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Steroid Intermediates: (1) 3,4-Dinor-2,5-seco-9α-estrane-1,5,17-trione, $C_{16}H_{22}O_3$; (2) *D*-Homo-4-norestr-3(5)-ene-2,17-dione, $C_{18}H_{24}O_2$; and (3) 1,2,3,4-Tetranorestr-9-ene-5,17-dione, $C_{14}H_{18}O_2$

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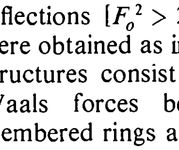
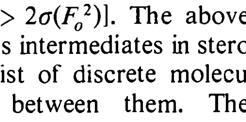
Abstract. (1) $M_r = 262{\cdot}4$, $P2_12_12_1$, $a = 9{\cdot}326\,(2)$, $b = 10{\cdot}355\,(4)$, $c = 14{\cdot}824\,(5)$ Å, $V = 1431{\cdot}6\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}217\,(1)$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}89$ cm^{-1}, $F(000) = 568$, $T = 295\,(1)$ K, $R = 0{\cdot}044$, 1156 reflections $[F_o^2 > 2\sigma(F_o^2)]$. (2) $M_r = 272{\cdot}4$, $P2_1/n$, $a = 11{\cdot}383\,(6)$, $b = 11{\cdot}645\,(2)$, $c = 11{\cdot}859\,(2)$ Å, $\beta = 107{\cdot}83\,(2)°$, $V = 1496{\cdot}5\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}209\,(1)$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}83$ cm^{-1}, $F(000) = 592$, $T = 295\,(1)$ K, $R = 0{\cdot}046$, 1605 reflections $[F_o^2 > 2\sigma(F_o^2)]$. (3) $M_r = 218{\cdot}3$, $P2_1$, $a = 8{\cdot}947\,(3)$, $b = 7{\cdot}031\,(1)$, $c = 9{\cdot}557\,(3)$ Å, $\beta = 100{\cdot}60\,(2)°$, $V = 590{\cdot}9\,(5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}227\,(1)$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}87$ cm^{-1}, $F(000) = 236$, $T = 295$ K, $R = 0{\cdot}041$, 997 reflections $[F_o^2 > 2\sigma(F_o^2)]$. The above three molecules were obtained as intermediates in steroid syntheses. The structures consist of discrete molecules with van der Waals forces between them. The saturated six-membered rings are all in the usual chair conformation while the saturated five-membered rings in (1) and (3) are in the envelope conformation (C_s), and the unsaturated six-membered ring in (3) has the sofa (C_s) conformation. Distances and angles are normal.

Introduction. In the course of a total synthesis of novel steroids, some interesting intermediates were obtained. The stereochemical features and the chemical behavior of these compounds have been reported (Nassim, Schlemper & Crabbé, 1983; Li, Nassim & Crabbé, 1983; Ding, Nassim & Crabbé, 1983).* In this paper we present the X-ray crystallographic results for three of these compounds. The X-ray data were used to establish their correct structure and configuration and served as a guide for additional synthetic steps.



(1)



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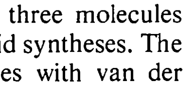

(3)

