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The Structure of Cholesteryl Palmitoleate at 295 K

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Abstract

Cholesteryl palmitoleate, $C_{43}H_{74}O_2$, $M_r = 623{\cdot}1$, m.p. 325 K, is monoclinic, space group $P2_1$, with cell dimensions $a = 12{\cdot}873\,(7)$, $b = 9{\cdot}173\,(4)$, $c = 35{\cdot}424\,(13)$ Å, $\beta = 93{\cdot}47\,(1)°$ and $Z = 4$ [two molecules (A, B) in the asymmetric unit], $V = 4175\,(3)$ Å^3. $D_c = 0{\cdot}991\,(1)$ Mg m^{-3}. Integrated intensities for 2383 reflections with $I > 2\sigma(I)$ were measured at 295 K, using an automatic diffractometer and Cu $K\alpha$ graphite-monochromated radiation ($\lambda = 1{\cdot}5418$ Å). Atomic coordinates for the rigid tetracyclic ring systems, taken from cholesteryl laurate, were used as an initial model for structure determination. Atoms of the hydrocarbon chains were located in subsequent Fourier maps. Refinement by block-diagonal least-squares methods gave a final R factor of 0·122. The molecules are packed in an antiparallel array in the crystal structure forming monolayers of thickness $d_{(001)} = 35{\cdot}4$ Å. The central regions of the monolayers are characterized by efficient molecular packing of cholesteryl rings while the layer interface regions are more loosely packed. Within the interface region there is a conformational disordering of the terminal isopropyl group in the C(17) (A) tail and a five-atom segment of the (B) ester chain around the *cis* double bond. One of the major conformational differences in the two independent molecules comes from a difference of 47° in the rotation about the ester bond. The conformation of the palmitoleate ester chains is also quite different, with molecule (A) having a kinked nearly extended chain. The disordered (B) chains have two different conformations which are both bent like boomerangs.

Introduction

A series of X-ray crystal structure determinations of unsaturated fatty acid esters of cholesterol has been undertaken. The primary aim in this study is to determine the conformation of the unsaturated fatty acid chains when they are incorporated in a close-packed lipid environment. Aspects of these structures may help in providing models for molecular associations in less ordered lipid systems.

At room temperature, the crystal structure of cholesteryl palmitoleate and the saturated esters with chain lengths C_9–C_{12} (Sawzik & Craven, 1980*a*) have the same crystal structure type, which has been designated type I monolayer in order to distinguish it from other structure types (Guerina & Craven, 1979). A notable feature of the type I monolayer structures is the contrast between the molecular close packing within the layer and the relatively loose packing in the interface region between layers. In the cholesteryl laurate structure at 298 K (Sawzik & Craven, 1979*a*) atoms in the interface region have large apparent thermal vibrational averaging and are also possibly disordered. At this temperature, there is a desirable compromise in that the crystal structure is near a phase transition, yet the number of available X-ray intensity data is adequate for structure determination. We report here the room-temperature (295 K) structure of cholesteryl palmitoleate, for which similar conditions prevail.

The crystalline and liquid-crystalline phases of cholesteryl palmitoleate undergo phase transformations which have been summarized by Small (1970) as follows:

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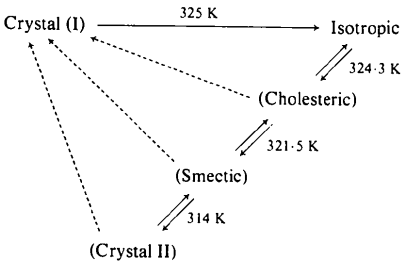

(⟶ indicates that transformation takes place on supercooling.) The cholesteric and smectic mesophases as well as a second crystalline form are monotropic with respect to the stable crystalline form. That is, their transition temperatures are lower than the crystal melting point, so that they do not appear when the crystal is heated to melting. Crystal form (I) is stable at room temperature and has the monolayer type I crystal structure reported in this paper.

