (36), 57 (19) and 46 (NS, 19).

(ii) Ammonia gas was passed through a solution of the thione 18 (62 mg, 0.368 mmol) in THF (50 cm³) protected from light, until all the starting material had been consumed. The red reaction mixture was adsorbed onto silica and was purified by dry flash column chromatography (Et_2O) affording the *title compound 19* (30 mg, 55%) identical with that prepared previously.

5-Anilino-1- $\lambda^4\delta^2$,3,2-dithiazole-4-thione 20.—A suspension of the salt 7 (162 mg, 0.931 mmol) in dichloromethane (30 cm³) under Ar at 25 °C was treated with aniline (510 mm³, 0.560 mmol); the yellow suspension turned red and the reaction mixture was stirred for 6 h protected from light. Flash column chromatography (20–50% CH_2Cl_2 –light petroleum) gave the *title compound 20* (71 mg, 66%) as bronze lustrous crystals;

136–137 °C (Found: M^+ , 225.9693. $C_8H_6N_2S_3$ requires M , 225.9693); $\nu_{max}(CHCl_3)/cm^{-1}$ 3368w, 1620m, 1596m, 1576m, 1499m, 1446m and 693m; $\lambda_{max}(EtOH)/nm$ (log ϵ) 519 (3.60), 312 (3.95) and 239 (4.12); δ_H (250 MHz; $CDCl_3$) 8.77 (1 H, br s, NH), 7.57–7.50 (2 H, m, Ph-H), 7.31–7.23 (3 H, m, Ph-H); δ_C (62.9 MHz; $CDCl_3$) 192.8 (C=S), 174.7, 137.8, 130.2, 125.4 and 118.6; m/z (180 °C) 226 (M^+ , 59%), 194 (M^+ - S, 15), 180 (M^+ - NS, 12), 153 (4), 136 (15), 104 (100), 77 (Ph, 84), 65 (9), 51 (36) and 46 (5).

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References

- 1 Part 17, C. W. Rees and J. R. J. Surtees, *J. Chem. Soc., Perkin Trans. 1*, 1991, 2945.
- 2 G. K. Maclean, J. Passmore, M. N. S. Rao, M. J. Schriver, P. S. White, D. Bethell, R. S. Pilkington and L. H. Sutcliffe, *J. Chem. Soc., Dalton Trans.*, 1985, 1405; E. G. Ewere, N. Burford, C. Mailer, J. Passmore, P. S. White, A. J. Banister, H. Oberhammer and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 66; M. Sammes in *Comprehensive Heterocyclic Chemistry*, eds. A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1984, vol. 6, p. 897.
- 3 S. Parsons, J. Passmore, M. J. Schriver and P. S. White, *Can. J. Chem.*, 1990, **68**, 852.
- 4 P. J. Dunn and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1989, 2489.
- 5 R. L. Greene, G. B. Street and L. J. Suter, *Phys. Rev. Lett.*, 1975, **34**, 577; M-H. Whangbo, R. Hoffmann and R. B. Woodward, *Proc. R. Soc. London, Ser. A*, 1979, **366**, 23; M. M. Labes, P. Love and L. F. Nichols, *Chem. Rev.*, 1979, **79**, 6.
- 6 R. Appel, H. Janssen, M. Siray and F. Knoch, *Chem. Ber.*, 1985, **118**, 1632.
- 7 R. F. English, Ph.D. Thesis, University of London, 1989.
- 8 J. L. Morris and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 211.
- 9 G. Wolmershäuser, M. Schaubert and T. Wilhelm, *J. Chem. Soc., Chem. Commun.*, 1984, 573.
- 10 R. T. Oakley, H. Koenig and A. W. Cordes, *Acta Crystallogr., Sect. C*, 1987, **43**, 2468.
- 11 D. J. Williams, Imperial College, unpublished results.

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