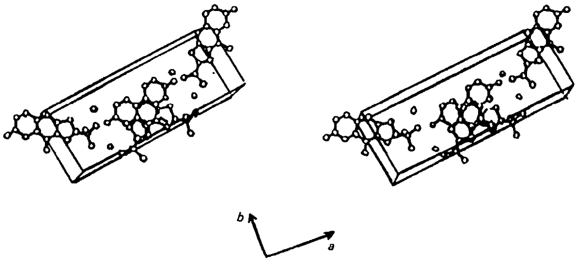

Fig. 2. Stereoview of the packing of the molecules in the unit cell.

The protons available from the water molecule and the two hydroxyl groups take part in hydrogen bonding [C(19)—H(19)—O*w* 2·705 (5), H···*A* 1·93 (5) Å, *D*—H···*A* 168 (5)°; O*w*—H(O*w*)1—O(11) 2·846 (6), H···*A* 2·05 (7) Å, *D*—H···*A* 135 (4)°; O(12)—H(12)—O(19) 2·737 (4), H···*A* 1·93 (3) Å, *D*—H···*A* 151 (2)°; O*w*—H(O*w*)2—O(11) 2·836 (6), H···*A* 2·24 (4) Å *D*—H···*A* 134 (2)°]. The molecules are stabilized by the hydrogen bonds and stacking forces.

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Structures of Two Aza-Steroids: 17β-Hydroxy-4-aza-5β-androst-1-en-3-one (I) and 17β-Acetoxy-3-aza-*A*-homo-4a-androsten-4-one (II)

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Abstract. (I): $C_{18}H_{27}NO_2$, $M_r = 289{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}801$ (2), $b = 11{\cdot}691$ (3), $c = 20{\cdot}134$ (4) Å, $V = 1601$ (1) Å^3, $D_x = 1{\cdot}201$ Mg m^{-3}, $Z = 4$, $F(000) = 632$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 7{\cdot}2$ mm^{-1}, 298 K. (II): $C_{21}H_{31}NO_3$, $M_r = 345{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}562$ (2), $b = 9{\cdot}979$ (2), $c = 25{\cdot}510$ (3) Å, $V = 1925$ (1) Å^3, $D_x = 1{\cdot}192$ Mg m^{-3}, $Z = 4$, $F(000) = 752$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 8{\cdot}5$ mm^{-1}, 298 K. Both structures were solved by direct methods and refined by full-matrix least squares to $R = 0{\cdot}066$ and $0{\cdot}056$, respectively, for 1078 and 882 reflections. Rings *B* and *C* show a chair conformation, while rings *D* show a skew-envelope form. The *A*-ring conformation of (I) is a distorted half-chair, while in (II) C(1), C(3), C(4), C(5) and C(10) atoms are in a plane. The acetate moiety of

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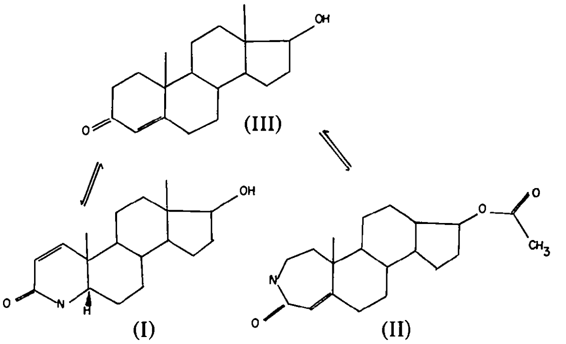
(II) shows a β-orientation with an antiperiplanar conformation with respect to the C(13)—C(17) bond. The pseudo-torsion angles C(19)—C(10)···C(13)—C(18) are 2·0 (8) in (I) and 0·0 (8)° in (II).

Introduction. The molecules (I) and (II) studied in the present work have been synthesized from testosterone (III). In the case of the 3-oxo-4-aza derivative (I) the main step of the synthetic pathway is a Leuckart reaction (Cánovas, Fonrodona, Bonet, Briansó & Briansó, 1980), while the synthesis of (II) involves a Beckmann transposition (Servera, 1975). Both molecules have been modified in positions 3 and 17 of the steroidal framework using substituents with strong alkylating activity in order to test their potential antineoplastic activity (Dalmases, Gómez-Belinchón, Bonet, Giner-Sorolla & Schmid, 1983; Dalmases, Serra, Lupón & Bonet, 1983; Casellas, Serra, Quintana, Bonet, Giner-Sorolla & Schmid, 1985). The structure determinations have been carried out to obtain the precise geometry of these molecules, which represent the rigid moiety of the potential antineoplasic agents mentioned above.