Experimental. Compounds prepared as described (Li, Nassim & Crabbé, 1983; Ding, Nassim & Crabbé, 1983). Enraf–Nonius CAD-4 diffractometer, 25 reflections ($15 < 2\theta < 30°$) used for cell dimensions, scattering factors including f' and f'' from *International Tables for X-ray Crystallography* (1974), computations on PDP11/34 computer using Enraf–Nonius (1979) *SDP* programs. All three structures solved using *MULTAN* (Germain, Main & Woolfson, 1971) and difference Fourier methods. Full-matrix least-squares refinements minimizing $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = [\sigma^2_{\text{counting}} + (0{\cdot}05F_o^2)^2]/4F_o^2$. (1) Prisms, $\sim 0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}3$ mm, absent $h00(h = 2n + 1)$, $0k0(k = 2n + 1)$, $00l(l = 2n + 1)$, no absorption correction, estimated transmission range <2% based on ψ scans, $2\theta_{\max} = 50°$, $2\theta < 12°$ (all forms) and $2\theta \geq 12°$ (only hkl), three standards every 2 h of X-ray exposure (3% range), 1820 reflections measured (1464 unique), $R_{\text{int}} = 0{\cdot}035$, 308 reflections with $F_o^2 < 2\sigma(F_o^2)$ considered unobserved, hydrogen atoms from difference Fourier syntheses and/or chemical ideality (not refined), 172 variables (x, y, z, 6β's for each nonhydrogen atom), $S = 1{\cdot}66$, $R = 0{\cdot}044$, $wR = 0{\cdot}058$, max. $\Delta/\sigma = 0{\cdot}08$, max. $\Delta\rho$ on final difference Fourier synthesis $= 0{\cdot}4$ e Å^{-3}. The final parameters are in Table 1. (2) Prisms, $\sim 0{\cdot}1 \times 0{\cdot}15 \times 0{\cdot}15$ mm, absent $h0l(h + l = 2n + 1)$ and $0k0(k = 2n + 1)$, no absorption correction, estimated transmission range <2% based on ψ scans, $2\theta_{\max} = 50°$, $2\theta < 12°(h, \pm k, \pm l)$ and $2\theta \geq 12°(h, k, \pm l)$, three standards every 2 h of X-ray exposure (3% range), 2934 reflections measured (2638 unique), $R_{\text{int}} = 0{\cdot}034$, 1033 reflections with $F_o^2 < 2\sigma(F_o^2)$ considered unobserved, hydrogen atoms from difference Fourier synthesis and/or chemically reasonable positions, 253 variables (x, y, z all atoms, 6β's nonhydrogen atoms), $R = 0{\cdot}046$, $wR = 0{\cdot}063$, $S = 1{\cdot}71$, max. $\Delta/\sigma = 0{\cdot}06$, max. $\Delta\rho$ on final difference Fourier synthesis $= 0{\cdot}4$ e Å^{-3}. The final parameters are in Table 2. (3) Prisms, $\sim 0{\cdot}3 \times 0{\cdot}4 \times 0{\cdot}4$ mm, absent $0k0(k = 2n + 1)$, no absorption correction, estimated transmission range <2% based on ψ scans, $2\theta_{\max} = 50°$, $2\theta \leq 40°(h, \pm k, \pm l)$, $2\theta > 40°(h, k, \pm l)$, three standards every 2 h of X-ray exposure (3% range), 1880 reflections measured (1134 unique), $R_{\text{int}} = 0{\cdot}025$,

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* Nomenclature used in this work was taken from these references.

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Table 1. *Atomic parameters for compound* (1) *with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B_{eq}(Å^2)
O(1)	−0·0369 (3)	−0·2259 (2)	−0·0504 (2)	6·06 (6)
O(5)	0·1617 (3)	−0·1173 (3)	−0·2177 (2)	5·51 (6)
O(17)	−0·7022 (2)	0·1551 (3)	−0·1042 (2)	5·59 (6)
C(1)	0·0365 (3)	−0·1299 (3)	−0·0567 (2)	3·80 (6)
C(2)	0·1719 (4)	−0·1151 (4)	−0·0058 (3)	5·32 (8)
C(5)	0·0680 (3)	−0·0379 (3)	−0·2091 (2)	3·53 (6)
C(6)	0·0216 (3)	0·0467 (4)	−0·2846 (2)	4·46 (7)
C(7)	−0·1412 (3)	0·0472 (4)	−0·2950 (2)	3·97 (7)
C(8)	−0·2116 (3)	0·0854 (3)	−0·2069 (2)	2·95 (5)
C(9)	−0·1734 (3)	−0·0082 (3)	−0·1308 (2)	2·99 (6)
C(10)	−0·0092 (3)	−0·0204 (3)	−0·1188 (2)	2·95 (6)
C(11)	−0·2449 (3)	0·0294 (3)	−0·0417 (2)	4·01 (7)
C(12)	−0·4090 (3)	0·0471 (4)	−0·0495 (2)	4·22 (7)
C(13)	−0·4438 (3)	0·1398 (3)	−0·1254 (2)	3·30 (6)
C(14)	−0·3751 (3)	0·0914 (3)	−0·2125 (2)	3·11 (6)
C(15)	−0·4481 (3)	0·1676 (4)	−0·2872 (2)	4·31 (7)
C(16)	−0·6044 (3)	0·1672 (4)	−0·2544 (2)	4·54 (8)
C(17)	−0·5990 (3)	0·1518 (3)	−0·1537 (2)	3·98 (7)
C(18)	−0·4002 (4)	0·2797 (3)	−0·1019 (3)	4·63 (8)

