The crystal was mounted on a glass fibre. Data were collected at a scan speed of 16.0° min^{-1} in ω; ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.33° with a take-off angle of 6.0°. The weak reflections $[I < 15\sigma(I)]$ were rescanned to a maximum of five scans and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak to background counting time was 2:1.

The structure was solved by direct methods (Fan, 1991) and expanded using Fourier techniques (Beurskens *et al.*, 1992). The non-H atoms were refined anisotropically.

Anomalous dispersion effects were included in F_c (Ibers & Hamilton, 1964). The values for $\Delta f'$ and $\Delta f''$ were those of Creagh & McAuley (1992). The values for the mass attenuation coefficients were those of Creagh & Hubbell (1992). All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1985, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Oxopregnenyl 4-Allyloxybenzoate

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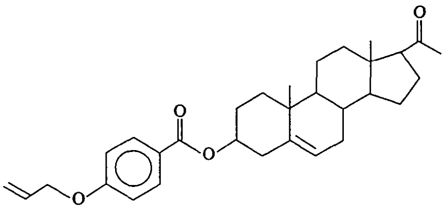
Abstract

The molecule of 20-oxo-5-pregnen-3-yl 4-allyloxybenzoate, $C_{31}H_{40}O_4$, is extended, with the benzoate moiety twisted by 34.0 (1)° from the least-squares plane through the tetracyclic core. The extended molecules pack in a parallel manner with respect to one another.

Comment

Polysiloxane backbones with pendant cholesterol ester groups are well known to produce liquid-crystalline behavior (Shibaev & Freidzon, 1989). The phase behavior of macromolecules based on liquid-crystalline cyclosiloxane backbones and cholesterol-based mesogens has also been examined extensively (Bunning & Kreuzer, 1995; Kreuzer *et al.*, 1991; Gresham *et al.*, 1994). These structures can be quenched into glassy transparent films which show promise for filter and storage applications. X-ray analysis of these materials has shown that a complex molecular architecture is present wherein two types of layered packing domains occur, each exhibiting characteristic X-ray diffraction features (Bunning, Klei, Samulski, Crane & Linville, 1991; Bunning, Klei, Samulski, Adams & Crane, 1993; Bunning, Socci, Farmer, Campbell & Adams, 1996). In systems with long spacer groups (the unit used to link the backbone to the tetracyclic core of the lath-shaped cholesterol molecule), a reflection corresponding approximately to the length of the extended mesogen is observed. In short spacer group compounds, a second reflection indicative of partial interdigitation of mesogens is also observed. Both reflections, corresponding to fully and partially interdigitated mesogens, appear with intermediate length spacer groups.

Previous examinations of two cholesteryl esters (Socci *et al.*, 1995; Chabinyc *et al.*, 1995) indicate some correlation between the solid-state conformation and the structure in the liquid-crystalline phase. In these two compounds, the length of the spacer unit was varied. In our continuing efforts to understand the key molecular interactions, several new steroidal mesogens, with different length and functionality units pendant on the 17β-C atom of the tetracyclic core, were synthesized. The structure of an allyloxybenzoate-substituted pregnenyl compound, (I), in which the C_8H_{17} tail of cholesterol is replaced by a $C({=}O)CH_3$ tail, is examined here.


(I)

Bond lengths and angles in (I) are normal. The conformation of the tetracyclic core is consistent with that found in other cholesterol analogs (Guerina & Craven, 1979; Sawzik & Craven, 1980; Chabinyc *et al.*, 1995; Socci *et al.*, 1995). The benzoate moiety is twisted out of the least-squares plane through the tetracyclic core by 34.0 (1)°. The molecules are packed in a parallel manner (Fig. 2). The long axis of the molecule makes an angle of 11.0° with the (001) plane. The completely interdigitated packing corresponds well to the layer spacing observed in the liquid-crystalline phase (24.7 Å).

