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Crystal structure of an optically active non-symmetric liquid crystal dimer: cholesteryl 5-[4-(4-*n*-heptylphenylethynyl)phenoxy]pentanoate

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The crystal structure of cholesteryl 5-[4-(4-*n*-heptylphenylethynyl)phenoxy]-pentanoate (C₅₃H₇₆O₃) was determined by direct methods using single crystal X-ray diffraction data. It crystallises in the triclinic system with space group P1 and Z = 2. The unit cell parameters are: $a = 10.6791(5)$, $b = 13.0903(7)$, $c = 18.6430(9)$ Å, $\alpha = 94.413(3)$, $\beta = 98.222(3)$, $\gamma = 112.987(3)^\circ$. The final reliability factor was $R = 0.0510$ for 7284 observed reflections and the goodness of fit was equal to 1.062. The asymmetric unit cell of the compound was found to contain two symmetry-independent molecules, A and B. In both molecules, the six-membered rings of the cholesterol moiety are conformationally very similar. However, pronounced differences were observed in the conformation of the five-membered ring, which is a half-chair in molecule A and assumes an envelope conformation in molecule B. In both molecules, the phenyl rings are planar. The dihedral angle between the two phenyl rings is $43.4(2)$ and $42.7(2)^\circ$ for molecules A and B, respectively. The packing of molecules in the crystalline state was found to be a precursor to the smectic A phase structure. The crystal structure is stabilised by inter-molecular C–H...O and C–H... π interactions.

Keywords: non-symmetric dimer; twist grain boundary; blue phase; crystal structure; dihedral angle; C–H... π interactions

1. Introduction

Optically active nonsymmetric dimers comprising cholesterol and aromatic mesogenic entities interlinked through a flexible spacer are well known to exhibit remarkable mesomorphic properties (1–8). Such properties of these cholesterol-based dimers primarily depend on the nature of the aromatic mesogenic unit, in addition to the length and parity of the spacer. For example, the achiral/chiral tolane (diphenylacetylene) moiety induces some interesting mesomorphism in such dimers. In particular, 4-*n*-alkoxytolane containing dimers show re-entrant twist grain boundary phase (TGB) (4), anomalies of periodicity in TGB structures (5), wide thermal range chiral nematic (N*) phase (6) and smectic A (SmA) phase associated with an electroclinic effect (7). In view of these findings and also to elucidate the structure-property correlations, we investigated four series of dimers in which the 4-*n*-alkyltolane moiety is employed instead of the 4-*n*-alkoxytolane core (8). Notably, depending upon the parity of the spacer of the resultant dimers, another variant of frustrated phase, the blue phase (BP), in addition to N*, SmA, chiral smectic C (SmC*) and TGB phases, is observed (8). Some of these systems during the recrystallisation process in a mixture of CH₂Cl₂-EtOH (2/10) form long defect-free crystals and therefore, their structures have been solved by X-ray diffraction analysis (9–12). In fact,

such studies have helped in providing unequivocal evidence that cholesterol-based dimers are relatively stable (pure) materials and thus, their thermal properties, especially the occurrence of frustrated phases, are genuine. In addition, some crystallographically interesting features have also been revealed by such investigations (9–12). In continuation of our work in this direction, we present the single crystal structure of cholesteryl 5-[4-(4-*n*-heptyl-phenylethynyl)phenoxy]-pentanoate (previously referred to as DTA-4,7) (8) (Figure 1). The phase sequence established with the aid of optical polarising microscopy and differential scanning calorimetry for this dimer is: *heating* – Cr 103 (48.2) SmA 142.2 (2) TGB^a-N* 146.5 (1.2) I; *cooling* – I 146 (1.1) BP^a-N*-TGB^a 141.5 SmA 51.6 (22.6) Cr (^atransient phase; Cr = crystal; SmA = smectic A phase; TGB = twist grain boundary phase; N* = chiral nematic phase; BP = blue phase; I = isotropic phase). On slow cooling (0.2°C), the compound exhibits a blue pattern of low birefringence immediately below the isotropic phase; on further cooling, a platelet texture consisting of blue plates grows quickly on top of the blue background suggesting the presence of blue phase (BPI or BPII). Upon cooling the sample further or subjecting to mechanical stress, the platelet texture transforms to the N* phase with a brightly coloured texture having oily streaks. On lowering the temperature, the transitions to TGB and SmA