997 reflections with $F_o^2 > 2\sigma(F_o^2)$ considered observed, hydrogen atoms from difference Fourier synthesis and/or chemically reasonable positions, 144 variables (x, y, z, 6β's nonhydrogen atoms), $R = 0{\cdot}041$, $wR = 0{\cdot}056$, $S = 1{\cdot}69$, max. $\Delta/\sigma = 0{\cdot}01$, max. $\Delta\rho$ on final difference Fourier synthesis = 0·4 e Å^{-3}. The final parameters are in Table 3.*

Discussion. The structure of (1) is shown in Fig. 1, and the bond distances and angles are given in Table 4. Both of the saturated six-membered rings are in the usual chair conformation while the saturated five-membered ring has C(13), C(15), C(16) and C(17) coplanar while C(14) is 0·621 (3) Å from that plane (envelope conformation). All bond distances are quite normal. The puckering of the five-membered ring results in internal angles less than tetrahedral, 101·2 (2) to 108·4 (2)°. The largest angle is at the sp^2 carbonyl carbon C(17) as might be expected.

The structure of (2) is shown in Fig. 2, and the bond distances and angles are given in Table 5. All three saturated six-membered rings are in the usual chair conformation. The unsaturated five-membered ring is nearly planar with C(1) only 0·090 (3) Å from the plane containing the other four ring atoms. Bond distances are normal with a short C(2)—C(3) single bond [1·422 (3) Å] between the carbonyl and the C(3)=C(5) double bond [1·333 (3) Å]. Angles in the five-membered ring range from 103·8 (2) to 111·9 (2)° with both angles at the double bond largest.

Table 2. *Atomic parameters for compound* (2) *with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B_{eq}(Å^2)
O(2)	0·2962 (2)	0·4539 (2)	0·6192 (2)	8·62 (6)
O(17)	0·2648 (2)	−0·2496 (2)	0·2457 (1)	7·33 (5)
C(1)	0·2144 (2)	0·2636 (2)	0·5551 (2)	5·81 (6)
C(2)	0·3018 (2)	0·3503 (2)	0·6338 (2)	5·95 (6)
C(3)	0·3893 (3)	0·2875 (2)	0·7242 (2)	5·88 (6)
C(5)	0·3640 (2)	0·1755 (2)	0·7172 (2)	4·76 (6)
C(6)	0·4326 (3)	0·0786 (2)	0·7899 (2)	5·82 (7)
C(7)	0·4537 (2)	−0·0178 (2)	0·7110 (2)	4·89 (6)
C(8)	0·3365 (2)	−0·0523 (2)	0·6125 (2)	3·65 (5)
C(9)	0·2805 (2)	0·0531 (2)	0·5387 (2)	3·84 (5)
C(10)	0·2517 (2)	0·1482 (2)	0·6159 (2)	4·62 (5)
C(11)	0·1673 (2)	0·0226 (2)	0·4355 (2)	4·79 (6)
C(12)	0·1944 (2)	−0·0714 (2)	0·3588 (2)	4·51 (5)
C(13)	0·2460 (2)	−0·1795 (2)	0·4286 (2)	3·90 (5)
C(14)	0·3610 (2)	−0·1483 (2)	0·5338 (2)	3·64 (5)
C(15)	0·4222 (3)	−0·2554 (2)	0·6011 (2)	5·21 (6)
C(16)	0·4605 (3)	−0·3387 (2)	0·5206 (2)	6·38 (7)
C(16′)	0·3555 (3)	−0·3684 (2)	0·4107 (2)	6·15 (7)
C(17)	0·2872 (2)	−0·2646 (2)	0·3509 (2)	4·81 (6)
C(18)	0·1456 (2)	−0·2387 (2)	0·4698 (2)	5·66 (6)

