Synthesis and X-Ray Structure of a Novel 1,2,4-Trithiolane

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Photolysis of 1,2-dithiole-3-thione derivative **1** results in the formation of the 1,2,4-trithiolane derivative **2**, the structure of which was established by single crystal X-ray analysis. Interesting bond delocalisation is observed in the molecular structure. A mechanism involving dimerisation of **1** followed by loss of sulfur is proposed.

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In the continuation of our studies on the chemistry of 1,2-dithiole-3-thiones [1] we have synthesised the known compound 4,5-dithiomethyl-1,2-dithiole-3-thione **1** [2]. During routine nmr characterisation of **1** a sample dissolved in deuteriochloroform was left in sunlight at room temperature for 48 hours. Small, shiny, black crystals appeared on the interior walls of the nmr tube. The crystals were insoluble in a range of common solvents and only small quantities were obtained. Subsequent controlled experiments in dichloromethane and chloroform solution established that this product was formed in a maximum of *ca.* 5% yield under pyrex-filtered uv irradiation, but not formed in the dark even after 10 days. The yield of product was not raised by performing the photolysis in refluxing dichloromethane or chloroform solution. Elemental analysis of the crystals indicated the formula $C_{10}H_{12}S_9$, *i.e.* a dimer of **1** minus one sulfur atom. X-Ray structural analysis revealed the unusual 1,2,4-trithiolane structure **2** (Figure 1).

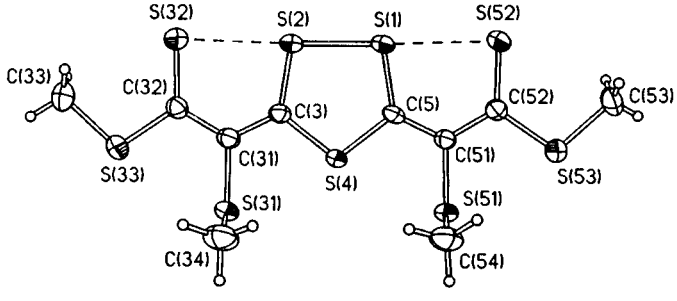
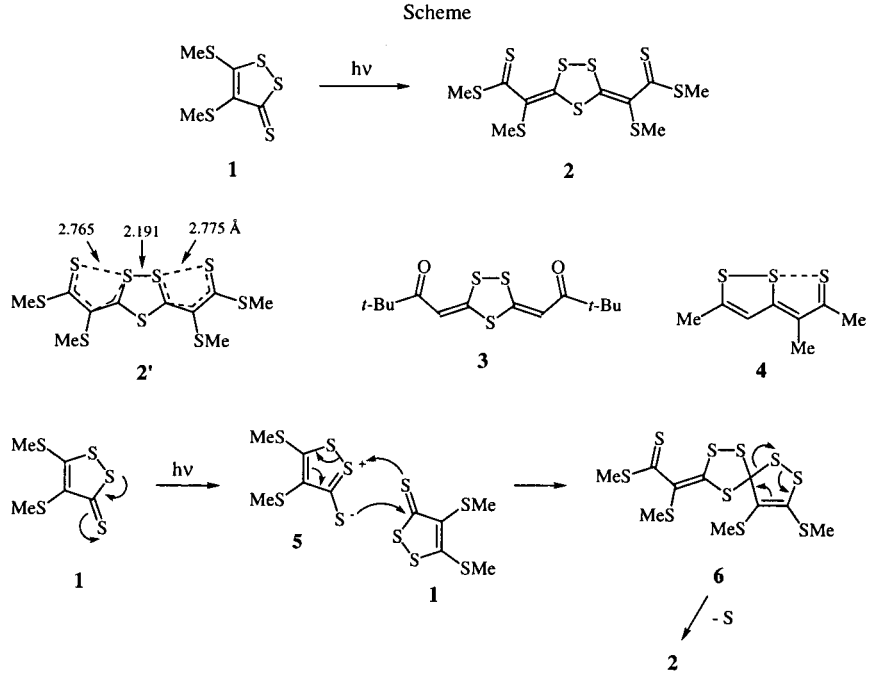


Fig. 1. Molecular structure of **2** (50% thermal ellipsoids).

