# Synthesis of *N*-unsubstituted bis[1,2]dithiolo[1,4]thiazines and bis[1,2]dithiolopyrroles

**Lidia S. Konstantinova,[a] Natalia V. Obruchnikova,[a] Oleg A. Rakitin,[a] Charles W. Rees[b] and Tomás Torroba[c]**

[a] *N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences, Leninsky Prospect, 47, 117913 Moscow, Russia*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY*
[c] *Departamento de Química, Facultad de Ciencias, Universidad de Burgos, 09001 Burgos, Spain*

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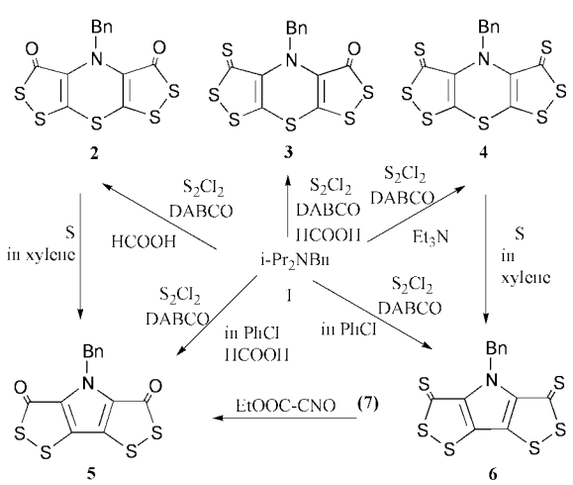
The parent bis[1,2]dithiolo[1,4]thiazine-3,5-dione **8**, -3,5-dithione **11**, the unsymmetrical 3-oxo-5-thione **10** and the bis[1,2]dithiolopyrrole-3,5-dione **9** are synthesised by acid catalysed cleavage of their various *N*-benzyl, ethyl, ethoxycarbonylethyl and propanoic acid derivatives. These *N*-alkyl compounds are prepared in the usual way from the appropriate *N*-alkyldiisopropylamine and $S_2Cl_2$. *N*-Benzyl derivatives **2** and **5** of the thiazine and pyrrole diones give **8** (100%) and **9** (58%) respectively with conc. $H_2SO_4$ in dilute DCM solution, and the *N*-ethyl thiazine derivatives of the dione **12** and the keto-thione **13** give **8** (89%) and **10** (75%) respectively in conc. $H_2SO_4$ at 120 °C. Ethyl 3-(diisopropylamino)propanoate **16** with $S_2Cl_2$ gives the three thiazines **17** (30%), **18** (15%) and **19** (13%), and **17** and **19** are converted into the pyrroles **20** (95%) and **21** (90%) respectively by thermal extrusion of sulfur in refluxing xylene. All five ethyl esters, **17**–**21**, are hydrolysed with aqueous acid to **22**–**26** respectively in 92–100% yield, and the *N*-propanoic acids **22**–**25** with hot conc. hydrochloric or hot 80–90% sulfuric acid are dealkylated to the corresponding parent products **8**–**11**. It is also shown that the hydrolysis and dealkylation steps **17**→**22**→**8** can be combined in one operation (75%).

We have previously described a remarkable one-pot transformation of Hünig's base and related diisopropylamines with disulfur dichloride, $S_2Cl_2$, into bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*]-[1,4]thiazines (*cf.* **2**–**4**) and, at higher temperature, into bis[1,2]dithiolo[4,3-*b*:3,4-*d*]pyrroles (*cf.* **5**, **6**), new families of stable fully unsaturated heterocycles which are revealing a rich chemistry.[1–6] There has been greatly renewed interest in sulfur heterocycles as new materials since the discovery of superconducting tetrathiafulvalene charge-transfer complexes[7] and molecular switches,[8] thiazole and thiadiazole liquid crystals,[9] and thiophene nonlinear optical materials.[10] With such potential applications in mind, we wished to synthesise a wider range of the bisdithiolothiazines and bisdithiolopyrroles, particularly with various *N*-substituents, for which the *N*-unsubstituted parent ring systems would hopefully be key intermediates. We now describe various syntheses of these parent compounds **8**–**11**.[5]

Our standard conditions for the above conversions are treatment of the tertiary diisopropylamine with $S_2Cl_2$ and DABCO for 3 d at room temperature, in chloroform for the thiazines, and in chlorobenzene for the pyrroles; a final brief period of heating for the latter induces extrusion of sulfur. For the oxygenated products, like **2**, **3** and **5**, formic acid is added towards the end of the reaction. However, when these conditions were applied to *N*,*N*-diisopropylamine and its trimethylsilyl derivative, there was extensive decomposition and no *N*-unsubstituted dithiolothiazines or dithiolopyrroles could be isolated. Diisopropylamines with readily removable, electron withdrawing groups like acetyl or cyano on nitrogen were equally unsuccessful as starting materials, since they are inert towards $S_2Cl_2$; the electron withdrawing groups presumably suppress the initial oxidation of the amine by $S_2Cl_2$ to an iminium ion.[4] Since an *N*-benzyl group should be removable we turned our attention to the synthesis of *N*-benzyl derivatives of the ring systems, and their debenzylation.

### *N*-Debenzylation reactions

Under minor variations of our standard conditions *N*-benzyldiisopropylamine **1**,[11] $S_2Cl_2$ and DABCO gave the three *N*-benzyl bis[1,2]dithiolothiazines **2**, **3** and **4** and two symmetrical bis[1,2]dithiolopyrroles **5** and **6**, as shown in Scheme 1.




**Scheme 1**

When **1** was treated with $S_2Cl_2$ (10 equiv) and DABCO (7 equiv) in $CHCl_3$ for 3 d followed by formic acid (100 equiv), the bisdithiolothiazinedione **2** was obtained in 35% yield. With slightly more DABCO (9 equiv) the unsymmetrical keto-thione

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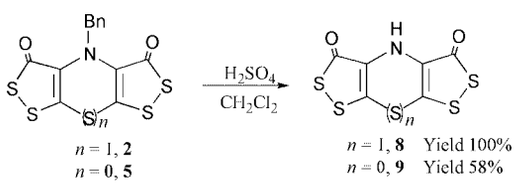
**3** was isolated in 14% yield. For the preparation of the dithione **4** (23%) we used a method developed for other bisdithiolothiazine-dithiones,[4] *i.e.* treatment of **1** with $S_2Cl_2$ and DABCO and finally with triethylamine.

