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Crystal structure of cholesteryl 5-(4′-(*n*-decyloxy)-2′,3′-difluoro-biphenyl-4-yloxy)pentanoate – a liquid crystalline non-symmetric dimer

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Cholesteryl 5-(4′-(*n*-decyloxy)-2′,3′-difluorobiphenyl-4-yloxy)pentanoate was found to crystallise in the triclinic space group *P*1 with unit cell parameters: $a=12.1282(4)$ Å, $b=14.2574(4)$ Å, $c=15.6294(5)$ Å, $\alpha=71.584(2)^\circ$, $\beta=79.929(2)^\circ$, $\gamma=77.645(2)^\circ$, $Z=2$. Three-dimensional X-ray intensity data were collected and the crystal structure solved by direct methods and refined by full-matrix least-squares procedures to a final *R*-value of 0.0383 for 5876 observed reflections. The asymmetric unit cell of the compound was found to contain two symmetry-independent molecules, A and B. In both the molecules, the six-membered rings of the cholesteryl moiety are conformationally very similar. However, pronounced differences are observed in the conformation of the five-membered ring, which is intermediate between half-chair and envelope in molecule A and assumes an envelope conformation in molecule B. In both the molecules, the phenyl rings are planar. The dihedral angle between the two phenyl rings is 36.3 and 38.9° for molecules A and B, respectively. The molecules in the unit cell are arranged in an antiparallel manner. The crystal structure is stabilized by intermolecular C–H…O, C–H…F and C–H…π interactions.

Keywords: twist grain boundary; cholesteryl derivative; crystal structure; dihedral angle; hydrogen bonding

1. Introduction

Recently, cholesterol-based oligomesogens have attracted much attention as a result of their rich and fascinating mesomorphic behaviour (*1–6*). In particular, non-symmetric dimers formed by covalently tethering a cholesteryl ester segment to an aromatic anisometric core via a central flexible spacer are in the limelight because they exhibit different kinds of frustrated fluid phases, such as blue (BP), twist grain boundary (TGB) and incommensurate smectic A (SmA_{ic}) phases (*2–6*). In addition, some of these stabilise technologically important SmA, chiral smectic C (SmC*) and chiral nematic (N*) phases over a wide thermal range (*2–6*). The occurrence of such complex fluid phases, especially the transient TGB phases, brings into doubt the purity of these dimers, given the fact that cholesterol-based compounds are sensitive to photochemical conditions and, thus, involve some fine impurities that are difficult to remove (*7*).

However, it is our and other research group's experimental experience (*2–6*) that cholesterol-based dimers are generally pure and reasonably stable. Indeed, such dimers are generally purified by repeated column chromatography and/or recrystallisation techniques; perhaps during this process the fine impurities are eliminated effectively. In order to demonstrate experimentally that dimers containing a cholesteryl segment are relatively free from impurities, we have been developing single crystals and subjecting them to X-ray diffraction analysis (*8*). In continuation of this work, in this paper we report the single crystal structure of cholesteryl 5-(4′-(*n*-decyloxy)-2′,3′-difluorobiphenyl-4-yloxy)pentanoate, a dimmer for which the molecular structure is shown in Figure 1. It should be noted that this dimer was prepared as described earlier and suitable single crystals were grown in a mixture of absolute ethanol/dichloromethane (9/1) (*3e*).

The phase sequence deduced for this dimer is, on heating, Cr 83.4°C (47.1 J g^{-1}) SmA 121°C (2.2 J g^{-1}) TGB-N* 121.7°C (0.7 J g^{-1}) I, and, on cooling, I 121.3°C (0.6 J g^{-1}) N*-TGB 120.4°C (2.2 J g^{-1}) SmA 65.9°C (42.4 J g^{-1}) Cr, where Cr, SmA, TGB, N* and I signify crystal, smectic A, twist grain boundary, chiral nematic and isotropic liquid phases, respectively. The sample, sandwiched between a pair of ordinary glass slides, when examined under polarising optical microscopy exhibited the characteristic focal-conic fan texture (which on shearing transforms into Grandjean planar texture composed of oily streaks) of the N* phase on cooling from the isotropic phase. On further cooling from the N* phase, the planar texture of the sample sharply changes to yield regions consisting of both focal-conic and pseudo-isotropic textures indicating the