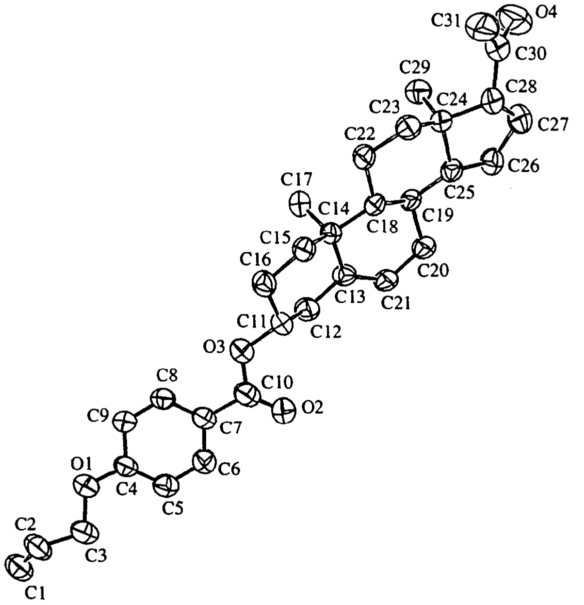


Fig. 1. The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

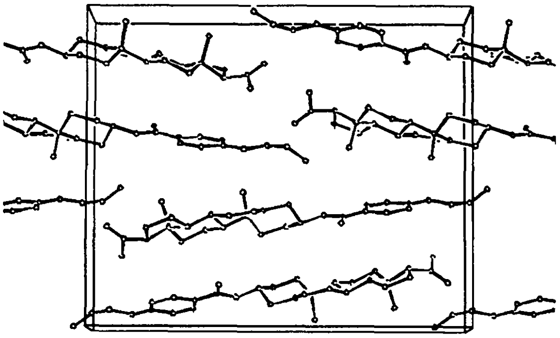


Fig. 2. Plot of the unit cell; the *a* axis is nearly perpendicular to the plane of the paper and the *b* and *c* axes horizontal and vertical, respectively.

Experimental

The title compound was synthesized *via* a room-temperature esterification reaction according to McHugh & Bunning (1995).

Crystal data

$C_{31}H_{40}O_4$
$M_r = 476.7$
Orthorhombic
$P2_12_12_1$
$a = 7.460\,(1)$ Å
$b = 17.118\,(3)$ Å
$c = 20.707\,(3)$ Å
$V = 2644.3\,(7)$ Å^3
$Z = 4$
$D_x = 1.197$ Mg m^{-3}
$D_m = 1.20$ Mg m^{-3}
D_m measured by flotation in a 45wt% sucrose solution

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4$–$11°$
$\mu = 0.08$ mm^{-1}
$T = 296$ K
Parallelepiped
0.45 × 0.40 × 0.30 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian
$T_{\min} = 0.9688$, $T_{\max} = 0.9736$
16 410 measured reflections
4320 independent reflections

2701 observed reflections [$I > 3\sigma(I)$]
$R_{\text{int}} = 0.074$
$\theta_{\max} = 29.97°$
$h = 0 \rightarrow 10$
$k = -24 \rightarrow 24$
$l = -29 \rightarrow 29$
2 standard reflections frequency: 240 min intensity decay: 0.9%

Refinement

Refinement on F
$R = 0.079$
$wR = 0.053$
$S = 2.473$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.421$ e Å^{-3}
$\Delta\rho_{\min} = -0.447$ e Å^{-3}
Extinction correction: none

2701 reflections
316 parameters
H-atom positions calculated
and refined as riding
$w = 1/[\sigma^2(F) + 0.000025F^2]$