Table 3. *Atomic parameters for compound* (3) *with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B_{eq}(Å^2)
O(5)	−0·0924 (2)	0·2480 (4)	0·1750 (2)	5·44 (4)
O(17)	0·3446 (3)	0·0571 (5)	−0·5419 (2)	6·90 (6)
C(5)	0·0023 (3)	0·2526 (4)	0·0958 (3)	3·99 (5)
C(6)	0·1676 (4)	0·2715 (5)	0·1558 (3)	4·32 (6)
C(7)	0·2675 (3)	0·1971 (5)	0·0542 (3)	3·74 (5)
C(8)	0·2241 (3)	0·2779 (4)	−0·0952 (2)	3·06 (5)
C(9)	0·0539 (3)	0·2666 (4)	−0·1488 (2)	3·16 (5)
C(10)	−0·0431 (3)	0·2500	−0·0572 (3)	3·57 (5)
C(11)	−0·0045 (3)	0·2862 (5)	−0·3054 (3)	3·91 (6)
C(12)	0·0895 (3)	0·1838 (5)	−0·4024 (3)	3·83 (6)
C(13)	0·2558 (3)	0·2337 (5)	−0·3549 (2)	3·51 (5)
C(14)	0·3061 (3)	0·1731 (4)	−0·1986 (2)	3·31 (5)
C(15)	0·4799 (3)	0·1814 (6)	−0·1745 (3)	4·90 (7)
C(16)	0·5122 (3)	0·1008 (7)	−0·3162 (3)	5·84 (8)
C(17)	0·3675 (3)	0·1224 (5)	−0·4226 (3)	4·59 (6)
C(18)	0·2854 (3)	0·4451 (5)	−0·3819 (3)	4·81 (6)

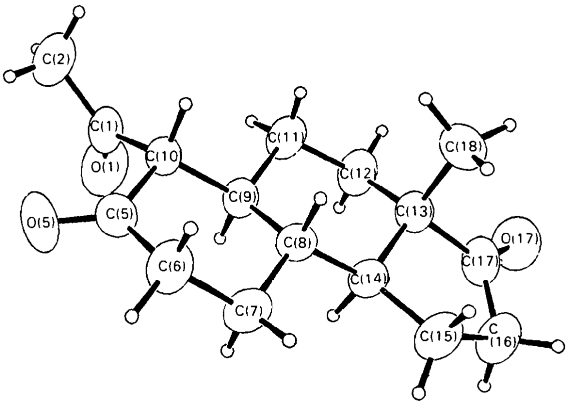

Fig. 1. Perspective view of compound (1) showing the atom labeling and thermal ellipsoids (50% probability).

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* Lists of structure factors, H-atom parameters, and anisotropic thermal parameters for all three compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39403 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond distances* (Å) *and bond angles* (°) *for compound* (1) *with e.s.d.'s in parentheses*

O(1)C(1)	1·211 (3)	C(9)C(10)	1·547 (3)
O(5)C(5)	1·207 (3)	C(9)C(11)	1·530 (3)
O(17)C(17)	1·211 (3)	C(11)C(12)	1·545 (4)
C(1)C(2)	1·479 (4)	C(12)C(13)	1·515 (4)
C(1)C(10)	1·521 (4)	C(13)C(14)	1·526 (4)
C(5)C(6)	1·485 (4)	C(13)C(17)	1·513 (4)
C(5)C(10)	1·531 (4)	C(13)C(18)	1·544 (4)
C(6)C(7)	1·526 (4)	C(14)C(15)	1·521 (4)
C(7)C(8)	1·515 (4)	C(15)C(16)	1·537 (4)
C(8)C(9)	1·530 (3)	C(16)C(17)	1·502 (4)
C(8)C(14)	1·528 (3)		

