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Structure of an Epipolysulfide: 3a,6-Dihydro-1-methylcyclopenta[6,7][1,2]dithiepino[5,4-*b*][1]benzothiophen-2(3*H*)-one

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Abstract. $C_{15}H_{12}OS_3$, $M_r = 304{\cdot}4$, m.p. 441–443 K, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}747\,(1)$, $b = 8{\cdot}787\,(2)$, $c = 18{\cdot}173\,(6)$ Å, $U = 1396{\cdot}8\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}445$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}458$ mm^{-1}, $F(000) = 632$, $T = 296$ K, final $R = 0{\cdot}062$ for 767 observed [$I > 3\sigma(I)$] diffractometer data. The S atoms of the dithiepine ring are disordered, as a result of which the ring conformation adopted is a chair for the major component (75%) and a twist-boat for the minor.

Introduction. Cyclodehydration of the *C*-secosteroid, *B*-nor-6,12-bisthia-*B*,14-secoestra-1,3,5(10),8-tetraene-14,17-dione with excess of *p*-toluenesulfonic acid in refluxing benzene afforded the unexpected title compound (I) in 20% yield, along with the expected compound *B*-nor-6,12-bisthiaestra-1,3,5(10),8,14-pentaen-17-one (II) in 10% yield (Ramadas, Appa Rao, Chenchaiah & Kumaresan, 1983). Because of the possibility of its being a member of a new type of tetracyclic organosulfur system and the current interest in the conformation of epipolysulfides, the X-ray crystal structure determination was undertaken.

Experimental. Light-pink crystals from 2-propanol, $0{\cdot}30 \times 0{\cdot}25 \times 0{\cdot}25$ mm. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator. 1484 reflections ($\omega/2\theta$ scan mode, $6° < 2\theta < 52°$), 767 unique observed reflections [$I > 3\sigma(I)$]. Reflections $2\bar{2}2$, $0\bar{2}2$ maintained intensity within 8% during data collection. Lp correction applied; absorption and extinction neglected. Structure solved by direct methods for nonhydrogen atoms. A difference Fourier map with phases of non-hydrogen atoms revealed two extra peaks, close to the S atoms of the dithiepine ring. With occupancy factors based on peak heights (Hamilton, 1959), refinement led to occupancies of 0·750 (4) and 0·250 (4) for the two S atoms. Refinement on F: non-hydrogen atoms with anisotropic temperature factors and H atoms (from ΔF map) with isotropic temperature factors. Final $R = 0{\cdot}062$, $wR = 0{\cdot}040$, $R_G = 0{\cdot}029$, $w^{-1} = \sigma^2|F_o|$. $(\Delta/\sigma)_{\max}$ in final cycle 0·100. Final difference map: no electron density $>0{\cdot}15$ e Å^{-3}. Programs: *MULTAN*80 (Main *et al.*, 1980), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Discussion. Table 1 gives the coordinates of the atoms of the structure.† The atom numbering and thermal ellipsoids are given in Fig. 1. Bond lengths and bond angles are in Table 2.

The bond lengths and bond angles in the thianaphthene and the dithiepin fragments, with the exception of C(5)—S(1) (in the major conformer), correspond closely to similar parameters in heterocyclic compounds containing S as hetero-atom: *e.g.*

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† Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42288 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3,12,13-tetrathia[4.4]metacyclophane (Beveridge, Bushnell & Mitchell, 1983); 3,4-dihydro-2*H*-[1]benzothieno[3,2-*b*]pyran-2-spiro-2′(3′*H*)-(benzo[*b*]-thiophen)-3′-one (Cox & Howie, 1982). The C(5)–S(1) bond length [1·959 (13) Å] and the low C–S–S bond angles (Table 2) probably reflect internal strain in the ring, as in the thiete ring of 2-chloroxanthene-9-spiro-2′-[3′,4′-bis(*tert*-butylthio)thiete] (Schreurs, Kroon, Bos & Brouwer, 1981) with a C–S bond of 1·907 (3) Å and C–S–S angle of 86·5°.

The thiophene ring, C(13)–S(3)–C(14)–C(7)–C(8), deviates slightly from planarity, assuming an envelope conformation with the flap at C(8), the junction with the fused benzene ring. The deviations of the atoms from the plane formed by the atoms C(7), C(13), C(14) and S(3) are: C(7) −0·002 (11), C(13) 0·002 (12), C(14) 0·003 (11), S(3) 0·002 (4) and C(8) 0·055 (10) Å. The disordered dithiepin ring exists in the chair and the twist-boat conformations (Fig. 2), when the S atoms are respectively on sites of occupancy 0·75 and 0·25. The characteristic features of these conformations are described in terms of the torsion angles of cycloheptane (Hendrickson, 1961). The torsion angle τ[C(6)–S(2)–S(1)–C(5)] (97·6°) in the major conformer and its counterpart in the minor conformer (−76·5°), involving the S atoms, are normal, *i.e.* within the range (70–110°) of values reported for such torsion angles in cyclic polysulfides (Abrahams, 1956).

