Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

1,8-Dioxa-4,11-dithiacyclotetradecane-2,9-dione

Jorma Koskimies,[a] Matti Näsäkkälä[b] and Ilpo Mutikainen[b]*

[a]Laboratory of Organic Chemistry, Department of Chemistry, PO Box 55 (A. I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland, and [b]Laboratory of Inorganic Chemistry, Department of Chemistry, PO Box 55 (A. I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

Correspondence e-mail:
ilpo.mutikainen@helsinki.fi

Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.004 Å
R factor = 0.048
wR factor = 0.129
Data-to-parameter ratio = 10.3

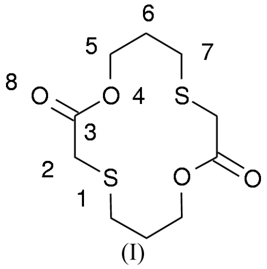
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 1 February 2001
Accepted 13 February 2001
Online 19 February 2001

The title compound, $C_{10}H_{16}O_4S_2$, was formed in a reaction of allyl alcohol and thioglycolic acid followed by acid-catalyzed esterification of the resulting hydroxy acid. The compound forms triclinic crystals and there is an inversion center in the middle of the molecule The structure was determined to be a 14-membered dilide which in the solid state assumes a centrosymmetric conformation where the S—C—C—O—C—C—C—S chain is roughly *gauche-gauche-anti-anti-gauche-anti-gauche*. Molecular-mechanics calculations showed that the X-ray conformation is 10 kJ above the global minimum.

Comment

In an attempt to prepare 1,4-oxathian-2-one (Koskimies, 1984), allyl alcohol and thioglycolic acid were reacted followed by acid-catalyzed esterification of the resulting hydroxy acid. A crystalline product, believed to be 1,4-thiepan-2-one (Davies *et al.*, 1977) on the basis of its NMR spectrum, was obtained. However, its mass spectrum showed a molecular ion peak of 264, suggesting the dimer. The structure of the dimer was confirmed by X-ray structure analysis as a 14-membered dilide, (I).



(I)

The formation of the 14-membered ring rather than the seven-membered lactone is probably facilitated by the presence of sulfur with long C—S bonds in the hydroxy acid chain: the seven-membered lactone is more strained than the corresponding carbocyclic lactone or the 14-membered dilide. In the solid state, the compound assumes a centrosymmetric conformation where the S1—C2—C3—O4—C5—C6—C7—S1A chain is roughly *gauche-gauche-anti-anti-gauche-anti-gauche*. The conformation may be classified as [77] using Dale's nomenclature (Dale, 1973) with corner points at both S atoms. This unusual structure is made possible by two parallel planar ester groups: C2, C3, O8, O4 and C5 are practically in the plane. The corresponding carbon dilide 1,8-dioxacyclotetradecane-2,9-dione (Groth, 1985), as well as tridecanolactone (Wiberg *et al.*, 1991), both crystallize in the [3434] conformation. The latter diamond-lattice conformation is also

DOI: 101107/S1600536801003038

preferred by the parent hydrocarbon cyclotetradecane (Ounsworth & Weiler, 1987). Molecular-mechanics calculations (Mohamadi *et al.*, 1990) show that the X-ray conformation is 10 kJ above the global minimum. This minimum-energy conformer is also centrosymmetric and of the [3434] type, the corner points at 2, 6, 2′ and 6′. The conformation is very similar to that of 1,8-dioxacyclotetradecane-2,9-dione (Groth, 1985). The main difference between the X-ray structure and the minimum conformation is that the latter is square-shaped with carbonyl bonds axial with respect to the molecular plane while the X-ray conformation is oval-shaped with S atoms at both ends and the carbonyl O atoms in the ring plane. Molecular-mechanics calculations suggest that the solid-state conformation is favored in more polar media. Analysis of vicinal coupling constants in the ^{1}H NMR spectrum indicate that in solution no single conformation is dominant, a fact also predicted by molecular-mechanics calculations.

Experimental

The title compound was prepared by mixing aqueous (80%) thioglycolic acid (10 ml, 0.15 mol) and allyl alcohol (13.5 ml, 0.15 mol). When the reaction had subsided, benzene (100 ml) and *p*-toluenesulfonic acid (0.2 g) were added and the reaction flask fitted with a Dean–Stark trap and condenser. The solution was refluxed until no water was collected in the trap. The solid obtained was recrystallized from benzene and dried *in vacuo*; yield 2.1 g (11%), m.p. 403.5–404.0 K. NMR (250 MHz) (CDCl$_3$): 4.30 (*t, J* = 5 Hz), 3.27 (*s*), 2.86 (*t, J* = 5 Hz), 2.0 (m). Mass spectrum: 264,133, 132, 114, 89, 88, 87, 61, 46, 45. IR (ATR): 2964 (*m*), 1722 (*s*), 1460 (*w*), 1419 (*m*), 1376 (*w*), 1273 (*m*) 1220 (*m*), 1178 (*m*), 1127 (*s*), 1058 (*m*), 1015 (*m*), 951 (*w*), 876 (*w*), 847 (*w*), 797 (*w*), 740 (*w*), 713 (*w*). A crystal suitable for X-ray diffraction was obtained from acetonitrile and mounted on a glass fiber using the oil-drop method (Kottke & Stalke, 1993) and data were collected at 193 K.

