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15,30-Dihydroxy-12,27-dimethyl-5,20-dioxa-2,8,17,23-tetrathia[9.9]metacyclophane* (β Form), $C_{26}H_{36}O_4S_4$, and 15-Hydroxy-12-methyl-5-oxa-2,8-dithia[9]metacyclophane, $C_{13}H_{18}O_2S_2$

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Abstract. $C_{26}H_{36}O_4S_4$, $M_r = 540.83$, triclinic, $P\bar{1}$, $a = 14.85$ (2), $b = 9.18$ (2), $c = 5.17$ (1) Å, $\alpha = 103.4$ (3), $\beta = 98.7$ (3), $\gamma = 90.3$ (3)°, $V = 677$ (2) Å^3, $Z = 1$, $D_m = 1.32$, $D_x = 1.33$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 33.2$ cm^{-1}, $F(000) = 288$, $T = 293$ K, $R = 0.079$ for 1427 observed reflections. $C_{13}H_{18}O_2S_2$, $M_r = 270.42$, monoclinic, $P2_1/c$, $a = 12.61$ (2), $b = 7.72$ (1), $c = 14.14$ (2) Å, $\beta = 102.8$ (3)°, $V = 1342$ (4) Å^3, $Z = 4$, $D_m = 1.33$, $D_x = 1.34$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 33.5$ cm^{-1}, $F(000) = 576$, $T = 293$ K, $R = 0.083$ for 1721 observed reflections. The latter molecule is a 12-membered metacyclophane macrocycle derived by introducing 5-oxa-2,8-dithianonane on the 2,6 positions of 4-methylphenol; the former, formally the dimer of the latter, is a centrosymmetric 24-membered crown metacyclophane macrocycle. In both compounds the molecular conformation is stabilized by transannular hydrogen bonds involving the hydroxyl groups.

Introduction. Polycondensation in benzyl alcohol of 2,6-bis[(dimethylamino)methyl]-4-methylphenol with 2,2'-oxydiethanedithiol gives both linear polymers and macrocycles (Costa Bizzarri, Della Casa, Ferruti, Ghedini, Pilati & Scapini, 1984). The latter were crystallized from toluene and from methanol giving rise to orthorhombic and triclinic crystals, respectively, both melting about 420 K. Sublimation of the crude product and successive crystallization from toluene gives monoclinic crystals with m.p. 380 K. NMR, IR and mass spectra were not conclusive in the elucidation of the molecular structures and single-crystal X-ray analyses were therefore undertaken. In a previous paper (Cannas, Marongiu & Pintori, 1984) it was shown that the molecules present in the orthorhombic crystals are 24-membered macrocycles; herewith the structure determinations of the other two crystalline forms are reported.

Experimental. $C_{26}H_{36}O_4S_4$. Colourless needle-shaped twinned crystal, twin axis [001]; approximate dimensions $0.07 \times 0.10 \times 2.0$ mm mounted along **c**; automatic Siemens AED diffractometer, Ni-filtered Cu $K\alpha$ radiation; accurate cell dimensions from least-squares fitting of 15 reflections $27 \le \theta \le 38°$; θ–2θ scan; three standard reflections (142, $1\bar{3}2$, 722) recorded every 200 reflections showed linear isotropic decrease of 25%; 1675 unique reflections $2\theta \le 110°$ ($-15 \le h \le 15$, $-9 \le k \le 10$, $0 \le l \le 5$); 1427 reflections with $I \ge 2.5\sigma(I)$ used in structure determination and refinement; intensities corrected for decomposition, Lorentz and polarization, not for absorption; structure solved by direct methods (*MULTAN*78; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined on F by block-diagonal least squares (Immirzi, 1967, 1973); separate scale factors for $hk0$ and $hk1$ reflections applied to take into account twinning effects on intensities; difference Fourier synthesis in final stages of refinement clearly indicated positions of all H atoms except those of methyl group; residual electron density within 0.31 e Å^{-3}. H contribution included and held fixed in final least-squares cycles, S atoms refined anisotropically; $R = 0.079$, $wR = 0.085$, $S = 0.70$; $|\Delta/\sigma|_{max} = 0.8$, $|\Delta/\sigma|_{av} = 0.25$, $w = 1/(5.2 + F_o + 0.0185F_o^2)$.

