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2,5-Dithiahexane-1,6-diyl-4,4'-bis(1,3-dioxolan-2-one)

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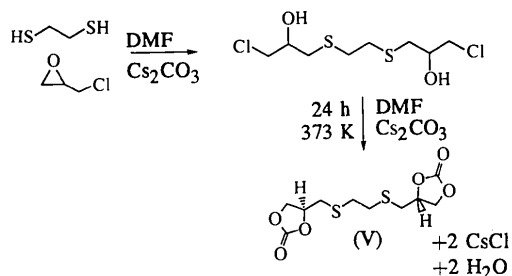
(Received 8 January 1996; accepted 1 February 1996)

Abstract

Molecules of the title compound, $C_{10}H_{14}O_6S_2$, possess crystallographically imposed inversion symmetry, with the central S—C—C—S moiety assuming an ideal *trans* conformation. Molecular-geometry parameters within the 1,3-dioxolan-2-one substituent are compared with those found in the small number of related compounds whose structures have been determined.

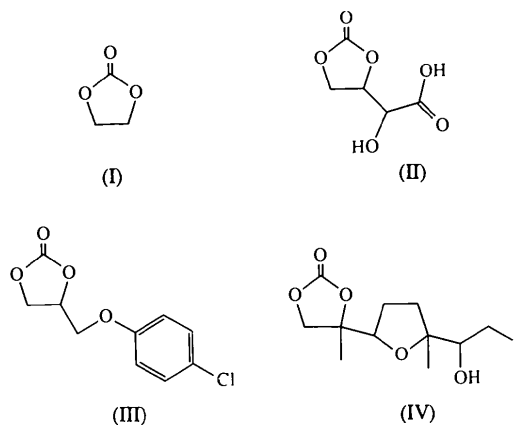
Comment

The title compound, (V), is a product of the reaction shown below (Pett *et al.*, 1988).



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The molecule occupies a crystallographic inversion centre and therefore possesses C_i molecular symmetry. A small number of structures containing 1,3-dioxolan-2-one units have been reported and some relevant molecular-geometry parameters are given in Table 3. Compound (I) has no reported e.s.d.'s and those for (IV) are high, presumably due in part to the presence of the I atom. The useful comparisons are therefore with compounds (II) and (III), and the title compound shows a very similar geometry to these compounds.



The 1,3-dioxolan-2-one ring is not planar; an excellent least-squares plane may be defined by atoms O1, C2, O2 and O3 [mean deviation 0.005 (3) Å], but atoms C4 and C5 lie 0.122 (5) below and 0.158 (5) Å above this plane, respectively. This imparts a twist conformation to the ring which is distinct from the conformation seen in compound (II) where atoms C4 and C5 are displaced unequally (by 0.04 and 0.13 Å, respectively), but in the same direction, from the carbonate plane (Moen, 1982). In compound (III), the ring conformation is essentially planar (Katzhendler, Ringel, Goldblum, Gibson

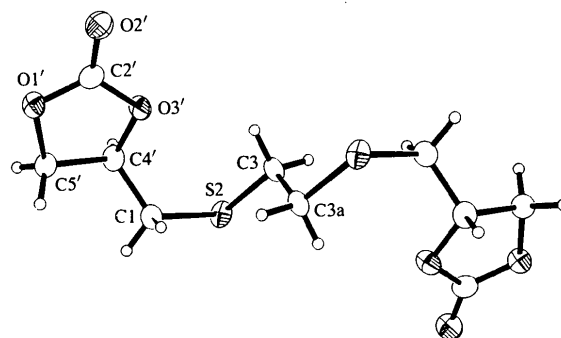


Fig. 1. A view of the title molecule with the atom-numbering scheme; atom C3a is related to atom C3 by inversion through $(\frac{1}{2}, 0, 0)$. Displacement ellipsoids enclose 50% probability surfaces and H atoms are represented by small spheres of arbitrary radii.

& Tashma, 1989). Bond lengths and angles within the thioether chain of (V) assume expected values (Blake & Schröder, 1990).

