

Short Note

3,5-Dithiatricyclo[5.2.1.0^{2,6}]decan-4-one

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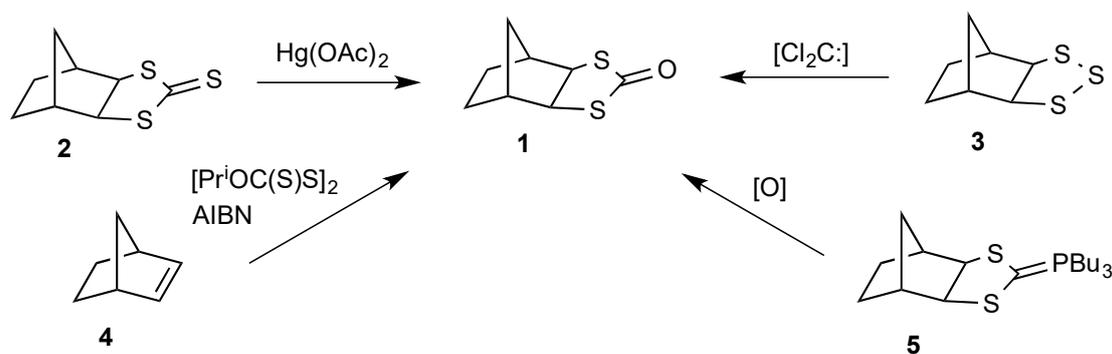


Abstract: The X-ray structure of the title compound has been determined and the structure shows an *exo*-configured planar dithiolanone ring. This is in contrast to the few previous dithiolanones to be characterised crystallographically, which are all twisted.

Keywords: 3,5-dithiatricyclo[5.2.1.0^{2,6}]decan-4-one; X-ray structure; ring planarity

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, ¹H and ¹³C-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 dihydrotetrathiafulvalenes [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**.

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, $\text{HC}\equiv\text{C}-\text{CHO}$, and CS_2 (<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 sp^3 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 sp^3 centre and one sp^2 centre.

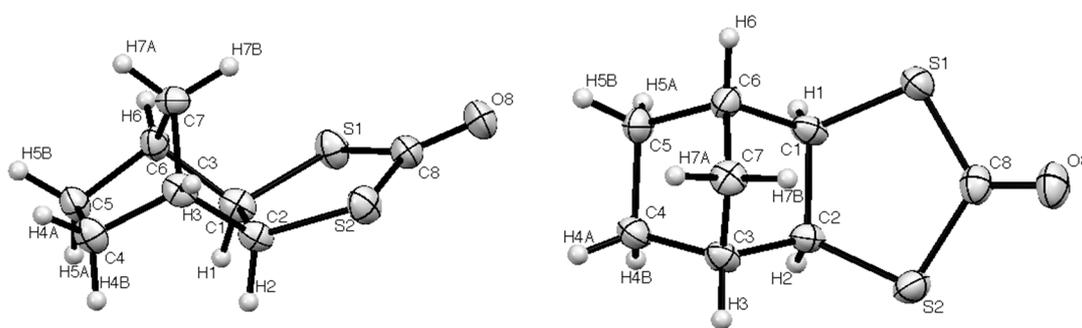


Figure 1. Two views of the molecular structure of **1** with numbering scheme (ORTEP probability ellipsoids at 50%).

Table 1. Selected bond lengths and angles.

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)	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.

