The C(1)–C(2) bond of 1·36(1) Å is apparently shorter than a normal aromatic C–C bond (1·395 Å).

This has previously been described in tryptamine hydrochloride, a radiation protector (Wakahara, Fujiwara & Tomita, 1973) and tryptamine picrate (Gartland, Freeman & Bugg, 1974). However, in another derivative of tryptophan, the potent mutagenic 3-amino-1,4-dimethyl-5*H*-pyrido[4,3-*b*]indole (Itai & Iitaka, 1978), the C(1)–C(2) bond is 1·428 (4) Å. Most torsion angles (Klyne & Prelog, 1960) are close to 0 or 180°. The non-hydrogen atoms lie in two different planes connected through the C(9)–C(10) single bond.

The C(2)–C(9)–C(10)–N(2) torsion angle (179°) indicates an antiperiplanar relationship across the C(9)–C(10) bond. Other significant torsion angles are −54° (synclinal), 129° (anticlinal) and −111° (anticlinal) for C(1)–C(2)–C(9)–C(10), C(3)–C(2)–C(9)–C(10) and C(11)–N(2)–C(10)–C(9) respectively.

An intramolecular hydrogen bond is found between the N(2) atom and the oxygen atom of the phenol ring. The N···H–O distance is 2·60 (2) Å and the angle is 131·9 (3)°.

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Structure of the Acetone Solvate of 17α-Hydroxy-3,11,20-trioxo-4-pregnen-21-yl Acetate (Cortisone Acetate, Modification IV*ac*)

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Abstract. $C_{23}H_{30}O_6.C_3H_6O$, M_r=460·57, monoclinic, $P2_1$, a = 9·820 (2), b = 7·661 (5), c = 16·648 (1) Å, β = 94·65 (1)°, V = 1248·3 (9) Å^3, Z = 2, D_x = 1·225 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ (Mo $K\alpha$) = 0·8 cm^{-1}, $F(000)$ = 496, room temperature, R = 0·063 for 1587 unique reflections with $I \geq 2{\cdot}5\sigma(I)$. The crystal structure of the acetone solvate, which is rather unstable, is isomorphous with the ethanol solvate. The conformation of the steroid molecule is identical to that of anhydrous modification II and deviates from that of anhydrous modification I by the conformation of ring *D* and the side-chain orientation with respect to the steroid skeleton. The acetone solvate is disordered over two positions (2:1) and hydrogen bonded with O(17) of the steroid molecule.

Introduction. In the crystalline state three anhydrous polymorphs of cortisone acetate (CA) exist (*e.g.* Callow & Kennard, 1961) and numerous pseudo-polymorphic forms (solvates) have been reported (Callow & Kennard, 1961; Carless, Moustafa & Rapson, 1966; Kuhnert-Brandstätter & Grimm, 1968; Shirotani & Sekiguchi, 1981). Structure analyses of anhydrous modifications I (CA I) and II (CA II) have been reported by Kanters, de Koster, van Geerestein & van Dijck (1985) and Declercq, Germain & Van Meerssche (1972), respectively. In the literature there is confusion about the correct description and designation of the different forms of CA because of possible interconversions (Mesley, 1968; van Geerestein, Kanters, van Dijck & van Wendel de Joode, 1985). The nomenclature of Carless, Moustafa & Rapson (1966) will be followed here. This paper reports the analysis of the acetone solvate of CA and is intended to be the first paper in a series on the X-ray structures of solvates of CA. The monoacetonate has not yet been described in

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the literature and will be called modification IV*ac* (CA IV*ac*), because we found its cell dimensions to be identical to those of the ethanol solvate (van Geerestein *et al.*, 1985), which is known in the literature as modification IV.