Atomic scattering factors
from *International Tables for X-ray Crystallography*
(1974, Vol. IV, Tables
2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	$U_{\rm eq}$
O1	0.6617 (4)	0.5654 (2)	−0.4059 (2)	0.069 (2)
O3	0.4420 (3)	0.6217 (2)	−0.1197 (1)	0.061 (2)
O2	0.1801 (4)	0.6560 (2)	−0.1645 (2)	0.084 (2)
O4	0.2322 (5)	0.6661 (3)	0.4593 (2)	0.107 (3)
C1	0.6926 (7)	0.5277 (3)	−0.5679 (3)	0.081 (3)
C2	0.7137 (6)	0.5706 (3)	−0.5185 (2)	0.073 (3)
C3	0.5764 (6)	0.5802 (3)	−0.4669 (2)	0.065 (3)
C4	0.5701 (5)	0.5796 (2)	−0.3511 (2)	0.051 (2)
C5	0.3932 (5)	0.6019 (3)	−0.3480 (2)	0.059 (2)
C6	0.3194 (5)	0.6176 (3)	−0.2879 (2)	0.057 (3)
C7	0.4153 (5)	0.6109 (2)	−0.2319 (2)	0.051 (2)
C8	0.5919 (5)	0.5864 (2)	−0.2368 (2)	0.056 (2)
C9	0.6688 (5)	0.5716 (3)	−0.2937 (2)	0.058 (3)
C10	0.3305 (6)	0.6314 (3)	−0.1703 (2)	0.059 (3)
C11	0.3863 (5)	0.6495 (2)	−0.0563 (2)	0.052 (2)
C12	0.2536 (5)	0.5943 (2)	−0.0249 (2)	0.057 (2)
C13	0.2179 (5)	0.6156 (2)	0.0446 (2)	0.045 (2)
C14	0.3822 (4)	0.6277 (2)	0.0868 (2)	0.043 (2)
C15	0.5125 (4)	0.6820 (2)	0.0508 (2)	0.050 (2)
C16	0.5555 (5)	0.6568 (2)	−0.0181 (2)	0.058 (2)
C17	0.4725 (5)	0.5482 (2)	0.0981 (2)	0.057 (2)
C18	0.3308 (4)	0.6666 (2)	0.1513 (2)	0.042 (2)
C19	0.1605 (4)	0.6318 (2)	0.1815 (2)	0.042 (2)
C20	0.0053 (4)	0.6397 (2)	0.1339 (2)	0.050 (2)
C21	0.0536 (4)	0.6237 (2)	0.0670 (2)	0.050 (2)
C22	0.4847 (4)	0.6705 (3)	0.1999 (2)	0.056 (2)
C23	0.4353 (5)	0.7085 (2)	0.2637 (2)	0.056 (2)
C24	0.2760 (5)	0.6683 (2)	0.2946 (2)	0.044 (2)
C25	0.1222 (4)	0.6704 (2)	0.2453 (2)	0.043 (2)
C26	−0.0423 (5)	0.6470 (2)	0.2848 (2)	0.060 (3)
C27	−0.0042 (5)	0.6782 (3)	0.3527 (2)	0.065 (3)
C28	0.1847 (5)	0.7113 (2)	0.3519 (2)	0.052 (2)
C29	0.3234 (6)	0.5847 (3)	0.3149 (2)	0.066 (3)
C30	0.2811 (6)	0.7060 (3)	0.4148 (2)	0.068 (3)
C31	0.4454 (7)	0.7559 (3)	0.4227 (3)	0.094 (4)

Table 2. *Selected torsion angles (°)*

C3—O1—C4—C5	5.5 (6)	C22—C18—C19—C20	172.3 (3)
C11—O3—C10—O2	−6.6 (6)	C22—C23—C24—C29	66.5 (4)
C6—C7—C10—O2	−1.9 (7)	C23—C24—C25—C26	−167.1 (3)
C12—C13—C14—C17	−70.2 (4)	C27—C28—C30—O4	14.0 (7)
C21—C13—C14—C15	−131.2 (4)	C27—C28—C30—C31	−163.9 (4)

All non-H atoms were refined anisotropically by full-matrix least-squares methods.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.2 *DIFDAT ADDREF ABSORB SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *Xtal*3.2 *GENTAN*. Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2 *ORTEP*. Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1161). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Bicyclo[2.2.1]heptenone System

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Abstract

The crystal and molecular structure of the title compound, 1,2,3,4-tetraphenyl-5-(4-pyridyl)bicyclo[2.2.1]-hept-2-en-7-one, $C_{36}H_{27}NO$, has been determined to confirm the stereochemistry and investigate its potential inclusion behavior.

Comment

Interest in the systematic design and application of organic clathrates has increased markedly in recent years. Studies have shown that sterically encumbered compounds may exhibit inclusion behavior without the cohesive force of hydrogen bonding (Atwood, Davies & MacNicol, 1984, 1991). These inclusion complexes, stabilized by weak van der Waals interactions, are controlled primarily by the topological complementarity of the guest and host molecules.

1,2,3,4-Tetraphenyl-5-(4-pyridyl)bicyclo[2.2.1]hept-2-en-7-one, (I), was prepared by a Diels–Alder reaction (Wasserman, 1965; Huisgen, Grashey & Sauer,