The molecule is essentially planar except for the out-of-plane orientations of the two methyl groups, C(34) and C(54), lying at 1.75 and 1.77Å from the mean plane. Intramolecular distances S(1)...S(52) 2.775Å and S(2)...S(32) 2.765Å are much shorter than twice the Van der Waals radius of sulfur (1.81 Å)[3]. The S(1)-S(2) bond (2.191Å) is longer than that found in 1,2,4-trithiolane derivatives which have no additional S...X interactions (2.04-2.07Å)[4] or in compound **3** (2.10 Å) where short intramolecular S...O contacts of 2.51Å exist[5]. Bonds C(32)=S(32) and C(52)=S(52) are longer than those usually

Scheme



found in dithioesters (average 1.62Å)[6] and the C-C bonds between them and the ring show π-delocalisation.

Compound **2** thus shows both types of bond delocalization which are characteristic of derivatives of thiathiophthene **4** [7] *viz.* a hypervalent bonding or bond/no-bond resonance in the linear S-S-S chain and π-delocalization in a 'fused' system of 5-membered ring and pseudo-ring. The degree of delocalization in **2** is lower than in asymmetric thiathiophthenes, where the difference between the 'long' and the 'short' S-S distances does not exceed 0.4 Å. However, similar compounds with a linear tetra- (rather than tri-) sulfur chain S...S-S...S, reported earlier [8] show even larger differences. Thus system **2** is actually a thiathiophthene-like S_3 chain plus one weaker contact with an extra S atom, as represented in structure **2'**, rather than a conjugated structure depicted in **2**.

A plausible mechanism for the formation of compound **2** from **1** is shown in the Scheme. This route involves the reaction of a zwitterionic canonical form **5** in a 1,3-dipolar addition to the thiocarbonyl group of another molecule of **1** to generate the spiro-intermediate **6**, which then rearranges as shown and expels a sulfur atom to form the product **2**. A radical mechanism is also possible. We do not understand why the reaction does not proceed in higher yield: after the crystals of **2** are removed from the reaction mixture by filtration, unreacted compound **1** is present in the filtrate, from which it can be recovered in high yield. Photolysis of this filtrate containing **1** did not afford any more of the product **2** (no reaction occured) suggesting that an inhibitor of this reaction (possibly derived from the sulfur which has been eliminated) is produced during the conversion of **1** into **2**.

Table 1

Bond Lengths (Å) and Angles (°) in **2**

S(1)-C(5)	1.722(2)	S(1)-S(2)	2.191(1)
S(1)...S(52)	2.775(1)	S(2)...S(32)	2.765(1)
S(2)-C(3)	1.722(2)	S(4)-C(5)	1.746(2)
S(4)-C(3)	1.752(3)	S(31)-C(31)	1.777(3)
S(31)-C(34)	1.803(4)	S(32)-C(32)	1.658(3)
S(33)-C(32)	1.742(3)	S(33)-C(33)	1.793(3)
S(51)-C(51)	1.781(2)	S(51)-C(54)	1.804(3)
S(52)-C(52)	1.660(3)	S(53)-C(52)	1.750(2)
S(53)-C(53)	1.793(3)	C(3)-C(31)	1.381(3)
C(5)-C(51)	1.386(4)	C(31)-C(32)	1.435(4)
C(51)-C(52)	1.425(3)		
C(5)-S(1)-S(2)	99.2(1)	C(3)-S(2)-S(1)	99.1(1)
C(5)-S(4)-C(3)	103.1(1)	C(31)-S(31)-C(34)	100.6(2)
C(32)-S(33)-C(33)	102.4(2)	C(51)-S(51)-C(54)	101.2(1)
C(52)-S(53)-C(53)	103.1(2)	C(31)-C(3)-S(2)	125.5(2)
C(31)-C(3)-S(4)	115.3(2)	S(2)-C(3)-S(4)	119.2(1)
C(51)-C(5)-S(1)	125.0(2)	C(51)-C(5)-S(4)	115.6(2)
S(1)-C(5)-S(4)	119.4(2)	C(3)-C(31)-C(32)	122.8(2)
C(3)-C(31)-S(31)	117.9(2)	C(32)-C(31)-S(31)	119.3(2)
C(31)-C(32)-S(32)	121.6(2)	C(31)-C(32)-S(33)	114.9(2)
S(32)-C(32)-S(33)	123.5(2)	C(5)-C(51)-C(52)	123.1(2)
C(5)-C(51)-S(51)	117.4(2)	C(52)-C(51)-S(51)	119.5(2)
C(51)-C(52)-S(52)	122.1(2)	C(51)-C(52)-S(53)	114.6(2)
S(52)-C(52)-S(53)	123.3(2)		