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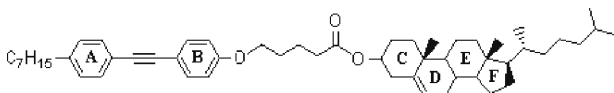


Figure 1. Chemical structure of cholesteryl 5-[4-(4-*n*-heptylphenylethynyl)phenoxy]-pentanoate.

phases occur as established by the observation of blurred planar and focal conic textures, respectively. For the homeotropic alignment, the SmA and TGB phases display pseudoisotropic and filamentary patterns, respectively. When a homeotropically aligned sample was heated at 3–5°C/min, the N* and SmA phases coexist along with the TGB phase as evident from the fact that the textures corresponding to these three mesophases, appeared simultaneously for a short while.

2. Experimental

A crystal with a good morphology ($0.3 \times 0.2 \times 0.2 \text{ mm}^3$) was chosen for three-dimensional intensity data collection using a Bruker CCD area-detector diffractometer. X-ray intensity data from 29,653 reflections (of which 8939 were unique) were recorded and from this number 7284 reflections ($-10 \ h \ 10, -12 \ k \ 12, -18 \ l \ 18$) were treated as observed. The structure was solved by direct methods using SHELXS97 software (13). The unit cell of the compound contains two symmetry-independent molecules, A and B. The structure was tested carefully for a relationship with a higher-symmetry space group using the program PLATON (14), but none could be found. All non-hydrogen atoms of the molecule were obtained from the E-map. Full-matrix least-squares refinement was carried out using SHELXL97 software (13). Hydrogen atoms were placed at geometrically fixed positions and allowed to ride on the corresponding non-H atoms with C–H = 0.93–0.98 Å, and Uiso = 1.5 Ueq of the attached C atom for methyl H atoms and 1.2 Ueq for other H atoms. The final reliability factor was $R = 0.0510$, and the goodness of fit was 1.062. The weight was $1/\sigma^2(F_o^2) + (0.0705P)^2 + 0.9270P$ where $P = [F_o^2 + 2F_c^2]/3$. The minimum and maximum residual electron densities were -0.145 and 0.153 e \AA^{-3} , respectively. The calculated density of 1.076 Mg m^{-3} is very low, as is the case for most mesogenic compounds. The linear absorption coefficient is $\mu = 0.064 \text{ mm}^{-1}$ for MoK α radiation (0.71073 Å) at room temperature (293(2) K). Atomic scattering factors were taken from the International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). Important crystallographic data and refinement parameters are summarised in Table 1. CCDC-708336 contains the supplementary crystallographic data for this paper.

Table 1. Crystal data and structure refinement.

CCDC deposition no.	CCDC-708336
Crystal description	White transparent rectangular
Crystal size	$0.3 \times 0.2 \times 0.2 \text{ mm}^3$
Chemical formula	$\text{C}_{53} \text{H}_{76} \text{O}_3$
Molecular weight	761.14
Radiation, wavelength	MoK α , 0.71073 Å
Cell parameters	$a = 10.6791(5), b = 13.0903(7),$ $c = 18.6430(9) \text{ \AA}$ $\alpha = 94.413(3), \beta = 98.222(3),$ $\gamma = 112.987(3)^\circ$
Unit cell volume	$2349.2(2) \text{ \AA}^3$
Crystal system	Triclinic
Space group	<i>P</i> 1
Density (calculated)	1.076 Mg m^{-3}
No. of molecules per unit cell, <i>Z</i>	2
Absorption coefficient (μ)	0.064 mm^{-1}
F(000)	836
Refinement of unit cell	6831 reflections, ($2.22 < \theta < 20.46^\circ$)
Scan mode	ϕ and ω
θ range for entire data collection	$2.11 < \theta < 20.67^\circ$
Range of indices	$h = -10$ to $10, k = -12$ to $12,$ $l = -18$ to 18
No. of measured reflections	29,624
No. of unique reflections	8939
No. of observed reflections	7284 [$I > 2 \sigma(I)$]
Structure determination	Direct methods
Refinement method	Full-matrix least-squares on F^2
No. of parameters refined	1010
Final R-factor	0.0510
wR(F^2)	0.1279
Weight	$1/\sigma^2(F_o^2) + (0.0705P)^2 + 0.9270P$ where $P = [F_o^2 + 2F_c^2]/3$
Goodness-of-fit on F^2	1.062
$(\Delta/\sigma)_{\text{max}}$	-0.003 [for $\times \text{C1A}$]
Final residual electron density	$-0.145 < \Delta \rho < 0.153 \text{ e \AA}^{-3}$

