

ORGANIC COMPOUNDS

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Cholesteryl 4-Vinylbenzoate

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Abstract

The structure of cholest-5-en-3-yl 4-vinylbenzoate, $C_{36}H_{52}O_2$, was determined by X-ray diffraction. The molecule is extended along the *b* axis, with the benzoate group orientated out of the plane of the tetracyclic core by $48.1(1)^\circ$. The molecules are packed in an antiparallel manner. The packing of antiparallel pairs of molecules in the unit cell is correlated to two types of interactions that coexist in the liquid-crystalline phase of cholesterol-based cyclic siloxane macromolecules.

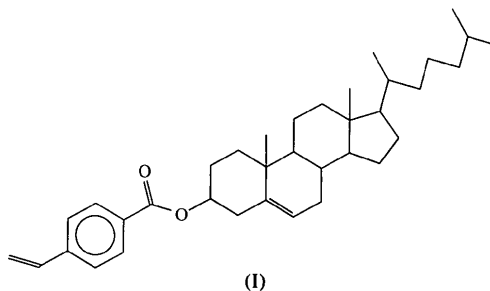
Comment

The first compound exhibiting liquid crystallinity was an ester of cholesterol discovered by Reinitzer in 1888 (Reinitzer, 1888). Since then, the liquid crystalline properties of a number of steroid-based esters (Shibaev & Freidzon, 1989) have been examined. The crystal structures of cholesterol-based materials, most notably those with pendant *n*-alkanoate ester groups, have also been studied in an attempt to obtain information relating the conformation and packing in the crystalline state to interactions in the liquid-crystalline state.

Craven and co-workers (Guerina & Craven, 1979; Pattabhi & Craven, 1979; Sawzik & Craven, 1979*a,b*, 1980*a,b*) have observed three distinct packing modes which are dependent upon the length of the pendant *n*-alkanoate spacer group. Compounds with short spacer lengths (6–8 C atoms) exhibit monolayer structures in which the molecules pack in an antiparallel fashion. The methyl side groups pendant on the tetracyclic core interlock, leading to efficient packing. Structures of com-

pounds with medium length spacers (9–12 C atoms) contain two non-symmetry-related molecules that differ mainly in the conformations of the *n*-alkanoate groups. The tetracyclic cores of these antiparallel molecules are approximately orthogonal. Compounds with longer spacer groups (13–18 C atoms) pack to form bilayer structures in which the molecules have an antiparallel orientation. The tetracyclic cores between adjacent molecules do not overlap. Differences in these three packing types have been compared with the variations in packing behaviour observed in the liquid-crystalline phases (Sawzik & Craven, 1979*b*). Others workers (Sato & Yano, 1987) have correlated molecular conformations in the crystalline state with the ability of a compound to exhibit a liquid-crystalline state.

As part of a program to develop ordered optically clear thin films, a series of cholesteryl 4-alkenebenzoate-based compounds were synthesized (Bunning, 1992; Gresham, McHugh, Bunning, Klei, Samulski & Crane, 1993). These compounds were attached to cyclic siloxane cores. X-ray diffraction measurements of these macromolecules in the liquid-crystalline state indicate the coexistence of two molecular-packing schemes (Bunning, Klei, Samulski, Crane & Linville, 1991; Bunning, Klei, Samulski, Adams & Crane, 1993). Type I packing consists of nearly fully interdigitated cholesteryl mesogens packed antiparallel, with a repeat distance (as measured from X-ray diffraction) corresponding to the calculated length of an extended molecule. Type II packing consists of antiparallel mesogens packed with overlap only between the aliphatic tails. The relative amounts of type I and II packing can be controlled by altering several variables, including the terminal alkene spacer length. This paper examines the structure of a vinylbenzoate-substituted cholesteryl compound (I). Materials with other *n*-alkenebenzoate spacer groups are also being studied.



