



Short Note

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

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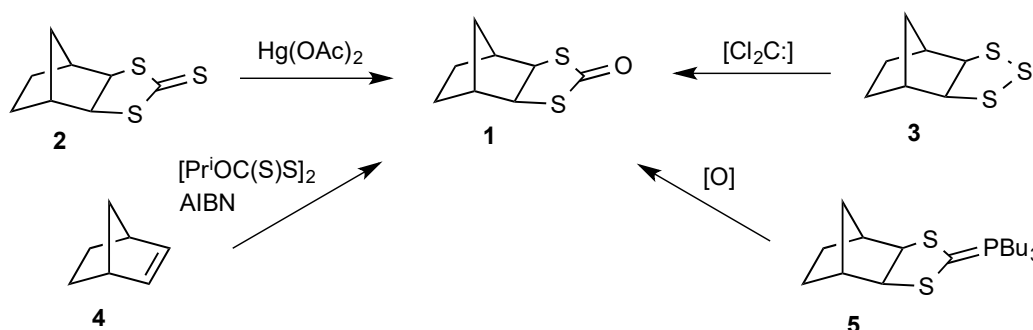
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Abstract: The x-ray structure of the title compound has been determined and the structure shows an *exo*-configured planar dithiolanone ring. This is in contrast to the few previous dithiolanones to be characterised crystallographically, which are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

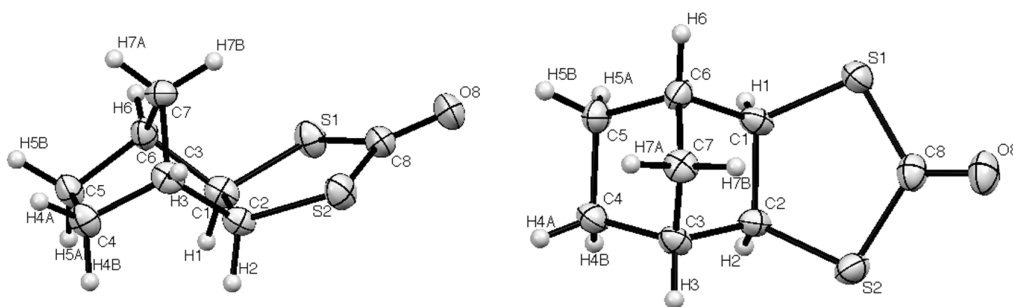


Figure 1. Two views of the molecular structure of **1** with numbering scheme (ORTEP probability ellipsoids at 50%).

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)

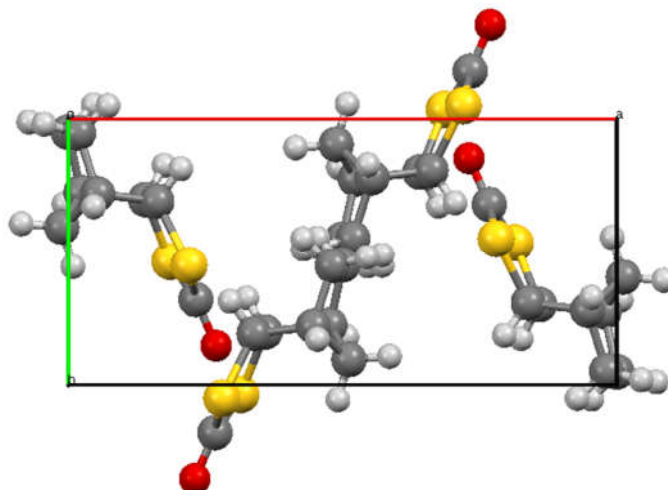


Figure 2. Unit cell of **1** viewed along the *c*-axis showing the four molecules present.

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.