Experimental

Cholesteryl palmitoleate was obtained from Serdary Research Laboratories, Inc., London, Ontario, and recrystallized slowly (2 months) at 277 K by slow evaporation of an acetone solution. A plate-like crystal elongated along the crystal *b* axis melted at 325 K which is in agreement with the melting point reported by Small (1970) for crystals of form (I). X-ray data were collected at 295 K using a Nonius CAD-4 diffractometer and Cu $K\alpha$ graphite-monochromated radiation. A crystal with dimensions 0·5 × 0·3 × 0·6 mm was mounted with the b^* axis 1·5° from the diffractometer φ axis. Unit-cell parameters as determined by a least-squares fit of $\sin^2\theta$ values for 17 reflections with $15° \leq 2\theta \leq 28°$ are given in the *Abstract*. X-ray intensities for 3906 non-symmetry-related reflections with $\sin\theta/\lambda < 0{\cdot}46$ Å^{-1} were collected using $\theta/2\theta$ scans. Three standard reflections, collected every 100 reflections, showed a maximum variation of 5% throughout the data collection. Reflections with $I > 2\sigma(I)$, of which there were 2383, were used for the structure determination and refinement. The variance in an integrated intensity was assumed to be $\sigma^2(I) = \sigma^2 + (0{\cdot}04I)^2$ where σ^2 is the variance due to counting statistics.

The cell data for cholesteryl palmitoleate indicated that this crystal structure was of the same type as cholesteryl laurate (Sawzik & Craven, 1979*a*, 1980*b*). Atomic positional parameters for the tetracyclic ring systems [atoms C(1)–C(19)] of the two independent molecules (*A*, *B*) of cholesteryl laurate at 198 K (Sawzik & Craven, 1980*b*) were used as a starting model for the palmitoleate structure determination. During the subsequent eight cycles of Fourier refinement, all the remaining atoms were located. A structure factor calculation with the resulting model gave an *R* factor of 0·29.

The structure refinement was carried out by an atomic block-diagonal least-squares procedure (Shiono, 1971) in which the function minimized was $\sum w\Delta^2$ where $\Delta = |F_{obs}| - |F_{calc}|$ and $w = 1/\sigma^2(F_{obs})$. The X-ray scattering factors used were those of Cromer & Waber (1965) for C and O and Stewart, Davidson & Simpson (1965) for H. Atomic positional and anisotropic thermal parameters for all 90 of the C and O atoms refined to an *R* of 0·20 after five cycles. At this

Table 1. *Atomic parameters for cholesteryl palmitoleate at* 293 K

Positional parameters are given as fractional coordinates (×10^3). Isotropic equivalent *B* values are given according to the expression: $B_{eq} = \frac{1}{3}\sum_{i=1}^{3} B_{ii}$. Estimated standard deviations are in parentheses.