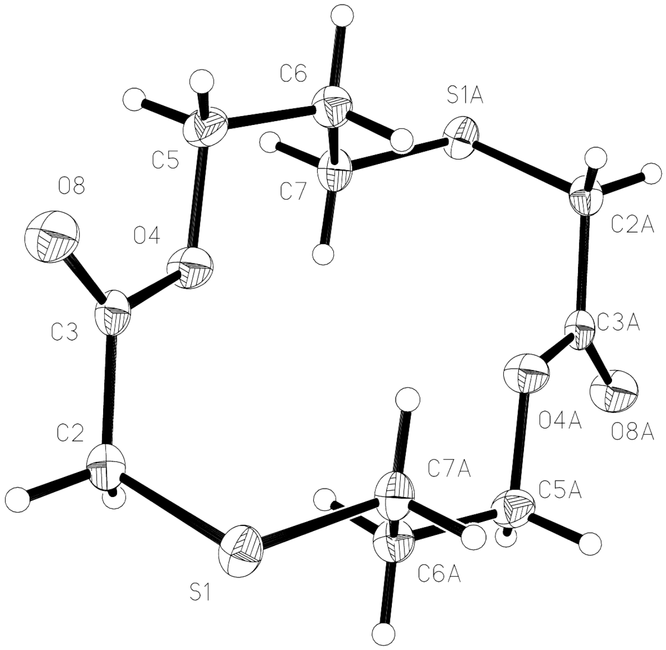


Figure 1
View of the title molecule. The displacement ellipsoids are drawn at the 30% probability level.

Crystal data

$C_{10}H_{16}O_4S_2$
$M_r = 264.35$
Triclinic, $P\bar{1}$
$a = 5.3920\ (18)$ Å
$b = 6.858\ (3)$ Å
$c = 8.960\ (6)$ Å
$\alpha = 71.88\ (4)^\circ$
$\beta = 74.04\ (3)^\circ$
$\gamma = 85.41\ (4)^\circ$
$V = 302.8\ (3)$ Å^3
$Z = 1$
$D_x = 1.450$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 3.5$–7.5°
$\mu = 0.44$ mm^{-1}
$T = 193\ (2)$ K
Plate, colorless
0.40 × 0.37 × 0.20 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.885$, $T_{\max} = 1.000$
2360 measured reflections
1082 independent reflections
1017 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.076$
$\theta_{\max} = 25.2^\circ$
$h = -6 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = -10 \rightarrow 10$
3 standard reflections every 200 reflections intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.129$
$S = 1.04$
1082 reflections
105 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0741P)^2 + 0.1359P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.59$ e Å^{-3}

Table 1
Selected geometric parameters (°).

C7$^{\rm i}$—S1—C2—C3	−66.99 (18)	C3—O4—C5—C6	150.67 (19)
S1—C2—C3—O8	−86.9 (2)	O4—C5—C6—C7	61.0 (3)
S1—C2—C3—O4	92.61 (19)	C5—C6—C7—S1$^{\rm i}$	174.15 (16)
O8—C3—O4—C5	0.1 (3)	S1—C2—C3—O4	92.61 (19)
C2—C3—O4—C5	−179.42 (17)	C3—O4—C5—C6	150.67 (19)

Symmetry code: (i) $1-x, 1-y, 1-z$.

The intensity data were corrected for Lorentz and polarization effects and for absorption. All non-H atoms were refined anisotropically. H atoms were located from difference Fourier maps and were refined isotropically.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*); cell refinement: *TEXSAN* (Molecular Structure Corporation, 1993*b*); data reduction: *TEXSAN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

References

Dale, J. (1973). *Acta Chem. Scand.* **23**, 1115.
Davies, D. I., Hughes, L., Vankar, Y. D. & Baldwin, J. E. (1977). *J. Chem. Soc. Perkin Trans.* 1, pp. p. 2476.
Groth, P. (1985). *Acta Chem. Scand. Ser. A*, **39**, 659.
Koskimies, J. K. (1984). *Acta Chem. Scand. Ser. B*, **38**, 101.
Kottke, T. & Stalke, D. (1993). *J. Appl. Cryst.* **26**, 615–619.
Mohamadi, F, Richards, N. G. J., Guida, W. C., Liskamp, R., Lipton, M., Caulfield, C., Chang, G. & Still, W. C. (1990). *J. Comput. Chem.* **11**, 440.

Molecular Structure Corporation (1993*a*). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993*b*). *TEXSAN*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Ounsworth, J. P. & Weiler, J. (1987). *J. Chem. Ed.* **64**, 568.

Wiberg, K. W., Waldron, R. F., Schulte, G. & Saunders, M. (1991). *J. Am. Chem. Soc.* **113**, 971.

Sheldrick, G. M. (1994). *SHELXTL/PC*. Release 5.03. Siemens Analytical X-ray Instruments Inc. Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.