3. Results and discussion

The atomic coordinates and equivalent isotropic displacement parameters are presented in Table 2. Selected bond lengths, bond angles, and torsion angles are given in Table 3. C–H...O and C–H... π hydrogen bonding geometry is given in Table 4. An ORTEP view of the molecules, A and B, is shown in Figure 2 (15). From the figure it is evident that both the asymmetric molecules are extended and have the same molecular length (calculated length of molecule A in the crystalline state is 43.499 Å and 43.437 Å for molecule B). This can be attributed to the presence of a triple bond between the phenyl groups which reduces the flexibility.

The geometry of both the asymmetric molecules, A and B, is similar in terms of bond distances and angles. A comparison of these parameters with mesogenic non-symmetric dimers indicates a good agreement (9–12). The average aromatic bond lengths in the phenyl rings A and B are respectively, 1.379(8) and 1.373(7) Å for molecule A and 1.375(7) and

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for non-hydrogen atoms (esds given in parentheses).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Molecule A				
C1A	-1.2771(12)	-1.5378(7)	1.2718(7)	0.156(6)
C2A	-1.1995(9)	-1.4221(6)	1.2508(5)	0.149(4)
C3A	-1.0644(7)	-1.4050(6)	1.2305(3)	0.099(3)
C4A	-0.9869(7)	-1.2917(6)	1.2111(3)	0.098(3)
C5A	-0.8594(6)	-1.2801(6)	1.1818(3)	0.086(2)
C6A	-0.7777(7)	-1.1663(6)	1.1623(3)	0.091(3)
C7A	-0.6526(6)	-1.1606(6)	1.1317(3)	0.086(3)
C8A	-0.5619(6)	-1.0490(6)	1.1129(3)	0.077(3)
C9A	-0.5063(6)	-1.0413(6)	1.0505(3)	0.081(3)
C10A	-0.4248(6)	-0.9406(6)	1.0321(3)	0.080(2)
C11A	-0.3907(6)	-0.8398(6)	1.0767(3)	0.080(3)
C12A	-0.4445(7)	-0.8478(6)	1.1408(3)	0.084(3)
C13A	-0.5252(7)	-0.9479(7)	1.1585(3)	0.087(3)
C14A	-0.3095(7)	-0.7348(8)	1.0553(4)	0.085(3)
C15A	-0.2464(7)	-0.6473(8)	1.0371(3)	0.084(3)