$C_{13}H_{18}O_2S_2$. Crystal fragment $0.07 \times 0.24 \times 0.40$ mm cut from larger colourless crystal, mounted

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along **b**; automatic Siemens AED diffractometer, Ni-filtered Cu $K\alpha$ radiation; accurate cell dimensions from least-squares fit of 7 pairs of reflections $30 \leq 2\theta \leq 52°$; three standard reflections ($61\bar{2}$, 414, $4\bar{1}4$) recorded every 200 reflections with $\pm 5\%$ fluctuation; 1989 unique reflections, $2\theta \leq 120°$ ($-14 \leq h \leq 14, 0 \leq k \leq 8, 0 \leq l \leq 15$); 1721 reflections with $F_o \geq 5\sigma(F_o)$ used in structure determination and refinement; intensities corrected for Lorentz and polarization, not for absorption; structure solved by direct methods (*MULTAN*78; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined on F by full-matrix least squares (*SHELX*76; Sheldrick, 1976). All H atoms except those of methyl group located from difference Fourier synthesis, held fixed in final stages of refinement, anisotropic thermal parameters for S atoms. $R = 0.083$, $R_w = 0.11$, S

$= 1.11$, $w = 1/(\sigma^2 + 0.0204F^2)$; $|\Delta\rho|_{max}$ in final difference Fourier map $= 0.30 \text{ e Å}^{-3}$; $(\Delta/\sigma)_{max} = 0.08$, $(\Delta/\sigma)_{av} = 0.035$. Scattering factors for both structures from *International Tables for X-ray Crystallography* (1974).*

Discussion. Positional and isotropic thermal parameters for $C_{26}H_{36}O_4S_4$ (hereafter β dimer) and for $C_{13}H_{18}O_2S_2$ (hereafter monomer) are given in Tables 1 and 2; Tables 3 and 4 give the values of bond distances and angles.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39846 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters with e.s.d.'s in parentheses for* $C_{26}H_{36}O_4S_4$

$$B_{eq} = (B_{11} + B_{22} + B_{33})/3.$$

	x	y	z	$B/B_{eq}(\text{Å}^2)$
C(1)	4091 (9)	3150 (6)	9871 (12)	3.69 (11)
S(2)	4494 (1)	1472 (2)	7842 (4)	4.03 (07)
C(3)	5713 (4)	1829 (7)	8432 (12)	3.82 (11)
C(4)	5975 (4)	2563 (6)	6255 (11)	3.46 (11)
O(5)	6935 (3)	2864 (4)	6546 (8)	3.61 (07)
C(6)	7440 (4)	1544 (13)	5911 (13)	4.30 (12)
C(7)	8418 (4)	1972 (7)	6008 (12)	3.77 (11)
S(8)	8608 (1)	3044 (2)	3585 (3)	3.30 (07)
C(9)	8584 (4)	4974 (11)	5526 (11)	3.50 (11)
C(10)	8203 (4)	5958 (6)	3676 (11)	3.03 (10)
C(11)	8778 (4)	6889 (6)	2847 (11)	3.35 (10)
C(12)	8448 (6)	7809 (6)	1128 (12)	3.57 (11)
C(13)	7522 (4)	7740 (6)	0235 (11)	3.30 (10)
C(14)	6926 (4)	6822 (6)	1037 (11)	3.20 (10)
C(15)	7275 (6)	5938 (11)	2775 (11)	3.96 (10)
O(H)	6657 (4)	5077 (4)	3557 (8)	3.83 (07)
C(H3)	9104 (4)	8811 (8)	0241 (14)	4.74 (13)

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters with e.s.d.'s in parentheses for* $C_{13}H_{18}O_2S_2$

$$B_{eq} = (B_{11} + B_{22} + B_{33})/3.$$

	x	y	z	$B/B_{eq}(\text{Å}^2)$
C(1)	-3087 (5)	3646 (7)	77 (4)	4.46 (10)
S(2)	-3524 (2)	5874 (2)	266 (1)	4.33 (7)
C(3)	-2392 (4)	6732 (7)	1151 (4)	4.04 (10)
C(4)	-2451 (4)	6332 (3)	2166 (3)	3.46 (8)
O(5)	-1437 (3)	6728 (4)	2802 (2)	3.73 (7)
C(6)	-1404 (4)	6348 (7)	3788 (4)	3.92 (9)
C(7)	-1450 (4)	4422 (7)	4008 (4)	3.89 (9)
S(8)	-341 (2)	3263 (2)	3656 (1)	4.05 (7)
C(9)	-942 (7)	1197 (7)	3209 (4)	4.12 (9)
C(10)	-1988 (4)	1323 (4)	2456 (6)	3.17 (8)
C(11)	-2946 (4)	571 (3)	2604 (3)	3.59 (8)
C(12)	-3931 (4)	706 (7)	1923 (3)	3.96 (10)
C(13)	-3937 (4)	1681 (7)	1109 (4)	4.15 (10)
C(14)	-3016 (4)	2460 (6)	926 (4)	3.46 (8)
C(15)	-2038 (6)	2222 (6)	1585 (3)	3.19 (8)
O(H)	-1111 (3)	2934 (5)	1389 (2)	4.39 (8)
C(H3)	-4943 (5)	-192 (9)	2079 (5)	5.72 (13)

