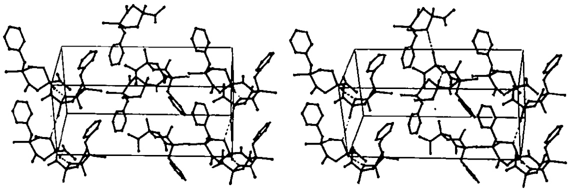

Fig. 2. Anordnung der Moleküle in der Elementarzelle. Stereo-Zeichnung, *a* von links nach rechts (um +30° gedreht), *b* von unten nach oben (um −5° gedreht); Wasserstoffbrücken gestrichelt.

Auch hier enthält der Ring zwei Phosphoratome der Oxidationsstufe +III. Der exocyclische P—N-Abstand ist in der Titelverbindung mit 1,627 (3) Å deutlich kürzer als die entsprechenden Bindungen im Ring, die mit bisher gefundenen Werten auch in ihrer Schwankungsbreite gut übereinstimmen. Der intramolekulare Kontaktabstand P(1)···P(2) über den Ring hinweg ist mit 3,314 (1) Å vergleichbar dem in anderen Twist-Konformationen und deutlich größer als in entsprechenden Sessel-Konformationen (Engelhardt & Stromburg, 1985).

Die Moleküle sind in der Elementarzelle über Wasserstoffbrücken zwischen N(2)—H(1)···O(2^{i}) bzw. O(2)···H(1^{ii})—N(2^{ii}) in Richtung der *b*-Achse zu unendlichen Ketten verbunden (Fig. 2): *r*N(2)···O(2) 2,793 (4) Å; *r*H(1)···O(2) 1,97 (3) Å mit *r*N(2)—H(1) 0,86 (3) Å [(i) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$].

Wir danken Herrn Kollegen J. Fuchs für seine freundliche Hilfe bei den Messungen. Der Deutschen Forschungsgemeinschaft und dem Fonds der Chemischen Industrie gilt unser Dank für finanzielle Unterstützung.

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Structure of a Steroid Oxetane Derivative With a Highly Strained and Unusual Ring Arrangement

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Abstract. 17,25-Epoxy-20-oxo-21,22,23,27-tetranor-16,25-cyclocholest-5-en-3-yl acetate, $C_{25}H_{34}O_4$, $M_r = 398{\cdot}55$, monoclinic, $P2_1$, $a = 6{\cdot}357\ (2)$, $b = 26{\cdot}203\ (6)$, $c = 6{\cdot}730\ (1)$ Å, $\beta = 103{\cdot}06\ (2)^\circ$, $V = 1092{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}212$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\bar{\alpha}) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}604$ mm^{-1}, $F(000) = 432$, $T =$

0108-2701/86/121833-04\$01.50

295 K. $R = 0·036$ for 1729 observed reflections. The 5-androstene skeleton of this molecule bears a fused cyclopentanone ring at the C(16) and C(17) positions of the *D* ring and an oxetane bridge between C(17) and C(22). The two five-membered rings are *trans*-fused while the oxetane ring is α to the steroid ring system.

Introduction. In a study of the photolysis of 5,16,20-pregnatrienyl 3β,20-diacetate Gutkowska (1973) isolated seven new photoproducts, the structure of five of which could be established unambiguously by spectroscopy and chemical correlation. The remaining two photoproducts were shown to be a photooxetane and its ring-opening product; however, the exact point of attachment of the four-membered ring and its stereochemistry on the steroid skeleton could not be established unambiguously. In a later study, Cavallo (1980) was able to show by thorough ^{1}H and ^{13}C NMR the exact point of attachment of the oxetane ring but its relative stereochemistry (α or β) remained uncertain. In an effort to resolve this problem and better understand the mechanism of formation of the oxetane and its ring-opening product, a crystal structure determination was undertaken.