Experimental. Both structures: colourless prismatic crystals (0·2 × 0·2 × 0·25 mm). Enraf–Nonius CAD-4. Cell parameters from 25 reflections ($2 \leq \theta \leq 15°$), graphite monochromator, Mo $K\alpha$ radiation, $\theta/2\theta$ scan technique. Three check reflections measured every 2 h, no significant intensity decay observed. 2234 reflections for (I) with $\theta \leq 25°$ and hkl range: 0 to 17, 0 to 13 and 0 to 23. 1988 reflections for (II) with $\theta \leq 29·5°$ and hkl range: 0 to 9, 0 to 10 and 0 to 29. 1078 (I) and 882 (II) reflections with $I \geq 2·5\sigma(I)$ regarded as observeds. Lorentz–polarization corrections applied, absorption ignored.

Both structures were solved by use of the *MULTAN* system (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement (*SHELX*76; Sheldrick, 1976), $\sum(w|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(F_o) + k|F_o|^2]^{-1}$, where k = 0·0 and 0·016, respectively, for (I) and (II), f, f' and f'' from *International Tables for X-ray Crystallography* (1974). The H atoms of (I) were computed, and obtained from a $\Delta\rho$ synthesis for (II); they were refined with an overall isotropic temperature factor, with C, N and O anisotropic. Final $R(wR)$ are 0·066 (0·066) and 0·056 (0·057) for all observed reflections. Max. $\Delta/\sigma = -0·02$ [x of C(7)] in (I) and $-0·28$ [x of C(1)] in (II). Max. and min. $\Delta\rho$ peak 0·4 and $-0·8$ e Å^{-3} for (I) and 0·2 and $-0·2$ e Å^{-3} for (II).

Table 1. *Final atomic coordinates* (× 10^4) *and* B_{eq} *values* (Å^2)

