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Structure of 3-Hydroxy-1-methyl-1,3,5(10)-estratriene-11,17-dione

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(*Received* 10 *November* 1989; *accepted* 16 *January* 1990)

Abstract. $C_{19}H_{22}O_3$, $M_r = 298{\cdot}39$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}332\,(6)$, $b = 14{\cdot}596\,(7)$, $c = 9{\cdot}567\,(4)$ Å, $V = 1582{\cdot}6\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}252$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}0778$ mm^{-1}, $F(000) = 640$, $T = 273$ K, $R = 0{\cdot}067$ for 1762 unique observed reflections where $F > 2\sigma(F)$. The structure was studied to observe the effect of 1-methyl and 11-keto substitution. The 3-hydroxyl is hydrogen bonded to O11 at 2·76 Å. The *B* ring is in a $7\alpha,8\beta$ half-chair conformation. The molecule twists about the C(9)—C(10) bond to relieve the steric interaction between the 1-methyl and 11-keto groups. The C1—C10—C9—C11 torsion angle is 55 *vs* 33·5°, the average of 38 estradiol analogue structures.

Experimental. Rectangular rod-shaped crystals by evaporation from methanol, 0·18 × 0·20 × 0·30 mm, Nicolet *P*3 diffractometer. ω-scan method, lattice parameters from the 2θ values of 24 reflections with $19 < 2\theta < 28°$, intensity measurements performed up to $2\theta = 60°$; range of *hkl* 0 to 16, −1 to 21, 0 to 14; variable scan speed from 3 to 30° min^{-1} (2θ). Four standard reflections (442, 620, 280, 015) varied in intensity by 2% throughout the experiment. 3746 reflections measured, 2627 unique reflections, $R_{\text{int}} = 0{\cdot}018$, 1762 observed reflections with $F > 2\sigma(F)$.

Structure solved by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Hydrogens found from difference map and refined with isotropic displacement parameters; final $R = 6{\cdot}7\%$, $wR = 5{\cdot}7\%$, $S = 1{\cdot}78$, $(\Delta/\sigma)_{\max} = 0{\cdot}17$. Weighting scheme based on estimates of experimental errors from counting statistics was used to calculate *w*. $(\Delta\rho)_{\max} = 0{\cdot}5$ e Å^{-3}, $(\Delta\rho)_{\min} = -0{\cdot}3$ e Å^{-3} from final difference Fourier synthesis. No corrections for absorption or extinction were made. Atomic scattering factors were taken

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† Deceased.

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Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
C(1)	0·5087 (3)	0·6651 (2)	0·6718 (4)	2·7 (1)
C(2)	0·5299 (3)	0·7573 (3)	0·6868 (4)	3·1 (1)
C(3)	0·6202 (3)	0·8006 (2)	0·6160 (4)	2·8 (1)
C(4)	0·6932 (3)	0·7488 (3)	0·5312 (4)	2·8 (1)
C(5)	0·6726 (3)	0·6551 (2)	0·5105 (4)	2·6 (1)
C(6)	0·7614 (3)	0·6010 (3)	0·4273 (5)	3·4 (1)
C(7)	0·7513 (3)	0·4980 (3)	0·4517 (5)	3·3 (1)
C(8)	0·6226 (3)	0·4717 (2)	0·4298 (4)	2·7 (1)
C(9)	0·5453 (3)	0·5141 (2)	0·5467 (4)	2·4 (1)
C(10)	0·5756 (3)	0·6144 (2)	0·5766 (4)	2·5 (1)
C(11)	0·4183 (3)	0·4986 (2)	0·5002 (4)	3·0 (1)
C(12)	0·3805 (4)	0·3994 (3)	0·4841 (5)	3·3 (1)
C(13)	0·4640 (4)	0·3559 (3)	0·3785 (4)	3·4 (1)
C(14)	0·5937 (3)	0·3695 (2)	0·4234 (4)	3·1 (1)
C(15)	0·6635 (5)	0·3054 (3)	0·3281 (6)	4·7 (1)
C(16)	0·5832 (6)	0·2201 (4)	0·3199 (8)	5·9 (2)
C(17)	0·4605 (5)	0·2528 (3)	0·3637 (5)	4·9 (1)
C(18)	0·4384 (5)	0·3942 (4)	0·2298 (5)	4·9 (1)
C(1*M*)	0·4181 (5)	0·6221 (4)	0·7666 (6)	4·3 (1)
O(3)	0·6349 (3)	0·8921 (2)	0·6384 (3)	4·2 (1)
O(11)	0·3532 (2)	0·5610 (2)	0·4678 (3)	4·5 (1)
O(17)	0·3759 (3)	0·2038 (2)	0·3848 (4)	6·9 (1)

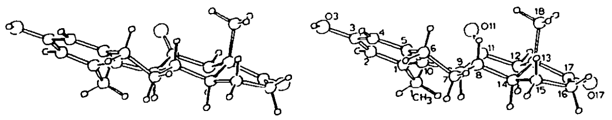

Fig. 1. *ORTEP*II (Johnson, 1976) stereoview of the molecule with atomic numbering.

from *International Tables for X-ray Crystallography* (1974).