A displacement ellipsoid plot of the molecule (without H atoms) showing the atom-numbering scheme is presented in Fig. 1. Bond lengths and angles in the phenyl ring of the benzoate ester compare well with conventional aromatic bond lengths and

angles. The benzoate moiety is out of the plane of the tetracyclic core, as indicated by a dihedral angle of $48.1(1)^\circ$ between the least-squares plane through the tetracyclic core and the benzoate group. The C35—C36 bond length [$1.30(1) \text{ \AA}$] is consistent with accepted values for C=C bonds, indicating that dimerization did not occur during X-ray exposure. The C28=O28 [$1.199(8) \text{ \AA}$] carbonyl and C28—O3 [$1.352(8) \text{ \AA}$] ester bonds are in agreement with accepted values. Large r.m.s. anisotropic displacement amplitudes are observed in the two terminal methyl groups of the aliphatic tail (C26 and C27). This observation is consistent with the large displacement parameters found for the same methyl groups in the *n*-alkanoate series (Guerina & Craven, 1979; Sawzik & Craven, 1979*a*, 1980*a,b*) and in other cholesterol-based compounds (Sato & Yano, 1987). The conformation of the tetracyclic core is consistent with those of the *n*-alkanoate series.

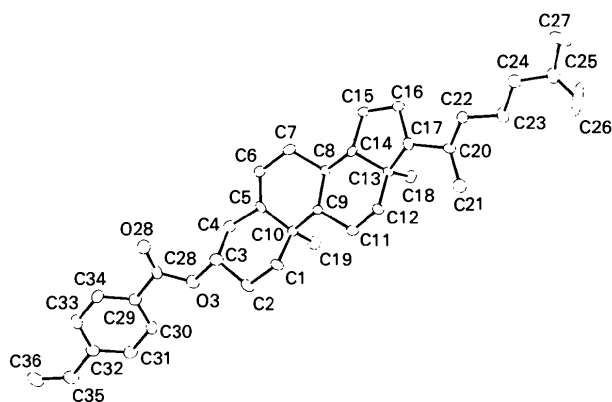


Fig. 1. Molecular structure of the title compound along with the atom-numbering scheme. H atoms are omitted. Displacement ellipsoids (ORTEP II; Johnson, 1976) are drawn at the 50% probability level.

The molecules adopt extended conformations along the *b* axis and are orientated antiparallel, as shown in Fig. 2. As a consequence of the benzoate group being twisted out of the plane of the tetracyclic core, the molecules pack in a herringbone pattern, which allows overlap of the phenyl group with the tetracyclic core of an adjacent molecule. The terminal aliphatic tails prefer proximate regions of the unit cell, overlapping partially. No direct overlap of tetracyclic cores is observed.

The two types of interactions that are observed in the liquid-crystalline state of cholesterol 4-vinylbenzoate-substituted siloxanes are similar to the interactions observed between cholesterol 4-vinylbenzoate molecules in the solid state. Type I packing (interdigitated molecules, side-by-side, antiparallel) is approximated by the antiparallel molecules on the right-hand side of the unit cell in Fig. 2. The end-to-end spacing (along the *b* axis) of 27.5 \AA between equivalent C25 atoms agrees qualitatively with the 26 \AA reflection observed in the

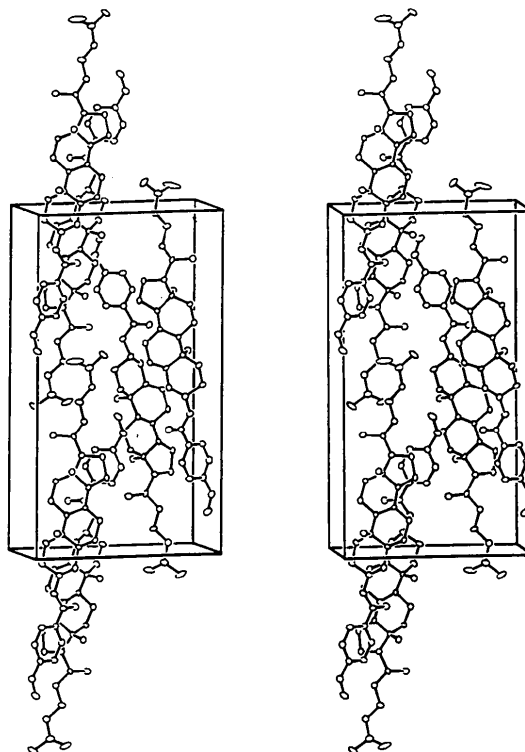


Fig. 2. An ORTEP II (Johnson, 1976) plot of the unit cell. The *c* axis is nearly perpendicular to the plane of the paper; the *a* and *b* axes are horizontal and vertical, respectively.

liquid-crystalline state. Type II packing (partially interdigitated molecules) is observed in the cholesteric and smectic liquid-crystalline phases. This interaction, identified by overlapping aliphatic tails, is represented by the antiparallel molecules on the left-hand side of the cell in Fig. 2. The end-to-end spacing (along the *b* axis) of 45.1 \AA between equivalent C36 atoms agrees qualitatively with the 47 \AA spacing observed in type II packing. In the liquid-crystalline phase, the amount of type II packing is dictated by steric interactions among aliphatic tails of neighbouring molecules. An increase in the mobility of the cholesterol molecules (*e.g.* modification of spacer group length) will lead to a decrease in the amount of type II packing relative to type I.