The bisdithiolopyrroles **5** and **6** were prepared by the reaction of **1** with $S_2Cl_2$ in chlorobenzene with a final period of heating with and without formic acid, respectively. The yield of the dione **5** was very low however (3%) and this compound was prepared alternatively in excellent yield from the dithione **6** by treatment with an excess of ethoxycarbonylnitrile oxide **7** generated *in situ* from ethyl chlorooximinoacetate and triethylamine,[4] and from the bisdithiolothiazinedione **2** by sulfur extrusion in boiling xylene for 7 h (86% and 92% yield respectively). The bisdithiolothiazinedithione **4** underwent similar but faster thermolysis (in boiling xylene for 1 h) to give the corresponding pyrrole **6** (88%).

The structures of these five *N*-benzyl derivatives, **2**–**6**, followed from their analytical and spectroscopic data and their close similarity to the analogous *N*-ethyl compounds;[4] the structure of **2** was confirmed by X-ray crystallography.[5] In general the yields of *N*-benzyl derivatives from the $S_2Cl_2$ reactions were lower than for the corresponding *N*-ethyl compounds, probably because of their greater sensitivity to heat and to acid (see below).

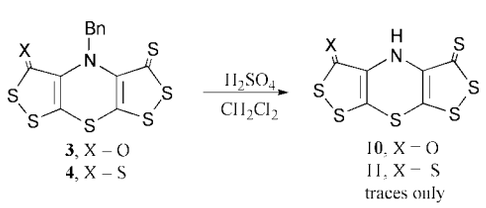
Very little is known about the *N*-debenzylation of 1,4-thiazines, 1,4-oxazines and piperazines, but cleavage of *N*-benzyl tertiary amines is usually achieved by palladium catalysed reductions. Compounds **2**–**6** are not stable to these reductive, nor to strongly basic, conditions and so we examined their behaviour under acidic conditions. Treatment of dilute solutions of the two diketo compounds **2** and **5** in DCM with conc. sulfuric acid gave the desired *N*-unsubstituted compounds **8** and **9** respectively (Scheme 2); **8** (100%) was formed rapidly, at




**Scheme 2**

5–10 °C for 5 min, and **9** (58%) at room temperature overnight. Their structures are based upon spectroscopic and analytical data and confirmed for **8** by X-ray crystallography.[5]

However, when one or more of the keto groups in **2** and **5** are replaced by thioketo groups, *i.e.* with compounds **3**, **4** and **6**, the analogous debenzylations were unsuccessful. The bisdithiolothiazines **3** and **4** were decomposed by conc. sulfuric acid in DCM solution at room temperature within 10 min (Scheme 3);

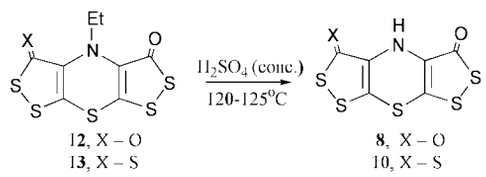



**Scheme 3**

the NH compounds **10** and **11** (see below) were obtained only in trace amounts and were identified by mass spectrometry. The bisdithiolopyrrole **6** did not react under the same conditions; the fused pyrroles are generally more stable than the thiazines. Thus cleavage of the *N*-benzyl compounds was successful only with the diketo compounds **2** and **5**.

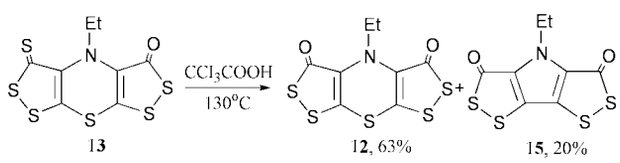
### *N*-De-ethylation reactions

Since *N*-ethylbisdithiolothiazines **12**–**14** and bisdithiolopyrrole **15** are readily available from Hünig's base,[4] we have investigated their possible *N*-de-ethylation reactions. Whilst such reactions are rare there is one report of the loss of an *N*-ethyl group accompanying *O*-demethylation in a phenothiazine derivative upon boiling in pyridine hydrochloride.[12] However the diketo derivative **12** was extensively decomposed under these conditions, giving substantial amounts of sulfur but no clean products of de-ethylation or sulfur extrusion. It was found that compounds **12**–**15** are very sensitive to alkali but remarkably stable to acid. The thiazines **12**–**14** were stable to dilute and conc. hydrochloric acid, even at reflux, and to dilute and conc. sulfuric acid at room temperature. But on heating in conc. sulfuric acid at 120 °C for 2 h, the diketo derivative **12** was smoothly dealkylated to **8** in high yield (89%) (Scheme 4). The



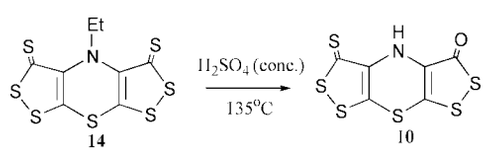

**Scheme 4**

monoketo derivative **13** behaved similarly to give the unsymmetrical parent compound **10** (obtained in trace amounts only from its *N*-benzyl derivative) in high yield (75%); this de-ethylation of **13** was accompanied by a little oxidation to give some of the diketo compound **8** as a minor product. When **13** was heated in trichloroacetic acid at 130 °C for 1 h it was oxidised, without dealkylation, to give **12** (63%) together with some extrusion of sulfur to the diketo pyrrole **15** (20%) (Scheme 5).




**Scheme 5**

The dithione **14** in conc. sulfuric acid at 135 °C for 3 h also suffered some oxidation and de-ethylation to give the unsymmetrical compound **10** (20%), together with traces of the two symmetrical compounds **8** and **11** (Scheme 6). The




**Scheme 6**

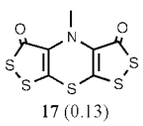
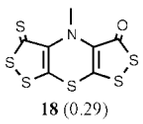
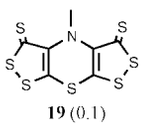
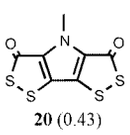
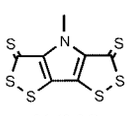
*N*-ethylbisdithiolopyrroles were unstable to hot conc. sulfuric acid (125–130 °C) and compound **15** gave none of the *N*-H compound **9**.