Experimental. Recrystallization from a methanol solution, m.p. 451 K, crystal size 0·12 × 0·20 × 0·50 mm, unit-cell dimensions from 25 well-centered reflections, $13 \leq 2\theta \leq 57°$, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, ω–2θ scan, $\Delta\omega = (1·00 + 0·35\tan\theta)°$, $2\theta_{\max} = 140°$ ($0 \leq h \leq 7$, $-31 \leq k \leq 31$, $-8 \leq l \leq 7$), orientation verified every 100 reflections, intensity checked every hour using three standard reflections, intensity fluctuations 0·9, 1·2, 3·1%. 2115 unique reflections measured of which 1729 with $I \geq 1·90\sigma(I)$ are considered observed, 386 unobserved, $R_{\rm int} = 0·045$. Lp correction, no absorption corrections, direct methods (*MULTAN*),* full-matrix then block-diagonal least squares based on F. Parameters refined, scale factor, atomic coordinates and anisotropic temperature factors for non-H atoms, H-atoms found on difference Fourier syntheses kept at fixed positions at first then refined isotropically. Function minimized $\sum w(|F_o| - |F_c|)^2$. Final $R = 0·036$, $wR = 0·035$, $S = 2·93$. Maximum $(\Delta/\sigma) = 0·45$, average $(\Delta/\sigma) = 0·10$, min., max. residual electron density on final difference Fourier synthesis −0·14, +0·11 e Å^{-3}. Scattering curves for non-H atoms from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965).

Table 1. *Final atomic coordinates for the photooxetane derivative* (× 10^4) *and* $U_{\rm eq}$ (Å^2, × 10^4)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O(3)	4118 (4)	−167	15004 (4)	59
O(17)	1332 (4)	3019 (1)	6118 (4)	45
O(20)	−3742 (5)	3204 (1)	3679 (5)	81
O(24)	7590 (6)	63 (1)	15954 (6)	103
C(1)	1494 (7)	586 (1)	10290 (6)	51
C(2)	1985 (7)	123 (1)	11736 (6)	56
C(3)	3663 (6)	269 (1)	13592 (6)	50
C(4)	2884 (6)	705 (1)	14722 (6)	51
C(5)	2335 (5)	1161 (1)	13317 (5)	42
C(6)	3254 (6)	1610 (2)	13890 (5)	46
C(7)	2844 (6)	2093 (1)	12672 (5)	46
C(8)	833 (5)	2054 (1)	10956 (5)	39
C(9)	822 (5)	1534 (1)	9829 (5)	38
C(10)	762 (5)	1072 (1)	11278 (5)	40
C(11)	−933 (6)	1508 (1)	7836 (5)	45
C(12)	−999 (6)	1972 (1)	6422 (5)	42
C(13)	−1170 (5)	2466 (1)	7598 (5)	40
C(14)	800 (5)	2483 (1)	9436 (5)	39
C(15)	947 (6)	3044 (1)	10196 (5)	45
C(16)	−86 (6)	3369 (1)	8334 (5)	44
C(17)	−826 (5)	2968 (1)	6622 (5)	43
C(18)	−3357 (6)	2508 (2)	8223 (6)	53
C(19)	−1517 (6)	987 (2)	11651 (6)	56
C(20)	−2095 (6)	3280 (2)	4861 (6)	54
C(21)	−570 (7)	3753 (2)	5003 (6)	56
C(22)	1216 (6)	3554 (1)	6800 (6)	49
C(23)	3330 (7)	3819 (2)	7323 (7)	59
C(24)	6100 (8)	−189 (2)	16198 (7)	67
C(25)	6219 (10)	−577 (2)	17862 (8)	87

Discussion. The atomic coordinates of the photooxetane derivative, presented in Table 1, correspond to the known absolute configuration.* The atomic numbering and a stereoview of the molecule are shown in Figs. 1 and 2 respectively. The bond distances and angles are given in Table 2.

