Table 2. *Selected geometric parameters* (Å, °)

O1—C1	1.435 (5)	O16—C25	1.187 (6)
O1—C11	1.355 (5)	O17—C9	1.453 (4)
O2—C11	1.184 (7)	O17—C27	1.359 (5)
O3—C2	1.433 (5)	O18—C27	1.192 (5)
O3—C13	1.354 (7)	C1—C2	1.516 (6)
O4—C13	1.169 (9)	C2—C3	1.526 (5)
O5—C3	1.440 (4)	C3—C4	1.533 (5)
O5—C15	1.347 (5)	C4—C5	1.517 (4)
O6—C15	1.195 (6)	C5—C6	1.522 (4)
O7—C4	1.428 (4)	C6—C7	1.513 (4)
O7—C17	1.358 (5)	C7—C8	1.538 (5)
O8—C17	1.194 (6)	C8—C9	1.515 (5)
O9—C5	1.455 (4)	C9—C10	1.495 (6)
O9—C19	1.356 (5)	C11—C12	1.504 (8)
O10—C19	1.186 (5)	C13—C14	1.475 (11)
O11—C6	1.447 (4)	C15—C16	1.481 (7)
O11—C21	1.368 (5)	C17—C18	1.469 (8)
O12—C21	1.192 (6)	C19—C20	1.484 (6)
O13—C7	1.439 (4)	C21—C22	1.476 (8)
O13—C23	1.349 (5)	C23—C24	1.475 (8)
O14—C23	1.195 (6)	C25—C26	1.488 (7)
O15—C8	1.448 (4)	C27—C28	1.483 (6)
O15—C25	1.352 (5)		
C1—O1—C11	116.1 (3)	O17—C9—C8	105.5 (2)
C2—O3—C13	117.9 (3)	C8—C9—C10	114.4 (3)
C3—O5—C15	116.8 (3)	O17—C9—C10	110.1 (3)
C4—O7—C17	118.2 (3)	O1—C11—O2	123.6 (4)
C5—O9—C19	117.9 (2)	O2—C11—C12	126.9 (4)
C6—O11—C21	117.4 (2)	O1—C11—C12	109.3 (4)
C7—O13—C23	117.9 (2)	O3—C13—O4	123.0 (6)
C8—O15—C25	117.8 (2)	O4—C13—C14	126.0 (7)
C9—O17—C27	115.9 (2)	O3—C13—C14	110.4 (5)
O1—C1—C2	109.7 (3)	O5—C15—O6	122.0 (3)
O3—C2—C1	105.6 (3)	O6—C15—C16	126.1 (4)
C1—C2—C3	113.5 (3)	O5—C15—C16	111.8 (3)
O3—C2—C3	108.9 (3)	O7—C17—O8	123.1 (3)
O5—C3—C2	107.6 (2)	O8—C17—C18	125.8 (4)
C2—C3—C4	113.3 (2)	O7—C17—C18	110.9 (4)
O5—C3—C4	108.5 (2)	O9—C19—O10	123.2 (3)
O7—C4—C3	108.8 (2)	O10—C19—C20	125.4 (3)
C3—C4—C5	112.3 (2)	O9—C19—C20	111.2 (3)
O7—C4—C5	108.7 (2)	O11—C21—O12	122.8 (3)
O9—C5—C4	110.7 (2)	O12—C21—C22	126.8 (3)
C4—C5—C6	115.2 (2)	O11—C21—C22	110.3 (3)
O9—C5—C6	103.8 (2)	O13—C23—O14	123.2 (3)
O11—C6—C5	108.4 (2)	O14—C23—C24	125.4 (4)
C5—C6—C7	110.9 (2)	O13—C23—C24	111.3 (4)
O11—C6—C7	109.1 (2)	O15—C25—O16	123.2 (3)
O13—C7—C6	108.4 (2)	O16—C25—C26	126.3 (3)
C6—C7—C8	115.3 (2)	O15—C25—C26	110.4 (3)
O13—C7—C8	106.2 (2)	O17—C27—O18	123.0 (3)
O15—C8—C7	104.7 (2)	O18—C27—C28	125.5 (4)
C7—C8—C9	113.0 (2)	O17—C27—C28	111.4 (3)
O15—C8—C9	110.4 (2)		