C16A	-0.1752(6)	-0.5375(6)	1.0189(3)	0.079(2)
C17A	-0.0562(6)	-0.5068(6)	0.9889(3)	0.081(3)
C18A	0.0110(6)	-0.4017(5)	0.9730(3)	0.075(2)
C19A	-0.0431(6)	-0.3237(6)	0.9844(3)	0.070(2)
C20A	-0.1603(7)	-0.3510(6)	1.0139(3)	0.086(3)
C21A	-0.2270(6)	-0.4575(7)	1.0296(3)	0.089(3)
O22A	0.0149(4)	-0.2161(4)	0.9709(2)	0.085(2)
C23A	0.1344(5)	-0.1808(5)	0.9361(3)	0.075(2)
C24A	0.1740(6)	-0.0622(5)	0.9267(3)	0.082(2)
C25A	0.2853(6)	-0.0194(5)	0.8832(3)	0.077(2)
C26A	0.3318(8)	0.1034(6)	0.8778(4)	0.109(3)
C27A	0.4453(8)	0.1522(6)	0.8369(3)	0.093(3)
O28A	0.5421(5)	0.1303(4)	0.8387(2)	0.097(2)
O29A	0.4264(7)	0.2253(6)	0.7983(4)	0.184(3)
C30A	0.5373(10)	0.2950(10)	0.7637(6)	0.155(5)
C31A	0.4909(9)	0.2756(6)	0.6831(5)	0.135(4)
C32A	0.6003(9)	0.3558(6)	0.6462(4)	0.122(3)
C33A	0.6405(6)	0.4816(5)	0.6739(3)	0.081(2)
C34A	0.6735(8)	0.4988(7)	0.7571(3)	0.096(3)
C35A	0.5701(8)	0.4138(9)	0.7938(4)	0.128(4)
C36A	0.5157(6)	0.5101(5)	0.6499(3)	0.096(2)
C37A	0.7670(6)	0.5533(5)	0.6435(3)	0.074(2)
C38A	0.8359(6)	0.6753(5)	0.6854(3)	0.076(2)
C39A	0.8862(6)	0.6704(7)	0.7646(3)	0.110(3)
C40A	0.7827(9)	0.5792(9)	0.7953(4)	0.125(4)
C41A	0.7411(7)	0.5517(5)	0.5615(3)	0.097(2)
C42A	0.8632(7)	0.6301(5)	0.5314(3)	0.096(3)
C43A	0.9169(6)	0.7530(5)	0.5695(3)	0.077(2)
C44A	0.9539(6)	0.7482(5)	0.6505(3)	0.077(2)
C45A	0.8065(6)	0.7982(6)	0.5538(4)	0.109(3)
C46A	1.0567(6)	0.8354(5)	0.5567(3)	0.088(2)
C47A	1.1108(6)	0.9240(6)	0.6267(3)	0.102(3)
C48A	1.0292(6)	0.8687(6)	0.6853(3)	0.110(3)
C49A	1.0671(7)	0.8924(6)	0.4875(3)	0.100(3)
C50A	1.0012(8)	0.8076(7)	0.4178(3)	0.133(3)
C51A	1.2206(7)	0.9655(7)	0.4877(4)	0.115(3)
C52A	1.2476(8)	1.0337(8)	0.4257(4)	0.136(4)
C53A	1.4061(8)	1.1066(8)	0.4354(4)	0.148(4)
C54A	1.4456(7)	1.1688(7)	0.3704(4)	0.163(5)
C55A	1.6038(7)	1.2155(11)	0.3825(7)	0.164(6)
C56A	1.3990(11)	1.2649(8)	0.3796(6)	0.173(6)

(Continued)