The molecule is constituted of a six-fused-ring system, the first four (*A*, *B*, *C*, *D*) of which are typical of the Δ^5-androstene steroid skeleton. The methyl groups at C(10) and C(13) are β to the steroid structure. The acetoxy group is also β to the skeleton and arranged in such a way that the carbonyl oxygen nearly eclipses the axial hydrogen atom at the 3-position of the ring. The torsion angles C(2)—C(3)—O(3)—C(24) and C(3)—O(3)—C(24)—C(25) have values of 151·2 (3) and 167·5 (4)° respectively. These are similar to the values of 155·6 and 168·5° found for cholesteryl acetate by Sawzik & Craven (1979). The cyclopentanone *E* ring is *trans*-fused to the cyclopentane *D* ring, *i.e.* the torsion angle C(15)—C(16)—C(17)—C(20) has a value of 173·0 (3)°. The torsion angle τ = O(17)—C(17)—C(16)—H(16) also indicates

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* The programs used here are modified versions of *NRC*-2, data reduction, *NRC*-10, bond distances and angles, *NRC*-22, mean planes (Ahmed, Hall, Pippy & Huber, 1983), *FORDAP*, Fourier and Patterson maps (A. Zalkin), *MULTAN*80, multisolution program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *NUCLS*, least-squares refinement (Doedens & Ibers, 1967) and *ORTEP*, stereodrawings (Johnson, 1965).

* Lists of structure factors, H-atom coordinates and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43215 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the *trans*-fusion of rings *D* and *E*. The actual value of τ, 147 (1)°, deviates significantly from 180°, and reveals the strain brought about by the four-member oxetane ring. This feature could not be established unambiguously by Cavallo (1980). The oxetane ring, made up of atoms C(16), C(17), O(17) and C(22), is on the α face of the steroid skeleton and is not planar since all the intracyclic bond angles are less than 90°. The dihedral angle between planes C(16), C(17), C(22) and C(17), O(17), C(22) is 44°. The four torsion angles in the oxetane ring have values around ±30°. This ring is the most puckered of those whose structures were established by X-ray diffraction. The average torsion angle is 16° for both the 3,5-dinitrobenzoate of *threo*-3,3,4,4-α-pentamethyl-2-oxetanemethanol (Hospital, Leroy, Bats & Moulines, 1978) and 2,2-bis(*p*-ethoxyphenyl)-3,3′-dimethyloxetan (Holan, Kowala & Wunderlich, 1973).

The bond distances and bond angles in rings *A*, *B* and *C* are within 4σ and 3σ respectively of their corresponding values in cholesteryl acetate. Not surprisingly C(14)—C(15) and C(13)—C(17) are found here to be significantly shorter, while the angles C(14)—C(15)—C(16), C(15)—C(16)—C(17) and C(13)—C(17)—C(16) deviate by 2·7, 3·5 and 5·0°, respectively, from the values reported for cholesteryl acetate.

There are no intermolecular contacts shorter than 3·40 Å, hence no other interaction than van der Waals type.

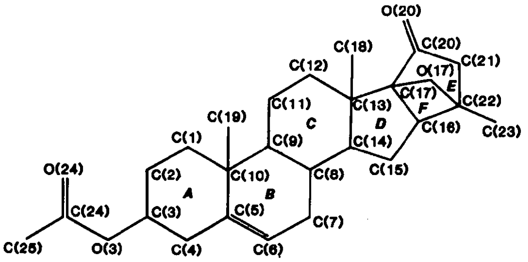

Fig. 1. Atomic and ring numbering for the photooxetane derivative.