Experimental

Crystal data

C₁₀H₁₄O₆S₂M_r = 294.33

Monoclinic

P2₁/c

a = 11.614 (14) Å

b = 5.288 (5) Å

c = 10.602 (15) Å

β = 110.02 (3)°

V = 611.8 (13) Å³

Z = 2

D_x = 1.598 Mg m⁻³D_m not measured

Data collection

Stoe Stadi-4 four-circle diffractometer

ω-2θ scans

Absorption correction:

ψ scans (North, Phillips & Mathews, 1968)

T_{min} = 0.574, T_{max} = 0.639

1615 measured reflections

1081 independent reflections

Refinement

Refinement on F²

R(F) = 0.0732

wR(F²) = 0.1948

S = 1.162

1078 reflections

83 parameters

H atoms were allowed to ride on their respective C atoms, with U_{iso}(H) = 1.2U_{eq}(C)w = 1/[σ²(F_o²) + (0.11P)² + 0.44P]where P = (F_o² + 2F_c²)/3

Mo Kα radiation

λ = 0.71073 Å

Cell parinolic reflections

θ = 12.0–13.5°

μ = 0.452 mm⁻¹

T = 150.0 (2) K

Column

0.45 × 0.20 × 0.20 mm

Colourless

868 observed reflections [I > 2σ(I)]

R_{int} = 0.0493θ_{max} = 25.03°

h = -13 → 13

k = -6 → 0

l = -12 → 12

3 standard reflections

frequency: 60 min

intensity decay: none

(Δ/σ)_{max} = 0.001Δρ_{max} = 0.75 e Å⁻³Δρ_{min} = -0.63 e Å⁻³

Extinction correction:

SHELXL93

Extinction coefficient:

0.017 (11)

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 2. Selected geometric parameters (Å, °)

C4'—C1	1.499 (6)	S2—C3	1.810 (5)
C1—S2	1.813 (5)	C3—C3'	1.521 (9)
C2'—O1'—C5'	109.7 (3)	O3'—C4'—C5'	102.4 (3)
C2'—O3'—C4'	109.6 (3)	O1'—C5'—C4'	103.3 (3)
C4'—C1—S2—C3	76.8 (4)	C1—S2—C3—C3'	69.8 (5)

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

Table 3. Comparison of the molecular-geometry parameters (Å, °) for 1,3-dioxolan-2-ones

Parameter ^a	(I)	(II)	(III)	(IV)	(V)
O1'—C2'	1.33	1.327 (2)	1.316 (6)	1.34 (2)	1.323 (5)
C2'—O2'	1.15	1.207 (2)	1.192 (6)	1.21 (2)	1.200 (6)
C2'—O3'	1.33	1.341 (2)	1.316 (6)	1.28 (2)	1.348 (6)
O3'—C4'	1.40	1.447 (2)	1.443 (5)	1.42 (2)	1.460 (6)
C4'—C5'	1.52	1.531 (2)	1.498 (7)	1.53 (2)	1.527 (6)
O1'—C5'	1.40	1.448 (2)	1.420 (6)	1.46 (2)	1.456 (5)
O1'—C2'—O3'	111	112.7 (1)	111.9 (4)	113 (1)	112.0 (4)

Notes: (a) numbering schemes have been standardized as for compound (V); (I) 1,3-dioxolan-2-one (Brown, 1954); (II) d-erythronic acid 3,4-carbonate (Moen, 1982); (III) 4-*p*-chlorophenylloxymethyl-1,3-dioxolan-2-one (Katzhendler *et al.*, 1989); (IV) 4-[5-(2-iodo-1-hydroxyethyl)-5-methyltetrahydro-2-furyl]-4-methyl-1,3-dioxolan-2-one (Wuts, D'Costa & Butler, 1984); (V) this work.

An ω-scan width of (1.8 + 0.35tanθ)° was used. The diffractometer was fitted with with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986).

Data collection: *STADI4* (Stoe & Cie, 1995a). Cell refinement: *STADI4*. Data reduction: *X-RED* (Stoe & Cie, 1995b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL93*.