Table 1. *Final positional parameters* (×10⁴, *for* H ×10³) *and equivalent isotropic U values* (×10³ Å²) *with* $U_{\rm eq} = \frac{1}{3}U_{ii}$ *for non-hydrogen atoms*

	x	y	z	$U_{\rm eq}$
C(1)	3268 (17)	1800 (16)	3644 (7)	68 (9)
C(2)	4091 (14)	3282 (12)	3795 (6)	39 (7)
C(3)	4566 (15)	4203 (14)	3182 (6)	51 (8)
C(4)	5444 (17)	5583 (14)	3487 (7)	63 (9)
C(5)	5317 (15)	5414 (12)	4312 (6)	50 (7)
C(6)	2677 (13)	5369 (11)	5853 (6)	39 (7)
C(7)	3531 (12)	3859 (13)	5775 (7)	41 (7)
C(8)	3568 (14)	2814 (14)	6398 (7)	42 (8)
C(9)	2976 (17)	2975 (14)	7116 (6)	56 (8)
C(10)	3271 (16)	1844 (18)	7634 (6)	64 (9)
C(11)	4146 (16)	571 (17)	7458 (9)	74 (11)
C(12)	4712 (19)	378 (14)	6759 (7)	65 (9)
C(13)	4397 (13)	1470 (15)	6231 (6)	49 (7)
C(14)	4180 (12)	3295 (12)	5174 (6)	39 (7)
C(15)	4444 (13)	3936 (13)	4416 (6)	42 (8)
O(1)	4363 (10)	3985 (10)	2531 (4)	74 (7)
S(1)*	3973 (8)	7108 (5)	4581 (3)	67 (4)
S(2)	3966 (7)	6990 (5)	5692 (3)	65 (3)
S(1′)	5038 (21)	6816 (15)	4953 (10)	71 (11)
S(2′)	2760 (17)	6549 (14)	5043 (8)	55 (9)
S(3)	4973 (5)	1483 (3)	5322 (2)	58 (2)
H(1)	251 (7)	369 (7)	722 (3)	46 (24)
H(2)	317 (9)	196 (7)	815 (3)	61 (26)
H(3)	438 (6)	−20 (6)	787 (2)	44 (22)
H(4)	610 (7)	554 (7)	470 (3)	85 (25)
H(5)	536 (8)	−68 (7)	665 (3)	119 (25)
H(6)	651 (8)	562 (7)	330 (3)	80 (25)
H(7)	516 (8)	655 (7)	329 (3)	80 (23)
H(8)	182 (8)	526 (7)	596 (3)	117 (25)
H(9)	307 (8)	584 (7)	628 (3)	120 (25)
H(10)	263 (12)	192 (9)	311 (5)	143 (44)
H(11)	259 (7)	125 (7)	396 (3)	93 (27)
H(12)	417 (7)	93 (7)	342 (3)	82 (26)

* S(1) and S(2) have site-occupation factors 0·750, S(1′) and S(2′) 0·250.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·513 (18)	C(5)–S(1′)	1·713 (19)
C(2)–C(3)	1·438 (16)	S(1)–S(2)	2·022 (8)
C(3)–C(4)	1·539 (18)	S(1′)–S(2′)	2·013 (24)
C(3)–O(1)	1·212 (13)	C(7)–C(8)	1·458 (18)
C(4)–C(5)	1·511 (17)	C(8)–C(9)	1·411 (17)
C(5)–C(15)	1·518 (16)	C(8)–C(13)	1·419 (18)
C(2)–C(15)	1·304 (16)	C(9)–C(10)	1·393 (18)
C(6)–C(7)	1·529 (15)	C(10)–C(11)	1·393 (21)
C(7)–C(14)	1·327 (16)	C(11)–C(12)	1·374 (21)
C(14)–C(15)	1·506 (15)	C(12)–C(13)	1·385 (18)
C(6)–S(2)	1·840 (12)	C(13)–S(3)	1·727 (12)
C(6)–S(2′)	1·802 (17)	C(14)–S(3)	1·757 (11)
C(5)–S(1)	1·959 (13)		

C(1)–C(2)–C(3)	118·8 (9)	C(5)–S(1)–S(2)	102·2 (5)
C(1)–C(2)–C(15)	130·5 (9)	C(15)–C(5)–S(1)	108·5 (8)
C(3)–C(2)–C(15)	110·7 (9)	C(6)–C(7)–C(8)	119·0 (9)
C(2)–C(3)–C(4)	108·0 (9)	C(7)–C(8)–C(13)	111·7 (9)
C(2)–C(3)–O(1)	128·7 (9)	C(7)–C(14)–S(3)	112·4 (8)
O(1)–C(3)–C(4)	123·3 (9)	C(13)–S(3)–C(14)	92·1 (6)
C(3)–C(4)–C(5)	104·1 (9)	C(8)–C(13)–S(3)	110·4 (8)
C(4)–C(5)–C(15)	104·2 (8)	C(8)–C(7)–C(14)	113·2 (9)
C(2)–C(15)–C(5)	112·9 (8)	S(3)–C(14)–C(15)	114·7 (7)
C(2)–C(15)–C(14)	126·2 (9)	C(12)–C(13)–S(3)	127·5 (9)
C(5)–C(15)–C(14)	120·7 (8)	C(7)–C(8)–C(9)	130·3 (10)
C(7)–C(14)–C(15)	132·8 (9)	C(8)–C(9)–C(10)	119·0 (10)
C(6)–C(7)–C(14)	127·5 (9)	C(9)–C(10)–C(11)	121·3 (10)
C(7)–C(6)–S(2′)	113·8 (9)	C(10)–C(11)–C(12)	120·6 (10)
C(7)–C(6)–S(2)	110·8 (8)	C(11)–C(12)–C(13)	118·8 (10)
C(6)–S(2′)–S(1′)	100·0 (10)	C(8)–C(13)–C(12)	122·0 (9)
C(6)–S(2)–S(1)	101·6 (5)	C(9)–C(8)–C(13)	118·0 (9)
C(5)–S(1′)–S(2′)	96·5 (10)		