Atomic parameters are listed in Table 1. Distances, angles and selected torsion angles are listed in Table 2.* A stereoscopic view of the molecule showing the atomic numbering and the molecular conformation is given in Fig. 1. Fig. 2 shows a stereoview of the molecular packing.

Related literature. Related structures were reported by Duax, Griffin, Strong & Wood (1989) and Segaloff, Gabbard, Flores, Borne, Baker, Duax, Strong & Rohrer (1980).

A sample of the title compound was provided by the late Dr A. Segaloff. This work was supported by

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

C(1)—C(2)	1·376 (5)	C(9)—C(10)	1·531 (5)
C(1)—C(10)	1·397 (5)	C(9)—C(11)	1·523 (5)
C(1)—C(1*M*)	1·507 (6)	C(11)—C(12)	1·519 (5)
C(2)—C(3)	1·381 (5)	C(11)—O(11)	1·212 (4)
C(3)—C(4)	1·384 (5)	C(12)—C(13)	1·523 (6)
C(3)—O(3)	1·362 (4)	C(13)—C(14)	1·544 (5)
C(4)—C(5)	1·401 (5)	C(13)—C(17)	1·512 (6)
C(5)—C(6)	1·506 (5)	C(13)—C(18)	1·556 (7)
C(5)—C(10)	1·401 (5)	C(14)—C(15)	1·528 (7)
C(6)—C(7)	1·526 (6)	C(15)—C(16)	1·544 (8)
C(7)—C(8)	1·523 (5)	C(16)—C(17)	1·529 (8)
C(8)—C(9)	1·549 (5)	C(17)—O(17)	1·213 (6)
C(8)—C(14)	1·529 (5)		

C(2)—C(1)—C(10)	119·5 (3)	C(1)—C(10)—C(9)	120·4 (3)
C(2)—C(1)—C(1*M*)	117·6 (3)	C(5)—C(10)—C(9)	119·8 (3)
C(10)—C(1)—C(1*M*)	122·8 (3)	C(9)—C(11)—C(12)	115·9 (3)
C(1)—C(2)—C(3)	121·8 (3)	C(9)—C(11)—O(11)	122·6 (3)
C(2)—C(3)—C(4)	118·7 (3)	C(12)—C(11)—O(11)	121·3 (3)
C(2)—C(3)—O(3)	117·5 (3)	C(11)—C(12)—C(13)	106·8 (3)
C(4)—C(3)—O(3)	123·8 (3)	C(12)—C(13)—C(14)	110·7 (3)
C(3)—C(4)—C(5)	121·1 (3)	C(12)—C(13)—C(17)	117·4 (3)
C(4)—C(5)—C(6)	118·3 (3)	C(12)—C(13)—C(18)	110·0 (3)
C(4)—C(5)—C(10)	118·7 (3)	C(14)—C(13)—C(17)	100·3 (3)
C(6)—C(5)—C(10)	122·8 (3)	C(14)—C(13)—C(18)	112·7 (3)
C(5)—C(6)—C(7)	112·7 (3)	C(17)—C(13)—C(18)	105·5 (3)
C(6)—C(7)—C(8)	107·4 (3)	C(8)—C(14)—C(13)	109·9 (3)
C(7)—C(8)—C(9)	110·0 (3)	C(8)—C(14)—C(15)	120·7 (3)
C(7)—C(8)—C(14)	117·2 (3)	C(13)—C(14)—C(15)	104·4 (3)
C(9)—C(8)—C(14)	107·3 (3)	C(14)—C(15)—C(16)	102·7 (4)
C(8)—C(9)—C(10)	112·9 (3)	C(15)—C(16)—C(17)	105·7 (4)
C(8)—C(9)—C(11)	105·3 (2)	C(13)—C(17)—C(16)	108·2 (4)
C(10)—C(9)—C(11)	114·1 (3)	C(13)—C(17)—O(17)	126·3 (3)
C(1)—C(10)—C(5)	119·7 (3)	C(16)—C(17)—O(17)	125·4 (4)