Experimental. Sample obtained through the Scientific Development Group of Organon, Oss, The Netherlands. CA was dissolved in boiling dry acetone and crystals were obtained by slow cooling to room temperature. The stability of the crystals was very variable and both needles and block-shaped crystals were obtained. Weissenberg photographs showed both types of crystals to have the same cell dimensions. However, the needles were twinned by pseudo-merohedry and therefore a block-shaped crystal of dimensions 0·4 × 0·2 × 0·2 mm was selected for data collection on an Enraf–Nonius CAD-4 diffractometer with Zr-filtered Mo $K\alpha$ radiation. Lattice parameters were refined by least-squares fitting of 2θ values of 25 reflections in the range $10 < \theta < 15°$; ω–2θ scan mode, $\Delta\omega = (0{\cdot}90 + 0{\cdot}35\tan\theta)°$. 2918 independent reflections were measured up to $\theta = 27°$, $\pm h,k,l$ (max. range 12,9,21), 1587 of these were considered observed [$I \geq 2{\cdot}5\sigma(I)$] and used for structure refinement. Three periodically measured standard reflections ($3\bar{2}4$, $\bar{3}2\bar{4}$, $1\bar{3}5$) showed a steady decrease in intensity up to 29% in 47 h of total X-ray exposure time, possibly partly due to loss of solvent. However, data collection on crystals which were sealed in a capillary also showed a large decrease of scattered intensity. Intensities were rescaled for this decay and Lp corrected, but not corrected for absorption.

Runs of *MULTAN*80 (Main *et al.*, 1980) failed, but the E maps revealed obviously correctly oriented fragments. A partial structure of two *trans*-fused six-membered rings was used to modify the normalized structure factors in the way suggested by Messerschmidt, Reck & Kutschabsky (1982):

$$|E_{\rm mod}(\mathbf{h})|^2 = |E_{\rm obs}(\mathbf{h})|^2 - p^2[|E_{\rm frag}(\mathbf{h})|^2 - 1],$$

where $E_{\rm obs}$ are the E values obtained through normalization by a conventional method, p^2 is the fractional scattering power and $E_{\rm frag}$ is calculated in the same way as the group scattering factor for a correctly oriented but randomly positioned partial structure given by Main (1976); for an equal-atom fragment:

$$|E_{\rm frag}(\mathbf{h})|^2 = \sum_{p=1}^{P}\sum_{i=1}^{N}\sum_{j=1}^{N}\cos[2\pi\mathbf{h}R_p(\mathbf{r}_i - \mathbf{r}_j)],$$

where R_p are the point-group symmetry operations, P the number of operations, N the number of atoms in the partial structure and $\mathbf{r}_i - \mathbf{r}_j$ the vector between atoms i and j. It is superfluous to rescale the E values modified in this way, when the conditions $\langle |E_{\rm obs}(\mathbf{h})|^2 \rangle = 1$ and $\langle |E_{\rm frag}(\mathbf{h})|^2 \rangle = 1$ are fulfilled. These modified E values will contain relatively more information with regard to the position than to the orientation of the molecule and with a more or less centrosymmetric fragment the distribution of the modified values will be more acentric than that of the original E values. A *MULTAN*80 run using the modified E values revealed an almost complete structure which was expanded by a difference Fourier synthesis. Meanwhile, a preliminary version of the *PATSEE* Patterson search program (Egert & Sheldrick, 1985) became available and the structure could easily be solved using the fused *A*, *B* and *C* rings of CA II as a search fragment.

H atoms were placed at calculated positions, except the OH group H atom which was located on a difference map. During refinement it became clear that the acetone solvent molecule is in statistical disorder, which was resolved by refining acetone as a rigid body distributed over two positions with coupled site occupation factors (s.o.f.) normalized to 1. In the final cycles of four-block least-squares refinement, using *SHELX*76 (Sheldrick, 1976), 82, 67, 67 and 76 parameters varied respectively including an overall scale factor, positional and individual anisotropic thermal parameters for C and O atoms, positional parameters for H[O(17)], positional and orientational parameters for the rigid acetone molecules with coupled thermal parameters and s.o.f.'s. The mean-square amplitude of vibration for H atoms was kept fixed at 0·1 Å^2. The refinement on F converged at $R = 0{\cdot}063$ and $wR = 0{\cdot}057$ where $w = 1/\sigma^2(F)$ and for 1587 unique data. The s.o.f.'s for the acetone solvent refined to 0·71 (1) and 0·29 (1) respectively. $\Delta/\sigma_{\rm av} = 0{\cdot}002$ (2) and $\Delta/\sigma_{\rm max} = 0{\cdot}007$ for all refined parameters. $\Delta\rho = \pm 0{\cdot}2$ e Å^{-3}. Scattering factors were taken from Cromer & Mann (1968) for C and O atoms and from Stewart, Davidson & Simpson (1965) for H atoms.

