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Low-temperature phase of bis(2-methoxycarbonyl-2-methylpropyl) 2,5-diisopropylidene-3,4-bis(2-methoxycarbonyl-2-methylpropoxycarbonyl)hex-3-enedioate, a crystal structure with six independent pseudo-related molecules

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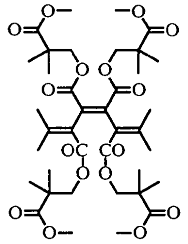
Abstract

The crystal structure of the title compound, $C_{38}H_{56}O_{16}$, is disordered above 298 K. A tripling of the unit cell is observed on cooling. The structure at 136 K contains six ordered molecules related by pseudo-translation vectors of $(\frac{1}{3},0,-\frac{1}{3})$, pseudo-inversion centers and pseudo-twofold screw axes.

Comment

The title compound, (I), shows a reversible phase transition at about 298 K. A data set collected at about 305 K revealed a monoclinic unit cell with $a = 12.254(2)$, $b = 26.241(4)$, $c = 13.461(3)$ Å, $\beta = 93.52(3)°$ and $V = 4320(1)$ Å^3 with $Z = 4$. The systematic absences showed the space group to be $P2_1/n$. The resulting structure, however, was seriously disordered, especially in the side chains. Below the phase-transition temperature a new unit cell is found with a volume three times as large as the high-temperature cell. The cell constants transform according to $a_{\rm low} = 2a_{\rm high} + c_{\rm high}$, $b_{\rm low} = b_{\rm high}$ and $c_{\rm low} = -a_{\rm high} + c_{\rm high}$. To collect data of the low-temperature phase a crystal mounted on a glass fiber was slowly cooled to 136 K. The $h0l$ reflections were absent for l odd. The $0k0$ reflections with k odd were weak but not absent. Thus, the space group is either Pc or $P2/c$. The structure was determined in the Pc space group.

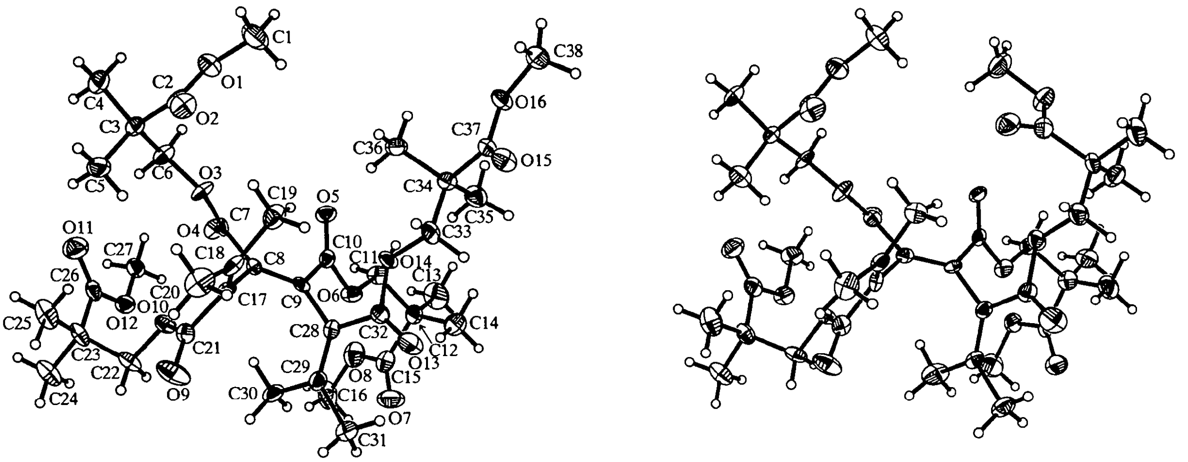


(I)

The resulting structure has six independent molecules in the asymmetric unit. All six molecules are ordered at low temperature. The crystal structure contains no twofold axes parallel to the b axis. Thus the resulting structure can not be transformed to the centrosymmetric space group $P2/c$. The tripling of the unit cell below the phase-transition point results in pseudo-translation vectors of approximately $(\frac{1}{3},0,\frac{2}{3})$ and $(\frac{2}{3},0,\frac{1}{3})$ which relate molecule A with molecules C and F, and molecule B with molecules D and E.