Table 3. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses for* $C_{26}H_{36}O_4S_4$ (β dimer)

C(1)—S(2)	1.811 (8)	C(10)—C(11)	1.384 (10)
S(2)—C(3)	1.805 (7)	C(11)—C(12)	1.401 (10)
C(3)—C(4)	1.534 (10)	C(12)—C(13)	1.379 (9)
C(4)—O(5)	1.429 (8)	C(13)—C(14)	1.389 (10)
O(5)—C(6)	1.428 (9)	C(14)—C(15)	1.391 (9)
C(6)—C(7)	1.493 (9)	C(14)—C(1)	1.514 (9)
C(7)—S(8)	1.815 (9)	C(15)—C(10)	1.385 (9)
S(8)—C(9)	1.826 (8)	C(12)—C(H3)	1.525 (11)
C(9)—C(10)	1.514 (10)	C(15)—O(H)	1.372 (9)

S(2)—C(1)—C(14^i)	107.4 (6)	C(11)—C(10)—C(15)	118.9 (8)
C(1)—S(2)—C(3)	102.7 (5)	C(10)—C(11)—C(12)	121.9 (11)
S(2)—C(3)—C(4)	109.0 (7)	C(11)—C(12)—C(H3)	120.4 (10)
C(3)—C(4)—O(5)	112.8 (8)	C(11)—C(12)—C(13)	117.6 (9)
C(4)—O(5)—C(6)	113.4 (9)	C(13)—C(12)—C(H3)	122.0 (8)
O(5)—C(6)—C(7)	109.6 (9)	C(12)—C(13)—C(14)	121.9 (8)
C(6)—C(7)—S(8)	114.0 (8)	C(13)—C(14)—C(15)	119.0 (11)
C(7)—S(8)—C(9)	102.4 (4)	C(13)—C(14)—C(1^i)	120.0 (8)
S(8)—C(9)—C(10)	109.6 (5)	C(15)—C(14)—C(1^i)	120.9 (10)
C(9)—C(10)—C(15)	120.7 (9)	C(14)—C(15)—O(H)	116.8 (9)
C(9)—C(10)—C(11)	120.5 (9)	C(10)—C(15)—O(H)	122.5 (8)
		C(10)—C(15)—C(14)	120.7 (11)

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

Table 4. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses for* $C_{13}H_{18}O_2S_2$

C(1)—S(2)	1.844 (6)	C(10)—C(11)	1.397 (8)
S(2)—C(3)	1.803 (7)	C(11)—C(12)	1.397 (8)
C(3)—C(4)	1.486 (8)	C(12)—C(13)	1.374 (7)
C(4)—O(5)	1.424 (7)	C(13)—C(14)	1.382 (8)
O(5)—C(6)	1.416 (7)	C(14)—C(15)	1.383 (8)
C(6)—C(7)	1.522 (8)	C(15)—C(10)	1.403 (6)
C(7)—S(8)	1.820 (6)	C(12)—C(H3)	1.511 (9)
S(8)—C(9)	1.818 (6)	C(14)—C(1)	1.497 (8)
C(9)—C(10)	1.504 (8)	C(15)—O(H)	1.374 (7)

C(14)—C(1)—S(2)	114.9 (4)		
C(1)—S(2)—C(3)	103.1 (3)	C(10)—C(11)—C(12)	122.1 (5)
S(2)—C(3)—C(4)	113.1 (5)	C(11)—C(12)—C(H3)	121.1 (5)
C(3)—C(4)—O(5)	109.6 (5)	C(11)—C(12)—C(13)	117.2 (7)
C(4)—O(5)—C(6)	113.8 (6)	C(13)—C(12)—C(H3)	121.7 (6)
O(5)—C(6)—C(7)	114.2 (5)	C(12)—C(13)—C(14)	123.1 (6)
C(6)—C(7)—S(8)	111.0 (5)	C(13)—C(14)—C(15)	118.5 (6)
C(7)—S(8)—C(9)	103.9 (4)	C(13)—C(14)—C(1)	120.9 (6)
S(8)—C(9)—C(10)	115.0 (4)	C(15)—C(14)—C(1)	120.5 (6)
C(9)—C(10)—C(15)	121.0 (7)	C(14)—C(15)—O(H)	118.8 (5)
C(9)—C(10)—C(11)	121.3 (5)	C(10)—C(15)—O(H)	120.0 (5)
C(11)—C(10)—C(15)	117.7 (6)	C(10)—C(15)—C(14)	121.1 (6)

Crystals of β dimer, obtained by evaporation of a methanol solution, are a polymorphic form of crystals of α dimer, crystallized from toluene (Cannas, Marongiu & Pintori, 1984).