	x	*y*	*z*	*B* (Å^2)
Molecule *A*				
C(*A*1)	−528 (2)	−216 (3)	−146 (1)	8 (2)
C(*A*2)	−576 (1)	−174 (2)	−110 (1)	6 (1)
C(*A*3)	−542 (1)	−22 (3)	−98 (1)	8 (2)
C(*A*4)	−573 (2)	86 (2)	−128 (1)	6 (1)
C(*A*5)	−533 (2)	44 (3)	−167 (1)	7 (2)
C(*A*6)	−478 (2)	153 (3)	−185 (1)	9 (2)
C(*A*7)	−438 (2)	121 (3)	−221 (1)	7 (1)
C(*A*8)	−478 (2)	−21 (3)	−243 (1)	8 (2)
C(*A*9)	−481 (2)	−144 (3)	−213 (1)	7 (2)
C(*A*10)	−552 (2)	−111 (2)	−178 (1)	6 (1)
C(*A*11)	−505 (2)	−292 (3)	−229 (1)	8 (2)
C(*A*12)	−438 (2)	−331 (3)	−262 (1)	9 (2)
C(*A*13)	−444 (2)	−202 (4)	−292 (1)	10 (2)
C(*A*14)	−415 (2)	−56 (3)	−274 (1)	10 (2)
C(*A*15)	−401 (2)	52 (3)	−307 (1)	11 (2)
C(*A*16)	−359 (2)	−37 (4)	−336 (1)	11 (2)
C(*A*17)	−357 (2)	−211 (4)	−325 (1)	12 (2)
C(*A*18)	−554 (2)	−196 (4)	−314 (1)	13 (2)
C(*A*19)	−670 (1)	−124 (3)	−192 (1)	7 (1)
C(*A*20)	−373 (2)	−303 (6)	−359 (1)	18 (3)
C(*A*21)	−381 (3)	−470 (5)	−345 (1)	17 (3)
C(*A*22)	−277 (2)	−305 (5)	−381 (1)	16 (3)
C(*A*23)	−274 (3)	−355 (5)	−419 (1)	20 (4)
C(*A*24)	−177 (3)	−325 (7)	−441 (1)	22 (4)
C(*A*25)	−167 (4)	−336 (7)	−478 (1)	25 (5)
C(*A*26,1)	−250 (6)	−242 (15)	−488 (3)	26 (9)
C(*A*26,2)	−156 (8)	−508 (13)	−478 (3)	27 (9)
C(*A*27)	−75 (4)	−230 (7)	−489 (1)	27 (5)
C(*A*28)	−563 (1)	−17 (3)	−34 (1)	7 (1)
C(*A*29)	−618 (1)	24 (3)	0 (1)	7 (1)
C(*A*30)	−603 (2)	−22 (3)	40 (1)	8 (2)
C(*A*31)	−676 (2)	25 (3)	70 (1)	9 (2)
C(*A*32)	−657 (2)	−43 (3)	108 (1)	9 (2)
C(*A*33)	−732 (2)	7 (3)	134 (1)	9 (2)
C(*A*34)	−705 (2)	−40 (3)	171 (1)	12 (2)
C(*A*35)	−789 (2)	−16 (3)	201 (1)	12 (2)
C(*A*36)	−897 (2)	−81 (4)	198 (1)	11 (2)
C(*A*37)	−930 (2)	−166 (4)	226 (1)	12 (2)
C(*A*38)	−871 (3)	−213 (5)	260 (1)	17 (3)
C(*A*39)	−940 (3)	−197 (5)	294 (1)	16 (3)
C(*A*40)	−895 (3)	−256 (5)	330 (1)	18 (3)
C(*A*41)	−955 (3)	−272 (5)	360 (1)	20 (4)
C(*A*42)	−884 (4)	−301 (8)	393 (1)	27 (5)
C(*A*43)	−987 (4)	−325 (8)	421 (1)	28 (5)
O(*A*3)	−599 (1)	26 (2)	−65 (1)	7 (1)
O(*A*28)	−491 (1)	−109 (2)	−28 (1)	8 (1)

Table 1 (*cont.*)