Table 2

Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å x 10^4) for **2**

	x	y	z	U_{eq}
S(1)	2038.6(9)	3366.4(8)	4309.4(5)	304(2)
S(2)	1550.3(9)	4088.6(8)	5934.8(5)	313(2)
S(4)	3395.6(8)	7164.2(8)	5588.4(5)	291(2)
S(31)	3542.2(9)	9647.3(8)	7778.2(6)	362(2)
S(32)	903.1(10)	4897.3(9)	7975.9(6)	408(2)
S(33)	2004.7(10)	8636.7(9)	9444.2(6)	408(2)
S(51)	4665.4(9)	7897.0(8)	3812.2(5)	329(2)
S(52)	2600.0(10)	2340.1(8)	2235.2(5)	368(2)
S(53)	4316.2(10)	5161.8(9)	1598.8(6)	401(2)
C(3)	2461(3)	6276(3)	6423(2)	264(5)
C(5)	3062(3)	5375(3)	4388(2)	254(5)
C(31)	2527(3)	7443(3)	7441(2)	301(6)
C(32)	1823(3)	6942(3)	8229(2)	300(6)
C(33)	970(6)	7556(5)	10193(3)	528(9)
C(34)	1759(5)	10461(5)	7258(3)	551(9)
C(51)	3663(3)	5712(3)	3558(2)	279(5)
C(52)	3497(3)	4407(3)	2524(2)	278(5)
C(53)	3957(6)	3223(5)	426(3)	515(9)
C(54)	2843(5)	8747(4)	3409(3)	473(8)

U(eq) is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

In summary, the unexpected formation of a new 1,2,4-trithiolane derivative **2** is described, and its X-ray crystal structure reveals interesting bond delocalisation within the molecule.

EXPERIMENTAL

Synthesis of 1,2,4-Trithiolane **2**.

Compound **1** [2] (50 mg, 0.10 mmole) was dissolved in chloroform (*ca.* 10 ml) and the solution irradiated with a uv lamp for 24 hours. After this time small insoluble black crystals of **2** (*ca.* 5 mg, 5%) were removed by filtration, mp 167°; m/z (CI) 389 (M^+-2S+1, 100%).

Anal. Calcd. for $C_{10}H_{12}S_9$: C, 28.5; H, 2.9. Found: C, 28.4; H, 2.8.

Unreacted starting material (*ca.* 40 mg) was recovered by evaporation of the filtrate.

The crystal data for **2** are: $C_{10}H_{12}S_9$, M = 420.74, triclinic, space group P$\bar{1}$ (No.2), a = 8.2446(5), b = 8.3436(5), c = 13.2504(9) Å, α = 108.099(5), β = 102.375(5), γ = 98.552(5)°, V = 823.2(1) Å^3, Dx = 1.70 g cm^{-3}, T = 295 K, $\bar{\lambda}$ (Mo-K_α) = 0.71073 Å, μ = 11.9 cm^{-1}, 3680 reflections (2θ ≤55°), 3034 unique, least squares refinement of 220 parameters against F^2 (SHELXL93 software, G. M. Sheldrick, University of Göttingen, Germany, 1993), R = 0.032 for 2438 data with $F^2 \geq 2\sigma(F^2)$, $wR(F^2)$ = 0.088. Related relevant data has been deposited at the Cambridge Crystallographic Database.

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