The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Difference Fourier maps showed rotational disorder in all the acetylic methyl groups. For each CH_3 group the positions of uniformly distributed H atoms were calculated and refined with fixed occupancies of 0.5 as a rigid group. The positions of the other H atoms were calculated and included using a riding model in the structure-factor calculations. Individual isotropic displacement factors for the H atoms and anisotropic displacement factors for all other atoms were used in a block-diagonal-matrix refinement. The absolute configuration was assigned to agree with the known chirality of the substrates. Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86. Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1073). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). C**50**, 1368–1370

Refinement of a Twinned Structure with *SHELXL*93: *meso*-2,2′-[1,6-Bis(methylamino)-3,4-dithia-1,6-hexanediyl]diphenol

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Abstract

Crystals of the title compound appeared to be twinned, but a new option in the program *SHELXL*93 [Sheldrick (1993). Univ. of Göttingen, Germany] has made a successful refinement possible. One hydroxyl O atom forms an intramolecular hydrogen bond to an amino N atom and a short contact to an aromatic H atom can be found. The other hydroxyl O atom acts as an acceptor for one intra- and one intermolecular hydrogen bond from the NH groups.

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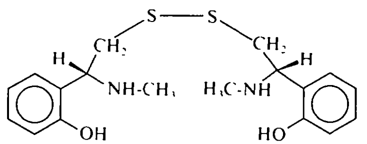
Comment

The title compound (I) is a synthetic intermediate *en route* to transition-metal complexes used for enzyme modelling. The structure analysis was undertaken to determine the relative configuration of its two stereogenic centres. The molecule turned out to be a *meso* form, *i.e.* C3 and C8 show a different configuration. A non-crystallographic mirror plane intersects the S—S bond. Details of the synthetic work will be published elsewhere (Berkessel, Neumann & Seidel, 1994).



(I)

The dihedral angle about the S—S bond is 95.9 (5)°. The hydrogen bond pattern is shown in Fig. 1.

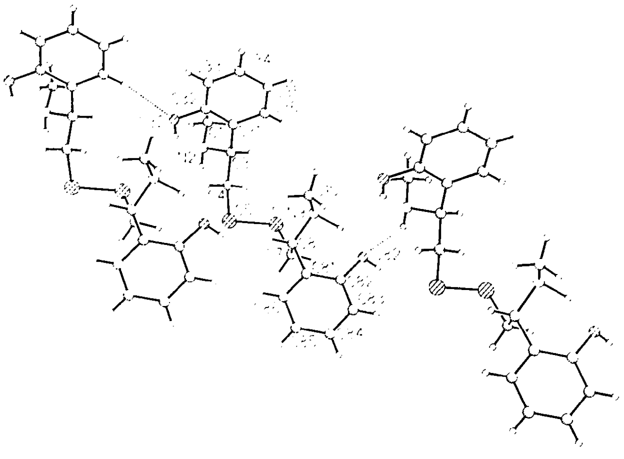


Fig. 1. Packing diagram of $C_{18}H_{24}N_2O_2S_2$ showing the hydrogen bonds as dashed lines and short contacts as dotted lines.

Experimental

Crystal data

$C_{18}H_{24}N_2O_2S_2$
$M_r = 364.51$
Monoclinic
$P2_1$
$a = 6.618$ (3) Å
$b = 7.436$ (1) Å
$c = 19.242$ (8) Å
$\beta = 92.36$ (2)°
$V = 946.1$ (6) Å^3
$Z = 2$
$D_x = 1.280$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 25.30$–46.60°
$\mu = 2.648$ mm^{-1}
$T = 293$ K
Transparent block
0.50 × 0.30 × 0.10 mm
Colourless
Crystal source: ether

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
ω scans
Absorption correction: none
2026 measured reflections
2026 independent reflections
1930 observed reflections [$I > 2\sigma(I)$]