### *N*-Ethoxycarbonylethyl derivatives

Given the above dealkylation reactions of the *N*-ethylbisdithiolothiazines in hot sulfuric acid, we wondered whether compounds with functionalised ethyl groups would cleave similarly, possibly under milder conditions. Such compounds, with *N*-$CH_2CH_2X$ groups, are generally readily available from the appropriate diisopropylamine, $Pr^i_2NCH_2CH_2X$, where X = Cl, PhS, and phthalimido, for example.[6] We were particularly interested in the propanoic acids (X = $CO_2H$) and their derivatives, with the aim of investigating intramolecular attraction between the ethyl group functionality and the sulfur atom in the

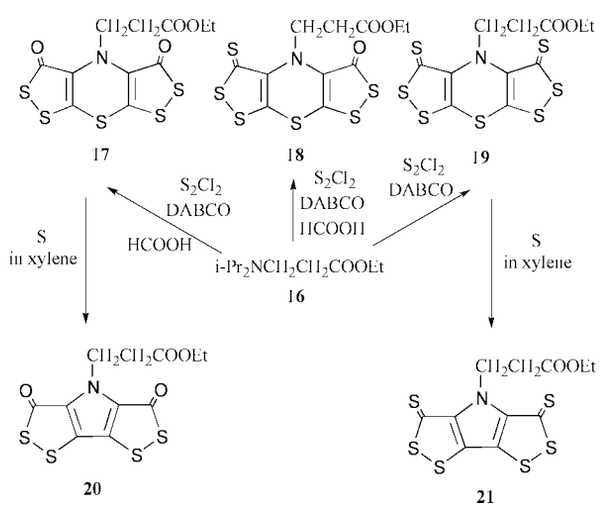
**Table 1** Hydrolysis of esters **17**–**21** to the corresponding acids **22**–**26**

$$\underset{\textbf{17–21}}{R–CH_2CH_2COOEt} \xrightarrow{acid} \underset{\textbf{22–26}}{R–CH_2CH_2COOH}$$

| Ester (mmol) R | Reaction conditions: Reagent | Reaction temperature/°C | Reaction time/h | Product (yield %) |
|---|---|---|---|---|
|  **17** (0.13) | HCl (20%), 20 ml | 60 | 15 | **22** (95) |
|  **18** (0.29) | $H_2SO_4$ (80%), 60 ml | 60 | 1 | **23** (94) |
|  **19** (0.1) | $H_2SO_4$ (80%), 20 ml | 60 | 1 | **24** (93) |
|  **20** (0.43) | HCl (20%), 60 ml | 60 | 18 | **25** (100) |
|  **21** (0.26) | $H_2SO_4$ (80%), 40 ml | 60 | 1 | **26** (92) |

1,4-thiazine ring in the "scorpion" conformation adopted by bisdithiolothiazines in the crystal lattice.[4–6]

We therefore studied the reaction of ethyl 3-(diisopropylamino)propionate **16**[13] with $S_2Cl_2$ under our standard conditions, and the results (Scheme 7) proved to be similar to those




**Scheme 7**

of the *N*-ethyl and *N*-benzyl compounds. The symmetrical diketo compound **17** and the unsymmetrical monothione **18** were obtained from the amine **16**, $S_2Cl_2$ and DABCO, with subsequent treatment with formic acid. If the formic acid was added after 3 d at room temperature compound **17** was obtained in 30% yield, but if added after 7 d at room temperature (in the presence of more DABCO) compound **18** was isolated (15%). If formic acid was replaced by triethylamine and the reaction mixture was then heated under reflux for 3 h, only the dithione **19** was isolated, though in disappointing yield (13%). The bisdithiolopyrroles **20** and **21** were obtained in high yield (95 and 90% respectively) by sulfur extrusion from the corresponding 1,4-thiazines upon heating in xylene. As with the *N*-benzyl compounds above, the extrusion of sulfur from dithione **19** was considerably faster than from the dione **17**, requiring 1 h and 18 h respectively for complete reaction.

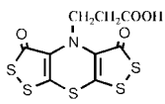
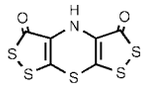
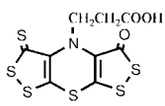
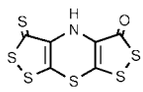
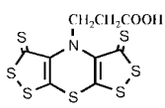
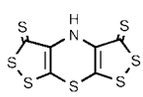
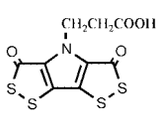
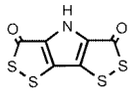
The reaction of bisdithiolothiazines **17**, **18** and **19** and bisdithiolopyrroles **20** and **21** with aqueous hydrochloric and sulfuric acids was then studied. In each case the first step was a very high yielding hydrolysis to the corresponding propanoic acid (Table 1). The diketo compounds **17** and **20** were hydrolysed more readily (with more dilute hydrochloric acid) than any of the thioketo analogues **18**, **19** and **21**. 1,4-Thiazino and pyrrolo derivatives with the same number of thio and keto groups had practically the same reactivity.

All the propanoic acids so produced are stable, high melting, coloured compounds, practically insoluble in common organic solvents and water. The diketo compounds **22** and **25** are yellow, the monothione **23** is deep red and the dithiones **24** and **26** are deep purple. Their structures are based on spectroscopic and analytical data and comparison with the corresponding *N*-ethyl derivatives,[4] and the structure of the diketo bisdithiolothiazine acid **22** was confirmed by X-ray crystallography.[14]

### *N*-Propanoic acid cleavage

We next studied the conversion of these propanoic acids into the parent *N*-unsubstituted systems by more vigorous acidic treatment; this was achieved in reasonable to high yields with conc. hydrochloric acid (36%) at 100 °C, sulfuric acid (80 and 90%) at up to 135 °C and trichloroacetic acid at 130 °C (Table 2).

**Table 2** *N*-Dealkylation of propanoic acids **22**–**25**

| Propanoic acid (mmol) | Reaction conditions: Reagent | Reaction temp./°C | Reaction time/h | Product (yield %) |
|---|---|---|---|---|
|  **22** (0.3) | HCl (36%) 50 ml | 100 | 10 |  **8** (80) |
|  **23** (0.1) | $H_2SO_4$ (80%) 15 ml | 107 | 26 |  **10** (40) |
|  **24** (0.3) | $H_2SO_4$ (96%) 50 ml | 135 | 2 |  **11** (78) |
| **24** (0.3) | $Cl_3CCO_2H$ 14 g | 130 | 2 | **8** (69) |
|  **25** (0.3) | HCl (36%) 45 ml | 100 | 35 |  **9** (56) |

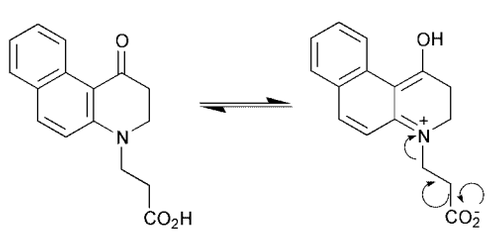
The symmetrical diketo acid **22** with conc. hydrochloric acid at 100 °C gave bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-3,5-dione **8** in high yield (80%). The monothione **23** required more vigorous conditions, 80% sulfuric acid and a longer reaction time, and the yield of 3-oxobis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazine-5-thione **10** was substantially lower (40%). Under still more vigorous conditions the dithione **24** gave a high yield of the parent bisthione **11** (78%) though the reaction now had to be performed under argon since **11** is unstable in air. Dithione **24** was also heated in trichloroacetic acid at 130 °C for 2 h, when the only product isolated was the diketo compound **8** (69%), oxidation of both thio groups having accompanied cleavage of the *N*-propanoic acid chain. Bisdithiolopyrrole derivatives required more vigorous conditions for the same cleavage. The pyrrolo-propanoic acid **25** in conc. hydrochloric acid at 100 °C had to be heated for longer than the thiazino-propanoic acid **22** and the yield of the pyrrole **9** (56%) was lower than that of the thiazine **8** (80%). In conc. sulfuric acid at 130 °C both pyrrole derivatives **25** and **26** decomposed within a few hours.