The authors thank SERC for provision of a four-circle diffractometer and for a postdoctoral fellowship (SP).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: HA1158). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
O1'	0.9150 (3)	-0.5334 (6)	0.2877 (3)	0.0240 (8)
C2'	0.8593 (4)	-0.4815 (9)	0.1590 (5)	0.0265 (11)
O2'	0.8715 (3)	-0.6010 (7)	0.0681 (3)	0.0367 (10)
O3'	0.7898 (3)	-0.2715 (6)	0.1410 (3)	0.0285 (9)
C4'	0.8047 (4)	-0.1571 (9)	0.2709 (4)	0.0230 (10)
C5'	0.8696 (4)	-0.3657 (8)	0.3691 (4)	0.0217 (10)
C1	0.6823 (4)	-0.0860 (9)	0.2786 (4)	0.0244 (10)
S2	0.61256 (10)	0.1960 (2)	0.18693 (11)	0.0242 (5)
C3	0.5542 (4)	0.0897 (9)	0.0143 (4)	0.0229 (10)

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4-Methylpyridinium Hydrogen Sulfide

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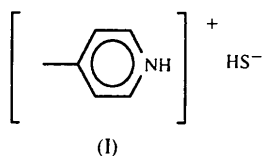
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Abstract

4-Methylpyridinium hydrogen sulfide, $C_6H_7NH^+ \cdot HS^-$, was obtained as a by-product of the reaction between $GaCl_3$ and thioglycolic acid in a 4-methylpyridine solution. The compound consists of heterocyclic $C_6H_7NH^+$ cationic rings and HS^- anions. Both the $C_6H_7NH^+$ cation and the HS^- anion lie on crystallographic mirror planes with the N, S, two C and two H atoms positioned in the planes. The H atom of the HS^- anion was not located.

Comment

As part of our program to study the reactions of indium and gallium compounds in nitrogen-donor solvents, we have isolated, crystallized and structurally characterized a number of by-products derived from reactions of the solvents, including piperidinium hydrogen sulfide (Andras, Hepp, Fanwick, Duraj & Gordon, 1994), 4-methylpyridinium bromide (Andras, Hepp, Fanwick, Martuch & Duraj, 1993) and 4-methylpyridinium hydrogen sulfide, (I), the structure of which is reported here.



† This work was performed while the author held a National Research Council–NASA Research Associateship.

4-Methylpyridinium hydrogen sulfide, also known as γ -picolinium hydrogen sulfide, retains the basic structure of the 4-methylpyridine ring (Ohms *et al.*, 1985), but its structure varies from that of 4-methylpyridine in several small ways. These variations include an increase in the C—N—C bond angle as the lone pair on the N atom of 4-methylpyridine is replaced with the N—H bond of the 4-methylpyridinium ring and a slight shortening (0.03 Å) of the C(2)—C(3) bond length between the neutral and protonated rings.

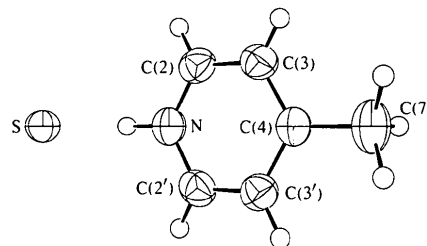


Fig. 1. ORTEP (Johnson, 1965) drawing of the title molecule (without the undetected H atom of HS^-) showing the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level, while isotropic H-atom displacement parameters are represented by spheres of arbitrary size.

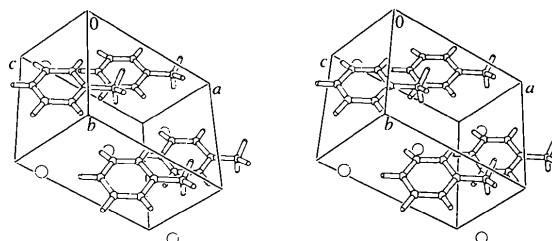


Fig. 2. Packing diagram of the title compound.

Experimental

4-Methylpyridinium hydrogen sulfide was obtained as a by-product of the reaction between $GaCl_3$ and thioglycolic acid ($HSCH_2CO_2H$) in a 4-methylpyridine solution. The reaction was carried out under an argon atmosphere. 2.0 ml (18.7 mmol) of $HSCH_2CO_2H$ was slowly added to a solution of 0.87 g of $GaCl_3$ in 30 ml of 4-methylpyridine. After reacting for 24 h, the precipitate which formed was removed by filtration. The filtrate solution was layered with 30 ml of freshly distilled hexanes. This produced colorless crystals of 4-methylpyridinium hydrogen sulfide which were allowed to grow for 80 d. The crystals were then collected, washed with three 10 ml aliquots of hexanes and dried *in vacuo*.

Crystal data

$C_6H_8N^+ \cdot HS^-$
 $M_r = 127.21$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$