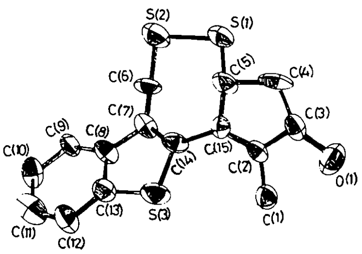

Fig. 1. *ORTEP* plot of the molecule (thermal ellipsoids of 50% probability), with the dithiepin ring in the chair conformation.

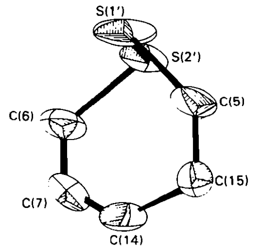

Fig. 2. The dithiepin ring in the twist-boat conformation.

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Structure of 1,3-Dihydro-3-methyl-4-(4-thio-β-D-erythrofuranosyl)-1-(*p*-tolyl)-2*H*-imidazole-2-thione, $C_{15}H_{18}N_2O_2S_2$

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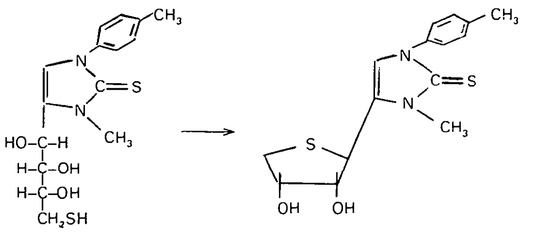
Abstract. $M_r = 322\cdot4$, orthorhombic, $P2_12_12_1$, $a = 11\cdot408\,(2)$, $b = 17\cdot502\,(3)$, $c = 7\cdot846\,(2)$ Å, $V = 1566\cdot5$ Å^3, $Z = 4$, $D_x = 1\cdot36$, D_m(flotation in benzene/CCl$_4$) = $1\cdot35$ Mg m^{-3}, graphite-monochromated Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 0\cdot36$ mm^{-1}, $F(000) = 680$, $T = 293$ K, final $R = 0\cdot040$ for 2172 independent reflections. The thiotetrafuranose-ring conformation is intermediate between twist ${}^2_3T$ and envelope E_3. The phenyl–imidazole and thiofuranose–imidazole dihedral angles are 46·7 (1) and 52·9 (1)°. The packing of the molecules is governed only by van der Waals contacts.

Introduction. Heterocyclic imidazole *C*-nucleosides are interesting because of their structural analogies with natural *C*-nucleosides. Sugars with S in the ring and nucleosides with this modification are not very common. The base–sugar bond in these analogues is more stable towards enzymic cleavage than in the naturally occurring compounds and the substitution of S for O markedly affects the conformation of the sugar ring (McCormick & McElhinney, 1978); interesting biological differences have been observed (Bloch, 1975; Bobek, Bloch, Parthasarathy & Whistler, 1975). The crystal structure of the title compound has been determined as part of a systematic structural investigation of the conformational properties of imidazole *C*-nucleosides with a view to assessing the influence of these sugar moieties on antitumour and antiviral properties. Compound (II) has been obtained by formation of the anhydride of 1,3-dihydro-3-methyl-4-(D-*arabino*-1,2,3-trihydroxy-4-mercaptobutyl)-1-(*p*-tolyl)-2*H*-imidazole-2-thione (I) catalysed by trifluoracetic acid.



(I) (II)

A previous ^{1}H NMR study in solution (Fernandez-Bolaños, Fuentes-Mota & Fernández-Bolaños Guzmán, 1984) showed the same configuration as obtained by the present X-ray study.

Experimental. Single crytals in form of colourless prisms. Crystal approximately $0\cdot29 \times 0\cdot20 \times 0\cdot49$ mm. Preliminary studies indicated orthorhombic symmetry, systematic absences consistent with $P2_12_12_1$. Lattice parameters refined using 25 reflections in the range $6 < \theta < 12°$. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ mode. $2\theta_{\max} = 60°$ ($h \le 16$, $k \le 24$, $l \le 11$). Two standard reflections (400 and $\bar{4}00$) monitored every 100 reflections showed only statistical fluctuations. 2172