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
(I) $C_{18}H_{27}NO_2$				
C(1)	640 (20)	2119 (10)	11618 (5)	4·48 (60)
C(2)	−825 (19)	2741 (9)	11868 (5)	3·92 (55)
C(3)	−2724 (19)	2204 (9)	12021 (5)	3·79 (54)
O(3)	−4205 (13)	2793 (6)	12177 (4)	4·47 (39)
N(4)	−2817 (13)	1048 (7)	11995 (4)	3·03 (37)
C(5)	−1080 (15)	327 (8)	11937 (5)	2·87 (44)
C(6)	−1757 (18)	−834 (9)	11706 (4)	3·63 (51)
C(7)	−2400 (17)	−879 (8)	10971 (4)	3·33 (46)
C(8)	−809 (15)	−443 (8)	10517 (4)	2·61 (40)
C(9)	−266 (15)	818 (8)	10713 (4)	2·63 (40)
C(10)	436 (15)	866 (8)	11451 (5)	2·98 (45)
C(11)	1110 (17)	1439 (9)	10224 (4)	3·74 (49)
C(12)	469 (16)	1343 (8)	9506 (4)	3·05 (46)
C(13)	85 (15)	75 (8)	9302 (4)	2·71 (42)
C(14)	−1466 (15)	−453 (8)	9781 (4)	2·82 (43)
C(15)	−2073 (18)	−1595 (8)	9470 (5)	3·75 (51)
C(16)	−1911 (19)	−1309 (8)	8705 (5)	3·96 (52)
C(17)	−1001 (16)	−108 (8)	8626 (4)	3·15 (44)
O(17)	171 (13)	−18 (6)	8060 (3)	1·38 (31)
C(18)	2036 (17)	−642 (9)	9288 (5)	4·21 (54)
C(19)	2393 (17)	258 (11)	11567 (6)	4·88 (61)
(II) $C_{21}H_{31}NO_3$				
C(1)	6538 (13)	454 (11)	6122 (3)	4·71 (46)
C(2)	6897 (14)	236 (14)	5534 (4)	5·32 (52)
N(2)	7988 (16)	1286 (9)	5323 (3)	3·78 (43)
C(3)	9509 (20)	1636 (9)	5520 (3)	5·63 (58)
O(3)	10440 (13)	2574 (8)	5340 (3)	8·18 (47)
C(4)	10379 (15)	825 (11)	5956 (4)	5·01 (47)
C(5)	9763 (11)	58 (8)	6334 (3)	3·53 (35)
C(6)	11116 (11)	−577 (10)	6708 (4)	4·65 (44)
C(7)	10798 (11)	−111 (11)	7268 (4)	4·52 (47)
C(8)	8938 (11)	−337 (9)	7443 (3)	3·40 (37)
C(9)	7586 (12)	257 (8)	7057 (3)	3·34 (36)
C(10)	7863 (10)	−246 (8)	6478 (3)	3·24 (32)
C(11)	5697 (11)	180 (10)	7249 (3)	3·72 (41)
C(12)	5442 (14)	722 (10)	7799 (3)	3·98 (42)
C(13)	6677 (12)	52 (8)	8178 (3)	3·57 (37)
C(14)	8594 (10)	269 (9)	7989 (3)	3·43 (36)
C(15)	9725 (12)	−155 (11)	8462 (3)	4·70 (43)
C(16)	8640 (13)	331 (12)	8949 (3)	5·33 (52)
C(17)	6838 (14)	763 (9)	8718 (4)	4·43 (42)
C(18)	6227 (19)	−1421 (11)	8279 (4)	5·44 (54)
C(19)	7528 (16)	−1784 (9)	6453 (4)	4·89 (45)
O(20)	5322 (9)	377 (7)	9044 (2)	5·21 (31)
C(21)	4943 (17)	1193 (12)	9442 (4)	5·54 (55)
C(22)	3303 (14)	690 (13)	9713 (4)	6·69 (59)
O(22)	5773 (12)	2145 (10)	9545 (3)	8·17 (52)

Discussion. Final atomic coordinates are given in Table 1.* Figs. 1 and 2 show views of the molecules (I) and (II), respectively, with their numbering schemes. Bond lengths and angles are given in Table 2. Both structures show chair conformations for rings *B* and *C*. The *D* rings show a skew-envelope conformation with C(13)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44277 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

deviating by 0·70 (1) (I) and 0·71 (1) Å (II) from the plane defined by the other four atoms. The *A*-ring conformation of molecule (I) is a distorted half chair [ΔC_2^{2-3} = 8·7 (9)° (Duax, Weeks & Rohrer, 1976)], due to the planar Δ^1-3-oxo-4-aza system. The *A*/*B* ring junction is *cis*. In molecule (II), the presence of the Δ^4 double bond conjugated with the carbonyl induces considerable planarity in this zone with C(1)—C(10)—C(5)—C(4) = 0·0 (8)°; the atoms C(3), C(4), C(5), C(10) and C(1) are in a plane [largest deviation 0·01 (1) Å]. The *A*/*B* ring junction is pseudo-*trans*. Bond lengths and angles are similar in (I) and (II) and are normal for this type of molecule. There are, however, some differences: The different ring conformation in (II) influences the *B*—*C*—*D* skeleton, producing an enlargement of the C(7)—C(8)—C(9) angle [112·2 (7); 109·5 (7)° in (I)] and a contraction of C(5)—C(10)—C(9) and C(5)—C(6)—C(7) angles [106·9 (6) and 110·6 (7)° in (II) and 112·4 (8) and 114·3 (8)° in (I)]. The differing substitution at C(17) in (II) produces an enlargement in the angles C(13)—C(17)—C(16) and C(14)—C(15)—C(16) [106·3 (8) and 104·2 (7)° respectively in (II); 103·0 (8) and 101·2 (8)° in (I)] and a contraction of C(15)—C(16)—C(17) [104·2 (7)° in (II) and 108·7 (8)° in (I)]. The intermolecular hydrogen bonding is also different. In (I), O(17) is hydrogen bonded to O($3^{\rm i}$) [(i) = $\frac{1}{2}+x$, $\frac{1}{2}-y$, $2-z$] with O(17)···O(3) at 2·68 (1) Å, while in (II),