$\theta_{max} = 55.08°$
$h = -7 \rightarrow 0$
$k = -7 \rightarrow 7$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 92 min
intensity variation: 1.70%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0777$
$wR(F^2) = 0.2039$
$S = 1.133$
2002 reflections
224 parameters
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.131P)^2 + 1.4059P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.610$ e Å^{-3}
$\Delta\rho_{min} = -0.405$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter 0.04 (7)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.7638 (19)	1.0179 (14)	0.6389 (5)	0.070 (3)
N2	0.7937 (12)	0.8796 (11)	0.6931 (4)	0.054 (2)
C3	0.6508 (13)	0.7240 (16)	0.6850 (4)	0.050 (2)
C4	0.6617 (14)	0.6158 (15)	0.7506 (4)	0.059 (3)
S5	0.5779 (4)	0.7268 (5)	0.82756 (10)	0.0748 (9)
S6	0.2723 (4)	0.7300 (4)	0.81376 (10)	0.0628 (7)
C7	0.1995 (15)	0.5331 (13)	0.8618 (4)	0.055 (2)
C8	0.2646 (12)	0.3565 (13)	0.8314 (4)	0.044 (2)
N9	0.1785 (11)	0.3353 (10)	0.7593 (3)	0.051 (2)
C10	0.2756 (19)	0.1940 (15)	0.7214 (5)	0.078 (3)
C31	0.7015 (12)	0.6117 (12)	0.6237 (4)	0.042 (2)
C32	0.8972 (14)	0.5757 (13)	0.6060 (4)	0.048 (2)
O32	1.0579 (8)	0.6475 (11)	0.6430 (3)	0.059 (2)
C33	0.9386 (16)	0.4595 (16)	0.5519 (5)	0.064 (3)
C34	0.7811 (17)	0.3857 (16)	0.5142 (5)	0.067 (3)
C35	0.5869 (16)	0.4130 (13)	0.5309 (5)	0.060 (3)
C36	0.5440 (14)	0.5280 (15)	0.5850 (4)	0.057 (2)
C81	0.1950 (11)	0.2046 (12)	0.8781 (3)	0.038 (2)
C82	−0.0008 (13)	0.1376 (14)	0.8730 (4)	0.050 (2)
O82	−0.1320 (8)	0.1933 (12)	0.8211 (3)	0.068 (2)
C83	−0.0636 (15)	0.0112 (13)	0.9200 (4)	0.054 (2)
C84	0.0685 (20)	−0.0522 (15)	0.9720 (5)	0.068 (3)
C85	0.2610 (19)	0.0100 (17)	0.9774 (5)	0.072 (3)
C86	0.3266 (16)	0.1383 (12)	0.9302 (4)	0.056 (2)

Table 2. *Selected geometric parameters* (Å, °)

C1—N2	1.472 (12)	C32—O32	1.364 (11)
N2—C3	1.498 (13)	C32—C33	1.388 (13)
C3—C31	1.495 (12)	C33—C34	1.361 (14)
C3—C4	1.496 (12)	C34—C35	1.353 (14)
C4—S5	1.803 (9)	C35—C36	1.385 (13)
S5—S6	2.029 (4)	C81—C82	1.388 (11)
S6—C7	1.807 (10)	C81—C86	1.391 (11)
C7—C8	1.508 (13)	C82—O82	1.361 (10)
C8—N9	1.487 (10)	C82—C83	1.380 (13)
C8—C81	1.526 (12)	C83—C84	1.385 (14)
N9—C10	1.444 (12)	C84—C85	1.35 (2)
C31—C32	1.379 (12)	C85—C86	1.399 (15)
C31—C36	1.401 (12)		
O82···N2^{i}	3.41 (1)	O32···N2	2.67 (1)
O82···N9	2.637 (9)	O32···C36^{ii}	3.56 (1)
C1—N2—C3	113.5 (7)	O32—C32—C33	117.4 (8)
C31—C3—C4	111.1 (9)	C31—C32—C33	121.5 (9)
C31—C3—N2	110.7 (7)	C34—C33—C32	118.7 (10)
C4—C3—N2	108.6 (7)	C35—C34—C33	121.8 (10)