	x	*y*	*z*	*B* (Å²)
Molecule *B*				
C(*B*1)	−277 (1)	−86 (2)	44 (1)	5 (1)
C(*B*2)	−308 (2)	−65 (3)	83 (1)	7 (1)
C(*B*3)	−221 (2)	−74 (3)	112 (1)	7 (1)
C(*B*4)	−136 (2)	49 (2)	101 (1)	7 (1)
C(*B*5)	−103 (1)	33 (2)	61 (1)	5 (1)
C(*B*6)	−6 (2)	35 (2)	59 (1)	7 (1)
C(*B*7)	39 (1)	22 (2)	19 (1)	7 (1)
C(*B*8)	−46 (1)	45 (2)	−16 (1)	5 (1)
C(*B*9)	−150 (1)	−28 (2)	−7 (1)	5 (1)
C(*B*10)	−191 (1)	19 (2)	30 (1)	4 (1)
C(*B*11)	−224 (1)	−27 (2)	−42 (1)	5 (1)
C(*B*12)	−187 (1)	−79 (3)	−78 (1)	7 (1)
C(*B*13)	−85 (2)	−2 (2)	−86 (1)	6 (1)
C(*B*14)	−6 (1)	−13 (2)	−53 (1)	6 (1)
C(*B*15)	91 (1)	44 (2)	−66 (1)	5 (1)
C(*B*16)	91 (1)	−8 (3)	−108 (1)	7 (1)
C(*B*17)	−18 (1)	−64 (2)	−117 (1)	5 (1)
C(*B*18)	−116 (2)	162 (3)	−95 (1)	9 (2)
C(*B*19)	−237 (2)	180 (3)	25 (1)	7 (1)
C(*B*20)	−53 (1)	−44 (3)	−159 (1)	7 (1)
C(*B*21)	−172 (2)	−73 (3)	−170 (1)	8 (1)
C(*B*22)	7 (2)	−132 (3)	−184 (1)	9 (2)
C(*B*23)	−4 (2)	−100 (3)	−226 (1)	10 (2)
C(*B*24)	66 (2)	−216 (4)	−245 (1)	13 (2)
C(*B*25)	58 (2)	−183 (5)	−291 (1)	16 (3)
C(*B*26)	−47 (3)	−203 (5)	−305 (1)	20 (3)
C(*B*27)	150 (3)	−241 (7)	−304 (1)	21 (4)
C(*B*28)	−228 (2)	−143 (4)	178 (1)	9 (2)
C(*B*29)	−271 (2)	−92 (3)	213 (1)	10 (2)
C(*B*30)	−250 (2)	−195 (3)	245 (1)	10 (2)
C(*B*31)	−308 (2)	−155 (4)	282 (1)	12 (2)
C(*B*32)	−271 (3)	−235 (5)	314 (1)	16 (3)
C(*B*33)	−330 (3)	−202 (4)	348 (1)	15 (3)
C(*B*34)	−321 (3)	−299 (5)	382 (1)	17 (3)
C(*B*35)	−384 (3)	−274 (6)	417 (1)	20 (4)
C(*B*36,1)	−487 (6)	−269 (9)	408 (2)	18 (6)
C(*B*37,1)	−575 (5)	−296 (12)	428 (3)	23 (8)
C(*B*38,1)	−540 (7)	−441 (14)	450 (2)	26 (9)
C(*B*39,1)	−544 (5)	−373 (11)	487 (2)	21 (7)
C(*B*40,1)	−636 (7)	−342 (13)	499 (2)	23 (8)
C(*B*36,2)	−355 (7)	−391 (12)	440 (2)	25 (8)
C(*B*37,2)	−459 (6)	−425 (11)	455 (2)	21 (8)
C(*B*38,2)	−586 (6)	−436 (12)	437 (2)	22 (8)
C(*B*39,2)	−650 (8)	−344 (16)	462 (2)	27 (8)
C(*B*40,2)	−635 (7)	−385 (12)	502 (2)	23 (8)
C(*B*41)	−666 (4)	−327 (9)	547 (2)	37 (8)
C(*B*42)	−782 (6)	−293 (9)	538 (1)	38 (8)
C(*B*43)	−822 (7)	−234 (10)	575 (2)	43 (9)
O(*B*3)	−254 (1)	−50 (2)	149 (1)	8 (1)
O(*B*28)	−169 (1)	−229 (2)	173 (1)	11 (1)