Experimental

Crystal data

C₃₆H₅₂O₂
M_r = 516.81
 Orthorhombic
*P*2₁2₁2₁
a = 13.755 (2) \AA
b = 24.817 (3) \AA
c = 9.101 (2) \AA
V = 3106 (1) \AA^3
Z = 4
D_x = 1.10 Mg m⁻³

Mo *K* α radiation
 λ = 0.71073 \AA
 Cell parameters from 25 reflections
 θ = 9.01–11.74°
 μ = 0.061 mm⁻¹
T = 294 K
 Parallelepiped
 0.37 × 0.30 × 0.27 mm
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: numerical
 $T_{\min} = 0.977$, $T_{\max} = 0.991$
 5066 measured reflections
 5035 independent reflections
 1470 observed reflections
 $[I > 2.0\sigma(I)]$

Refinement

Refinement on F^2
 $R = 0.071$
 $wR = 0.064$
 $S = 1.912$
 1470 reflections
 343 parameters
 H-atom parameters refined as riding

$\theta_{\max} = 29.97^\circ$
 $h = 0 \rightarrow 19$
 $k = 0 \rightarrow 34$
 $l = 0 \rightarrow 12$
 3 standard reflections monitored every 120 reflections
 intensity decay: 1.79%

$w = 4F_o^2 / [\sigma^2(F_o^2) + 0.0016F_o^4]$
 $(\Delta/\sigma)_{\max} = 0.015$
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = 0.00 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
O3	0.3961 (3)	0.1037 (2)	0.4407 (5)	0.069 (2)
O28	0.2672 (3)	0.1459 (2)	0.3399 (6)	0.080 (2)
C1	0.4243 (5)	-0.0405 (3)	0.3309 (3)	0.074 (3)
C2	0.4511 (5)	0.0178 (2)	0.3715 (9)	0.076 (3)
C3	0.3609 (5)	0.0523 (3)	0.3872 (8)	0.064 (3)
C4	0.2907 (5)	0.0285 (3)	0.4934 (8)	0.065 (3)
C5	0.2676 (5)	-0.0305 (2)	0.4595 (7)	0.051 (2)
C6	0.1774 (5)	-0.0480 (3)	0.4510 (8)	0.062 (3)
C7	0.1485 (4)	-0.1050 (2)	0.4282 (9)	0.065 (3)
C8	0.2313 (4)	-0.1445 (2)	0.4498 (7)	0.046 (2)
C9	0.3219 (4)	-0.1225 (2)	0.3722 (8)	0.044 (2)
C10	0.3552 (4)	-0.0671 (2)	0.4400 (7)	0.047 (2)
C11	0.4032 (5)	-0.1639 (2)	0.3628 (8)	0.064 (3)
C12	0.3712 (5)	-0.2187 (2)	0.3078 (8)	0.056 (3)
C13	0.2875 (4)	-0.2415 (2)	0.3994 (6)	0.042 (2)
C14	0.2055 (4)	-0.1997 (2)	0.3912 (7)	0.046 (2)
C15	0.1180 (4)	-0.2288 (2)	0.4561 (8)	0.059 (3)
C16	0.1332 (4)	-0.2879 (2)	0.4098 (9)	0.062 (3)
C17	0.2346 (4)	-0.2917 (2)	0.3381 (8)	0.055 (2)
C18	0.3208 (5)	-0.2527 (3)	0.5578 (7)	0.066 (3)
C19	0.4039 (5)	-0.0752 (3)	0.5871 (8)	0.075 (3)
C20	0.2809 (4)	-0.3478 (3)	0.3536 (9)	0.060 (3)
C21	0.3822 (5)	-0.3514 (3)	0.290 (1)	0.105 (4)
C22	0.2148 (5)	-0.3906 (2)	0.2860 (8)	0.070 (3)
C23	0.2436 (5)	-0.4481 (3)	0.3086 (9)	0.084 (3)
C24	0.1694 (5)	-0.4888 (3)	0.259 (1)	0.084 (3)
C25	0.1874 (6)	-0.5461 (3)	0.275 (1)	0.127 (4)
C26	0.2671 (8)	-0.5670 (4)	0.294 (2)	0.345 (8)
C27	0.1041 (7)	-0.5805 (3)	0.227 (1)	0.167 (5)
C28	0.3425 (5)	0.1475 (3)	0.4059 (8)	0.058 (3)
C29	0.3908 (5)	0.1981 (3)	0.4526 (7)	0.054 (2)
C30	0.4756 (5)	0.1980 (3)	0.5340 (8)	0.066 (3)
C31	0.5192 (5)	0.2457 (3)	0.5715 (8)	0.071 (3)
C32	0.4818 (5)	0.2945 (3)	0.5275 (8)	0.060 (3)
C33	0.3966 (5)	0.2944 (3)	0.4489 (8)	0.068 (3)
C34	0.3513 (5)	0.2469 (3)	0.4125 (8)	0.065 (3)
C35	0.5325 (6)	0.3444 (3)	0.5643 (9)	0.082 (3)
C36	0.5071 (6)	0.3936 (3)	0.534 (1)	0.096 (4)