O(1)C(1)C(2)	121·9 (3)	C(9)C(11)C(12)	113·4 (2)
O(1)C(1)C(10)	120·0 (3)	C(11)C(12)C(13)	110·0 (2)
C(2)C(1)C(10)	118·1 (3)	C(12)C(13)C(14)	109·3 (2)
O(5)C(5)C(6)	122·2 (2)	C(12)C(13)C(17)	117·6 (2)
O(5)C(5)C(10)	120·9 (3)	C(12)C(13)C(18)	111·8 (2)
C(6)C(5)C(10)	116·9 (2)	C(14)C(13)C(17)	101·2 (2)
C(5)C(6)C(7)	111·6 (3)	C(14)C(13)C(18)	112·9 (2)
C(6)C(7)C(8)	110·2 (2)	C(17)C(13)C(18)	103·7 (2)
C(7)C(8)C(9)	111·7 (2)	C(8)C(14)C(13)	112·7 (2)
C(7)C(8)C(14)	113·3 (2)	C(8)C(14)C(15)	120·5 (2)
C(9)C(8)C(14)	107·4 (2)	C(13)C(14)C(15)	104·9 (2)
C(8)C(9)C(10)	111·5 (2)	C(14)C(15)C(16)	101·2 (2)
C(8)C(9)C(11)	111·9 (2)	C(15)C(16)C(17)	106·4 (2)
C(10)C(9)C(11)	110·7 (2)	O(17)C(17)C(13)	126·5 (3)
C(1)C(10)C(5)	108·0 (2)	O(17)C(17)C(16)	125·0 (3)
C(1)C(10)C(9)	114·0 (2)	C(13)C(17)C(16)	108·4 (2)
C(5)C(10)C(9)	112·0 (2)		

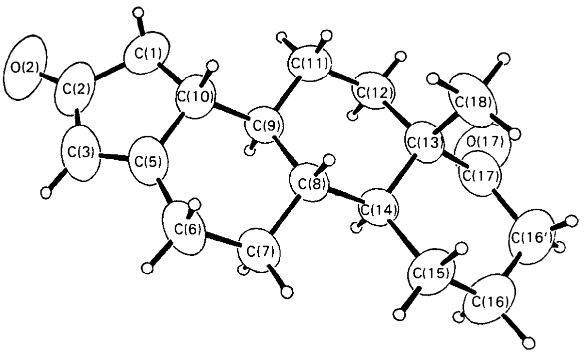

Fig. 2. Perspective view of compound (2) showing the atom labeling and thermal ellipsoids (50% probability).

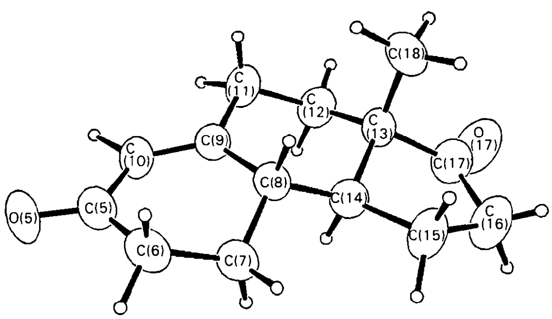

Fig. 3. Perspective view of compound (3) showing the atom labeling and thermal ellipsoids (50% probability).

Table 5. *Bond distances* (Å) *and bond angles* (°) *for compound* (2) *with e.s.d.'s in parentheses*

O(2)C(2)	1·218 (3)	C(9)C(10)	1·534 (3)
O(17)C(17)	1·207 (2)	C(9)C(11)	1·522 (3)
C(1)C(2)	1·520 (4)	C(11)C(12)	1·514 (3)
C(1)C(10)	1·523 (3)	C(12)C(13)	1·522 (3)
C(2)C(3)	1·422 (3)	C(13)C(14)	1·550 (2)
C(3)C(5)	1·333 (3)	C(13)C(17)	1·523 (3)
C(5)C(6)	1·488 (3)	C(13)C(18)	1·537 (3)
C(5)C(10)	1·496 (3)	C(14)C(15)	1·528 (3)
C(6)C(7)	1·527 (3)	C(15)C(16)	1·516 (3)
C(7)C(8)	1·533 (3)	C(16)C(16′)	1·514 (3)
C(8)C(9)	1·528 (2)	C(16′)C(17)	1·494 (3)
C(8)C(14)	1·536 (2)		