We have shown that the ethyl propanoate **17** is hydrolysed to the propanoic acid **22** (95%) in dilute hydrochloric acid at 60 °C for 15 h and that the acid **22** is cleaved to the parent compound **8** (80%) in conc. hydrochloric acid at 100 °C for 1 h. As one might expect these two steps can be combined and the ester **17** was converted directly into **8** in virtually the same overall yield (75%) by heating in conc. sulfuric acid at 95 °C for 20 h. The analogous sequence **18**→**23**→**10** could probably be combined in the same way. The parent compound **8** can also be prepared quite readily *via* its *N*-ethyl and *N*-benzyl derivatives, **12** and **2**, whilst the monothio analogue **10** is best prepared *via* its *N*-ethyl derivative **13**.

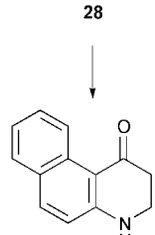
Of the three *N*-unsubstituted bisdithiolothiazines, **8** and **10** are thermally stable, and may be kept in air though both darken on storage in the light. Bisthione **11** however is unstable in air at room temperature or adsorbed onto silica gel, giving **10**; all operations involving **11** should be performed under argon.

All the above acid-catalysed dealkylation reactions presumably involve protonation of the substrates on one, or more, of the several available hetero atoms (N, S or O) followed by loss of the alkyl group by nucleophilic attack or by elimination. The benzyl group is cleaved most readily, as expected, followed by the propanoic acid group, and then the ethyl group. A rare acid-catalysed *N*-de-ethylation of a phenothiazine with boiling pyridine hydrochloride was mentioned earlier.[12]

A somewhat related, but thermal cleavage of an *N*-propanoic acid residue has been reported.[15] When **27** was heated neat at 250 °C under reduced pressure (0.1 mm) it gave **29** in almost quantitative yield. Curiously this transformation was structure specific, being observed only when both fused benzene rings were present. The reaction could possibly be self (acid) catalysed *via* the zwitterionic form **28** with the proton transferred to the carbonyl group, giving a tautomer which would be greatly stabilised by the second benzo ring. However this thermal cleavage did not extend to our *N*-propanoic acid **22**, nor its ethyl ester **17**, since on heating at 200–220 °C/0.5 mm both of these compounds underwent preferential sulfur extrusion and sublimation to give the corresponding pyrroles **25** and **20** quantitatively.



**27** **28**



**29**

## Experimental

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 298 instrument in KBr pellets. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DRX 400. CH groups were identified by DEPT experiments. *J*-values are given in Hz. Mass spectra were recorded on VG7070E and VG-AutoSpec instruments using electron impact ionisation. Light petroleum refers to the fraction bp 40–60 °C.

### 4-Benzyl-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4′,3′,-*e*][1,4]-thiazine-3,5-dione 2

Disulfur dichloride (4.0 ml, 50 mmol) was added dropwise at −15 to −20 °C to a stirred solution of *N*-benzyldiisopropylamine **1** (5 mmol) and DABCO (3.92 g, 35 mmol) dissolved in chloroform (100 ml). Then the mixture was stirred for 15 min at −20 °C and at room temperature for 72 h. Formic acid (3.76 ml, 100 mmol) was added dropwise at 5 °C, the mixture was stirred for 1 h at room temperature, refluxed for 1 h, filtered and solvent was removed under reduced pressure. The residue was separated by column chromatography (silica, light petroleum, and then light petroleum–DCM mixtures) to give the *title compound* **2** (650 mg, 35%) as yellow crystals (from light petroleum–$CHCl_3$), mp 200–202 °C (Found $M^+$, 368.9080. $C_{13}H_7NO_2S_5$ requires *M*, 368.9080) (Found: C, 42.5; H, 1.8; N, 3.5. $C_{13}H_7NO_2S_5$ requires C, 42.2; H, 1.9; N, 3.8%); $\delta_H$ ($CDCl_3$) 4.85 (2H, s, $CH_2$), 7.34 (5H, m, Ph); $\delta_C$ ($CDCl_3$) 182.31 (C=O), 147.00, 137.33 and 136.49 (3 × sp$^2$ tertiary C), 128.83, 128.62 and 128.35 (3 C–H), 50.77 ($CH_2$); $\nu_{max}$/cm$^{-1}$ 3020 and 2960 (CH), 1630 (C=O), 1550, 1510, 1450, 1340, 1260, 1130, 1050, 940, 710; *m*/*z* 369 ($M^+$, 27%), 278 (20), 218 (6), 126 (10), 114 (23), 102 (11), 91 (100), 65 (82).

### 4-Benzyl-3-oxo-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazine-5-thione 3

Disulfur dichloride (4.0 ml, 50 mmol) was added dropwise at −15 to −20 °C to a stirred solution of *N*-benzyldiisopropylamine **1** (5 mmol) and DABCO (5.04 g, 45 mmol) dissolved in chloroform (100 ml). Then the mixture was stirred for 15 min at −20 °C and at room temperature for 144 h. Formic acid (3.76 ml, 100 mmol) was added dropwise at 5 °C, the reaction mixture was refluxed for 1 h, filtered and solvent was removed under reduced pressure. The residue was separated by column chromatography (silica, light petroleum, and then light petroleum–DCM mixtures) to give the *title compound* **3** (260 mg, 14%) as orange crystals (from light petroleum–$CHCl_3$), mp 209–210 °C (Found $M^+$, 384.8864. $C_{13}H_7NOS_6$ requires *M*, 384.8852) (Found: C, 40.4; H, 1.8; N, 3.5. $C_{13}H_7NOS_6$ requires C, 40.5; H, 1.8; N, 3.6%); $\delta_H$ ($CDCl_3$) 4.97 (2H, br s, $CH_2$), 7.28 and 7.35 (5H, m, Ph); $\delta_C$ ($CDCl_3$) 203.21 (C=S), 183.90 (C=O), 159.11, 150.98, 147.46, 138.01 and 136.51 (5 × sp$^2$ tertiary C), 129.36, 129.02 and 128.32 (3 C-H), 51.76 ($CH_2$); $\nu_{max}$/cm$^{-1}$ 1620 (C=O), 1540, 1440, 1320, 1280, 1090, 1020, 700; *m*/*z* 385 ($M^+$, 27%), 369 (7), 353 (10), 294 (29), 276 (13), 263 (16), 234 (14), 192 (8), 149 (11), 126 (7), 114 (12), 91 (100), 65 (21).