Table 2. Selected geometric parameters (Å , $^\circ$)

O3—C3	1.449 (8)	C13—C18	1.537 (9)
O3—C28	1.352 (8)	C14—C15	1.522 (8)
O28—C28	1.199 (8)	C15—C16	1.542 (9)
C1—C2	1.537 (9)	C16—C17	1.542 (9)
C1—C10	1.53 (1)	C17—C20	1.537 (9)
C2—C3	1.515 (9)	C20—C21	1.51 (1)
C3—C4	1.49 (1)	C20—C22	1.528 (9)
C4—C5	1.528 (9)	C22—C23	1.494 (9)
C5—C6	1.317 (9)	C23—C24	1.51 (1)
C5—C10	1.520 (9)	C24—C25	1.45 (1)
C6—C7	1.484 (9)	C25—C26	1.23 (1)
C7—C8	1.516 (8)	C25—C27	1.50 (1)
C8—C9	1.534 (8)	C28—C29	1.483 (9)
C8—C14	1.512 (8)	C29—C30	1.382 (9)
C9—C10	1.574 (8)	C29—C34	1.38 (1)
C9—C11	1.522 (8)	C30—C31	1.370 (9)
C10—C19	1.51 (1)	C31—C32	1.375 (9)
C11—C12	1.513 (9)	C32—C33	1.37 (1)
C12—C13	1.530 (9)	C32—C35	1.46 (1)
C13—C14	1.534 (8)	C33—C34	1.37 (1)
C13—C17	1.548 (9)	C35—C36	1.30 (1)
C3—O3—C28	116.5 (5)	C8—C14—C13	115.0 (5)
C2—C1—C10	113.6 (6)	C8—C14—C15	118.5 (5)
C1—C2—C3	110.9 (6)	C13—C14—C15	104.0 (5)
O3—C3—C2	104.7 (5)	C14—C15—C16	103.7 (5)
O3—C3—C4	110.4 (6)	C15—C16—C17	107.2 (5)
C2—C3—C4	111.6 (6)	C13—C17—C16	102.9 (5)
C3—C4—C5	112.6 (6)	C13—C17—C20	120.1 (5)
C4—C5—C6	121.7 (6)	C16—C17—C20	113.0 (5)
C4—C5—C10	115.6 (5)	C17—C20—C21	113.7 (5)
C6—C5—C10	122.8 (6)	C17—C20—C22	110.2 (5)
C5—C6—C7	125.2 (6)	C21—C20—C22	110.8 (6)
C6—C7—C8	113.3 (5)	C20—C22—C23	116.8 (6)
C7—C8—C9	108.7 (5)	C22—C23—C24	114.8 (6)
C7—C8—C14	111.3 (5)	C23—C24—C25	120.8 (7)
C9—C8—C14	110.6 (5)	C24—C25—C26	125.7 (8)
C8—C9—C10	111.5 (5)	C24—C25—C27	113.6 (7)
C8—C9—C11	112.4 (5)	C26—C25—C27	119.0 (8)
C10—C9—C11	113.5 (5)	O3—C28—O28	124.2 (6)
C1—C10—C5	108.1 (5)	O3—C28—C29	111.7 (6)
C1—C10—C9	107.7 (5)	O28—C28—C29	124.0 (6)
C1—C10—C19	111.0 (5)	C28—C29—C30	122.0 (6)
C5—C10—C9	109.7 (5)	C28—C29—C34	119.5 (6)
C5—C10—C19	109.2 (5)	C30—C29—C34	118.5 (6)
C9—C10—C19	111.1 (5)	C29—C30—C31	120.2 (6)
C9—C11—C12	114.4 (5)	C30—C31—C32	121.5 (6)
C11—C12—C13	111.7 (5)	C31—C32—C33	118.1 (6)
C12—C13—C14	106.0 (5)	C31—C32—C35	120.0 (6)
C12—C13—C17	117.1 (5)	C33—C32—C35	121.9 (6)
C12—C13—C18	110.7 (5)	C32—C33—C34	120.9 (6)
C14—C13—C17	100.4 (5)	C29—C34—C33	120.8 (6)
C14—C13—C18	112.8 (5)	C32—C35—C36	128.3 (8)
C17—C13—C18	109.4 (5)		