Table 2. (Continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Molecule B				
C1B	2.1461(13)	2.3688(8)	0.4959(6)	0.197(6)
C2B	2.0682(11)	2.2484(7)	0.5095(5)	0.175(5)
C3B	1.9383(8)	2.2457(7)	0.5385(4)	0.139(4)
C4B	1.8575(8)	2.1295(6)	0.5548(4)	0.126(3)
C5B	1.7411(6)	2.1201(5)	0.5928(3)	0.095(3)
C6B	1.6585(7)	2.0038(6)	0.6082(4)	0.103(3)
C7B	1.5413(6)	1.9943(5)	0.6448(3)	0.088(3)
C8B	1.4546(6)	1.8799(5)	0.6623(3)	0.069(2)
C9B	1.4115(6)	1.8690(5)	0.7288(3)	0.076(2)
C10B	1.3298(6)	1.7666(5)	0.7457(3)	0.073(2)
C11B	1.2839(5)	1.6711(5)	0.6961(3)	0.065(2)
C12B	1.3257(6)	1.6822(5)	0.6286(3)	0.080(2)
C13B	1.4090(7)	1.7852(5)	0.6131(3)	0.083(2)
C14B	1.2032(6)	1.5640(6)	0.7149(3)	0.073(2)
C15B	1.1392(6)	1.4769(6)	0.7327(3)	0.074(2)
C16B	1.0715(5)	1.3677(5)	0.7532(3)	0.068(2)
C17B	0.9657(6)	1.3419(5)	0.7938(3)	0.073(2)
C18B	0.9036(5)	1.2364(5)	0.8135(3)	0.073(2)
C19B	0.9486(5)	1.1549(5)	0.7930(3)	0.068(2)
C20B	1.0531(6)	1.1785(5)	0.7527(3)	0.077(2)
C21B	1.1131(6)	1.2832(5)	0.7333(3)	0.077(2)
O22B	0.8972(4)	1.0475(4)	0.8096(2)	0.091(2)
C23B	0.7924(6)	1.0161(5)	0.8523(3)	0.081(2)
C24B	0.7411(6)	0.8914(5)	0.8488(3)	0.086(3)
C25B	0.6286(6)	0.8409(5)	0.8935(3)	0.076(2)
C26B	0.5694(6)	0.7150(5)	0.8808(3)	0.081(2)
C27B	0.4527(6)	0.6592(5)	0.9190(3)	0.078(2)
O28B	0.3761(4)	0.6990(3)	0.9374(2)	0.087(2)
O29B	0.4397(4)	0.5556(4)	0.9289(2)	0.086(2)
C30B	0.3292(6)	0.4883(5)	0.9636(3)	0.074(2)
C31B	0.2980(6)	0.3678(4)	0.9373(3)	0.074(2)
C32B	0.1871(5)	0.2912(4)	0.9742(3)	0.068(2)
C33B	0.2237(5)	0.3095(4)	1.0577(3)	0.055(2)
C34B	0.2699(5)	0.4333(4)	1.0844(3)	0.072(2)
C35B	0.3736(6)	0.5145(5)	1.0450(3)	0.084(2)
C36B	0.3447(5)	0.2773(5)	1.0832(3)	0.081(2)
C37B	0.0939(5)	0.2394(4)	1.0897(3)	0.060(2)
C38B	0.1083(5)	0.2776(4)	1.1705(3)	0.068(2)
C39B	0.1246(6)	0.3994(5)	1.1809(3)	0.086(2)
C40B	0.2241(6)	0.4705(5)	1.1391(3)	0.081(2)
C41B	0.0482(5)	0.1129(5)	1.0710(3)	0.073(2)
C42B	-0.0730(5)	0.0435(4)	1.1049(3)	0.071(2)
C43B	-0.0476(5)	0.0771(4)	1.1872(3)	0.060(2)
C44B	-0.0148(5)	0.2022(4)	1.1998(3)	0.070(2)
C45B	0.0717(5)	0.0495(5)	1.2247(3)	0.089(2)
C46B	-0.1723(5)	0.0309(5)	1.2259(3)	0.068(2)
C47B	-0.1267(6)	0.1172(5)	1.2955(3)	0.095(3)
C48B	-0.0177(7)	0.2276(5)	1.2805(3)	0.092(2)
C49B	-0.2291(5)	-0.0920(5)	1.2411(3)	0.076(2)
C50B	-0.2831(6)	-0.1751(5)	1.1713(3)	0.090(2)
C51B	-0.3395(6)	-0.1088(5)	1.2887(3)	0.083(2)
C52B	-0.4111(7)	-0.2285(6)	1.3045(3)	0.103(3)
C53B	-0.5173(6)	-0.2365(4)	1.3536(3)	0.100(3)
C54B	-0.6150(5)	-0.3564(4)	1.3591(3)	0.116(3)
C55B	-0.5374(9)	-0.4207(9)	1.3960(7)	0.155(6)
C56B	-0.7304(7)	-0.3591(8)	1.3999(4)	0.166(5)

$$*U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i \times a_j \times \mathbf{a}_i \cdot \mathbf{a}_j$$