point atomic thermal parameters for the palmitoleate chain of moelcules (*B*) and the C(17) hydrocarbon tail of molecule (*A*) were unusually large, suggesting that they might be disordered. Although the electron density was diffuse in this region of the crystal structure, it was possible to trace an alternate conformation for the mid-section [C(36)–C(40)] of the (*B*) chain in a difference Fourier map. A second position for C(26) of the (*A*) tail was also found. Close contacts restrict conformer (1) of the (*A*) tail to pack with conformer (1) of the (*B*) chain and conformer (2) of (*A*) with conformer (2) of (*B*) only. Otherwise, the disorder was assumed to be random, since a re-examination of the X-ray photographs showed no additional weak reflections or diffuse streaks. Disordered atoms were given a fixed occupancy of 0·5 and all atoms were refined for the next three cycles giving an R of 0·16. Occupancy factors for the disordered atoms were refined in the next two cycles but did not change significantly from 0·5 and were fixed thereafter. All H atoms were included with fixed parameters obtained by assuming C–H bond distances of 1·0 Å and standard bond angles. Isotropic thermal parameters were also fixed for H atoms with values equivalent to those of the C atoms to which each is bonded. Six cycles of refinement for all atoms followed, converging at $R = \sum|\Delta|/\sum|F_{obs}| = 0{\cdot}122$. The maximum electron density in the final difference map (0·3 e Å^{-3}) was located in the disordered region. Final atomic parameters are given in Table 1.*

Intramolecular geometry

Within experimental error, bond distances and angles* for the independent molecules (*A*) and (*B*) are consistent with those found in the cholesteryl laurate structure determinations at 198 K (Sawzik & Craven, 1980*b*) and at 298 K (Dahlén, 1979; Sawzik & Craven, 1979*a*). The averge least-squares standard deviation for bond distances is 0·05 Å, and 3° for bond angles.

The tetracyclic ring systems of molecules (*A*) and (*B*) have similar conformations. A best least-squares fit for superposition (Nyburg, 1974) of the C(1)–C(19) fragment from the two molecules results in an r.m.s. displacement of 0·10 Å. The effective steroid length (Duax & Norton, 1975), taken as the C(3)–C(16) distance, is 8·88 (6) Å for molecule (*A*) and 9·01 (4) Å for molecule (*B*). A measure of the twist within the ring systems is given by the C(19)–C(10)–C(13)–C(18) torsion angle, which has a value of 9 (2)° for molecule (*A*) and 5 (1)° for (*B*). In related structures, this torsion angle ranges from 7·9–15·0° and the effective steroid length from 8·86–9·01 Å (Pattabhi & Craven, 1979). The length of the cholesteryl palmitoleate molecule, taken as the C(25)–C(43) distance, is 34·15 (8) Å for (*A*) and 33·33 (9) Å for (*B*). The rotation about the ester linkage determines the relation-

* Tables of interatomic bond distances and angles, anisotropic temperature factors, hydrogen-atom positional parameters, plane constants for the least-squares planes given in Table 2, and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36715 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2 HU, England.

Table 2. *Least-squares planes calculated for selected atoms*

Listed are distances (Å $\times 10^2$) from the plane. The e.s.d.'s are in parentheses. Values for molecule (*A*) precede those for (*B*); in disordered regions of the (*B*) chain, values are in the sequence (*A*), (*B*1), (*B*2). The plane constants have been deposited.

Plane (1)					
C(4)	C(5)	C(6)	C(7)	C(10)	
−1 (3)	2 (3)	−1 (4)	0 (3)	1 (3)	
1 (3)	−1 (3)	−1 (3)	1 (3)	0 (3)	
Plane (2)					
O(3)	C(28)	C(29)	O(28)		
2 (3)	−5 (3)	1 (3)	2 (3)		
−2 (3)	6 (3)	−2 (3)	−2 (3)		
Plane (3)					
C(35)	C(36)	C(37)	C(38)		
0 (4)	−10 (5)	10 (4)	0 (5)		
10 (8)	−19 (9)	15 (8)	−6 (8)		
7 (9)	−17 (8)	19 (9)	−9 (9)		
Plane (4)					
C(29)	C(30)	C(31)	C(32)	C(33)	C(34)
1 (3)	−2 (4)	−5 (4)	6 (3)	4 (4)	−5 (4)
−2 (4)	7 (4)	6 (5)	−14 (5)	−5 (4)	9 (4)
Plane (5)					
C(40)	C(41)	C(42)	C(43)		
3 (5)	−3 (5)	−1 (5)	2 (5)		
−9 (8)	7 (8)	13 (8)	−11 (8)		
−1 (8)	1 (9)	1 (8)	−1 (8)		