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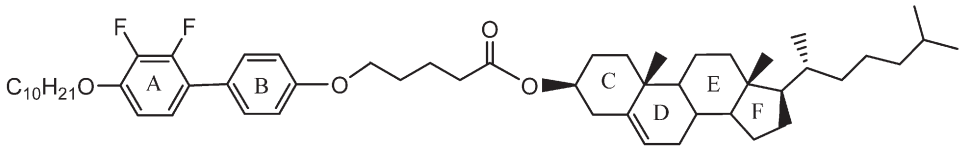

Figure 1. Chemical structure of cholesteryl 5-(4′-(*n*-decyloxy)-2′,3′-difluorobiphenyl-4-yloxy)pentanoate.

presence of the SmA phase. On very slow heating ($0.1^{\circ}C\,min^{-1}$) filaments grow steadily in the pseudo-isotropic regions of the SmA phase and quickly coalesce into the Grandjean planar texture. This indicates the occurrence of TGB phase over a short thermal range. As expected, the SmA–TGB and TGB–N* transitions were not resolved in the differential scanning calorimetry thermograms; hence, the enthalpy given in the phase sequence represents combined enthalpy for both SmA–TGB and TGB–N* transitions.

2. Experimental

X-ray intensity data of 24 222 reflections (of which 5876 were unique) were collected at room temperature using a Bruker CCD area-detector diffractometer equipped with graphite-monochromated Mo K_{α} radiation (λ=0.71073 Å). The structure was solved by direct methods using SHELXS97 software (*9*). All non-hydrogen atoms of the molecule were obtained from the E-map. Full-matrix least-squares refinement was carried out using SHELXL97 software (*9*). Hydrogen atoms were placed at geometrically fixed positions and allowed to ride on the corresponding non-H atoms with C–H=0.96–0.97 Å, and $U_{iso}=1.5U_{eq}$ of the attached C atom for methyl H atoms and $1.2U_{eq}$ for other H atoms. The final refinement cycles converged R=0.0383 and $wR(F^2)$=0.0984. The residual electron density in the final difference Fourier map ranges from −0.094 to 0.143e $Å^{-3}$. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). The crystallographic data are summarised in Table 1. CCDC-677850 contains the supplementary crystallographic data for this paper.

3. Results and discussion

The atomic coordinates and equivalent isotropic displacement parameters are presented in Table 2. Selected bond distances, bond angles and torsion angles are listed in Table 3. An ORTEP view of the independent molecules, with the atom labelling scheme, is shown in Figure 2 (*10*). The software used to prepare material for publication was SHELXL97 (*9*). The unit cell of the compound, which is asymmetric in this case, 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 (*11*), but none could be found.

The two independent molecules in the asymmetric unit are essentially identical, except for their torsion angles. A comparison of bond lengths and bond angles of the title compound with mesogenic non-symmetric dimers indicates a good agreement (*8*). The distance of the biphenyl bond (C15–C20) compares well with values usually observed for halogenated biphenyls (*12*). As in other biphenyl derivatives, the internal ring bond angle at C15 and C20 are considerably less than 120° and the adjacent angles are greater than 120° (Table 3). The biphenyl moiety displays non-planar behaviour. The dihedral

Table 1. Crystal data and other experimental details.

CCDC deposition No.	CCDC-677850
Crystal description	Colourless irregular
Crystal size	0.3 × 0.2 × 0.2 mm
Chemical formula	$C_{54}H_{80}F_2O_4$
Molecular weight	831.18
Radiation, wavelength	Mo K_{α}, 0.71073 Å
Cell parameters	a=12.1282(4), b=14.2574(4), c=15.6294(5) Å α=71.584(2), β=79.929(2), γ=77.645(2)°
Unit cell volume	2487.96(13) $Å^3$
Crystal system	Triclinic
Space group	$P1$
Density (calculated)	1.110 $Mg\,m^{-3}$
No. of molecules per unit cell, Z	2
Absorption coefficient (μ)	0.073 mm^{-1}
F(000)	908
θ range for entire data collection	1.74<θ<17.28°
Range of indices	h=−10 to 10, k=−11 to 11, l=−13 to 13
Reflections collected/Unique	24222/5876
No. of observed reflections	5202 [F_o>4σ (F_o)]
No. of parameters refined	1082
Refinement method	Full-matrix least-squares on F^2
Final R-factor	0.0383
$wR(F^2)$	0.0984
Weight	$1/[\sigma^2(F_o^2)+(0.0602P)^2+0.6569P]$ where $P=[F_o^2+2F_c^2]/3$
Goodness-of-fit on F^2	1.014
Final residual electron density	−0.094<$\Delta\rho$<0.143e $Å^{-3}$
$(\Delta/\sigma)_{max}$ in the final cycle	−0.074 [for y C58B]

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for non-hydrogen atoms (e.s.d.'s are given in parenthesis).

