Bis[1,2]dithiolo[3,4-*b*][4′,3′-*e*][1,4]thiazine-3,5-dione, a planar 1,4-thiazine

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***N*-Benzyldiisopropylamine 1 and S_2Cl_2 give the *N*-benzylbisdithiolothiazine 2, shown by X-ray crystallography to have the typically folded tricyclic structure; 2 is debenzylated by H_2SO_4 to give the title compound 4 which atypically has a rare near-planar 1,4-thiazine ring, gives a blue anion in solution and does not extrude sulfur thermally.**

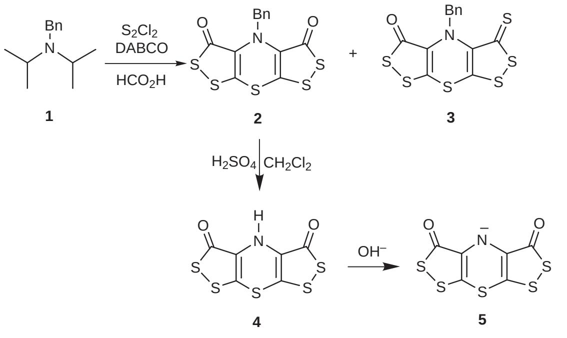
Sulfur–nitrogen heterocycles with a high proportion of heteroatoms are of theoretical and, when reasonable syntheses are available, practical interest in the chemistry of new materials. We have shown that Hünig's base and related diisopropylamines are fully sulfurated in both isopropyl groups by S_2Cl_2 in one-pot reactions to yield bis[1,2]dithiolo[3,4-*b*:4′,3′*e*]-[1,4]thiazines (*cf.* **2**, **3**)[1–4] and bis[1,2]dithiolo[4,3-*b*:3′,4′*d*]-pyrroles (*cf.* **6**, **8**),[2,4] new families of stable fully unsaturated heterocycles which are revealing a rich chemistry.

The *N*-unsubstituted parent ring systems would be particularly interesting from the structural point of view, and as intermediates in the preparation of *N*-substituted derivatives. Unfortunately these key compounds could not be prepared directly from Pr^i_2NH since this is decomposed by S_2Cl_2. Presumably the first step in the tertiary amine–S_2Cl_2 reaction is oxidation of an isopropyl group to give an iminium ion[5] which reacts further with S_2Cl_2 to form the 1,2-dithiole ring and ultimately the tricyclic system. Readily removable groups on nitrogen, such as acetyl and cyano, which would destabilise the iminium ion suppress the reaction with S_2Cl_2.[4]

We therefore treated *N*-benzyldiisopropylamine[6] **1** with S_2Cl_2 (10 equiv.) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (9 equiv.) in 1,2-dichloroethane for 3 d at room temperature. Formic acid (20 equiv.) was then added and the mixture heated under reflux for 1.5 h, since this treatment gives cleaner reactions by facilitating conversion of the 3-chlorodithiolium salts into dithiole-3-ones. Products **2**† [orange crystals, mp 200–202 °C (21%)] and **3**† [orange solid, mp 209–210 °C (7%)] were obtained after chromatography (Scheme 1).

Structure **2** was confirmed by X-ray crystallography‡ which shows the molecule (Fig. 1) to have a scorpion-like conformation very similar to the *N*-ethyl analogue,[4] the benzyl ring being folded back and partially overlaying the thiazine ring (Fig. 1). The molecule has crystallographic C_s symmetry about a plane passing through S(8), N(4), C(9), C(10) and C(13). The fold angle about the N···S axis of the thiazine ring is 32°, *cf.* 34° in the *N*-ethyl analogue. The pattern of bonding in the thiazine and dithiole ring systems does not differ significantly from that observed in the *N*-ethyl analogue. The molecules pack to form corrugated sheets (Fig. 2) dominated by strong intermolecular O···S interactions [3.02 Å]. There are no intersheet interactions of note.