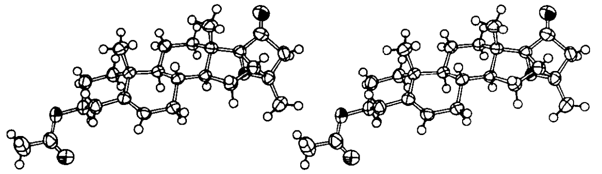

Fig. 2. Stereopair of the photooxetane derivative. For clarity, one octant of each oxygen atom has been shaded while the H-atoms are shown as small spheres. The ellipsoids of the non-H-atoms correspond to a 50% probability.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *for the photooxetane derivative*

C(1)—C(2)	1·542 (6)	C(12)—C(13)	1·534 (5)
C(1)—C(10)	1·556 (5)	C(13)—C(14)	1·549 (5)
C(2)—C(3)	1·497 (6)	C(13)—C(17)	1·508 (5)
C(3)—C(4)	1·516 (6)	C(13)—C(18)	1·545 (5)
C(3)—O(3)	1·472 (4)	C(14)—C(15)	1·552 (5)
O(3)—C(24)	1·334 (6)	C(15)—C(16)	1·535 (5)
C(4)—C(5)	1·515 (5)	C(16)—C(17)	1·552 (5)
C(5)—C(6)	1·331 (5)	C(16)—C(22)	1·540 (5)
C(5)—C(10)	1·522 (5)	C(17)—O(17)	1·492 (4)
C(6)—C(7)	1·498 (5)	C(17)—C(20)	1·514 (5)
C(7)—C(8)	1·520 (5)	O(17)—C(22)	1·482 (5)
C(8)—C(9)	1·559 (5)	C(20)—C(21)	1·563 (6)
C(8)—C(14)	1·517 (5)	C(20)—O(20)	1·180 (5)
C(9)—C(10)	1·560 (5)	C(21)—C(22)	1·550 (6)
C(9)—C(11)	1·540 (5)	C(22)—C(23)	1·483 (6)
C(10)—C(19)	1·541 (5)	C(24)—O(24)	1·196 (6)
C(11)—C(12)	1·539 (5)	C(24)—C(25)	1·502 (7)

C(3)—O(3)—C(24)	116·3 (3)	C(14)—C(13)—C(17)	98·8 (3)
C(17)—O(17)—C(22)	84·4 (2)	C(14)—C(13)—C(18)	113·3 (3)
C(2)—C(1)—C(10)	114·3 (3)	C(17)—C(13)—C(18)	106·5 (3)
C(1)—C(2)—C(3)	109·3 (3)	C(8)—C(14)—C(13)	113·7 (3)
O(3)—C(3)—C(2)	109·8 (3)	C(8)—C(14)—C(15)	119·3 (3)
O(3)—C(3)—C(4)	107·4 (3)	C(13)—C(14)—C(15)	105·5 (3)
C(2)—C(3)—C(4)	111·0 (3)	C(14)—C(15)—C(16)	105·9 (3)
C(3)—C(4)—C(5)	109·7 (3)	C(15)—C(16)—C(17)	103·5 (3)
C(4)—C(5)—C(6)	119·5 (3)	C(15)—C(16)—C(22)	121·8 (3)
C(4)—C(5)—C(10)	117·0 (3)	C(17)—C(16)—C(22)	80·5 (3)
C(6)—C(5)—C(10)	123·5 (3)	O(17)—C(17)—C(13)	114·1 (3)
C(5)—C(6)—C(7)	125·3 (3)	O(17)—C(17)—C(16)	88·2 (2)
C(6)—C(7)—C(8)	111·8 (3)	O(17)—C(17)—C(20)	97·4 (3)
C(7)—C(8)—C(9)	109·8 (3)	C(13)—C(17)—C(16)	108·5 (3)
C(7)—C(8)—C(14)	110·1 (3)	C(13)—C(17)—C(20)	135·1 (3)
C(9)—C(8)—C(14)	108·8 (3)	C(16)—C(17)—C(20)	103·5 (3)
C(8)—C(9)—C(10)	111·9 (3)	O(20)—C(20)—C(17)	132·2 (4)
C(8)—C(9)—C(11)	112·7 (3)	O(20)—C(20)—C(21)	128·2 (4)
C(10)—C(9)—C(11)	113·3 (3)	C(17)—C(20)—C(21)	99·6 (3)
C(1)—C(10)—C(5)	108·2 (3)	C(20)—C(21)—C(22)	96·7 (3)
C(1)—C(10)—C(9)	108·4 (3)	O(17)—C(22)—C(16)	89·0 (3)
C(1)—C(10)—C(19)	109·5 (3)	O(17)—C(22)—C(21)	99·0 (3)
C(5)—C(10)—C(9)	109·9 (3)	O(17)—C(22)—C(23)	114·2 (3)
C(5)—C(10)—C(19)	109·0 (3)	C(16)—C(22)—C(21)	102·7 (3)
C(9)—C(10)—C(19)	111·8 (3)	C(16)—C(22)—C(23)	125·7 (3)
C(9)—C(11)—C(12)	114·6 (3)	C(21)—C(22)—C(23)	119·5 (3)
C(11)—C(12)—C(13)	110·1 (3)	O(3)—C(24)—O(24)	124·3 (4)
C(12)—C(13)—C(14)	107·3 (3)	O(3)—C(24)—C(25)	111·1 (4)
C(12)—C(13)—C(17)	118·5 (3)	O(24)—C(24)—C(25)	124·6 (5)
C(12)—C(13)—C(18)	112·0 (3)		