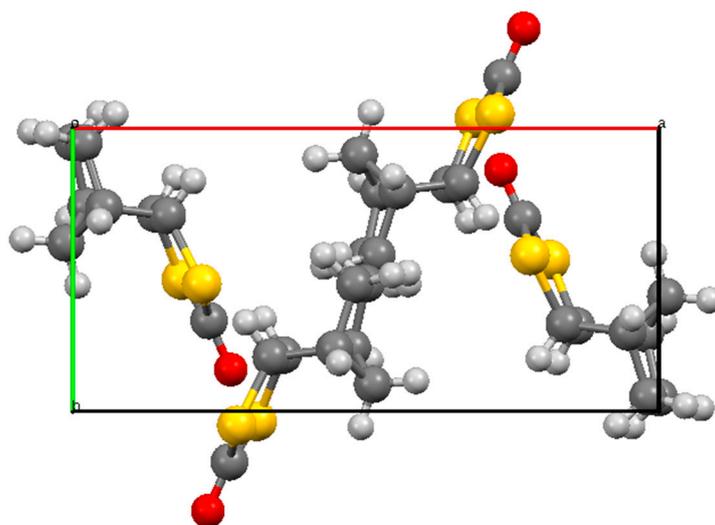


Figure 2. Unit cell of **1** viewed along the *c*-axis showing the four molecules present.

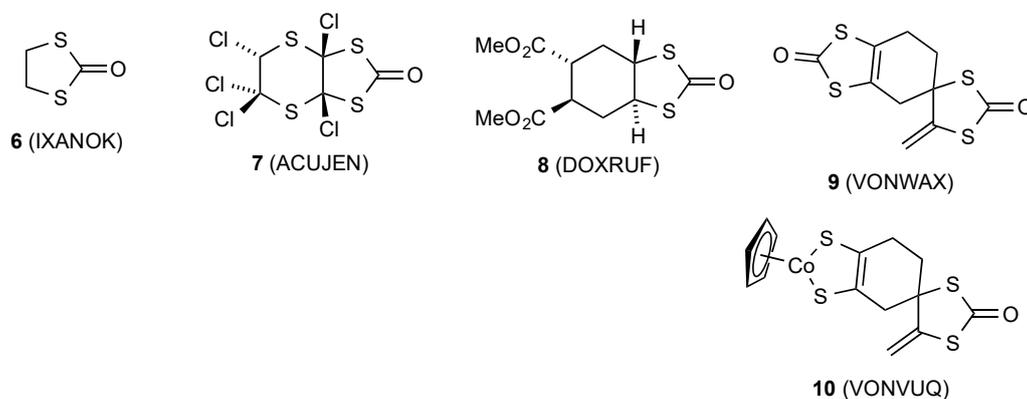


Figure 3. A survey of crystallographically characterised 1,3-dithiolan-2-ones with Cambridge Structural Database (CSD) reference codes.

Table 2. Key angles in the structures of dithiolanones (°).

Compound	C–S–C Internal Angle	S–C(O)–S Internal Angle	S–C–C–S Torsion Angle	Reference
1	100.4(3), 99.7(3)	114.4(3)	1.9(5)	This work
6	96.61(5), 96.57(5)	113.41(6)	44.44(9)	[10]
7	95.7(2), 94.6(2)	114.8(2)	48.2(3)	[11]
8	94.7(2), 94.5(2)	113.6(2)	51.3(3)	[12]
9	99.67(8), 98.62(8)	114.1(1)	11.6(2)	[13]
10	97.9(2), 97.2(3)	113.7(3)	36.2(4)	[13]

In summary, the X-ray crystal structure of the norbornane-fused 1,3-dithiolan-2-one **1** shows it to adopt an *exo* configuration with a planar heterocyclic ring, in contrast to the twisted shape adopted by the small number of other 1,3-dithiolan-2-ones for which crystal structures are known.

3. Experimental

3,5-Dithiatricyclo[5.2.1.0^{2,6}]decan-4-one (**1**): Crystal data for C₈H₁₀OS₂, M = 186.28 g mol⁻¹, colourless prism, crystal dimensions 0.25 × 0.12 × 0.05 mm, orthorhombic, space group *Pna*2₁, *a* = 13.134(6), *b* = 6.336(3), *c* = 9.999(4) Å, *V* = 832.1(6) Å³, *Z* = 4, *D*_{calc} = 1.487 g cm⁻³, *T* = 93 K, *R*₁ = 0.0430, *R*_w2 = 0.1051 for 1350 reflections with *I* > 2σ(*I*), and 101 variables, *R*_{int} 0.0530, Goodness of

fit on F^2 1.122. Data were collected using graphite monochromated Mo $K\alpha$ radiation $\lambda = 0.71075 \text{ \AA}$ 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 <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.