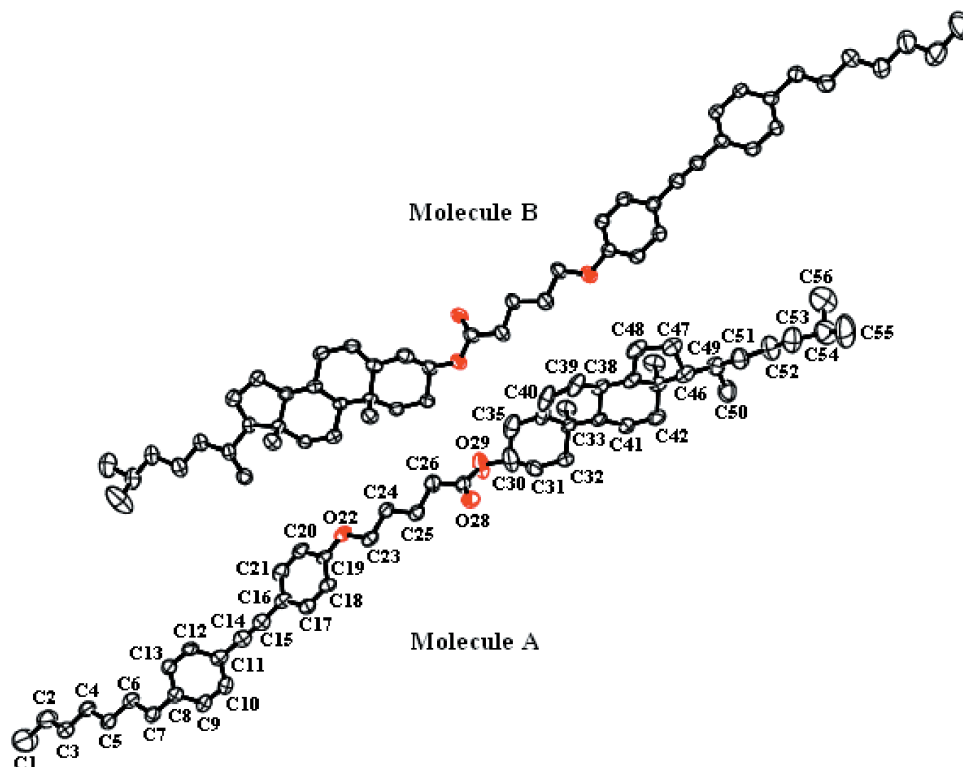


Figure 2. A view of the two independent molecules showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity.

1.383(7) Å for molecule B. For both molecules, the average observed bond angle in each of the two phenyl rings is 120.0(6)°. In both asymmetric molecules, the bond angles C10–C11–C12 and C17–C16–C21 are smaller than 120°, as was also observed in related compounds (9–11). The CO double bond (C27=O28) was found to be 1.173(6) Å (molecule A) and 1.201(6) Å (molecule B), whereas the CO single bonds were: molecule A 1.300(7) (C27–O29) and 1.454(9) Å (O29–C30); molecule B 1.338(6) (C27–O29) and 1.443(6) Å (O29–C30). In cholesteryl 4-[4-(4-*n*-butylphenylethynyl)phenoxy]butanoate (DTA-3,4), the respective bonds were found to be 1.167(8), 1.330(7) and 1.459(5) Å (9); in cholesteryl 4-[4-(4-*n*-hexylphenylethynyl)-phenoxy]butanoate (DTA-3,6), the respective bonds were: molecule A 1.163(9) Å (I), 1.295(8), 1.474(8) Å and molecule B 1.207(9) Å, 1.297(8), 1.447(7) Å (8); in cholesteryl 4-[4-(4-*n*-heptylphenylethynyl)phenoxy]butanoate (DTA-3,7), the respective bonds were found to be 1.186(8), 1.308(8) and 1.454(6) Å (11). The CC triple bond (C14–C15) was found to be 1.185(9) Å (molecule A) and 1.180(8) Å (molecule B) and the angles C11–C14–C15 and C14–C15–C16 were respectively, 177.7(6)° and 175.4(7)° in molecule A and 177.7(6)° and 174.7(6)° in molecule B. The corresponding observed values in DTA-3,4 are respectively, 1.201(5) Å, 177.2(4) and 175.8(4)°; in DTA-3,6, the respective values were:

molecule A 1.202(9) Å, 178.4(8), 178.0(8)° and molecule B 1.230(9) Å, 177.3(8), 172.6(8)°; in DTA-3,7, the respective values were 1.208(8) Å, 179.3(7), 178.7(7)°. The bond length C34–C40 [1.290(10) Å (A), 1.329(7) Å (B)] indicates the double bond nature.