A Ring		*B* Ring	
C(10)—C(1)—C(2)—C(3)	−3·8 (6)	C(10)—C(5)—C(6)—C(7)	−13·8 (5)
C(1)—C(2)—C(3)—C(4)	−2·0 (6)	C(5)—C(6)—C(7)—C(8)	51·4 (4)
C(2)—C(3)—C(4)—C(5)	3·6 (5)	C(6)—C(7)—C(8)—C(9)	−67·5 (4)
C(3)—C(4)—C(5)—C(10)	0·5 (5)	C(7)—C(8)—C(9)—C(10)	44·7 (4)
C(4)—C(5)—C(10)—C(1)	−6·4 (5)	C(8)—C(9)—C(10)—C(5)	−6·2 (4)
C(5)—C(10)—C(1)—C(2)	8·0 (5)	C(9)—C(10)—C(5)—C(6)	−9·8 (5)
C Ring		*D* Ring	
C(14)—C(8)—C(9)—C(11)	−61·6 (3)	C(17)—C(13)—C(14)—C(15)	43·0 (4)
C(8)—C(9)—C(11)—C(12)	61·8 (4)	C(13)—C(14)—C(15)—C(16)	−39·1 (5)
C(9)—C(11)—C(12)—C(13)	−57·8 (4)	C(14)—C(15)—C(16)—C(17)	19·5 (5)
C(11)—C(12)—C(13)—C(14)	54·4 (4)	C(15)—C(16)—C(17)—C(13)	7·3 (6)
C(12)—C(13)—C(14)—C(8)	−61·5 (4)	C(16)—C(17)—C(13)—C(14)	−30·5 (5)
C(13)—C(14)—C(8)—C(9)	64·4 (4)		

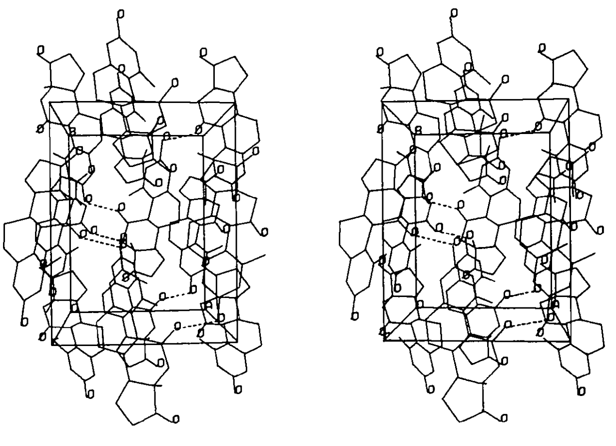

Fig. 2. Stereoview of the packing of the molecule down the *c* axis, showing the hydrogen bonding.

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* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52614 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the National Institute of Diabetes and Digestive and Kidney Diseases, Grant No. DK26546-22.

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Acta Cryst. (1990). C**46**, 1174–1176

Two Chlorinated Thiophene Derivatives, $C_{13}H_{11}Cl_4NO_6S$ and $C_9H_6Cl_4O_4S$

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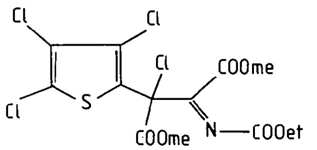
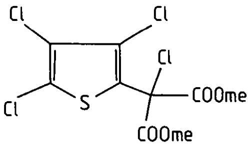
(*Received* 22 *November* 1989; *accepted* 17 *January* 1990)

Abstract. Dimethyl 2-chloro-3-ethoxycarbonylimino-2-(3,4,5-trichlorothien-2-yl)succinate, $C_{13}H_{11}Cl_4NO_6S$ (1), $M_r = 451{\cdot}1$, monoclinic, $P2_1/c$, $a = 12{\cdot}208\,(2)$, $b = 10{\cdot}413\,(1)$, $c = 14{\cdot}849\,(1)$ Å, $\beta = 104{\cdot}97\,(1)°$, $V = 1823{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}64$ g cm^{-3}, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71073$ Å), $F(000) = 912$, $\mu = 7{\cdot}2$ cm^{-1}, $T = 298$ K, $R = 0{\cdot}068$ for 4375 reflections. Dimethyl 2-chloro-2-(3,4,5-trichlorothien-2-yl)malonate, $C_9H_6Cl_4O_4S$ (2), $M_r = 352{\cdot}0$, monoclinic, $P2_1$, $a = 6{\cdot}742\,(3)$, $b = 8{\cdot}068\,(1)$, $c = 12{\cdot}555\,(1)$ Å, $\beta = 97{\cdot}84\,(2)°$, $V = 676{\cdot}5$ Å^3, $Z = 2$, $D_x = 1{\cdot}73$ g cm^{-3}, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71073$ Å), $F(000) = 352$, $\mu = 10{\cdot}3$ cm^{-1}, $T = 298$ K, $R = 0{\cdot}031$ for 1561 reflections. The S—C bond of the chlorinated thiophene ring is significantly shorter than the corresponding bond in related (S,N)-ylides.