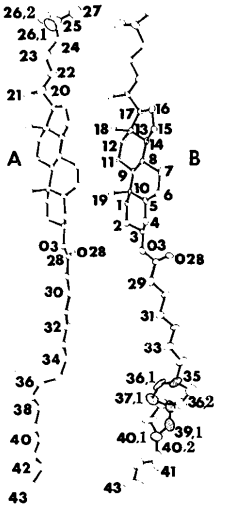

Fig. 1. Molecules (*A*) and (*B*) shown in their observed configuration with their tetracyclic ring systems in the same orientation. Atoms are represented as 10% probability thermal envelopes.

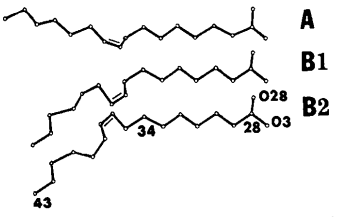

Fig. 2. The palmitoleate ester chain for molecule (*A*) and the two disordered conformers for molecule (*B*). In each chain the best least-squares line through atoms C(29)–C(34) is horizontal.

ship of the alkenoate chain to the cholesteryl moiety, and thus is important in describing the overall shape of the molecule. In molecule (*A*) the C(2)–C(3)–O(3)–C(28) torsion angle has a value of 82 (2)°; however, for (*B*) this value is 129 (2)°. Atoms of the ethylenic groups [C(4),C(5),C(6),C(7),C(10) and C(35), C(36),C(37),C(38)] and ester groups [O(3),C(28), C(29),O(28)] are coplanar within experimental error for both molecules (Table 2).

The C(17) side chains have an extended conformation in both (*A*) and (*B*) cholesteryl palmitoleate molecules (Fig. 1). However, in molecule (*A*) there is a conformational disordering of the terminal isopropyl group, which gives rise to two positions for carbon atom C(26). The C(23)–C(24)–C(25)–C(26,1) torsion angle is 56° while for C(26,2) this angle has a value of −79°. Both the (+)*gauche* and (−)*gauche* conformations have been observed for the terminal atoms of the C(17) tail in cholesterol and cholesteryl ester crystal structures (Craven, 1979; Sawzik & Craven, 1979*b*; Guerina & Craven, 1979). The preferred conformation about the C(24)–C(25) bond seems to be (−)*gauche* as found in the cholesteryl palmitoleate (*B*) tail and the second (2) conformer of the (*A*) tail.

The conformation of the palmitoleate ester chain is significantly different in the two molecules (*A*) and (*B*) (Figs. 1, 2). Each chain consists of two sections, atoms C(29)–C(34) and C(40)–C(43), which form almost planar zigzags (Table 2) on either side of the *cis* double bond. The relationship of the first planar section to the second determines the overall shape of the chain. Two parameters which describe this relationship are bending (angle between best least-squares lines through adjacent chain segments) and kinking (perpendicular separation of these lines). In molecule (*A*) the palmitoleate chain has a nearly extended conformation, with least-squares lines through the planar sections [atoms C(29)–C(34) and C(40)–C(43)] making an angle of 173° and having a perpendicular separation of −0·5 Å. The chain is slightly twisted with the least-squares planes through adjacent sections making an angle of 33°. Although molecule (*B*) is disordered, the relationship of the planar sections is similar for both conformers. Conformer (*B*1) has a bend of −133°, while for (*B*2) this value is −129°. The kink separation is 1·5 Å for (*B*1) and 1·9 Å for (*B*2). The best least-squares planes through adjacent hydrocarbon segments make dihedral angles of 42° for (*B*1) and 47° for (*B*2).