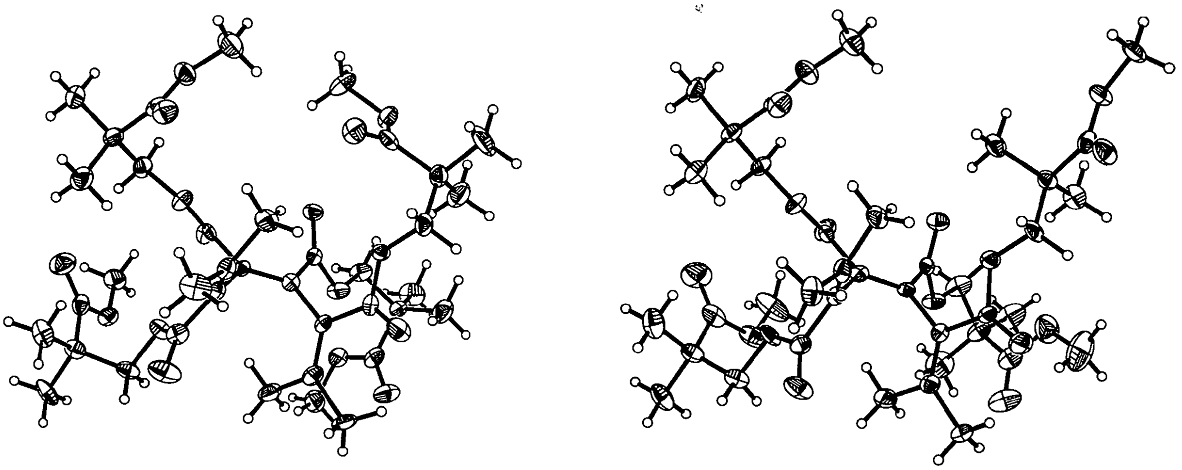
The conformations of the six molecules are very similar, except for the relative orientations of the side chains. The conformations of molecules B and C are identical. Molecule B can be transformed to molecule C by a pseudo-inversion center at 0.438,0.251,0.303. This pseudo-inversion center also relates the major part of molecule A to molecule D and the major part of molecule E to molecule F. Some side chains of those molecules, however, are not fitted by this pseudo-center. The conformations of molecules D and F are also almost identical, but differ considerably from the conformations of molecules B and C. In effect, molecule D can be transformed to molecule F by a pseudo-inversion center at 0.281,0.250,0.471. This pseudo-center also relates the major part of molecule A to molecule B and a large part of molecule C to molecule E. Again a number of side chains of those molecules are not fitted by this pseudo-center.

The conformations of molecules A and E are unique. The side chains attached to C7, C10 and C17 of molecule A are very similar to those of molecules B and C. The corresponding side chains of molecule E on the other hand are very similar to those of molecules D



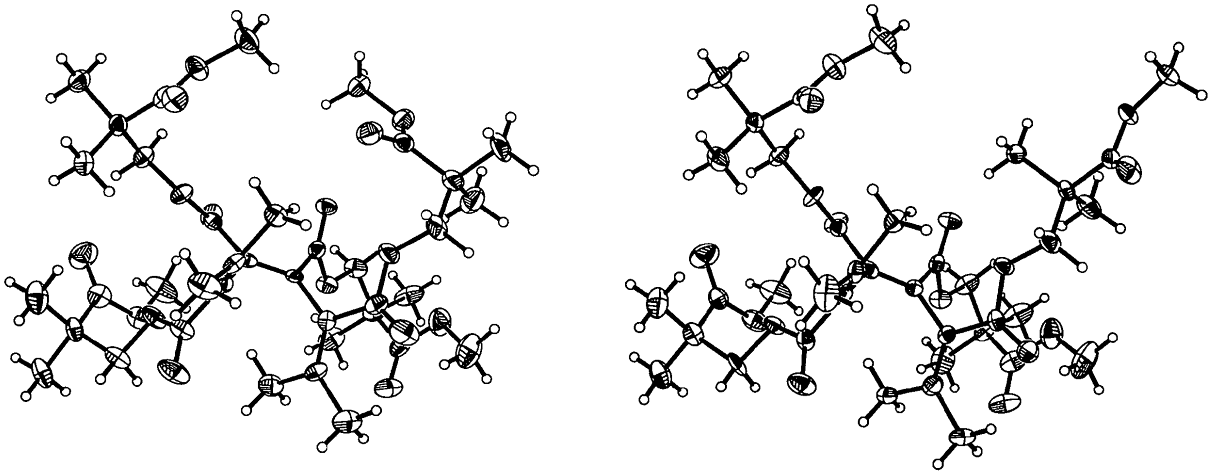
Molecule *A*

Molecule *B*



Molecule *C*

Molecule *D*



Molecule *E*

Molecule *F*

Fig. 1. The structures of the six independent molecules of (I) shown with 50% probability displacement ellipsoids. A similar numbering scheme has been used for each of the six molecules.