Ring *A*		Ring *B*	
C(1)—C(2)—C(3)—C(4)	60·2 (4)	C(5)—C(6)—C(7)—C(8)	15·0 (5)
C(2)—C(3)—C(4)—C(5)	−58·4 (4)	C(6)—C(7)—C(8)—C(9)	−45·1 (4)
C(3)—C(4)—C(5)—C(10)	53·6 (4)	C(7)—C(8)—C(9)—C(10)	61·7 (4)
C(4)—C(5)—C(10)—C(1)	−47·8 (4)	C(8)—C(9)—C(10)—C(5)	−43·9 (4)
C(5)—C(10)—C(1)—C(2)	48·4 (4)	C(9)—C(10)—C(5)—C(6)	12·9 (5)
C(10)—C(1)—C(2)—C(3)	−56·4 (4)	C(10)—C(5)—C(6)—C(7)	1·9 (4)

Ring *C*		Ring *D*	
C(8)—C(9)—C(11)—C(12)	48·7 (4)	C(13)—C(14)—C(15)—C(16)	−26·6 (4)
C(9)—C(11)—C(12)—C(13)	−53·5 (4)	C(14)—C(15)—C(16)—C(17)	1·6 (4)
C(11)—C(12)—C(13)—C(14)	57·9 (4)	C(15)—C(16)—C(17)—C(13)	25·0 (4)
C(12)—C(13)—C(14)—C(8)	−63·6 (4)	C(16)—C(17)—C(13)—C(14)	−40·3 (3)
C(13)—C(14)—C(8)—C(9)	58·2 (4)	C(17)—C(13)—C(14)—C(15)	40·2 (3)
C(14)—C(8)—C(9)—C(11)	−48·8 (4)		

Ring *E*		Oxetane ring	
C(16)—C(17)—C(20)—C(21)	43·0 (3)	O(17)—C(17)—C(16)—C(22)	30·8 (2)
C(17)—C(20)—C(21)—C(22)	2·3 (3)	C(17)—C(16)—C(22)—O(17)	−31·0 (2)
C(20)—C(21)—C(22)—C(16)	−47·6 (3)	C(16)—C(22)—O(17)—C(17)	32·0 (2)
C(21)—C(22)—C(16)—C(17)	68·0 (3)	C(22)—O(17)—C(17)—C(16)	−31·8 (2)
C(22)—C(16)—C(17)—C(20)	−66·4 (3)		

		Others	
		O(17)—C(17)—C(20)—C(21)	−46·9 (3)
		C(20)—C(21)—C(22)—O(17)	43·4 (3)
		C(21)—C(22)—O(17)—C(17)	−70·6 (3)
		C(22)—O(17)—C(17)—C(20)	71·7 (3)

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Structures of Two Isomers of Phenyl-3*H*-1,2-dithiole-3-thione*†