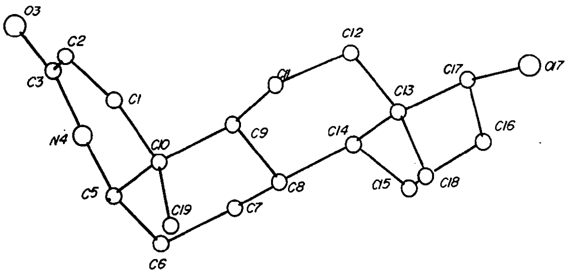

Fig. 1. View of a molecule of (I) with atom-numbering scheme.

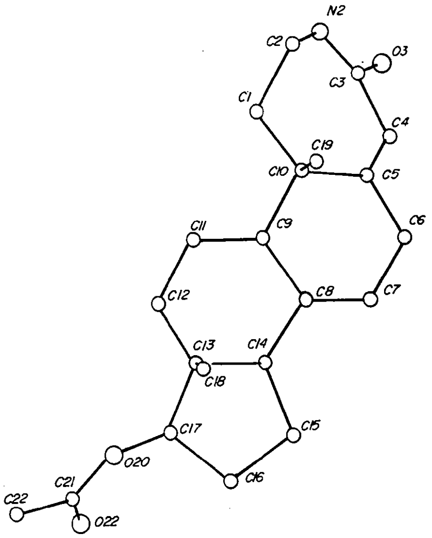

Fig. 2. View of a molecule of (II) with atom-numbering scheme.