### 4-Benzyl-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-3,5-dithione 4

Disulfur dichloride (4.0 ml, 50 mmol) was added dropwise at −15 to −20 °C to a stirred solution of *N*-benzyldiisopropylamine **1** (5 mmol) and DABCO (6.1 g, 50 mmol) dissolved in chloroform (100 ml). Then the mixture was stirred for 15 min at −20 °C and at room temperature for 72 h. Triethylamine (6.57 g, 50 mmol) was added dropwise, the mixture was stirred for 3 h at room temperature, filtered and solvent was removed under reduced pressure. The residue was separated by column chromatography (silica, light petroleum, and then light petroleum–DCM mixtures) to give the *title compound* **4** (460 mg, 23%) as dark red crystals (from light petroleum–$CHCl_3$), mp 221–222 °C (Found $M^+$, 400.8606. $C_{13}H_7NS_7$ requires *M*, 400.8624) (Found: C, 38.7; H, 1.6; N, 3.2. $C_{13}H_7NS_7$ requires C, 38.9; H, 1.8; N, 3.5%); $\delta_H$ ($d_5$-pyridine) 5.45 (2H, s, $CH_2$), 7.31 and 7.38 (5H, m, Ph); $\delta_C$ ($d_5$-pyridine) 203.87 (C=S), 159.74, 147.86 and 137.76 (3 × sp$^2$ tertiary C), 129.82, 128.82, and 128.42 (3 C-H), 51.76 ($CH_2$); $\nu_{max}$/cm$^{-1}$ 1630, 1480, 1450, 1330, 1300, 1110, 1050, 940, 850, 700; *m*/*z* 401 ($M^+$, 70%), 369 (45), 310 (52), 279 (50), 246 (53), 210 (85), 158 (36), 100 (40), 91 (100), 65 (50).

### 4-Benzyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3,4-*d*]pyrrole-3,5(4*H*)-dione 5

**Method A.** Disulfur dichloride (4.0 ml, 50 mmol) was added dropwise at −15 to −20 °C to a stirred solution of *N*-benzyldiisopropylamine **1** (0.95 g, 5 mmol) and DABCO (3.92 g, 35 mmol) dissolved in chlorobenzene (100 ml). The mixture was stirred for 15 min at −20 °C and at room temperature for 72 h. Formic acid (3.76 ml, 100 mmol) was added dropwise at 5 °C, the mixture was stirred for 1 h at room temperature, refluxed for 48 h, filtered and the solvent was removed under reduced pressure. The residue was separated by column chromatography (silica, light petroleum, and then light petroleum–DCM mixtures) to give the *title compound* **5** (50 mg, 3%) as yellow crystals (from light petroleum–$CHCl_3$), mp 211–213 °C (Found $M^+$, 336.9345. $C_{13}H_7NO_2S_4$ requires *M*, 336.9360) (Found: C, 46.2; H, 2.2; N, 4.0. $C_{13}H_7NO_2S_4$ requires C, 46.3; H, 2.1; N, 4.1%); $\delta_H$ ($CDCl_3$) 5.70 (2H, s, $CH_2$), 7.31 and 7.41 (5H, m, Ph); $\delta_C$ ($CDCl_3$) 181.49 (C=O), 136.53, 135.26 and 130.88 (3 × sp$^2$ tertiary C), 128.86, 128.50 and 128.38 (3 C-H), 47.02 ($CH_2$); $\nu_{max}$/cm$^{-1}$ 1640 (C=O), 1490, 1420, 1360, 1230, 1100, 1070, 850, 820, 770; *m*/*z* 337 ($M^+$, 41%), 304 (4), 215 (9), 182 (2), 149 (3), 123 (10), 91 (100), 65 (15).

**Method B.** Triethylamine (0.42 ml, 3.0 mmol) was added dropwise to a solution of dithione **6** (0.22 g, 0.6 mmol) and ethyl chlorooximidoacetate (0.36 g, 2.4 mmol) in dry THF (10 ml) at 0 °C. The mixture was stirred for 15 min at 0 °C and a further 15 min at room temperature. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. The residue was subjected to MPLC (petroleum ether to DCM) to give the title compound **5** (170 mg, 86%) identical with the above specimen.

### 4-Benzyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3,4-*d*]pyrrole-3,5(4*H*)-dithione 6

Disulfur dichloride (4.0 ml, 50 mmol) was added dropwise at −15 to −20 °C to a stirred solution of *N*-benzyldiisopropylamine **1** (0.95 g, 5 mmol) and DABCO (6.1 g, 50 mmol) dissolved in chlorobenzene (100 ml). Then the mixture was stirred for 15 min at −20 °C and at room temperature for 72 h. The mixture was boiled for 2 h, filtered and the solvent was removed under reduced pressure. The residue was separated by column chromatography (silica, light petroleum, and then light petroleum–DCM mixtures) to give the *title compound* **6** (240 mg, 13%) as black crystals (from light petroleum–$CHCl_3$), mp 223–224 °C (Found $M^+$ 368.8926. $C_{13}H_7NS_6$ requires *M*, 368.8903) (Found: C, 42.1; H, 1.9; N, 3.8. $C_{13}H_7NS_6$ requires C, 42.45; H, 1.9; N, 3.8%); $\delta_H$ ($d_5$-pyridine) 5.88 (2H, s, $CH_2$), 7.52 and 7.60 (5H, m, Ph); $\delta_C$ ($d_5$-pyridine) 200.44 (C=S), 143.52, 139.94 and 137.20 (3 × sp$^2$ tertiary C), 128.77, 127.47 and 127.22 (3 C-H), 42.69 ($CH_2$); $\nu_{max}$/cm$^{-1}$ 1470, 1450, 1350, 1100, 840, 730; *m*/*z* 369 ($M^+$, 75%), 336 (15), 305 (12), 272 (10), 247 (45), 138 (12), 121 (22), 112 (22), 100 (25), 91 (100), 65 (35).