Discussion. The final atomic parameters are given in Table 1*. The conformation of the steroid molecule and atom numbering are shown in Fig. 1. Bond lengths and bond angles involving non-H atoms of the steroid, which are given in Table 2, correspond to those observed in CA I and CA II.

The conformations of rings *A*, *B* and *C* are the same as in CA I and CA II, the *A* ring having a 1α-sofa conformation, as indicated by the asymmetry parameter $\Delta C_s[\mathrm{C}(1)] = 7{\cdot}9\ (6)°$ (Duax & Norton, 1975) and the *B* and *C* rings having chair conformations. The *D* ring has a 13β-envelope conformation {$\Delta C_s[\mathrm{C}(13)] = 5{\cdot}0\ (5)$, $\Delta C_2[\mathrm{C}(13)$–$\mathrm{C}(14)] = 16{\cdot}8\ (5)°$}, which was also found for CA II {$\Delta C_s[\mathrm{C}(13)] = 4{\cdot}3$,

* Lists of structure factors, torsion angles, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43271 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

ΔC_2[C(13)–C(14)] = 19·5°}, whereas in CA I the *D* ring adopts a 13β,14α-half-chair conformation {ΔC_s[C(13)] = 14·1 (5), ΔC_2[C(13)–C(14)] = 4·5 (5)°}.

The conformation of the side chain of CA is given by torsion angles C(17)–C(20)–C(21)–O(21) = 172·2 (5), O(20)–C(20)–C(21)–O(21) = −6·8 (8), C(20)–C(21)–O(21)–C(22) = −76·1 (7), C(21)–O(21)–C(22)–C(23) = −176·8 (6), C(21)–O(21)–C(22)–O(22) = −2 (1)° and its orientation with respect to the steroid skeleton is given by the torsion angles about C(17)–C(20), *e.g.* C(13)–C(17)–C(20)–C(21) = −89·1 (6)°. The orientations of the side chain of CA IV*ac* and CA II are nearly the same [mean difference of the C(17)–C(20) torsion angles being 4 (5)°], the larger difference between CA IV*ac* and CA I [corresponding mean difference 14 (5)°] suggests a relation between *D*-ring conformation and side-chain orientation.

Fig. 2 shows a stereoview down **b** and illustrates the easy dissolution of the crystals, the solvent molecules being dissipated through grooves in the crystal structure. The acetone solvent molecule acts as an acceptor in a hydrogen bond with O(17), with O···O distances of

Table 1. *Positional and equivalent isotropic thermal parameters* (Å²) *for non*-H *atoms with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/3\sin^2\beta$.