C(2)C(1)C(10)	105·1 (2)	C(5)C(10)C(9)	110·3 (2)
O(2)C(2)C(1)	125·1 (3)	C(9)C(11)C(12)	111·9 (2)
O(2)C(2)C(3)	127·7 (2)	C(11)C(12)C(13)	112·8 (2)
C(1)C(2)C(3)	107·3 (2)	C(12)C(13)C(14)	109·5 (2)
C(2)C(3)C(5)	111·6 (2)	C(12)C(13)C(17)	110·4 (2)
C(3)C(5)C(6)	129·8 (2)	C(12)C(13)C(18)	110·1 (2)
C(3)C(5)C(10)	111·9 (2)	C(14)C(13)C(17)	107·4 (2)
C(6)C(5)C(10)	118·2 (2)	C(14)C(13)C(18)	112·1 (2)
C(5)C(6)C(7)	110·8 (2)	C(17)C(13)C(18)	107·3 (2)
C(6)C(7)C(8)	113·4 (2)	C(8)C(14)C(13)	113·2 (1)
C(7)C(8)C(9)	109·8 (2)	C(8)C(14)C(15)	114·5 (1)
C(7)C(8)C(14)	112·1 (2)	C(13)C(14)C(15)	111·5 (2)
C(9)C(8)C(14)	111·0 (1)	C(14)C(15)C(16)	111·5 (2)
C(8)C(9)C(10)	111·5 (2)	C(15)C(16)C(16′)	112·6 (2)
C(8)C(9)C(11)	112·1 (2)	C(16)C(16′)C(17)	112·5 (2)
C(10)C(9)C(11)	111·4 (2)	O(17)C(17)C(13)	121·6 (2)
C(1)C(10)C(5)	103·8 (2)	O(17)C(17)C(16′)	121·6 (2)
C(1)C(10)C(9)	115·8 (2)	C(13)C(17)C(16′)	116·8 (2)

Table 6. *Bond distances* (Å) *and bond angles* (°) *for compound* (3) *with e.s.d.'s in parentheses*

O(5)C(5)	1·236 (3)	C(9)C(11)	1·498 (3)
O(17)C(17)	1·212 (3)	C(11)C(12)	1·540 (3)
C(5)C(6)	1·491 (4)	C(12)C(13)	1·515 (3)
C(5)C(10)	1·444 (3)	C(13)C(14)	1·539 (3)
C(6)C(7)	1·528 (3)	C(13)C(17)	1·506 (3)
C(7)C(8)	1·519 (3)	C(13)C(18)	1·540 (4)
C(8)C(9)	1·517 (3)	C(14)C(15)	1·530 (3)
C(8)C(14)	1·525 (3)	C(15)C(16)	1·544 (3)
C(9)C(10)	1·346 (3)	C(16)C(17)	1·499 (3)

O(5)C(5)C(6)	120·7 (2)	C(12)C(13)C(14)	108·8 (2)
O(5)C(5)C(10)	121·5 (2)	C(12)C(13)C(17)	116·3 (2)
C(6)C(5)C(10)	117·7 (2)	C(12)C(13)C(18)	111·3 (2)
C(5)C(6)C(7)	112·4 (2)	C(14)C(13)C(17)	100·0 (2)
C(6)C(7)C(8)	113·0 (2)	C(14)C(13)C(18)	113·7 (2)
C(7)C(8)C(9)	111·4 (2)	C(17)C(13)C(18)	106·3 (2)
C(7)C(8)C(14)	111·0 (2)	C(8)C(14)C(13)	113·9 (2)
C(9)C(8)C(14)	109·2 (2)	C(8)C(14)C(15)	118·8 (2)
C(8)C(9)C(10)	120·8 (2)	C(13)C(14)C(15)	104·1 (2)
C(8)C(9)C(11)	118·4 (2)	C(14)C(15)C(16)	101·7 (2)
C(10)C(9)C(11)	120·7 (2)	C(15)C(16)C(17)	106·3 (2)
C(5)C(10)C(9)	124·2 (2)	O(17)C(17)C(13)	126·2 (2)
C(9)C(11)C(12)	115·4 (2)	O(17)C(17)C(16)	125·1 (2)
C(11)C(12)C(13)	109·0 (2)	C(13)C(17)C(16)	108·7 (2)