### Sulfur extrusion from 2 and 4

A solution of **2** or **4** (1 mmol) in xylene (100 ml) was boiled for 7 or 1 h respectively. The solvent was removed in a rotary evaporator, the residue was washed with light petroleum and

crystallised from light petroleum–chloroform mixtures to give **5** (92%) or **6** (88%) identical with the above specimens.

### Treatment of 4-ethyl-3-oxo-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-5-thione 13 with trichloroacetic acid

A mixture of compound **13** (32 mg, 0.1 mmol) and trichloroacetic acid (15 g) was heated at 130 °C for 1 h. After cooling the reaction mixture was diluted with water (100 ml), extracted with DCM and the organic solution was dried over $MgSO_4$. After evaporation the residue was subjected to column chromatography (silica, light petroleum, and then light petroleum–DCM mixtures) to give 4-ethyl-3*H*-bis[1,2]dithiolo[4,3-*b*:3,4-*d*]-pyrrole-3,5-dione **15** (5 mg, 20%) with mp 199–200 °C and 4-ethylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-3,5(4*H*)-dione **12** (18 mg, 63%) with mp 191–193 °C.[4]

### Preparation of compounds 17–19

Ethyl 3-(diisopropylamine)propionate **16**[13] was treated with $S_2Cl_2$ exactly as for the conversions of *N*-benzyldiisopropylamine **1** into **2**, **3** and **4** to give compounds **17**, **18** and **19**, respectively.

**Ethyl 3-(3,5-dioxo-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*]-[1,4]thiazin-4-yl)propanoate 17.** Yellow crystals (30%), mp 135–136 °C (from light petroleum–$CHCl_3$) (Found $M^+$, 378.9125. $C_{11}H_9NO_4S_5$ requires *M*, 378.9135) (Found: C, 34.9; H, 2.4; N, 3.6. $C_{11}H_9NO_4S_5$ requires C, 34.8; H, 2.4; N, 3.7%); $\delta_H$ ($CDCl_3$) 1.21 (3H, t, *J* 7.1, $CH_3$), 2.64 (2H, t, *J* 6.4, $CH_2$), 4.10 (4H, m, 2 $CH_2$); $\delta_C$ ($CDCl_3$) 181.99 (C=O), 171.30 (C=O), 146.74 and 136.52 (2 × $sp^2$ tertiary C), 60.94 ($CH_2$), 42.34 ($CH_2$), 34.66 ($CH_2$), 14.16 ($CH_3$); $\nu_{max}/cm^{-1}$ 2980 (CH), 1730 (C=O), 1660, 1630, 1550, 1510, 1440, 1380, 1260, 1210, 1180, 1080, 1010, 830; *m*/*z* 379 ($M^+$, 100%), 292 (71), 279 (52), 262 (8), 251 (9), 219 (14), 175 (9), 114 (17), 101 (39), 88 (19), 73 (34), 55 (34).

**Ethyl 3-(3-oxo-5-thioxo-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-4-yl)propanoate 18.** Orange crystals (15%), mp 154–155 °C (from light petroleum–$CHCl_3$) (Found $M^+$, 394.8915. $C_{11}H_9NO_3S_6$ requires *M*, 394.8907) (Found: C, 33.6; H, 2.3; N, 3.4. $C_{11}H_9NO_3S_6$ requires C, 33.4; H, 2.3; N, 3.5%); $\delta_H$ ($d_5$-pyridine) 1.08 (3H, t, *J* 7.1, $CH_3$), 2.82 (2H, t, *J* 6.5, $CH_2$), 4.05 (2H, q, *J* 7.1, $CH_2$), 4.62 (2H, br s, $CH_2$); $\delta_C$ ($d_5$-pyridine) 203.37 (C=S), 183.78 (C=O), 171.85 (C=O), 158.70, 150.74, 147.84 and 136.98 (4 × $sp^2$ tertiary C), 61.01 ($CH_2$), 43.84 ($CH_2$), 34.60 ($CH_2$), 14.32 ($CH_3$); $\nu_{max}/cm^{-1}$ 2980 (CH), 1720 (C=O), 1620, 1540, 1470, 1440, 1340, 1290, 1180, 1060, 1010; *m*/*z* 395 ($M^+$, 100%), 307 (82), 295 (34), 263 (55), 235 (16), 126 (22), 114 (24), 100 (47), 88 (33), 70 (29), 55 (32).

**Ethyl 3-(3,5-dithioxo-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-4-yl)propanoate 19.** Dark red crystals (13%), mp 181–182 °C (from light petroleum–$CHCl_3$) (Found $M^+$, 410.8686. $C_{11}H_9NO_2S_7$ requires *M*, 410.8678) (Found: C, 31.9; H, 2.2; N, 3.4. $C_{11}H_9NO_2S_7$ requires C, 32.1; H, 2.2; N, 3.4%); $\delta_H$ ($d_5$-pyridine) 1.07 (3H, t, *J* 7.2, $CH_3$), 2.87 (2H, t, *J* 6.8, $CH_2$), 4.05 (2H, q, *J* 7.1, $CH_2$), 4.85 (2H, t, *J* 6.8, $CH_2$); $\delta_C$ ($d_5$-pyridine) 203.60 (C=S), 171.61 (C=O), 159.01 and 148.11 (2 × $sp^2$ tertiary C), 60.75 ($CH_2$), 43.70 ($CH_2$), 34.37 ($CH_2$), 14.07 ($CH_3$); $\nu_{max}/cm^{-1}$ 1730 (C=O), 1500, 1460, 1310, 1090, 1070, 1000, 980, 930; *m*/*z* 411 ($M^+$, 68%), 395 (21), 378 (23), 323 (31), 307 (20), 279 (29), 246 (32), 126 (31), 100 (96), 84 (100), 70 (60), 64 (48), 49 (100).

### Sulfur extrusion from 17 and 19

A solution of **17** or **19** (1 mmol) in xylene (100 ml) was boiled for 18 or 1 h respectively. The solvent was removed in a rotary evaporator, the residue was washed with light petroleum and crystallised from light petroleum–chloroform mixtures to give the following compounds.

**Table 3** Acid hydrolysis and cleavage of bisdithiolo-thiazines and -pyrroles

| Starting material (mmol) | Reaction conditions: Reagent | Reaction temp./°C | Reaction time/h | Product (yield %) |
|---|---|---|---|---|
| **2** (0.3) | $H_2SO_4$ (96%), 0.6 ml[a] | 5–10 | 0.08 | **8** (100) |
| **6** (0.3) | $H_2SO_4$ (96%), 0.6 ml[a] | 20 | 20 | **9** (58) |
| **12** (0.15) | $H_2SO_4$ (96%), 20 ml | 120 | 2 | **8** (89) |
| **13** (0.1) | $H_2SO_4$ (96%), 20 ml | 125 | 2 | **10** (75) |
| **14** (0.1) | $H_2SO_4$ (96%), 20 ml | 135 | 3 | **10** (40) |

[a] In dichloromethane (40 ml).