Atom	x	y	z	U_{eq}[a]
C1A	2.5276(9)	−1.8705(6)	0.7671(7)	0.166(4)
C2A	2.4230(7)	−1.8215(7)	0.7214(6)	0.127(3)
C3A	2.3960(6)	−1.7126(6)	0.7036(6)	0.104(2)
C4A	2.2990(7)	−1.6579(6)	0.6506(5)	0.096(2)
C5A	2.2625(6)	−1.5506(6)	0.6506(5)	0.081(2)
C6A	2.1637(6)	−1.4945(5)	0.5978(5)	0.080(2)
C7A	2.1194(6)	−1.3921(5)	0.6108(4)	0.0752(19)
C8A	2.0191(6)	−1.3339(6)	0.5616(4)	0.078(2)
C9A	1.9722(6)	−1.2354(5)	0.5821(4)	0.077(2)
C10A	1.8726(6)	−1.1788(7)	0.5323(4)	0.078(2)
O11A	1.8389(5)	−1.0838(5)	0.5489(3)	0.0810(14)
C12A	1.7477(8)	−1.0237(8)	0.5123(5)	0.062(2)
C13A	1.7184(8)	−0.9339(10)	0.5298(5)	0.070(2)
C14A	1.6251(9)	−0.8646(6)	0.4989(6)	0.066(2)
C15A	1.5526(8)	−0.8816(7)	0.4462(5)	0.065(2)
C16A	1.5849(7)	−0.9723(8)	0.4280(4)	0.0600(17)
C17A	1.6781(9)	−1.0414(6)	0.4587(5)	0.071(2)
F18A	1.7798(4)	−0.9077(3)	0.5820(3)	0.1022(13)
F19A	1.6032(3)	−0.7776(3)	0.5216(3)	0.0986(12)
C20A	1.4484(8)	−0.8111(7)	0.4180(4)	0.0609(18)
C21A	1.4390(8)	−0.7066(8)	0.3910(5)	0.0748(19)
C22A	1.3403(10)	−0.6452(6)	0.3673(4)	0.078(2)
C23A	1.2475(8)	−0.6870(9)	0.3670(4)	0.0668(19)
C24A	1.2548(8)	−0.7879(9)	0.3911(5)	0.070(2)
C25A	1.3529(10)	−0.8482(5)	0.4159(4)	0.0707(19)
O26A	1.1449(5)	−0.6306(5)	0.3429(3)	0.0871(14)
C27A	1.1237(6)	−0.5276(7)	0.3334(5)	0.086(2)
C28A	1.0078(7)	−0.4837(6)	0.3074(5)	0.090(2)
C29A	0.9715(7)	−0.3741(7)	0.3017(5)	0.098(2)
C30A	0.8582(7)	−0.3309(7)	0.2645(5)	0.098(2)
C31A	0.8079(7)	−0.2301(7)	0.2744(6)	0.091(2)
O32A	0.8179(4)	−0.1986(4)	0.3342(4)	0.1006(16)
O33A	0.7309(5)	−0.1818(4)	0.2140(3)	0.1087(17)
C34A	0.6594(8)	−0.0891(6)	0.2196(5)	0.099(2)
C35A	0.7156(6)	−0.0009(7)	0.1681(6)	0.109(3)
C36A	0.6354(7)	0.0970(5)	0.1638(5)	0.102(2)
C37A	0.5238(6)	0.1060(6)	0.1245(5)	0.0725(19)
C38A	0.4744(8)	0.0107(6)	0.1737(5)	0.075(2)
C39A	0.5517(7)	−0.0873(6)	0.1834(5)	0.101(2)
C40A	0.5515(6)	0.1092(5)	0.0232(4)	0.096(2)
C41A	0.4385(6)	0.1992(5)	0.1378(4)	0.0688(18)
C42A	0.3192(6)	0.1958(5)	0.1213(4)	0.0673(18)
C43A	0.2753(6)	0.1067(5)	0.1910(5)	0.086(2)
C44A	0.3638(9)	0.0140(6)	0.2051(5)	0.095(2)
C45A	0.4778(5)	0.2981(5)	0.0855(4)	0.0810(19)
C46A	0.3888(6)	0.3909(5)	0.0848(4)	0.082(2)
C47A	0.2773(6)	0.3852(5)	0.0551(4)	0.0643(17)
C48A	0.2386(6)	0.2913(5)	0.1211(4)	0.0717(19)
C49A	0.2998(5)	0.3797(5)	−0.0436(4)	0.088(2)
C50A	0.1751(6)	0.4663(5)	0.0677(4)	0.0742(19)
C51A	0.0706(5)	0.4141(6)	0.0779(5)	0.090(2)
C52A	0.1154(6)	0.3001(5)	0.1038(5)	0.093(2)
C53A	0.1601(6)	0.5692(6)	−0.0041(5)	0.095(2)
C54A	0.2600(7)	0.6226(6)	−0.0152(6)	0.150(3)
C55A	0.0488(7)	0.6365(6)	0.0126(6)	0.117(3)
C56A	0.0119(9)	0.7213(8)	−0.0715(6)	0.164(4)
C57A	−0.0925(8)	0.7877(8)	−0.0606(7)	0.149(4)
C58A	−0.1371(10)	0.8592(10)	−0.1432(11)	0.199(6)
C59A	−0.0586(14)	0.9090(10)	−0.2151(10)	0.213(8)
C60A	−0.2403(12)	0.9248(10)	−0.1146(9)	0.217(7)
C1B	0.4936(10)	0.6820(7)	0.1181(8)	0.173(5)