In both the asymmetric molecules, A and B, the two phenyl rings A and B are independently planar (highest displacement, 0.013(7) Å for the atom C8A and 0.010(7) Å for the atom C9B). However, unlike DTA-3,7, the phenyl rings in DTA-4,7 are not coplanar. The dihedral angle between the two phenyl rings in DTA-3,7 is 2.2(2)° and in DTA-4,7, it is 43.4(2)° for molecule A and 42.7(2)° for molecule B. The dihedral angles between the planes of the fused rings of the cholesterol moiety and the phenyl rings A and B are respectively, 24.1(2)° and 67.1(2)° for molecule A and 4.5(2)° and 39.0(1)° for molecule B.

In molecule A, ring C has a chair conformation with asymmetry parameters ΔC_5 (C31) = 3.27, ΔC_2 (C30–C31) = 2.59 (16, 17). Ring D adopts a half-chair conformation with asymmetry parameter ΔC_2 (C37–C38) = 1.23. Ring E has a chair conformation with the best rotational axis bisecting C37–C41 and C43–C44 and asymmetry parameter, ΔC_2 (C35–C39) = 6.80. The best mirror plane passes through C37 and C43, with ΔC_5 (C37) = 2.12. Ring F is in a half-chair conformation [ΔC_2 (C43–C44) = 7.50].

In molecule B, ring C has a chair conformation with asymmetry parameters ΔC_s (C31) = 2.10, ΔC_2 (C30–C31) = 3.89. Ring D adopts a half-chair conformation [ΔC_2 (C37–C38) = 1.90]. Ring E has a chair conformation [ΔC_2 (C37–C41) = 5.56, ΔC_s (C37) = 1.68]. The five-membered ring F is in an envelope conformation [ΔC_s (C43) = 6.74]. The pseudo-torsion angles C36A–C33A–C43A–C45A = 8.1° in molecule A, C36B–C33B–C43B–C45B = 7.0° in molecule B provide a quantitative measure of the twist about the length of the cholesteryl ester moiety, and show that the cholesteryl moiety in both the independent molecules is not twisted to any significant degree and that the moiety is quite flat, rather than being folded.

Unit cell packing of symmetry-independent molecules is shown in Figure 3. From this figure it is evident that the asymmetric molecules in the unit cell are arranged in an antiparallel manner. Packing of DTA-4,7 molecules is shown in Figure 4. It is clear that the molecules have a distinct smectic-like structure composed of monolayers. The crystal structure is stabilised by the presence of intermolecular short contacts of the type C–H...O involving O28 of the ester group. Five

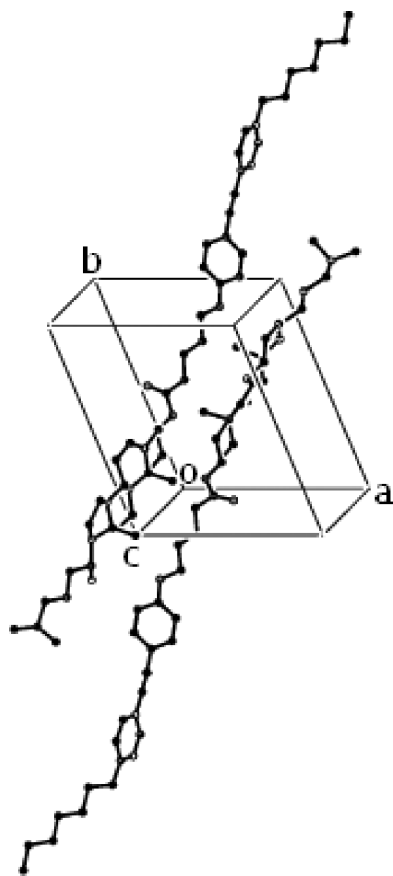


Figure 3. Packing of symmetry-independent molecules in the unit cell.