All non-H atoms were refined anisotropically by full-matrix least squares. H atoms were included as fixed riding atoms in geometrically calculated positions.

Data collection: *CAD-4* (Enraf–Nonius, 1989). Cell refinement: *CAD-4*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *BTABLE PTABLE CIF* in *MolEN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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***rac*-1,1,4-Trimethyl-5-trimethylsilyl-1,3,3a,4,6,7,8,9-octahydro-1-silaphtho[1,2-*c*]furan at 153 K**

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Abstract

The crystal structure of *rac*-1,1,4-trimethyl-5-trimethylsilyl-1,3,3a,4,6,7,8,9-octahydro-1-silaphtho[1,2-*c*]furan, C₁₇H₃₀OSi₂, has been determined at low temperature.

Comment

The title compound, (2), was obtained in 53% yield via an intramolecular cobalt-mediated [2 + 2 + 2] cycloaddition

of the alkenediyne (1) and subsequent oxidative demetallation of the resulting cobalt–cyclohexadiene complex. Further details will be published elsewhere (Eckenberg & Groth, 1995). The reaction proceeded in a stereospecific manner with regard to the geometry of the double bond in compound (1). The X-ray structure analysis was performed in order to establish the relative stereochemistry at atoms C3a and C4, and it confirmed our previous assignments based on NMR techniques (Eckenberg, 1992). The five-membered ring (Si1, O2, C3, C3a, C3b) adopts an envelope conformation. The first six-membered ring (C3b, C3a, C4, C5, C9b, C9a) adopts a twist conformation, whereas the second six-membered ring (C9a, C9b, C6, C7, C8, C9) is in a chair conformation. All bond lengths and angles in compound (2) are in the expected ranges.

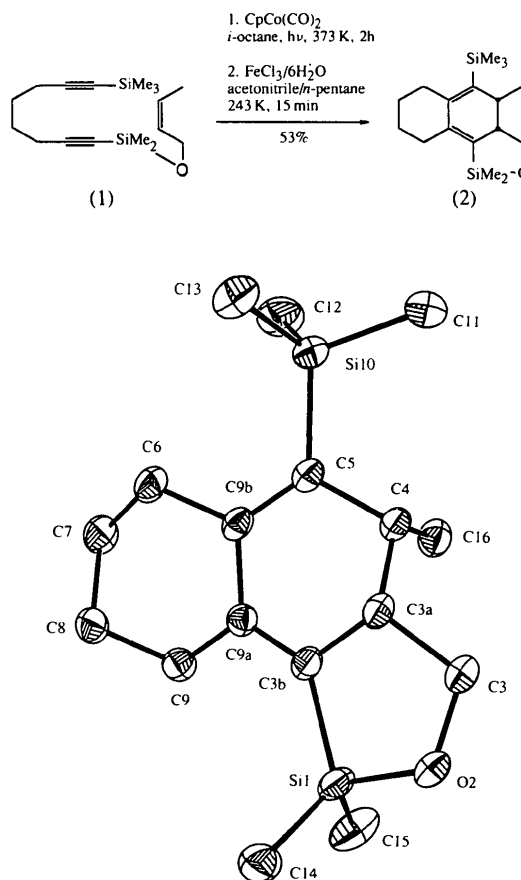


Fig. 1. Crystal structure of compound (2) showing 50% probability displacement ellipsoids. The H atoms are omitted for clarity.

Experimental

The compound was crystallized from a mixture of diethyl ether and pentane at room temperature.

Crystal data

C₁₇H₃₀OSi₂
M_r = 306.59

Mo K α radiation
 λ = 0.71073 Å