	x	*y*	*z*	U_{eq}
O(3)	0·5564 (6)	0·2710 (9)	0·1713 (3)	0·154 (3)
O(11)	0·8365 (4)	−0·0219 (5)	0·5132 (2)	0·084 (2)
O(17)	0·6033 (3)	0·2273 (6)	0·7540 (2)	0·072 (1)
O(20)	0·9226 (4)	0·2395 (7)	0·8634 (2)	0·097 (2)
O(21)	0·8596 (5)	−0·0937 (7)	0·8961 (2)	0·095 (2)
O(22)	0·9946 (4)	−0·1399 (7)	0·7970 (3)	0·107 (2)
C(1)	0·6857 (5)	0·0934 (8)	0·3631 (3)	0·062 (2)
C(2)	0·6807 (6)	0·1032 (9)	0·2700 (4)	0·082 (3)
C(3)	0·6103 (6)	0·265 (1)	0·2403 (4)	0·094 (3)
C(4)	0·6203 (6)	0·415 (1)	0·2927 (4)	0·083 (3)
C(5)	0·6850 (5)	0·4185 (8)	0·3657 (4)	0·061 (2)
C(6)	0·7005 (5)	0·5858 (7)	0·4100 (3)	0·072 (2)
C(7)	0·6676 (5)	0·5706 (7)	0·4982 (3)	0·065 (2)
C(8)	0·7527 (4)	0·4265 (7)	0·5413 (3)	0·054 (2)
C(9)	0·7186 (4)	0·2522 (7)	0·4955 (3)	0·046 (2)
C(10)	0·7501 (4)	0·2553 (7)	0·4059 (3)	0·048 (2)
C(11)	0·7762 (5)	0·0961 (7)	0·5433 (3)	0·056 (2)
C(12)	0·7500 (5)	0·0842 (7)	0·6317 (3)	0·056 (2)
C(13)	0·7913 (4)	0·2596 (8)	0·6735 (3)	0·052 (2)
C(14)	0·7169 (5)	0·4100 (7)	0·6284 (3)	0·054 (2)
C(15)	0·7399 (5)	0·5636 (7)	0·6848 (3)	0·065 (2)
C(16)	0·7499 (5)	0·4857 (8)	0·7712 (3)	0·071 (3)
C(17)	0·7411 (5)	0·2867 (8)	0·7595 (3)	0·063 (2)
C(18)	0·9495 (4)	0·2764 (8)	0·6764 (3)	0·065 (2)
C(19)	0·9045 (4)	0·2618 (9)	0·3958 (3)	0·071 (2)
C(20)	0·8201 (6)	0·1803 (9)	0·8257 (3)	0·069 (3)
C(21)	0·7682 (6)	0·001 (1)	0·8412 (4)	0·088 (3)
C(22)	0·9726 (7)	−0·1571 (9)	0·8662 (4)	0·086 (3)
C(23)	1·0583 (6)	−0·263 (1)	0·9269 (4)	0·124 (3)
Acetone molecule *a* [s.o.f. = 0·71 (1)]				
O|ac(1*a*)|	0·4994 (5)	0·2239 (9)	0·9058 (3)	0·102 (1)*
C|ac(1*a*)|	0·3880 (5)	0·1803 (9)	0·9563 (3)	0·102 (1)*
C|ac(2*a*)|	0·3719 (5)	0·0977 (9)	1·0053 (3)	0·154 (2)*
C|ac(3*a*)|	0·2607 (5)	0·2068 (9)	0·8737 (3)	0·154 (2)*
Acetone molecule *b* [s.o.f. = 0·29 (1)]				
O|ac(1*b*)|	0·468 (1)	0·282 (2)	0·8791 (8)	0·102 (1)*
C|ac(1*b*)|	0·392 (1)	0·253 (2)	0·9317 (8)	0·102 (1)*
C|ac(2*b*)|	0·431 (1)	0·138 (2)	1·0006 (8)	0·154 (2)*
C|ac(3*b*)|	0·254 (1)	0·332 (2)	0·9303 (8)	0·154 (2)*

* Thermal parameters for acetone atoms were coupled during refinement.