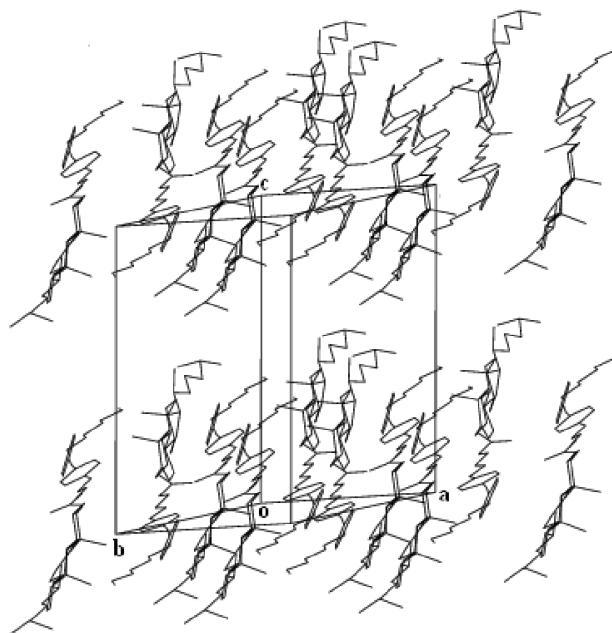


Figure 4. Crystal structure of DTA-4,7.

Table 3. Selected bond lengths (Å), bond angles (°) and torsion angles (°) (esds given in parentheses).

	Molecule A	Molecule B
Bond lengths		
C14–C15	1.185(9)	1.180(8)
C27–O28	1.173(6)	1.201(6)
C27–O29	1.300(7)	1.338(6)
O29–C30	1.454(9)	1.443(6)
C34–C40	1.290(10)	1.329(7)
Bond angles		
C10–C11–C12	116.1(6)	117.1(5)
C11–C14–C15	177.7(6)	177.7(6)
C14–C15–C16	175.4(7)	174.7(6)
C17–C16–C21	117.0(6)	117.4(5)
C44–C43–C46	100.0(4)	100.4(4)
C46–C43–C42	117.1(4)	117.6(4)
C48–C44–C43	104.8(5)	104.8(4)
C48–C44–C38	116.3(4)	118.0(4)
Torsion angles		
C46–C43–C44–C48	48.3(5)	46.4(4)
C43–C44–C48–C47	–35.9(5)	–31.6(5)
C46–C47–C48–C44	9.7(6)	4.7(6)
C43–C46–C47–C48	19.4(6)	23.3(5)
C44–C43–C46–C47	–40.2(5)	–41.7(4)

C–H... π interactions are also observed, which serve to link the molecules in the unit cell. Therefore, from this data it may be reasonable to assume that the dimers melt into a monolayered smectic A (SmA) phase; this presumption is supported by the general observation that the cholesterol-based non-symmetric dimers stabilise the monolayer SmA phase if the spacer length is less than the length of the terminal tail.

Table 4. C–H...O and C–H... π hydrogen bonding geometry. Cg3 and Cg4 represent the centre of gravity of the phenyl ring (A) in molecules A and B and Cg5 and Cg6 represent the centre of gravity of the phenyl ring (B) in molecules A and B, respectively.

D–H...A	D–H(Å)	D...A(Å)	H...A(Å)	D–H...A(°)
C9A– H9A...O28B ⁽ⁱ⁾	0.93	3.5027	2.60	165
C9B– H9B...O28A ⁽ⁱⁱ⁾	0.93	3.4972	2.58	168
C23A– H23B...O28B ⁽ⁱⁱⁱ⁾	0.97	3.3137	2.59	131
C5B–H52B...Cg6 ^{iv}	0.97	3.8839	3.0450	145.55
C40A– H40A...Cg5 ^{iv}	0.93	3.8776	2.9616	168.55
C31B– H31D...Cg6 ^v	0.97	3.7537	2.9505	140.92
C5A–H51A...Cg5 ^v	0.97	3.8174	3.0277	139.47
C46B– H46B...Cg3 ^{vi}	0.98	3.8999	2.9227	175.05

Symmetry code: (i) $-1+x, -2+y, z$; (ii) $1+x, 2+y, z$; (iii) $x, -1+y, z$; (iv) $1+x, 1+y, z$; (v) $-1+x, -1+y, z$; (vi) $x, 1+y, z$.

Supplementary material

CCDC-708336 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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