and *F*. The side chain attached to C28 of molecule *A*, however, has a conformation similar to that found in molecules *D* and *F*, while the corresponding side chain in molecule *E* is similar to that found in molecules *B* and *C*. Thus, only two possible orientations are found for each of the four side chains.

A combination of a crystallographic symmetry operation with a pseudo-symmetry operation generally results in a new pseudo-symmetry operation. In the present structure, the *c*-glide planes can be combined with the pseudo-inversion centers of pseudo-twofold screw axes parallel to the *b* axis. Thus, the low-temperature phase has pseudo-space group $P2_1/c$. The pseudo-inversion centers and the pseudo-screw axes are repeated in the unit cell after translation vectors of about $(\frac{1}{6},0,-\frac{1}{6})$. These repetitions of pseudo-symmetry elements are a result of the pseudo-translation symmetry of the crystal.

The central double bond (C8═C9) shows a small deviation from planarity. The C7—C8—C9—C10 torsion angle has an average value of 8.0°. The C17—C8—C9—C28 torsion angle has an average value of 3.4°. The C17═C18 and C28═C29 double bonds are almost planar. The triene system is non-planar; the torsion angle about the C18—C17—C8—C9 bond ranges from 84 to 96°. The torsion angle about the C8—C9—C28—C29 bond ranges from 75 to 86°. Thus, the planes of adjacent double bonds are almost perpendicular. Resonance in the triene system is prevented. The C8—C17 and C9—C28 bond lengths of 1.50 Å are rather long for single bonds between sp^2-hybridized C atoms. A value of 1.458 Å has been reported for a similar bond length in a related compound with a planar triene system (Baird *et al.*, 1987). Each of the molecules shows two rather short intramolecular C—H···O interactions: C20—H20···O9 with an H···O distance of about 2.30 Å and C31—H31···O13 with an H···O distance of about 2.20 Å. Desiraju (1991) has classified such short C—H···O interactions as weak hydrogen bonds. The crystal packing shows a considerable number of weak intermolecular electrostatic O···H interactions with distances of 2.4 Å and upwards.

Experimental

Compound (I) was prepared by the treatment of one equivalent of the corresponding 5-palladatricyclo[4.1.0.0^{2,4}]heptane (Hashmi, Naumann, Probst & Bats, 1997; Hashmi, Naumann & Bats, 1997; Hashmi *et al.*, 1998) with one equivalent of iodine in dichloromethane at 273 K. Silica-gel chromatography of the crude reaction mixture with hexane/ethyl acetate (3:1) provided (I) in 96% yield as a colorless solid [m.p. 337 K; R_f = 0.43 (hexane/ethyl acetate, 1:1)]. Crystals were grown from a solution of the title compound in *n*-hexane/ethyl acetate.

Crystal data

$C_{38}H_{56}O_{16}$
$M_r = 768.83$
Monoclinic
Pc
$a = 26.280\,(4)$ Å
$b = 26.285\,(3)$ Å
$c = 18.449\,(2)$ Å
$\beta = 102.696\,(10)^\circ$
$V = 12432\,(3)$ Å^3
$Z = 12$
$D_x = 1.232$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 235 reflections
$\theta = 3$–23°
$\mu = 0.096$ mm^{-1}
$T = 136\,(2)$ K
Rod
$0.80 \times 0.22 \times 0.14$ mm
Colorless

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: none
207 489 measured reflections
62 820 independent reflections
26 218 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.128$
$\theta_{\rm max} = 30.36^\circ$
$h = -36 \rightarrow 36$
$k = -34 \rightarrow 35$
$l = -26 \rightarrow 23$
775 standard reflections
frequency: 540 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.078$
$wR(F^2) = 0.157$
$S = 1.011$
62 820 reflections
2966 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.014$
$\Delta\rho_{\rm max} = 0.325$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.281$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00039 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