C3—C4—S5	116.2 (8)	C34—C35—C36	119.8 (9)
C4—S5—S6	103.7 (3)	C35—C36—C31	120.1 (9)
C7—S6—S5	102.1 (4)	C82—C81—C86	118.6 (8)
C8—C7—S6	114.9 (6)	C82—C81—C8	121.8 (7)
N9—C8—C7	110.5 (7)	C86—C81—C8	119.5 (7)
N9—C8—C81	111.0 (7)	O82—C82—C83	119.2 (8)
C7—C8—C81	108.6 (6)	O82—C82—C81	120.6 (8)
C10—N9—C8	112.7 (8)	C83—C82—C81	120.2 (8)
C32—C31—C36	118.0 (8)	C82—C83—C84	120.5 (9)
C32—C31—C3	123.1 (7)	C85—C84—C83	120.2 (10)
C36—C31—C3	118.7 (7)	C84—C85—C86	120.0 (10)
O32—C32—C31	121.0 (8)	C81—C86—C85	120.5 (10)

Symmetry codes: (i) $x-1, y-1, z$; (ii) $1+x, y, z$.

23 of 25 reflections found on a polaroid photograph could be used by the indexing procedure to obtain a preliminary cell. The indices of the remaining reflections ($-1\ -1\ -1.75$ and $-2\ 0\ -2.5$) gave a strong indication of twinning. The following conditions (confirmed by scanning the reciprocal space) for the additional reflections could be derived: for $h = 4m + 1$ there were reflections with $l = n + 0.75$, for $h = 4m + 2$ there were reflections with $l = n + 0.5$ and for $h = 4m + 3$ there were reflections with $l = n + 0.25$ (with m, n integers). These reflections of the two twin components were separated sufficiently for a satisfactory data collection, but overlap occurred for the reflections with $h = 4m$. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1985). For refinement the data were read in *via HKLF*5 and an additional variable was introduced (using the *BASF* command) describing the fractional contributions of the two twin components for the reflections with $h = 4m$; the ratio refined to 0.324 (6). Comparing this refinement with two other procedures leads to the following results: omitting all reflections with $h = 4m$ from refinement gives $wR(F^2) = 0.500$ and a mean e.s.d. of a C—C bond (σ) = 0.018 Å, while treating the reflections with $h = 4m$ as normal data, *i.e.* as if there was no twinning, gives $wR(F^2) = 0.4794$ and $\sigma = 0.02$ Å; for comparison, the twin refinement results in $wR(F^2) = 0.4129$ and $\sigma = 0.013$ Å.

All H atoms were located by a difference Fourier synthesis and refined with fixed individual displacement parameters [$U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C_{methyl}},\mathrm{O})$ or $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C,N})$] using a riding model with C—H(non aromatic) = 0.96 or C—H(aromatic) = 0.93 Å, respectively. The N—H distance was refined and the O—H distance was fixed to 0.82 Å but the torsion angle about the O—C bond was refined. Data collection: *SDP* (Enraf-Nonius, 1985). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL XP* (Sheldrick, 1991).

I thank Professor Dr A. Berkessel (University of Heidelberg) for providing the sample.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Configuration of (*E*)-2-(1-Hydroxy-1-methyl-2-oxopropyl)-2-(methylthio)thiolane *S*-Oxide†

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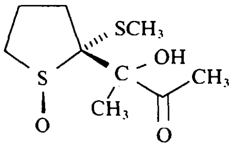
Abstract

The title compound, $C_9H_{16}O_3S_2$ (1), exhibits an (*E*)-configuration with a quasi-diaxial (*trans*) arrangement of the 1-oxido and 2-methylthio substituents. This clearly shows that the carbanion exhibits configurational stability under the reaction conditions. Pairs of molecules of (1) form dimers through two hydrogen bonds, with OH groups as donors and SO groups as acceptors.

Comment

The title hydroxyketone, (1), was formed by the reaction of 2-(methylthio)thiolane 1-oxide with butyllithium, followed by 2,3-butanedione (Brunck, 1993). Two diastereomers of (1) were obtained in a ratio of 3:1 and could be separated by column chromatography. Since their configuration could not be determined by spectroscopic methods, we have performed an X-ray analysis of the main diastereomer, which exhibits the (*E*)-configuration.



(1)

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† C,C-Coupling with Sulfur-Stabilized Carbanions. 5. Part 4: Böge, Schwär & Voss (1993).