**Ethyl 3-(3,5-dioxo-3*H*,5*H*-[4,3-*b*:3,4-*d*]bis[1,2]dithiolopyrrol-4-yl)propanoate 20.** Yellow crystals (95%), mp 147–148 °C (from light petroleum–$CHCl_3$) (Found $M^+$, 346.9404. $C_{11}H_9NO_4S_4$ requires *M*, 346.9414) (Found: C, 37.8; H, 2.5; N, 3.9. $C_{11}H_9NO_4S_4$ requires C, 38.0; H, 2.6; N, 4.0%); $\delta_H$ ($CDCl_3$) 1.21 (3H, t, *J* 7.1, $CH_3$), 2.84 (2H, t, *J* 7.0, $CH_2$), 4.09 (2H, t, *J* 7.1, $CH_2$), 4.82 (2H, t, *J* 7.0, $CH_2$); $\delta_C$ ($CDCl_3$) 181.24 (C=O), 170.02 (C=O), 135.53 and 130.51 (2 × $sp^2$ tertiary C), 60.97 ($CH_2$), 39.74 ($CH_2$), 35.65 ($CH_2$), 14.03 ($CH_3$); $\nu_{max}/cm^{-1}$ 2980 (CH), 1710 (C=O), 1660, 1620, 1440, 1330, 1290, 1190, 1100, 930, 850; *m*/*z* 347 ($M^+$, 65%), 302 (14), 287 (16), 273 (12), 259 (28), 247 (18), 231 (12), 182 (10), 126 (10), 96 (20), 55 (100).

**Ethyl 3-(3,5-dithioxo-3*H*,5*H*-bis[1,2]dithiolo[4,3-*b*:3,4-*d*]-pyrrol-4-yl)propanoate 21.** Black crystals (90%), mp 172–174 °C (from light petroleum–$CHCl_3$) (Found $M^+$, 378.8945. $C_{11}H_9NO_2S_6$ requires *M*, 378.8958) (Found: C, 34.6; H, 2.3; N, 3.45. $C_{11}H_9NO_2S_6$ requires C, 34.8; H, 2.4; N, 3.7%); $\delta_H$ ($d_5$-pyridine) 1.15 (3H, t, *J* 7.1, $CH_3$), 3.20 (2H, t, *J* 8.0, $CH_2$), 4.15 (2H, q, *J* 7.1, $CH_2$), 5.92 (2H, t, *J* 8.0, $CH_2$); $\delta_C$ ($d_5$-pyridine) 200.05 (C=S), 170.74 (C=O), 145.69 and 137.15 (2 × $sp^2$ tertiary C), 61.05 ($CH_2$), 37.06 ($CH_2$), 36.34 ($CH_2$), 14.36 ($CH_3$); $\nu_{max}/cm^{-1}$ 2920 (C-H), 1710 (C=O), 1430, 1410, 1350, 1280, 1180, 1040, 850; *m*/*z* 379 ($M^+$, 100%), 347 (12), 306 (32), 279 (22), 248 (18), 192 (15), 160 (23), 112 (21), 64 (32).

### General procedure for the hydrolysis and cleavage of bisdithiolo-thiazines and pyrroles

The bisdithiolo-thiazine or -pyrrole was mixed with acid and stirred at the temperature and for the time given in Tables 1, 2 and 3. Then the reaction mixture was diluted with water, extracted with DCM and the organic solution was dried over $MgSO_4$. After evaporation the residue was subjected to column chromatography (silica, light petroleum, and then light petroleum–DCM mixtures). Reaction details and product yields are given in Tables 1, 2 and 3.

Characterisation of products not already given are as follows.

**3*H*,4*H*,5*H*-Bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-3,5-dione 8.** Yellow crystals, mp 222–224 °C (Found $M^+$, 278.8600. $C_6HNO_2S_5$ requires *M*, 278.8611) (Found: C, 25.8; H, 0.3; N, 4.8. $C_6HNO_2S_5$ requires C, 25.8; H, 0.4; N, 5.0%); $\delta_H$ ($CDCl_3$) 5.99 (1H, br s, NH); $\delta_C$ ($CDCl_3$) 180.91 (C=O), 133.81 and 128.78 (2 × $sp^2$ tertiary C); $\nu_{max}/cm^{-1}$ 3320 (NH), 1640 C=O), 1590, 1550, 1470, 1280, 1060, 850, 800; *m*/*z* 279 ($M^+$, 100%), 251 (13), 219 (8), 175 (14), 159 (11), 115 (8), 88 (21).

**3*H*-Bis[1,2]dithiolo[4,3-*b*:3,4-*d*]pyrrole-3,5(4*H*)-dione 9.** Yellow crystals, mp 267–268 °C (Found $M^+$, 246.8873. $C_6HNO_2S_4$ requires *M*, 246.8890) (Found: C, 29.0; H, 0.3; N, 5.3. $C_6HNO_2S_4$ requires C, 29.1; H, 0.4; N, 5.7%); $\delta_H$ ($CDCl_3$)

3.77 (1H, br s, NH); $\delta_C$ ($D_2SO_4$) 182.80 (C=O), 140.27 and 138.96 (2 × sp² tertiary C); $\nu_{max}$/cm$^{-1}$ 3150 (NH), 1665 C=O), 1640, 1460, 1230, 1100, 840; *m*/*z* 247 ($M^+$, 100%), 251 (13), 219 (8), 191 (9), 126 (4), 100 (12), 96 (16), 83 (21).

**3-Oxo-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-5-thione 10.** Dark red crystals, mp 253–255 °C (Found $M^+$, 294.8379. $C_6HNOS_6$ requires *M*, 294.8382) (Found: C, 24.6; H, 0.3; N, 4.9. $C_6HNOS_6$ requires C, 24.4; H, 0.3; N, 4.7%); $\delta_H$ ($d_5$-pyridine) 6.61 (1H, br s, NH); $\delta_C$ ($d_5$-pyridine) 194.92 (C=S), 182.00 (C=O), 150.65, 144.55, 138.52 and 133.65 (4 × sp² tertiary C); $\nu_{max}$/cm$^{-1}$ 1640 (C=O), 1580, 1450, 1320, 1110, 1030, 860, 740; *m*/*z* 295 ($M^+$, 100%), 235 (15), 191 (27), 159 (22), 126 (18), 100 (37), 88 (29).