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

(I) $C_{18}H_{27}NO_2$		(II) $C_{21}H_{31}NO_3$	
C(2)—C(1)	1·332 (16)	C(2)—C(1)	1·540 (14)
C(10)—C(1)	1·509 (14)	C(10)—C(1)	1·522 (12)
C(3)—C(2)	1·469 (15)	N(2)—C(2)	1·438 (14)
O(3)—C(3)	1·260 (13)	C(3)—N(2)	1·304 (16)
N(4)—C(3)	1·354 (12)	O(3)—C(3)	1·258 (12)
C(5)—N(4)	1·456 (12)	C(4)—C(3)	1·524 (16)
C(5)—H(4)	1·535 (13)	C(5)—C(4)	1·316 (13)
C(6)—C(5)	1·506 (13)	C(6)—C(5)	1·535 (12)
C(10)—C(5)	1·554 (13)	C(10)—C(5)	1·513 (12)
C(7)—C(6)	1·545 (12)	C(7)—C(6)	1·522 (13)
C(8)—C(7)	1·506 (13)	C(8)—C(7)	1·493 (13)
C(9)—C(8)	1·571 (12)	C(9)—C(8)	1·537 (12)
C(14)—C(8)	1·547 (12)	C(14)—C(8)	1·541 (11)
C(10)—C(9)	1·562 (12)	C(10)—C(9)	1·575 (11)
C(11)—C(9)	1·541 (12)	C(11)—C(9)	1·512 (12)
C(19)—C(10)	1·527 (15)	C(19)—C(10)	1·557 (13)
C(12)—C(11)	1·514 (12)	C(12)—C(11)	1·517 (12)
C(13)—C(12)	1·561 (12)	C(13)—C(12)	1·502 (13)
C(14)—C(13)	1·557 (13)	C(14)—C(13)	1·544 (11)
C(17)—C(13)	1·562 (12)	C(17)—C(13)	1·553 (12)
C(18)—C(13)	1·570 (15)	C(18)—C(13)	1·530 (14)
C(15)—C(14)	1·531 (12)	C(15)—C(14)	1·538 (12)
C(16)—C(15)	1·580 (13)	C(16)—C(15)	1·567 (13)
C(17)—C(16)	1·543 (13)	C(17)—C(16)	1·546 (15)
O(17)—C(17)	1·395 (12)	O(20)—C(17)	1·468 (12)
		C(21)—O(20)	1·333 (12)
		C(22)—C(21)	1·506 (16)
		O(22)—C(21)	1·169 (14)
C(10)—C(1)—C(2)	123·1 (11)	C(10)—C(1)—C(2)	113·6 (8)
C(3)—C(2)—C(1)	120·2 (10)	N(2)—C(2)—C(1)	111·3 (9)
O(3)—C(3)—C(2)	121·4 (10)	C(3)—N(2)—C(2)	123·8 (9)
N(4)—C(3)—C(2)	117·4 (11)	O(3)—C(3)—N(2)	123·4 (10)
N(4)—C(3)—O(3)	121·2 (11)	C(4)—C(3)—N(2)	121·4 (9)
C(5)—N(4)—C(3)	122·9 (10)	C(4)—C(3)—O(3)	114·9 (12)
C(6)—C(5)—N(4)	107·4 (8)	C(5)—C(4)—C(3)	133·6 (11)
C(10)—C(5)—N(4)	110·7 (7)	C(6)—C(5)—C(4)	117·3 (8)
C(10)—C(5)—C(6)	112·0 (8)	C(10)—C(5)—C(4)	129·1 (9)
C(7)—C(6)—C(5)	114·3 (8)	C(10)—C(5)—C(6)	113·5 (7)
C(8)—C(7)—C(6)	111·5 (9)	C(7)—C(6)—C(5)	110·6 (7)
C(9)—C(8)—C(7)	109·5 (7)	C(8)—C(7)—C(6)	112·5 (8)
C(14)—C(8)—C(7)	111·8 (8)	C(9)—C(8)—C(7)	112·2 (7)
C(14)—C(8)—C(9)	108·5 (7)	C(14)—C(8)—C(7)	111·7 (7)
C(10)—C(9)—C(8)	110·2 (7)	C(14)—C(8)—C(9)	108·3 (7)
C(11)—C(9)—C(8)	115·1 (8)	C(10)—C(9)—C(8)	112·9 (7)
C(11)—C(9)—C(10)	114·0 (8)	C(11)—C(9)—C(8)	113·7 (7)
C(5)—C(10)—C(1)	108·4 (8)	C(11)—C(9)—C(10)	114·4 (7)
C(9)—C(10)—C(1)	106·0 (8)	C(5)—C(10)—C(1)	112·9 (7)
C(9)—C(10)—C(5)	112·4 (8)	C(9)—C(10)—C(1)	109·0 (7)
C(19)—C(10)—C(1)	109·8 (10)	C(9)—C(10)—C(5)	106·9 (6)
C(19)—C(10)—C(5)	107·0 (8)	C(19)—C(10)—C(1)	108·7 (8)
C(19)—C(10)—C(9)	113·2 (8)	C(19)—C(10)—C(5)	110·0 (7)
C(12)—C(11)—C(9)	113·6 (9)	C(19)—C(10)—C(9)	109·3 (7)
C(13)—C(12)—C(11)	111·7 (8)	C(12)—C(11)—C(9)	113·6 (7)
C(14)—C(13)—C(12)	109·1 (8)	C(13)—C(12)—C(11)	111·0 (8)
C(17)—C(13)—C(12)	116·0 (8)	C(14)—C(13)—C(12)	108·7 (7)
C(17)—C(13)—C(14)	99·5 (7)	C(17)—C(13)—C(12)	114·6 (7)
C(18)—C(13)—C(12)	111·7 (9)	C(17)—C(13)—C(14)	98·0 (7)
C(18)—C(13)—C(14)	111·8 (8)	C(18)—C(13)—C(12)	113·4 (9)
C(18)—C(13)—C(17)	108·1 (8)	C(18)—C(13)—C(14)	113·4 (8)
C(13)—C(14)—C(8)	113·2 (8)	C(18)—C(13)—C(17)	107·9 (7)
C(15)—C(14)—C(8)	118·4 (8)	C(13)—C(14)—C(8)	112·7 (7)
C(15)—C(14)—C(13)	106·0 (7)	C(15)—C(14)—C(8)	120·5 (7)
C(16)—C(15)—C(14)	101·2 (8)	C(15)—C(14)—C(13)	103·8 (7)
C(17)—C(16)—C(15)	108·7 (8)	C(16)—C(15)—C(14)	104·2 (7)
C(16)—C(17)—C(13)	103·0 (8)	C(17)—C(16)—C(15)	104·2 (7)
O(17)—C(17)—C(13)	115·6 (8)	C(16)—C(17)—C(13)	106·3 (8)
O(17)—C(17)—C(16)	112·5 (8)	O(20)—C(17)—C(13)	108·7 (8)
		O(20)—C(17)—C(16)	113·6 (7)
		C(21)—O(20)—C(17)	116·1 (8)
		C(22)—C(21)—O(20)	108·9 (11)
		O(22)—C(21)—O(20)	123·6 (12)
		O(22)—C(21)—C(22)	127·5 (11)