Table 2. (Continued)

Atom	*x*	*y*	*z*	U_{eq}[a]
C2B	0.5937(7)	0.6227(8)	0.1644(7)	0.148(3)
C3B	0.6117(8)	0.5146(7)	0.1729(6)	0.119(3)
C4B	0.7059(7)	0.4542(7)	0.2285(6)	0.108(3)
C5B	0.7354(7)	0.3455(6)	0.2287(5)	0.100(2)
C6B	0.8247(6)	0.2827(6)	0.2895(5)	0.086(2)
C7B	0.8621(6)	0.1771(6)	0.2830(5)	0.0755(19)
C8B	0.9574(5)	0.1166(6)	0.3381(4)	0.0714(19)
C9B	1.0008(6)	0.0154(6)	0.3267(5)	0.079(2)
C10B	1.0964(6)	−0.0430(6)	0.3786(4)	0.076(2)
O11B	1.1349(5)	−0.1360(5)	0.3595(3)	0.0817(13)
C12B	1.2315(8)	−0.1944(8)	0.3908(6)	0.072(2)
C13B	1.2724(10)	−0.2784(10)	0.3608(5)	0.070(2)
C14B	1.3678(10)	−0.3406(6)	0.3866(6)	0.070(2)
C15B	1.4339(8)	−0.3279(6)	0.4424(5)	0.0584(19)
C16B	1.3920(9)	−0.2446(8)	0.4732(4)	0.0749(19)
C17B	1.2926(9)	−0.1781(5)	0.4489(5)	0.0649(18)
F18B	1.2134(4)	−0.2952(3)	0.3025(3)	0.1185(15)
F19B	1.3991(4)	−0.4203(4)	0.3517(3)	0.1037(13)
C20B	1.5410(8)	−0.3959(7)	0.4681(4)	0.0570(18)
C21B	1.5561(7)	−0.4993(7)	0.4867(4)	0.0715(19)
C22B	1.6572(9)	−0.5610(6)	0.5129(4)	0.0733(19)
C23B	1.7468(9)	−0.5210(8)	0.5197(4)	0.0678(19)
C24B	1.7323(7)	−0.4184(8)	0.5008(5)	0.076(2)
C25B	1.6326(10)	−0.3566(5)	0.4753(4)	0.0701(19)
O26B	1.8494(5)	−0.5728(4)	0.5419(3)	0.0823(14)
C27B	1.8703(6)	−0.6791(6)	0.5543(4)	0.0737(19)
C28B	1.9886(6)	−0.7186(5)	0.5780(4)	0.077(2)
C29B	2.0274(6)	−0.8294(5)	0.5902(5)	0.082(2)
C30B	2.1405(6)	−0.8664(6)	0.6250(5)	0.082(2)
C31B	2.1997(7)	−0.9683(6)	0.6168(6)	0.071(2)
O32B	2.1788(4)	−1.0111(4)	0.5685(4)	0.0946(16)
O33B	2.2848(5)	−1.0010(4)	0.6673(3)	0.0859(14)
C34B	2.3657(6)	−1.0905(6)	0.6603(5)	0.0739(19)
C35B	2.4763(6)	−1.0788(5)	0.6834(5)	0.088(2)
C36B	2.5652(5)	−1.1723(5)	0.6891(4)	0.0763(19)
C37B	2.5286(6)	−1.2685(5)	0.7576(4)	0.0578(17)
C38B	2.4143(6)	−1.2752(6)	0.7352(4)	0.0641(18)
C39B	2.3242(6)	−1.1824(6)	0.7242(5)	0.080(2)
C40B	2.5136(5)	−1.2571(5)	0.8549(4)	0.0801(18)
C41B	2.6188(5)	−1.3590(5)	0.7477(4)	0.0589(17)
C42B	2.5735(6)	−1.4574(5)	0.7871(4)	0.0557(16)
C43B	2.4755(6)	−1.4541(5)	0.7369(4)	0.0703(18)
C44B	2.3944(5)	−1.3578(7)	0.7246(4)	0.0664(17)
C45B	2.7295(6)	−1.3638(5)	0.7832(5)	0.0805(19)
C46B	2.8181(5)	−1.4566(5)	0.7807(4)	0.080(2)
C47B	2.7716(5)	−1.5545(5)	0.8303(4)	0.0593(17)
C48B	2.6658(5)	−1.5454(5)	0.7844(4)	0.0614(17)
C49B	2.7387(5)	−1.5621(5)	0.9327(4)	0.086(2)
C50B	2.8430(6)	−1.6530(5)	0.8189(4)	0.0667(18)
C51B	2.7512(6)	−1.7202(5)	0.8340(4)	0.089(2)
C52B	2.6364(5)	−1.6496(5)	0.8174(4)	0.0731(18)
C53B	2.9426(6)	−1.7023(6)	0.8723(4)	0.0804(19)
C54B	3.0327(6)	−1.6381(6)	0.8491(5)	0.120(3)
C55B	2.9917(7)	−1.8049(7)	0.8632(6)	0.120(3)
C56B	3.0730(8)	−1.8667(8)	0.9325(8)	0.165(4)
C57B	3.1067(12)	−1.9710(9)	0.9437(11)	0.163(7)
C58B	3.1844(14)	−2.0370(9)	1.0121(10)	0.191(7)
C59B	3.1232(15)	−2.0928(12)	1.0956(10)	0.194(11)
C60B	3.3008(15)	−2.0507(18)	0.9695(13)	0.192(11)