**3*H*,4*H*,5*H*-Bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-3,5-dithione 11.** Black crystals, mp 270–272 °C (Found $M^+$, 310.8158. $C_6HNS_7$ requires *M*, 310.8154); $\delta_H$ ($d_5$-pyridine) 3.48 (1H, br s, NH); $\delta_C$ ($d_5$-pyridine) 199.62 (C=S), 158.32 and 148.52 (2 × sp² tertiary C); $\nu_{max}$/cm$^{-1}$ 3310 (NH), 1590, 1500, 1320, 1120, 1020, 890; *m*/*z* 311 ($M^+$, 8%), 279 (13), 175 (6), 124 (18), 115 (6), 88 (18), 76 (34), 62 (54), 44 (100).

**3-(3,5-Dioxo-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazin-4-yl)propanoic acid 22.** Yellow crystals, mp 209–210 °C (Found $M^+$, 350.8824. $C_9H_5NO_4S_5$ requires *M*, 350.8822) (Found: C, 30.8; H, 1.6; N, 3.9. $C_9H_5NO_4S_5$ requires C, 30.8; H, 1.4; N, 4.0%); $\delta_H$ ($d_5$-pyridine) 2.97 (2H, t, *J* 6.5, $CH_2$), 4.53 (2H, t, *J* 6.5, $CH_2$); $\delta_C$ ($d_5$-pyridine) 183.67 (C=O), 174.38 (C=O), 149.11 and 136.68 (2 × sp² tertiary C) 44.20 ($CH_2$), 35.07 ($CH_2$); $\nu_{max}$/cm$^{-1}$ 2960 (CH), 1710 (C=O), 1620, 1550, 1510, 1450, 1260, 1020, 980, 830, 800; *m*/*z* 351 ($M^+$, 12%), 327 (6), 292 (8), 279 (8), 236 (14), 213 (7), 105 (100), 91 (58), 77 (78), 70 (48).

**3-(3-Oxo-5-thioxo-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*]-[1,4]thiazin-4-yl)propanoic acid 23.** Dark red crystals, mp 218–219 °C (Found $M^+$, 366.8563. $C_9H_5NO_3S_6$ requires *M*, 366.8594) (Found: C, 29.4; H, 1.5; N, 3.6. $C_9H_5NO_3S_6$ requires C, 29.4; H, 1.4; N, 3.8%); $\delta_H$ ($d_5$-pyridine) 3.02 (2H, t, *J* 6.6, $CH_2$), 4.78 (2H, br s, $CH_2$); $\delta_C$ ($d_5$-pyridine) 203.10 (C=S), 183.90 (C=O), 174.40 (C=O), 158.74, 150.95, 148.09 and 137.19 (4 × sp² tertiary C), 44.60 ($CH_2$), 35.04 ($CH_2$); $\nu_{max}$/cm$^{-1}$ 2930 (CH), 1700 (C=O), 1630, 1470, 1340, 1290, 1260, 1100, 1020, 830; *m*/*z* 367 ($M^+$, 55%), 351 (52), 335 (100), 319 (25), 307 (30), 263 (42), 126 (27), 100 (100), 76 (100), 64 (100).

**3-(3,5-Dithioxo-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*]-[1,4]thiazin-4-yl)propanoic acid 24.** Black crystals, mp 216–217 °C (Found $M^+$, 382.8374. $C_9H_5NO_2S_7$ requires *M*, 382.8365) (Found: C, 28.6; H, 1.2; N, 3.5. $C_9H_5NO_2S_7$ requires C, 28.2; H, 1.3; N, 3.7%); $\delta_H$ ($d_5$-pyridine) 3.03 (2H, t, *J* 7.0, $CH_2$), 4.95 (2H, t, *J* 7.0, $CH_2$); $\delta_C$ ($d_5$-pyridine) 203.69 (C=S), 174.35 (C=O), 158.96 and 148.31 (2 × sp² tertiary C), 44.51 ($CH_2$), 34.86 ($CH_2$); $\nu_{max}$/cm$^{-1}$ 2930 (CH), 1700 (C=O), 1500, 1450, 1310, 1060, 930, 740; *m*/*z* 383 ($M^+$, 25%), 351 (100), 311 (10), 295 (8), 279 (12), 247 (15), 204 (8), 138 (8), 112 (6), 88 (10).

**3-(3,5-Dioxo-3*H*,5*H*-bis[1,2]dithiolo[4,3-*b*:3,4*H*-*d*]pyrrol-4-yl)propanoic acid 25.** Yellow crystals, mp 239–240 °C (Found: C, 33.8; H, 1.4; N, 4.2. $C_9H_5NO_4S_4$ requires C, 33.9; H, 1.6; N, 4.4%); $\delta_H$ ($d_5$-pyridine) 3.18 (2H, t, *J* 7.5, $CH_2$), 5.10 (2H, t, *J* 6.5, $CH_2$); $\delta_C$ ($d_5$-pyridine) 182.28 (C=O), 172.90 (C=O), 149.05 and 131.40 (2 × sp² tertiary C) 40.29 ($CH_2$), 36.31 ($CH_2$); $\nu_{max}$/cm$^{-1}$ 3250 (OH), 1720 (C=O), 1630, 1600, 1430, 1340, 1300, 1230, 1210, 1180, 1100, 860; *m*/*z* 319 ($M^+$, 88%), 247 (38), 231 (32), 182 (14), 126 (13), 100 (30), 94 (32), 88 (26), 70 (28), 64 (60), 55 (100).

**3-(3,5-Dithioxo-3*H*,5*H*-bis[1,2]dithiolo[4,3-*b*:3,4-*d*]pyrrol-4-yl)propanoic acid 26.** Black crystals, mp 273–274 °C (Found $M^+$, 378.8958. $C_9H_5NO_2S_7$ requires M, 378.8930) (Found: C, 30.5; H, 1.4; N, 3.8. $C_9H_5NO_2S_6$ requires C, 30.75; H, 1.4; N, 4.0%); $\delta_H$ ($d_5$-pyridine) 3.34 (2H, t, *J* 8.2, $CH_2$), 5.96 (2H, t, *J* 8.2, $CH_2$); $\delta_C$ ($d_5$-pyridine) 199.58 (C=O), 172.74 (C=O), 145.20 and 136.65 (2 × sp² tertiary C) 40.12 ($CH_2$), 36.14 ($CH_2$); $\nu_{max}$/cm$^{-1}$ 2920 (CH), 1710 (C=O), 1630, 1430, 1350, 1280, 1130, 1110, 1040, 930, 850; *m*/*z* 351 ($M^+$, 46%), 335 (12), 306 (22), 279 (22), 247 (30), 215 (21), 138 (30), 126 (42), 112 (100), 100 (88), 88 (45), 55 (78).

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