References

1. Russell, G.A.; Law, W.C.; Zaleta, M. Aliphatic semidiones. 44. Spin probes derived from dithiols. *J. Am. Chem. Soc.* **1985**, *107*, 4175–4182. [[CrossRef](#)]
2. Ghosh, T. Reaction of trithiolanes with dihalocarbenes under phase-transfer catalysis. A convenient synthesis of trithiocarbonates and thionocarbonates. *J. Org. Chem.* **1990**, *55*, 1146–1147. [[CrossRef](#)]
3. Bartlett, P.D.; Ghosh, T. Sulfuration of the norbornene double bond. *J. Org. Chem.* **1987**, *52*, 4937–4943. [[CrossRef](#)]
4. Gareau, Y.; Beauchemin, A. Free Radical Reaction of Diisopropyl Xanthogen Disulfide with Unsaturated Systems. *Heterocycles* **1998**, *48*, 2003–2017. [[CrossRef](#)]
5. Aitken, R.A.; Massil, T.; Raut, S.V. Cycloaddition of $\text{Bu}^n_3\text{P}\cdot\text{CS}_2$: direct one-pot conversion of strained double bonds to 2-alkylidene-1,3-dithiolanes. *J. Chem. Soc. Chem. Commun.* **1994**, 2603–2604. [[CrossRef](#)]
6. Aitken, R.A.; Carcas, K.; Hill, L.; Massil, T.; Raut, S.V. Cycloaddition of $\text{Bu}^n_3\text{P}\cdot\text{CS}_2$: Direct one-pot conversion of strained double bonds to 2-alkylidene-1,3-dithiolanes. *Tetrahedron* **1997**, *53*, 2261–2270. [[CrossRef](#)]
7. Aitken, R.; Hill, L.; Massil, T.; Hursthouse, M.B.; Malik, K. Cycloaddition of $\text{Bu}_3\text{P}\cdot\text{CS}_2$: Formation of extended bis- and tris-1,3-dithiolanes and dithiolane-containing polymers. *Tetrahedron* **1997**, *53*, 10441–10450. [[CrossRef](#)]
8. Aitken, R.A.; Hill, L.; Lightfoot, P. Direct one pot construction of norbornane-fused dihydrotetrafulvalenes. *Tetrahedron Lett.* **1997**, *38*, 7927–7930. [[CrossRef](#)]
9. Aitken, R.A.; Aitken, K.M.; Lambert, S.; Playfair, R.; Wilson, N.J. Synthesis of Norbornane-Fused 1,3-Dithiolanes and Evaluation of 1,3-Dithiolane-Containing Polymers as Absorbants for Mercury(II) Salts. *Heterocycles* **2012**, *84*, 1113–1122. [[CrossRef](#)]
10. Reinheimer, E.; Bacsá, J.; Dunbar, K.R. 1,3-Dithiolan-2-one. *Acta Crystallogr. Sect. E* **2004**, *60*, o1206–o1207. [[CrossRef](#)]
11. Dautel, O.J.; Fourmigué, M. Polyhalogenated BEDT-TTF through chlorination (SO_2Cl_2 , Cl_2) and fluorination ($^{\text{®}}$ Selectfluor, XeF_2) of 5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one. *J. Chem. Soc. Perkin Trans. 1* **2001**, 3399–3402. [[CrossRef](#)]
12. Dotsenko, I.A. Convenient synthesis of 1,3-dithiolane-2-thiones: Cyclic trithiocarbonates as conformational locks. *Arkivoc* **2014**, 16–41. [[CrossRef](#)]
13. Masui, T.; Nomura, M.; Kobayashi, Y.; Terada, K.; Fujita-Takayama, C.; Sugiyama, T.; Kajitani, M. CpCo^{I} -mediated Diels–Alder Reaction Forming Dimeric 1,3-Dithiol-2-one Derivative with Spiro Structure and Successive Formation of Novel Cobalt Dithiolene Complex. *Chem. Lett.* **2008**, *37*, 1032–1033. [[CrossRef](#)]
14. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122. [[CrossRef](#)] [[PubMed](#)]



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