Though the overall shape of the two cholesteryl palmitoleate (*B*) conformers is similar as determined by the relationship of the two planar zigzag segments, the section of chain that separates these segments is quite different. Beginning at the C(30)–C(31)–C(32)–C(33) torsion angle, the sequence of rotations about C–C bonds for conformer (*B*1) is [*tttgtΔsgttt*] and for (*B*2) this sequence is [*ttttsΔs̄ḡtgt*] where *t* is *trans*, *s* is *skew*, *g* is *gauche*, with negative sense indicated as $\bar{s}$ or $\bar{g}$, and *Δ* is the double bond (Fig. 2). The cholesteryl palmitoleate (*B*1) and (*B*2) conformers may be said to lie between an extended conformation as in the (*A*) chain and that of a boomerang which is observed in the low-temperature oleic acid crystal structure (Abrahamsson & Ryderstedt-Nahringbauer, 1962). The extended palmitoleate chain of molecule (*A*) has an overall conformation similar to that observed in the crystal structure of cholesteryl oleate (Craven & Guerina, 1979), yet the sequence of rotations about C–C bonds beginning with C(31)–C(32) is [*tttgsΔstttt*] while for the oleate chain these rotations are [*ttttsΔggt̄s̄tt*]. Thus rather different kinds of dislocations in the double-bond region can give rise to the same general shape in these *cis* unsaturated fatty acid chains.

Molecular packing

In the crystal structure of cholesteryl palmitoleate molecules are arranged to form monolayers that are parallel to the crystal planes (001) and have a thickness $d_{(001)} = 35{\cdot}4$ Å (Fig. 3). The two molecules (*A*,*B*) which are not related by symmetry have their tetracyclic ring systems almost perpendicular to one another and all molecular long axes are nearly parallel to the [10$\bar{1}$] direction. Within the monolayers hydrocarbon chains of (*A*) and (*B*) molecules have close-neighbor cholesteryl ring systems. There is efficient cholesteryl packing of the (*B*) molecules with each other along the crystallographic *b* axis. In contrast, the interface region between layers is more loosely packed. It is within this region that the disordered C(17) (*A*) tail and (*B*) ester chain are located.

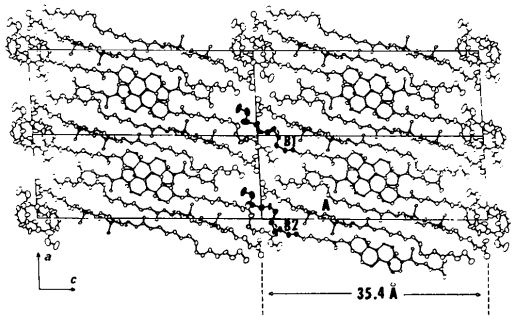

Fig. 3. Crystal structure of cholesteryl palmitoleate in projection down the *b* axis. The two molecules not related by symmetry are (*A*) (ring system viewed on edge) and (*B*). Adjacent monolayers extend vertically with the interface region occurring in vertical strips at the center and edge of the figure. The disordered conformers (*B*1) and (*B*2) are shown separately (shaded) and together (unshaded). Only one of the disordered methyl groups [C(26,1)] of molecule (*A*) is visible in projection, the other [C(26,2)] lies below C(25).

Values of thermal parameters for the atoms of the cholesteryl palmitoleate molecules are consistent with the crystal-packing arrangement. The ester chains of (*A*) molecules and the C(17) tails of (*B*) molecules are surrounded by cholesteryl ring systems (Fig. 3) and have a smaller average amplitude of vibration than the (*B*) chains and (*A*) tails which project into the layer interface (Fig. 1). This difference has been observed for other type I monolayer cholesteryl ester structures and may be related to the stiffening effect that cholesterol has on phospholipid membranes (Pattabhi & Craven, 1979).

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