N(2) is hydrogen bonded to O($3^{\rm ii}$) [(ii) = $\frac{1}{2}+x$, $-y-\frac{1}{2}$, $1-z$] with N···O and H···O lengths of 2·80 (2) and 2·16 (8) Å, respectively. The acetate group at C(17) in (II) shows a β-orientation. The C(13)—C(17)—O(20)—C(21) torsion angle is −160·9 (7)°, thus the acetate moiety is antiperiplanar with respect to the C(13)—C(17) bond and the O(22) atom is oriented to the α side of the molecule. The O(22) atom is synperiplanar to C(17) [C(17)—O(20)—C(21)—O(22) −1·1 (7)°]. The pseudo-torsion angles C(19)—C(10)···C(13)—C(18) are 2·0 (8)° in (I) and 0·0 (8)° in (II).

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Structure of Plumbagin*

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Abstract. $C_{11}H_8O_3$, $M_r = 188{\cdot}2$, monoclinic, $P2_1/a$, $a = 19{\cdot}067$ (3), $b = 7{\cdot}057$ (2), $c = 13{\cdot}370$ (3) Å, $\beta = 91{\cdot}17$ (2)°, $V = 1798{\cdot}6$ Å^3, $Z = 8$, $D_m = 1{\cdot}37$ (3), $D_x = 1{\cdot}390$ (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}110$ mm^{-1}, $F(000) = 784$, $T = 298$ K, $R = 0{\cdot}066$ for 1426 reflections. There are two molecules in the asymmetric unit and they have slightly different geometry. The packing of the molecules is due to van der Waals forces and there are no intermolecular hydrogen bonds.

Introduction. Plumbagin is the active principle of chita, the root of plants under three distinct botanical classifications: (1) *Plumbago rosea*, (2) *P. zeylanica* and (3) *P. europoea*. Plumbagin is known for its chemotherapeutic properties. It is used in various prescriptions for dyspepsia, paralysis, rheumatism, coughs and leprosy (Roy & Dutt, 1928). The structure and synthesis of this compound has been carried out by Fieser & Dunn (1936) and its biosynthesis has been described by Durand & Zenk (1971).

Experimental. D_m by flotation, dark-yellow needles (from methanol) 0·4 × 0·5 × 0·4 mm, Enraf–Nonius CAD-4 diffractometer (at the Indian Institute of Technology, Madras), $\omega/2\theta$ scan technique, Mo $K\alpha$ radiation, cell parameters refined from 14 strong accurately centred reflections in the range $18 < 2\theta < 26°$, Lp correction, absorption ignored, 3220 unique reflections with $0 \le h \le 16$, $0 \le k \le 8$, $-16 \le l \le 16$ and with $2\theta \le 54°$, 1426 reflections with $|F_o| \ge 0{\cdot}5\sigma(|F_o|)$. Two standard reflections monitored every 100 reflections during data collection, intensity variation less than 5%. Structure solution using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), 290 reflections with $|E| \ge 1{\cdot}278$ for phase generation, most H atoms located from $\Delta\rho$ map. Full-matrix refinement on F (Gantzel, Sparks & Trueblood, 1961) with anisotropic temperature factors for non-H atoms and isotropic for H atoms, final $R = wR = 0{\cdot}066$, Cruickshank weighting scheme (Cruickshank, Bujosa, Lovell & Truter, 1961) with $w = 1/\sigma^2$ where $\sigma^2 = A + B|F_o| + C|F_o|^2$

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* 5-Hydroxy-2-methyl-1,4-naphthoquinone.

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