A view of the β dimer molecule is shown in Fig. 1 together with atom labelling; values of torsion angles are given in Table 5. The dimeric molecules are centrosymmetric and in both of them the hydroxyl groups are hydrogen bonded to the oxa ring atoms; these bonds play an important role in stabilizing the macrocycle structure and they force the O—H··· O(5)—C(6)—C(7)—S(8)—C(9)—C(10)—C(15) rings to maintain very close conformation in the two polymorphs: O(H)···O(5) distances are 2·75 (1) and 2·82 (1) Å and O(H)—H···O(5) angles are 135 (5) and 152 (5)° in α and β forms respectively. Significant differences are instead present in the conformation of O(5)—C(4)—C(3)—S(2)—C(1) moieties, as shown by the values of torsion angles. As a consequence, the molecules in the crystals of the α form are more flattened, as is also evidenced by the values of the interplanar distance of the 4-methylphenol rings: 0·38 (2) Å in α dimer and 2·10 (2) Å in β dimer.

Both α and β forms crystallize in a closest-packed space group (Kitaigorodskii, 1961), regulated by

Fig. 1. Projection of the molecular structure of $C_{26}H_{36}O_4S_4$ (β dimer) along the axis perpendicular to the phenyl ring.
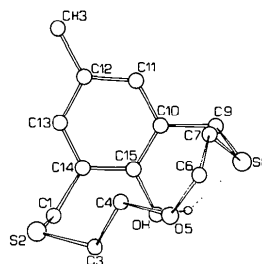

Fig. 2. Projection of the molecular structure of monomer $C_{13}H_{18}O_2S_2$ along the axis perpendicular to the phenyl ring.

normal van der Waals contacts. The molar volume in the α form [663 (1) Å³] is slightly smaller than in the β form [677 (2) Å³], the flattened molecules giving rise to a closer packing.

A view of the monomer molecule is shown in Fig. 2; the plane through the 4-methylphenol atoms forms an angle of 68·9 (2)° with that through the twelve atoms of the macrocycle ring. Atoms in the 4-methylphenol group deviate at most 0·029 (6) Å from the least-squares plane, while C(1) and C(9) are forced 0·186 (7) and 0·079 (7) Å, respectively, out of this plane; O(H) deviates 0·073 (5) Å in the opposite direction. The hydroxyl group points towards S(8) forming a rather strong intraannular hydrogen bond: S(8)···O(H) = 3·15 (1) Å, 'S(8)···H(OH)—O(OH) = 150 (3)°. The S(2)···O(H) distance is, on the other hand, 3·846 (9) Å; as a result the conformations of the two O(5)—C—C—S—C—C chains in the ring are different as shown by the sequence of torsion angles given in Table 5.

Packing is regulated by normal van der Waals contacts.

Table 5. Values of torsion angles in the three molecules

E.s.d.'s are within 1°.

	α dimer	β dimer	Monomer
C(14ⁱ)—C(1)—S(2)—C(3)	−170	165	68
C(1)—S(2)—C(3)—C(4)	−81	−92	−86
S(2)—C(3)—C(4)—O(5)	180	−179	168
C(3)—C(4)—O(5)—C(6)	161	71	−178
C(4)—O(5)—C(6)—C(7)	180	174	68
O(5)—C(6)—C(7)—S(8)	−68	−62	58
C(6)—C(7)—S(8)—C(9)	100	93	−144
C(7)—S(8)—C(9)—C(10)	−144	−148	52
S(8)—C(9)—C(10)—C(11)	−100	−103	−121
S(8)—C(9)—C(10)—C(15)	80	77	58
S(2)—C(1)—C(14ⁱ)—C(15ⁱ)	−152	−100	−95
S(2)—C(1)—C(14ⁱ)—C(13ⁱ)	28	77	81

Symmetry codes: α dimer (i) $-x$, $-y$, $-z$; β dimer (i) $1-x$, $1-y$, $1-z$; monomer (i) x,y,z.

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