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Abstract. Structures of two isomeric compounds are reported: 4-phenyl-3*H*-1,2-dithiole-3-thione (4-PDT) and 5-phenyl-3*H*-1,2-dithiole-3-thione (5-PDT). Both have formula $C_6H_5.C_3HS_3$, $M_r = 210{\cdot}339$, X-ray data collected with $\lambda(\text{Mo}\ K\alpha_1) = 0{\cdot}7093$ Å at 296 (1) K. The former belongs to the monoclinic space group $P2_1/c$, $a = 17{\cdot}827$ (4), $b = 5{\cdot}731$ (1), $c = 9{\cdot}272$ (2) Å, $\beta = 91{\cdot}93$ (2)°, $V = 946{\cdot}8$ (3) Å^3, $Z = 4$, $D_m = 1{\cdot}47$ (1), $D_x = 1{\cdot}475$ g cm^{-3}, $\mu = 6{\cdot}93$ cm^{-1}, $F(000) = 432$. Final $R(F) = 0{\cdot}031$ for 2255 counter data with $F_o^2 \geq 2\sigma(F_o^2)$. The latter crystallizes in the orthorhombic space group *Pbca*, $a = 19{\cdot}949$ (6), $b = 12{\cdot}188$ (3), $c = 7{\cdot}544$ (2) Å, $V = 1834{\cdot}2$ (9) Å^3, $Z = 8$, $D_m = 1{\cdot}51$ (1), $D_x = 1{\cdot}523$ g cm^{-3}, $\mu = 7{\cdot}16$ cm^{-1}, $F(000) = 864$. Final $R(F) = 0{\cdot}031$ for 1633 data with $F_o^2 \geq 2\sigma(F_o^2)$. The molecules are composed of a phenyl ring and a five-membered heterocyclic ring, the difference between the two isomers being the positions of the C atom of the 3*H*-1,2-dithiole-3-thione ring to which the phenyl ring is linked. The two molecules have bond lengths and angles resembling each other and other compounds containing 3*H*-1,2-dithiole-3-thione as a building unit. The phenyl rings and the five-membered-ring systems are both planar to within 0·01 Å in both structures, the angle between the two plane normals being 67·40 (9)° for 4-PDT and 29·36 (8)° for 5-PDT.

Introduction. The title compounds, 4-PDT and 5-PDT, contain 3*H*-1,2-dithiole-3-thione as a building unit which was considered by Bueding, Dolan & Leroy (1982) to be essential for the antischistosomal drug 4-methyl-5-(2-pyrazinyl)-3*H*-1,2-dithiole-3-thione (oltipraz) to function. In our previous studies, it was shown that the pyrazine ring is linked to 4-methyl-3*H*-1,2-dithiole-3-thione *via* a C—C bond to yield oltipraz (Wei, 1983), or to 4-methyl-3*H*-1,2-dithiol-3-one to form an oltipraz analog (Wei, 1985*a*). On the other hand, the 3*H*-1,2-dithiole-3-thione ring could be linked to a *p*-methoxyphenyl group, yielding 5-(*p*-methoxyphenyl)-3*H*-1,2-dithiole-3-thione (Wang, Lin & Wei, 1985). The present paper reports the structures in which a phenyl ring replaces an H atom of the 3*H*-1,2-dithiole-3-thione ring at two different positions. Thus, crystallographic elucidation of the stereochemistry of a variety of different compounds containing the six- and five-membered-ring systems afford considerable stereochemical insight into the molecular parameters, including the angle between plane normals for the two ring systems.

Experimental. Maroon crystals of 4-PDT were obtained from toluene solution and orange crystals of 5-PDT from ethyl acetate solution of the corresponding specimen, kindly furnished by Professor Ernest Bueding of The Johns Hopkins University. Crystal densities determined by flotation in mixtures of 2-bromobutyric acid and 1,2-dichloroethane. In each case, space group and approximate cell parameters established from Weissenberg and precession photographs. For 4-PDT,

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