Treatment of a dilute solution of the *N*-benzyl compound **2** in CH_2Cl_2 with concentrated H_2SO_4 at 5–10 °C for 5 min gave the debenzylated compound **4**† (orange–red crystals, mp 222–224 °C) in quantitative yield. All its properties, including a broad *N*–H absorption at 3474 cm^{-1} and one carbonyl absorption at 1640 cm^{-1} are in agreement with the parent bis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazine-3,5-dione structure **4**. X-Ray analysis of the N–H species **4** shows that removal of the *N*-benzyl substituent results in a dramatic flattening of the molecule, the non-hydrogen atoms being co-planar to within



Scheme 1

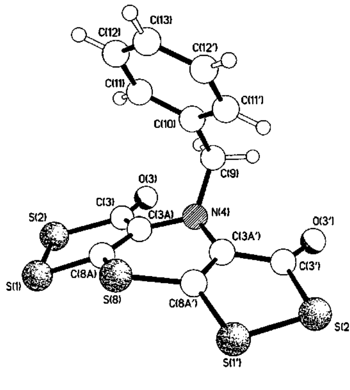


Fig. 1 The molecular structure of **2**. The geometry at N(4) is pyramidal, with the nitrogen atom lying 0.24 Å out of the plane of its substituents.

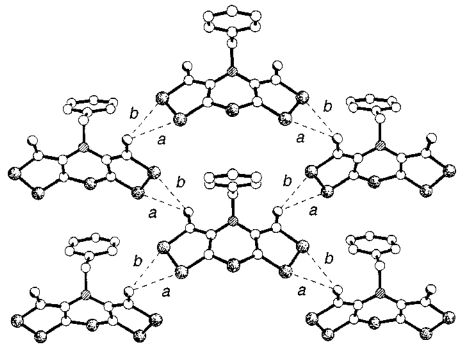


Fig. 2 Part of one of the corrugated sheets of molecules present in the crystals of **2**. The intermolecular O···S contacts (*a*) and (*b*) are both 3.02 Å.

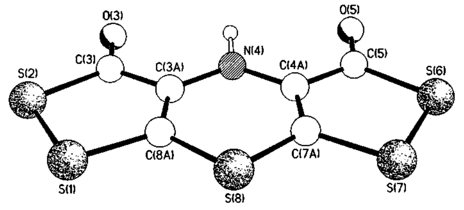


Fig. **3** The molecular structure of **4**.

0.11 Å with only a 5° fold about the thiazine N···S vector (Fig. 3)§ compared to greater than 30° for its *N*-alkyl derivatives and 27° for dibenzo-1,4-thiazine (phenothiazine).[7] The only significant change in the pattern of bonding, compared with **2**, is a small decrease in the C(3A)–N(4) distance and a slight increase in the C(8A)–S(8) bond length. The molecules pack as alternating bi-directional π–π stacked tapes, the planes of adjacent stacks being inclined by 89° (Fig. 4). The tapes are produced by head-to-tail linking of molecules *via* pairs of O···S interactions [3.08 and 3.09 Å], and orthogonal tapes by similar strength O···S, and weaker S···S, interactions [3.15 and 3.54 Å respectively]. The *N*–H hydrogen atom is not involved in any significant intermolecular interactions, possibly because of its steric congestion.

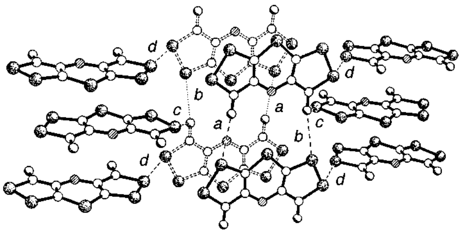


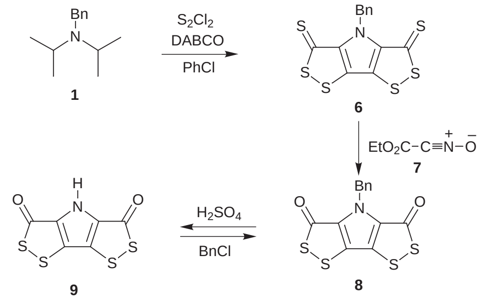
Fig. **4** Part of the array of orthogonally oriented p-stacked tapes present in the crystals of **4**, the mean interplanar separation being *ca*. 3.4 Å. The intermolecular O···S and S···S contacts are (*a*) 3.09, (*b*) 3.08, (*c*) 3.15 and (*d*) 3.54 Å.

The *N*-H compound **4** readily formed purple solutions of the lithium or sodium salt **5** by reaction with LiHMDS or NaH in THF from which a hygroscopic deep purple solid could be isolated by evaporation. Compound **4**, with a UV spectrum of λ_{max} = 310 nm, ε = 8860 in THF, gave a blue solution in aq. 0.1 M NaOH with λ_{max} = 600 nm, ε = 8000. The aqueous alkaline solution was stable for a few days, and the blue spot formed by immersion of TLC plates in aq. NaOH provides a good method of detection of **4**.