Table 2. *Bond distances* (Å) *and bond angles* (°) *for non*-H *atoms with e.s.d.'s in parentheses*

O(3)–C(3)	1·226 (8)	C(8)–C(9)	1·561 (7)
O(11)–C(11)	1·211 (6)	C(8)–C(14)	1·525 (7)
O(17)–C(17)	1·424 (6)	C(9)–C(11)	1·520 (7)
O(20)–C(20)	1·229 (7)	C(9)–C(10)	1·548 (7)
O(21)–C(22)	1·343 (8)	C(10)–C(19)	1·540 (6)
O(21)–C(21)	1·426 (8)	C(11)–C(12)	1·517 (7)
O(22)–C(22)	1·196 (8)	C(12)–C(13)	1·552 (8)
C(1)–C(10)	1·540 (8)	C(13)–C(14)	1·528 (8)
C(1)–C(2)	1·549 (8)	C(13)–C(17)	1·565 (7)
C(2)–C(3)	1·48 (1)	C(13)–C(18)	1·556 (6)
C(3)–C(4)	1·44 (1)	C(14)–C(15)	1·511 (7)
C(4)–C(5)	1·325 (9)	C(15)–C(16)	1·553 (7)
C(5)–C(6)	1·480 (8)	C(16)–C(17)	1·538 (9)
C(5)–C(10)	1·533 (8)	C(17)–C(20)	1·530 (8)
C(6)–C(7)	1·533 (7)	C(20)–C(21)	1·49 (1)
C(7)–C(8)	1·528 (7)	C(22)–C(23)	1·50 (1)

C(21)–O(21)–C(22)	116·2 (5)	O(11)–C(11)–C(12)	118·9 (5)
C(2)–C(1)–C(10)	113·7 (5)	C(11)–C(12)–C(13)	108·9 (4)
C(1)–C(2)–C(3)	110·5 (5)	C(14)–C(13)–C(18)	112·9 (4)
O(3)–C(3)–C(4)	122·7 (7)	C(12)–C(13)–C(17)	115·8 (4)
C(2)–C(3)–C(4)	117·2 (6)	C(14)–C(13)–C(17)	100·1 (4)
O(3)–C(3)–C(2)	119·8 (7)	C(17)–C(13)–C(18)	110·4 (4)
C(3)–C(4)–C(5)	125·1 (7)	C(12)–C(13)–C(14)	109·6 (4)
C(4)–C(5)–C(10)	122·4 (6)	C(12)–C(13)–C(18)	108·0 (4)
C(4)–C(5)–C(6)	119·8 (6)	C(8)–C(14)–C(15)	119·5 (4)
C(6)–C(5)–C(10)	117·8 (5)	C(13)–C(14)–C(15)	103·9 (4)
C(5)–C(6)–C(7)	113·0 (5)	C(8)–C(14)–C(13)	113·1 (4)
C(6)–C(7)–C(8)	110·8 (4)	C(14)–C(15)–C(16)	105·7 (4)
C(7)–C(8)–C(9)	107·5 (4)	C(15)–C(16)–C(17)	105·4 (4)
C(7)–C(8)–C(14)	110·3 (4)	O(17)–C(17)–C(16)	111·6 (4)
C(9)–C(8)–C(14)	109·7 (4)	O(17)–C(17)–C(13)	105·5 (4)
C(8)–C(9)–C(11)	111·2 (4)	C(16)–C(17)–C(20)	114·6 (4)
C(10)–C(9)–C(11)	114·9 (4)	O(17)–C(17)–C(20)	107·4 (4)
C(8)–C(9)–C(10)	114·0 (4)	C(13)–C(17)–C(16)	103·2 (4)
C(5)–C(10)–C(9)	108·9 (4)	C(13)–C(17)–C(20)	114·2 (4)
C(1)–C(10)–C(9)	109·1 (4)	O(20)–C(20)–C(17)	121·2 (6)
C(1)–C(10)–C(19)	110·3 (4)	C(17)–C(20)–C(21)	117·0 (5)
C(5)–C(10)–C(19)	107·8 (4)	O(20)–C(20)–C(21)	121·8 (6)
C(1)–C(10)–C(5)	108·3 (4)	O(21)–C(21)–C(20)	111·9 (5)
C(9)–C(10)–C(19)	112·4 (4)	O(21)–C(22)–C(23)	112·4 (5)
C(9)–C(11)–C(12)	118·0 (4)	O(22)–C(22)–C(23)	125·0 (6)
O(11)–C(11)–C(9)	123·0 (4)	O(21)–C(22)–O(22)	122·4 (6)

