**Short Note**

### 3,5-Dithiatricyclo[5.2.1.0<sup>2,6</sup>]decan-4-one

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**Abstract:** The X-ray structure of the title compound has been determined and the structure shows an *exo*-configured planar dithiolanone ring. This is in contrast to the few previous dithiolanones to be characterised crystallographically, which are all twisted.

**Keywords:** 3,5-dithiatricyclo[5.2.1.0<sup>2,6</sup>]decan-4-one; X-ray structure; ring planarity

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### 1. Introduction

The title compound 1 was first mentioned in 1985 [1], when it was formed by mercuric acetate oxidation of the corresponding 1,3-dithiolane-2-thione 2 (Scheme 1). However, in that report it was treated as a synthetic intermediate and no analytical or spectroscopic data were given. A short time later, a second preparative method was described [2] involving reaction of the 1,2,3-trithiolane 3, formed from norbornene 4 and sulfur [3], with dichlorocarbene under phase-transfer conditions. In this report it was suggested that the trithiolane 3 reacts with dichlorocarbene to give the thione, 2, but the mechanism by which 2 was converted into 1 was unclear. Perhaps the simplest preparation of 1 involves direct treatment of norbornene 4 with diisopropyl xanthogen disulfide and the radical initiator azobis(isobutyronitrile) (AIBN), which affords 1 directly in 74% yield [4]. Although compound 1 has been characterised by melting point, <sup>1</sup>H and <sup>13</sup>C-NMR and IR spectroscopy, and elemental analysis [2], its X-ray structure has not been investigated. We have obtained compound 1 repeatedly in low yield as a by-product arising from oxidative degradation of the adduct, 5, formed from norbornene 4 and Bu₃P × CS₂. The ylene 5 can be exploited synthetically in a Wittig reaction with aldehydes to give 2-alkylidene-1,3-dithiolanes [5–7] or, in the presence of extra CS₂, in a 1,3-dipolar cycloaddition process with dipolarophiles such as dimethyl acetylenedicarboxylate (DMAD) to give dihydrotetraethiafulvalenes [8]. Furthermore, it can also undergo hydrolysis to give the corresponding 1,3-dithiolane [9]. We describe here determination of the molecular and crystal structure of 1 by X-ray diffraction. The structure is compared with the few crystal structures previously reported for 1,3-dithiolan-2-ones.

![Scheme 1. Synthetic routes to 1.](image_url)

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2. Results

A sample of compound 1 suitable for X-ray diffraction was obtained from chromatographic purification of the product obtained by reaction of 5 with propargylaldehyde, HCC≡C–CHO, and CS₂ (<5% yield). The resulting molecular structure is shown in Figure 1 and selected bond lengths and angles are given in Table 1. The structure features an exo-configured dithiolanone ring, which is essentially planar with the expected long C-S bond lengths and correspondingly smaller internal angles at sulfur. The crystal structure features a centrosymmetric arrangement of four molecules in the unit cell (Figure 2). Rather surprisingly, a search of the Cambridge Structural Database (CSD, March 2020 update) revealed only five previous structures containing the 1,3-dithiolan-2-one fragment with at least one sp³ carbon in the ring (Figure 3). These are the parent compound 6 [10], the polychlorinated compound 7 in which the dithiolanone ring is tetrasubstituted [11], the bicyclic diester 8 with a trans-disubstituted dithiolanone ring [12], and the Diels–Alder dimer of 4,5-bis(methylene)-1,3-dithiolan-2-one 9 and the derived cobalt complex 10 [13], both of which have the dithiolanone ring fully substituted but with one spiro sp³ centre and one sp² centre.

![Figure 1. Two views of the molecular structure of 1 with numbering scheme (ORTEP probability ellipsoids at 50%).](image)

| Bond         | Length/Å | Angle       | Value/° |
|--------------|----------|-------------|---------|
| C(1)–C(2)   | 1.570(8) | C(1)–C(2)–S(2) | 113.2(4) |
| C(1)–S(1)   | 1.805(6) | C(2)–S(2)–C(8) | 99.7(3)  |
| S(1)–C(8)   | 1.753(6) | S(2)–C(8)–O(8) | 122.5(5) |
| C(8)–O(8)   | 1.206(7) | O(8)–C(8)–S(1) | 123.2(5) |
| C(8)–S(2)   | 1.775(6) | S(2)–C(8)–S(1) | 114.4(3) |
| S(2)–C(2)   | 1.798(6) | C(8)–S(1)–C(1) | 100.4(3) |
| S(1)–C(1)–C(2) |       | S(1)–C(1)–C(2) | 112.3(4) |

While comparison of the internal angles at sulfur and at C=O show all six compounds to have rather similar values, the key difference observed between the molecular structure of 1 and the previous structures 6–10 is the degree of planarity in the dithiolanone ring. This is readily quantified by examining the torsion angle S-C-C-S for the six compounds (Table 2). While the carbonyl C(2) carbon is completely planar in all cases, it is only in the case of 1 where the whole dithiolanone ring is fused cis to the rigid bicyclo[2.2.1] skeleton that all five ring atoms are essentially coplanar, corresponding to a S-C-C-S torsion angle near to zero. In all the other cases this torsion angle is significantly greater, corresponding to a twisting of the ring, and it appears that even in the absence of substituent effects in 6 this twisted conformation is preferred.
= colourless prism, crystal dimensions 0.25 × the small number of other 1,3-dithiolan-2-ones for which crystal structures are known.

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fit on $F^2$ 1.122. Data were collected using graphite monochromated Mo Kα radiation $\lambda = 0.71075$ Å and have been deposited at the Cambridge Crystallographic Data Centre as CCDC 1989785. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [link](http://www.ccdc.cam.ac.uk/getstructures). The structure was solved by direct methods and refined by full-matrix least-squares against $F^2$ (SHELXL Version 2018/3 [14]). Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealised geometries. The data did not allow determination of the polarity of the axis.

**Author Contributions:** N.S.K. prepared the compound; A.M.Z.S. collected the X-ray data and solved the structure; R.A.A. designed the experiments, analysed the data, and wrote the paper. All authors have read and agreed to the published version of the manuscript.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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