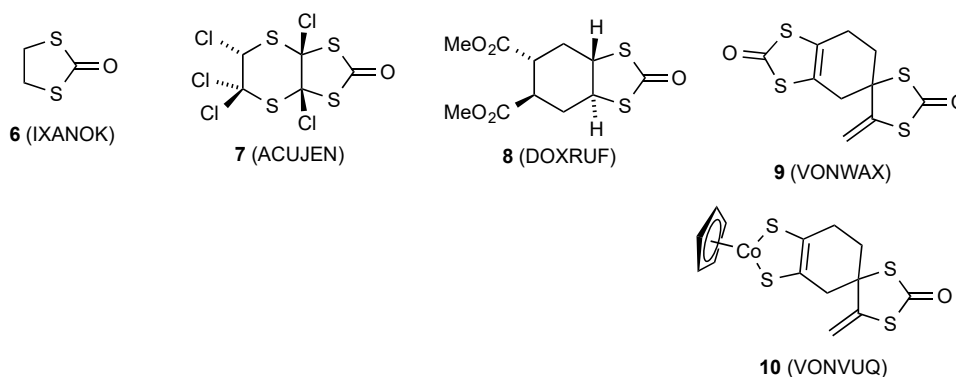


Figure 3. A survey of crystallographically characterised 1,3-dithiolan-2-ones with Cambridge Structural Database (CSD) reference codes.

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 Kα radiation λ = 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 <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.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1

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, doi:10.1021/ja00300a016.
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, doi:10.1021/jo00291a011.
3. Bartlett, P.D.; Ghosh, T. Sulfuration of the norbornene double bond. *J. Org. Chem.* **1987**, *52*, 4937–4943, doi:10.1021/jo00231a020.
4. Gareau, Y.; Beauchemin, A. Free Radical Reaction of Diisopropyl Xanthogen Disulfide with Unsaturated Systems. *Heterocycles*. **1998**, *48*, 2003–2017, doi:10.3987/com-98-8230.
5. Aitken, R.A.; Massil, T.; Raut, S.V. Cycloaddition of Buⁿ₃P-CS₂: direct one-pot conversion of strained double bonds to 2-alkylidene-1,3-dithiolanes. *J. Chem. Soc., Chem. Commun.* **1994**, 2603–2604, doi:10.1039/c39940002603.
6. Aitken, R.A.; Carcas, K.; Hill, L.; Massil, T.; Raut, S.V. Cycloaddition of Buⁿ₃P-CS₂: Direct one-pot conversion of strained double bonds to 2-alkylidene-1,3-dithiolanes. *Tetrahedron* **1997**, *53*, 2261–2270, doi:10.1016/s0040-4020(96)01128-3.
7. Aitken, R.; Hill, L.; Massil, T.; Hursthouse, M.B.; Malik, K. Cycloaddition of Buⁿ₃P-CS₂: Formation of extended bis- and tris-1,3-dithiolanes and dithiolane-containing polymers. *Tetrahedron* **1997**, *53*, 10441–10450, doi:10.1016/s0040-4020(97)00655-8.
8. Aitken, R.A.; Hill, L.; Lightfoot, P. Direct one pot construction of norbornane-fused dihydrotetrafulvalenes. *Tetrahedron Lett.* **1997**, *38*, 7927–7930, doi:10.1016/s0040-4039(97)10049-1.
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, doi:10.3987/com-11-s(p)93.

10. Reinheimer, E.; Bacsa, J.; Dunbar, K.R. 1,3-Dithiolan-2-one. *Acta Crystallogr. Sect. E.* **2004**, *60*, o1206–o1207, doi:10.1107/s1600536804014382.
11. Dautel, O.J.; Fourmigué, M. Polyhalogenated BEDT-TTF through chlorination (SO₂Cl₂, Cl₂) and fluorination (Selectfluor, XeF₂) of 5,6-dihydro[1,3]dithiolo[4,5-b][1,4]dithiin-2-one. *J. Chem. Soc. Perkin Trans. 1* **2001**, 3399–3402, doi:10.1039/b106144p.
12. Dotsenko, I.A. Convenient synthesis of 1,3-dithiolane-2-thiones: cyclic trithiocarbonates as conformational locks. *Arkivoc* **2014**, 16–41, doi:10.3998/ark.5550190.p008.671.
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, doi:10.1246/cl.2008.1032.
14. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122, doi:10.1107/S0108767307043930.



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