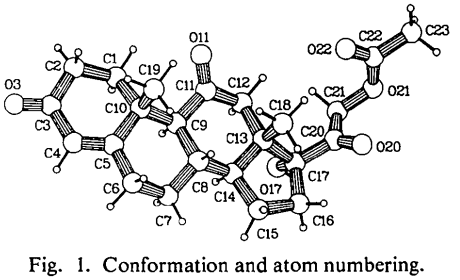

Fig. 1. Conformation and atom numbering.

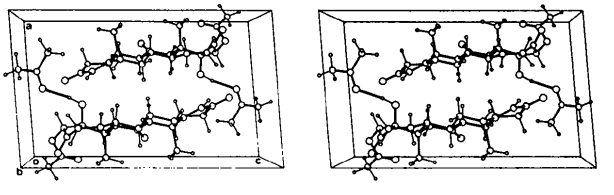

Fig. 2. Stereoview showing the molecular packing down **b**. For clarity only the acetone molecule with the highest site occupation is shown.

2·801 (6) and 2·59 (1) Å and O—H···O angles of 171 (4) and 163 (6)° for acetone molecules with s.o.f. 0·71 (1) and 0·29 (1), respectively. The inclusion of the solvent results in a packing that is different from that observed in anhydrous CA I and CA II, where the steroid molecules are hydrogen bonded head-to-tail [O(17)→O(3′)] and head-to-head [O(17)→O(22′)], respectively (Kanters *et al.*, 1985). The packing can be described as $M\,a_9b_9c_5\,211$ (Duax & Norton, 1975) indicating that the molecules are packed two thick, one wide and one long, with the steroid length parallel to **c**.

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The Structure of a Thioxanthodaunomycinone

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Abstract. 8-Acetyl-7,8,9,10-tetrahydro-6,11-dimethoxy-12*H*-5-thianaphthacen-12-one, $C_{21}H_{20}O_4S$, $M_r = 368{\cdot}45$, monoclinic, $P2_1/c$, $a = 9{\cdot}4586\ (6)$, $b = 9{\cdot}4246\ (5)$, $c = 20{\cdot}0674\ (9)$ Å, $\beta = 95{\cdot}361\ (5)°$, $V = 1781\ (1)$ Å^3, $Z = 4$, $F(000) = 776$, $D_x = 1{\cdot}375$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, Ni filter, $\mu = 17{\cdot}8$ cm^{-1}, 293 K, $R = 0{\cdot}043$, $wR = 0{\cdot}063$, 3195 observed reflections. The introduction of a sulfur atom in the *C* ring of the heteroanthracycline molecule buckles the xanthone skeleton. Owing to steric interactions with the heteroatoms on the *C* ring and the hydrogen atoms of the *A* ring, the methoxy groups on ring *B* are twisted out of the average molecular plane by approximately 90°. The conformation of the cyclohexene ring is distorted from a stable half-chair conformation towards a 1,2 diplanar or sofa conformer.

Introduction. A number of natural and synthetic anthracyclines have been successfully used as antitumor treatments; however, many of these products are cardiotoxic and prolonged administration leads to congestive heart failure. The antitumor effect of these compounds arises from their interaction with double-stranded DNA; the complex of one of these anthracyclines, daunomycin (1), and a DNA fragment has been structurally characterized by Quigley, Wang, Ughetto, Van der Marel, Van Boom & Rich (1980). In the complex, the daunomycin chromophore intercalates between base pairs and forms hydrogen bonds to the bases through the hydroxyl and acetyl groups on the cyclohexene ring. In contrast, the cardiotoxic effects of these compounds may arise from portions of the molecule that do not participate in binding to DNA; these effects are thought to be due to superoxide generation *via* the electron-accepting quinone portion of the molecule. It therefore seems reasonable that the intercalating properties of these molecules can be

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