Preparation and *X*-Ray Crystal Structure of a 2,1,3-Benzothiadiazine Derivative Containing a Dithiosulphone Group

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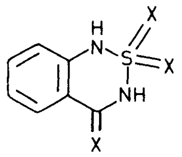
The 2,2-disulphide (**1b**) of 1*H*-2,1,3-benzothiadiazine-4(3*H*)-thione, a compound containing a novel dithiosulphone group, has been synthesised in a one-step reaction; the structure has been established by *X*-ray crystallography.

Shortly after the first synthesis of the 2,1,3-benzothiadiazine ring system,[1] it became clear that this heterocycle was of considerable biological importance. In the past decade attention has focused on the 2,2-dioxide (**1a**) of 1*H*-2,1,3-benzothiadiazine-4(3*H*)-one; there has been unabated interest in the synthesis and properties of new derivatives as they are among the most potent and versatile synergistic herbicides known. The standard route to compound (**1a**) involves cyclisation of an appropriately substituted methyl anthranilate with sulphamoyl chloride (NH_2SO_2Cl); the nitrogen atoms can then be functionalised in the normal way.[1,2] Surprisingly, no derivative of (**1a**) has been described where any of the oxygen atoms is replaced by sulphur. In a recent review[3] of compounds possessing the S=S bond there are several possible examples of thiosulphoxides and of compounds containing three contiguous sulphur atoms, and although a dithiosulphone structure was considered for some of the latter, an *X*-ray study in one case ($I[CH_2]_2$–S–S–S–$[CH_2]_2I$) showed that a linear trisulphide was present.[4] We now report the synthesis of (**1b**), a compound with the hitherto unknown dithiosulphone grouping.



(**1**) a; X = O
b; X = S

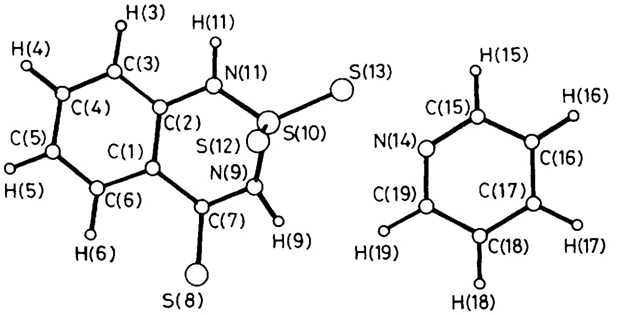


Figure 1. *X*-Ray structure of compound (**1b**)·C_5H_5N showing atom numbering scheme.

Treatment of 2-aminobenzamide with phosphorus pentasulphide (1 equiv.) in refluxing pyridine for 1.5 h yielded the compound of formula $C_{12}H_{11}N_3S_4$ in 56% yield. The crystal structure (Figure 1) was elucidated by *X*-ray analysis† which revealed the presence of the 2,2-disulphide (**1b**) of 1*H*-2,1,3-benzothiadiazine-4(3*H*)-thione and pyridine in a 1 : 1 molar ratio.‡

There is no intermolecular interaction within the crystal lattice: the shortest intermolecular contact for $C_7H_6N_2S_4$ molecules is between S(8) and N(9) (3.360 Å), and for $C_7H_6N_2S_4$ and the pyridine molecule is between S(13) and N(14) (3.374 Å). The thiadiazine ring adopts a conformation in which S(10) is 0.66 Å out of the mean plane through all the other atoms in the ring, although the N(9)–C(7)–C(1)–C(2)–N(11) unit is planar to within 0.04 Å. The heterocyclic system contains two S–N single bonds, S(10)–N(11) [1.666(7)] and S(10)–N(9) [1.718(4)], and partial double bonds for C(7)–S(8) [1.683(5)], C(2)–N(11) [1.380(9)], and S(10)–S(13) [1.947(2) Å]. The axial S(10)–S(12) bond is significantly longer [1.970(2) Å]. The torsion angles C(7)–N(9)–S(10)–S(13), C(7)–N(9)–S(10)–S(12), C(2)–N(11)–S(10)–S(13), and C(2)–N(11)–S(10)–S(12) are 155.4, −62.3, −144.0, and 77.4° respectively.

This provides the first structural study on the 2,1,3-benzothiadiazine ring system. A remarkable feature of the dithiosulphone group of (**1b**)·C_5H_5N is its stability; the compound can be recovered unchanged after 12 h in a refluxing mixture of water and toluene.

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† *Crystal data* of (**1b**)·C_5H_5N: $C_7H_6N_2S_4 \cdot C_5H_5N$, $M = 325.51$, triclinic, space group $P\bar{1}$, $a = 12.391(3)$, $b = 7.422(2)$, $c = 10.011(2)$ Å, $\alpha = 6.411(2)$, $\beta = 117.21(2)$, $\gamma = 111.79(2)^\circ$, $U = 719.5$ Å^3, $Z = 2$, $F(000)$ 336, D_c 1.502 g cm^{-3}, $R = 0.069$ for 1713 reflections. Diffracted intensities were recorded on a four-circle Hilger-Watts diffractometer controlled by PDP8 computer using the $\omega/2\theta$ scan mode, and the structure was solved by direct methods. The benzothiadiazine molecule was visible in the *E*-map and the pyridine molecule was found from a subsequent difference Fourier map. The structure was refined by blocked full-matrix least squares; during the refinement the bond lengths within the pyridine molecule were kept fixed because of high thermal vibrations (U_{iso} 0.10). The atomic co-cordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Satisfactory analytical data were obtained. Compound (**1b**)·C_5H_5N, yellow crystals, m.p. 189—190 °C (from ethanol–water); *m/z* 246 (M^+); $\nu_{\max}$ (Nujol) 1607, 1570, 1190—1179br., 1158, 1132, 992, 899, 747, 681, and 663 cm^{-1}; δ_H [300 MHz; $(CD_3)_2SO$], pyridine moiety: 8.94 (2H, q, *J* 6.5 and 1.4 Hz, 2-H), 8.60 (1H, m, 4-H), and 8.07 (2H, q, *J ca.* 6.4 and 6.7 Hz, 3-H); benzothiadiazine moiety: 10.66 and 10.22 (each 1H, s, NH, deuterium exchangeable, position varies a little with concentration), 8.27 (1H, q, *J* 8.1 and 1.4 Hz, 5-H), 7.27 (1H, t, *J ca.* 7.5 Hz, 7-H), 6.84 (1H, d, *J* 7.8 Hz, 8-H), and 6.74 (1H, t, *J ca.* 7.4 Hz, 6-H). Irradiation at δ 6.74 caused the quartet at δ 8.27 to collapse to a singlet, and irradiation at δ 8.27 caused the expected change to the triplet at δ 6.74.