The H atoms were placed at calculated positions and were refined with fixed individual displacement parameters [$U(\mathrm{H}) = 1.2U_{\rm eq}(\mathrm{C})$ and $U(\mathrm{H}) = 1.5U_{\rm eq}(\mathrm{C_{methyl}})$] using a riding model with fixed distances: H—C(methyl) = 0.96 and H—C(secondary) = 0.97 Å, respectively. Torsion angles about the C—C or C—O bonds of the methyl groups attached to planar groups were allowed to refine. The structure was refined by blocked least squares, refining three molecules per block. The Flack (1983) value was determined [−0.1 (7), 29 439 Friedel-related reflections], but does not reliably establish the absolute structure.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1996*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996*b*). Software used to prepare material for publication: *CIF* in *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1272). Services for accessing these data are described at the back of the journal.

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17-Oxo-17a-oxa-17a-homo-5α-androstan-3α,4β-diyl diacetate

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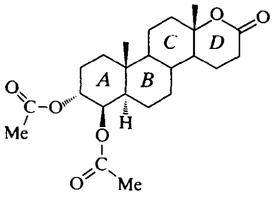
Abstract

The title compound, $C_{23}H_{34}O_6$, a ring *D* lactone, has two acetoxy groups in positions 3α and 4β. All ring junctions are *trans* which results in a planar molecule. The two acetoxy groups have different behaviour, one of them being disordered and exhibiting double-bond delocalization. The ordered acetoxy group is involved in two weak intramolecular C—H···O bonds.

Comment

The title compound, (I), is the diacetate form of the 3α,4β-dihydroxy-17a-oxa-17a-homo-5α-androstan-17-one, a key intermediate for the synthesis of a previously prepared potential aromatase inhibitor 4-hydroxy-17a-oxa-17a-homoandrost-4-ene-3,17-dione (Tavares da Silva *et al.*, 1997). It was prepared in order to study the conformation and molecular interactions of steroids related with aromatase inhibition (Paixão *et al.*, 1998).



(I)

The X-ray analysis gives ring bond lengths and angles in good agreement with expected values (Paixão *et al.*, 1998). The two acetoxy groups are in positions 3α and 4β. The 4β acetoxy group has bond lengths and valence angles within normal values and its constituent atoms (O4, C41, C42, O41) are highly coplanar [sum of the valence angles about C41 is 360.0 (7)°] as expected from the double bond between C41 and O41. In the 3α acetoxy group, the O3—C31 bond length approaches the value of a delocalized double bond similar to that of carboxylate anions. Furthermore, the structure refinement shows that this group is disordered over two positions in such a way that the 50.3 (8)% occupied site appears to have a normal C31—O31*B* double bond and the 49.7 (8)% occupied site appears to have a longer C31—O31*A* bond relative to the characteristic lengths in a *gem*-diol (*International Tables for Crystallography*, 1995, Vol. C). Both disordered components have a small distortion from the expected coplanarity of an acetoxy group [sums of valence angles around C31 are 346.7 (7) and 348.4 (7)°].

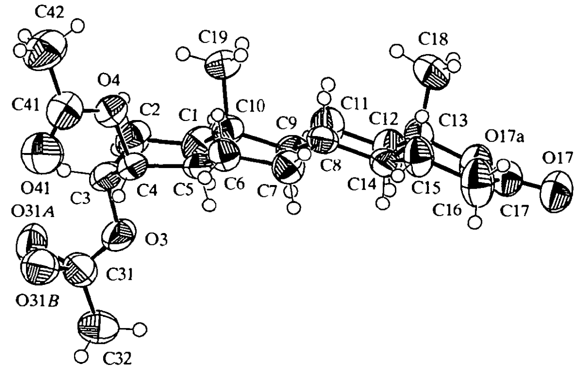


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

The distance between terminal-O atoms O31*A* and O17 is 12.424 (6) Å. The pseudo-torsion angle C19—C10—C13—C18 is −4.0 (3)°. All ring junctions are *trans*. Rings *A*, *B* and *C* have slightly flattened chair conformations [average torsion angles 52 (4), 56 (5) and 56 (2)°, respectively]. The six-membered ring *D* characteristic of a γ-lactone has a 14α-sofa conformation [$\Delta C_s(14) = 4.5(3)$, $\Delta C_2(13,14) = 15.8(4)$ and $\Delta C_2(15,16) = 41.0(4)°$; Duax & Norton, 1975].

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