Experimental. Both compounds were synthesized as described by Dillen, Meth-Cohn & van Vuuren (1987).



(1)



(2)

Compound (1), crystal *ca* 0·12 × 0·31 × 0·31 mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; ω scan; variable scan speed with a maximum of 5·49° min^{-1}, and a minimum corresponding to 50 s measuring time per reflection; the ω-scan angle changed as (0·53 +

Table 1. *Fractional coordinates* (× 10^4) *and equivalent thermal factors* (Å^2 × 10^3)

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

	x	y	z	U_{eq}
(*a*) Molecule (1)				
S(1)	379 (1)	1792 (1)	8828 (1)	49 (1)
C(2)	60 (2)	3338 (2)	8465 (2)	49 (1)
C(3)	674 (2)	4216 (2)	9045 (2)	48 (1)
C(4)	1428 (2)	3620 (2)	9823 (2)	44 (1)
C(5)	1381 (2)	2325 (2)	9810 (1)	39 (1)
C(6)	2074 (2)	1414 (2)	10519 (1)	38 (1)
C(7)	3344 (2)	1744 (2)	10744 (1)	37 (1)
N(8)	3851 (2)	2179 (2)	11528 (1)	44 (1)
C(9)	5007 (2)	2553 (3)	11767 (2)	50 (1)
O(10)	5089 (1)	3731 (2)	11473 (1)	63 (1)
C(11)	6235 (3)	4294 (3)	11742 (2)	88 (1)
C(12)	6186 (3)	5492 (4)	11225 (3)	102 (1)
O(13)	5735 (1)	1923 (2)	12266 (1)	68 (1)
C(14)	3938 (2)	1518 (2)	9975 (2)	45 (1)
O(15)	3211 (1)	1146 (2)	9200 (1)	50 (1)
C(16)	3651 (3)	883 (3)	8396 (2)	70 (1)
O(17)	4931 (2)	1639 (2)	10099 (1)	74 (1)
C(18)	1911 (2)	−11 (2)	10233 (2)	41 (1)
O(19)	2768 (1)	−691 (1)	10744 (1)	50 (1)
C(20)	2708 (3)	−2083 (3)	10578 (2)	63 (1)
O(21)	1125 (1)	−425 (1)	9663 (1)	57 (1)
Cl(22)	1589 (1)	1501 (1)	11569 (1)	52 (1)
Cl(23)	−956 (1)	3632 (1)	7459 (1)	73 (1)
Cl(24)	576 (1)	5838 (1)	8864 (1)	72 (1)
Cl(25)	2259 (1)	4544 (1)	10697 (1)	64 (1)
(*b*) Molecule (2)				
S(1)	876 (1)	3669	6361 (1)	49 (1)
C(2)	1271 (6)	3059 (5)	5098 (3)	49 (1)
C(3)	2959 (6)	2197 (5)	5091 (3)	45 (1)
C(4)	4002 (5)	2005 (5)	6146 (3)	43 (1)
C(5)	3052 (5)	2711 (5)	6921 (3)	37 (1)
C(6)	3743 (5)	2678 (4)	8114 (3)	36 (1)
C(7)	4513 (5)	944 (5)	8503 (3)	39 (1)
O(8)	3206 (4)	−187 (3)	8110 (2)	44 (1)
C(9)	3769 (8)	−1897 (5)	8382 (4)	53 (1)
O(10)	6030 (4)	700 (3)	9098 (2)	53 (1)
C(11)	2094 (5)	3248 (5)	8761 (3)	42 (1)
O(12)	2104 (4)	2345 (3)	9639 (2)	47 (1)
C(13)	603 (8)	2778 (6)	10319 (4)	59 (1)
O(14)	998 (4)	4375 (4)	8499 (2)	62 (1)
Cl(15)	5760 (1)	4135 (2)	8441 (1)	51 (1)
Cl(16)	−426 (2)	3599 (2)	4017 (1)	74 (1)
Cl(17)	3759 (2)	1359 (2)	3977 (1)	70 (1)
Cl(18)	6258 (1)	1007 (2)	6385 (1)	62 (1)

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