The structure of (3) is shown in Fig. 3, and the bond distances and angles are given in Table 6. Again, the saturated six-membered ring is in the chair conformation, the unsaturated six-membered ring has the sofa conformation (Duax, Weeks & Rohrer, 1976), and the five-membered ring has the envelope conformation. C(7) is 0·587 (3) Å out of the plane [max. deviation 0·020 (3) Å] of the other five atoms in the six-membered ring, and C(14) is 0·629 (3) Å out of the plane [max. deviation = 0·043 (3) Å] of the other four atoms in the five-membered ring. Bond distances and angles are normal with a short C(5)—C(10) single bond [1·444 (3) Å] between the carbonyl group and the C(9)=C(10) double bond [1·346 (3) Å]. This situation is similar to that in (2). At the three sp^2 carbon atoms, the internal angles are near 120° with C(5)—C(10)—C(9) = 124·2 (2)°.

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Structure of 3,3'-Dichlorodibenzoyl Peroxide, $C_{14}H_8Cl_2O_4$

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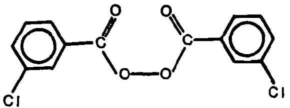
Abstract. $M_r = 311·12$, monoclinic, $C2/c$, $a = 14·655$ (2), $b = 9·318$ (3), $c = 10·373$ (2) Å, $\beta = 109·67$ (1)°, $V = 1333·96$ Å^3, $Z = 4$, $D_x = 1·549$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·494$ mm^{-1}, $T = 300$ K, $F(000) = 632$, final $R = 0·037$, $R_w = 0·054$ for 856 observed reflections with $F > 3\sigma(F)$. A twofold symmetry axis bisects the O—O peroxide bond. The peroxide bond distance is 1·453 (2) Å, and C—Cl is 1·734 (2) Å. The molecular structure shows an antiparallel arrangement of the C=O and C—Cl bonds yielding a *transoid* disposition. The molecules are held together by van der Waals forces, forming parallel chains.

Introduction. The structure elucidation of the title compound (I) was undertaken in conjunction with our interest in studying the nature of the peroxide (O—O) bond in various chemical and structural configurations. Of interest is the comparison of the O—O bond distance found in the present case to that recently observed in a strained environment in an ozonide molecule (Syed, Kirschenheuter, Jain, Griffin & Stevens, 1983).



(I)

Experimental. Crystals of the title compound were obtained by slow evaporation of a solution of the compound in ethanol. D_m not determined. Enraf–Nonius CAD-4 diffractometer. Approximate crystal dimensions 0·10 × 0·63 × 0·28 mm. Graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions from a least-squares analysis of 25 reflections with $20° \leq 2\theta \leq 36°$ accurately measured on diffractometer. Systematic absences: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$; space group $C2/c$. ω:2θ scan mode to measure 1333 reflections with $2\theta \leq 50°$; $-17 \leq h \leq 17$, $0 \leq k \leq 11$, $0 \leq l \leq 12$; 1181 unique of which 856 treated as observed with $I > 3\sigma(I)$, where $\sigma(I)$ is the e.s.d. based on counting statistics, and included in the least-squares refinement. Three intensity-control standards measured every 2 h of exposure time (maximum decay 3·9%) and crystal-orientation check after every 200 reflections. Lorentz–polarization correction applied; absorption correction

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