Compound **4** and its sodium salt **5** either did not react with common electrophiles such as BnCl, BzCl, MeI and TMSCl under standard conditions or gave unstable products which reverted to **4** during isolation. In striking contrast with its *N*-alkyl derivatives,[2,4] **4** did not extrude sulfur on heating in chlorobenzene for 6 h or in 1,2-dichlorobenzene for 2 h. The expected product **9** (below) was made alternatively. Attempted thiation of **4** with Lawesson's reagent in refluxing THF gave an unstable product that decomposed on work-up; debenzylation of the oxothione **3** by sulfuric acid also gave an unstable product, and we have not yet succeeded in preparing thiocarbonyl derivatives of the parent structure **4**.

Treatment of **1** with S_2Cl_2 (10 equiv) and DABCO (10 equiv) in chlorobenzene for 3 d at room temperature followed by heating under reflux for 2 h gave the pyrrole **6**† [black crystals, mp 223–224 °C (13%)] (Scheme 2) formed by selective sulfur extrusion from the intermediate 1,4-thiazine.[2,4]

The pyrrole **6** was not debenzylated by the sulfuric acid treatment that is so successful with the thiazine **2**. Treatment of **6** in THF at 0 °C for 15 min with excess of ethoxycarbonyl nitrile oxide **7** generated *in situ* from ethyl chlorooximidoacetate and Et_3N[4] readily gave the corresponding dioxo derivative **8** [yellow crystals, mp 211–213 °C (decomp.) (86%)], a structure supported by all its analytical and spectroscopic properties (Scheme 2). The sulfuric acid treatment of **8** in



Scheme 2

CH_2Cl_2 at room temperature overnight did now give the debenzylated compound **9** as yellow crystals [mp 267–268 °C (decomp.) (58%)]. The structure of **9** is based upon spectroscopic data and its almost quantitative reconversion to the *N*-benzyl compound **8** with Bu^tOK and BnCl in DMF (Scheme 2). Unexceptionally, **9** did not give a coloured solution in 0.1 M aq. NaOH.

Thus the parent bisdithiolopyrrole **9** and bisdithiolo-1,4-thiazine **4** have been prepared in very short sequences from **1**. Whilst the properties of the former are entirely normal, the thiazine **4** is abnormal in that it is almost planar, it readily gives a highly coloured anion which is inert to substitution on nitrogen, and it does not extrude the thiazine sulfur atom on heating. It is not yet clear how these unusual properties, which appear to indicate enhanced electronic delocalisation and stabilisation, result from simply replacing an *N*-alkyl group by hydrogen, nor why the analogous compounds with one or two thiocarbonyl groups should be unstable.

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Notes and references

† The structures of all new compounds are based upon IR, MS, HRMS, ^1H and ^{13}C NMR and elemental analysis.

‡ *Crystal data* for **2**: $C_{13}H_7NO_2S_5$, M = 369.5, orthorhombic, *Pnma* (no. 62), a = 11.573(3), b = 16.113(1), c = 8.064(1) Å, V = 1503.7(4) Å^3, Z = 4 (the molecule has crystallographic C_s symmetry), D_c = 1.632 g cm^{-3}, μ(Cu-Kα) = 71.3 cm^{-1}, $F(000)$ = 752, T = 293 K; orange hexagonal prisms 0.58 × 0.43 × 0.40 mm. For **4**: $C_6HNO_2S_5$, M = 279.4, monoclinic, $C2/c$ (no. 15), a = 11.323(1), b = 8.071(1), c = 20.066(2) Å, β = 104.49(1)°, V = 1775.4(3) Å^3, Z = 8, D_c = 2.090 g cm^{-3}, μ(Mo-Kα) = 12.7 cm^{-1}, $F(000)$ = 1120, T = 203 K; orange–red blocky needles 0.73 × 0.22 × 0.17 mm. 1232 (2601) Independent reflections were measured on Siemens P4/PC diffractometers using ω-scans for **2** (**4**) respectively. The structures were solved by direct methods and all of the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 with absorption corrected data to give R_1 = 0.036 (0.037), wR_2 = 0.093 (0.078) for 1118 (2063) independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 124°$ (60°)] and 104 (131) parameters for **2** (**4**) respectively. CCDC 182/1095.

§ In the thiazine ring the C and N atoms are coplanar to within 0.01 Å with the S atom lying 0.11 Å and the H atom 0.20 Å out of this plane.

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