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

Table 3. Selected bond lengths (Å), bond angles (°) and torsion angles (°) (e.s.d.'s are given in parentheses).

	Molecule A	Molecule B
Bond lengths		
C15–C20	1.474(9)	1.478(9)
C13–F18	1.373(8)	1.356(7)
C14–F19	1.356(7)	1.366(8)
C31–O32	1.192(8)	1.197(8)
C38–C44	1.341(8)	1.317(8)
Bond angles		
C13–C14–C15	122.5(7)	124.3(8)
C14–C15–C16	113.5(7)	113.7(7)
C15–C16–C17	123.9(6)	124.0(6)
C21–C20–C25	116.3(7)	116.6(6)
Torsion angles		
C16–C15–C20–C25	33.9(9)	−38.3(8)
C47–C50–C51–C52	19.2(6)	20.6(6)
C50–C51–C52–C48	8.1(7)	5.5(6)
C51–C52–C48–C47	−33.0(6)	−29.7(6)
C52–C48–C47–C50	45.3(6)	43.3(6)
C48–C47–C50–C51	−39.2(6)	−38.4(5)

angles between the rings of the biphenyl moiety are, for molecule A, 36.3(2)° and, for molecule B, 38.9(2)°. The distances between the F19 atom and an H atom geometrically placed on C21 are 2.465(4) Å (molecule A) and 2.443(4) Å (molecule B) (Table 3), indicating torsional strain on F19.

Whereas all three six-membered rings of the cholesteryl ester moiety in the four independent molecules possess the same conformation, the five-membered ring (F) conformation differs. In molecule A, ring C has a chair conformation with asymmetry parameters ΔC_s(C35)=1.26 and ΔC_2(C34–C35)=3.18 (*13, 14*). Ring D adopts a half-chair conformation with asymmetry parameter ΔC_2(C38–C44)=2.61. Ring E has a chair conformation with the best rotational axis bisecting C41–C45 and C47–C48 and asymmetry parameter ΔC_2(C41–C45)=6.84. The best

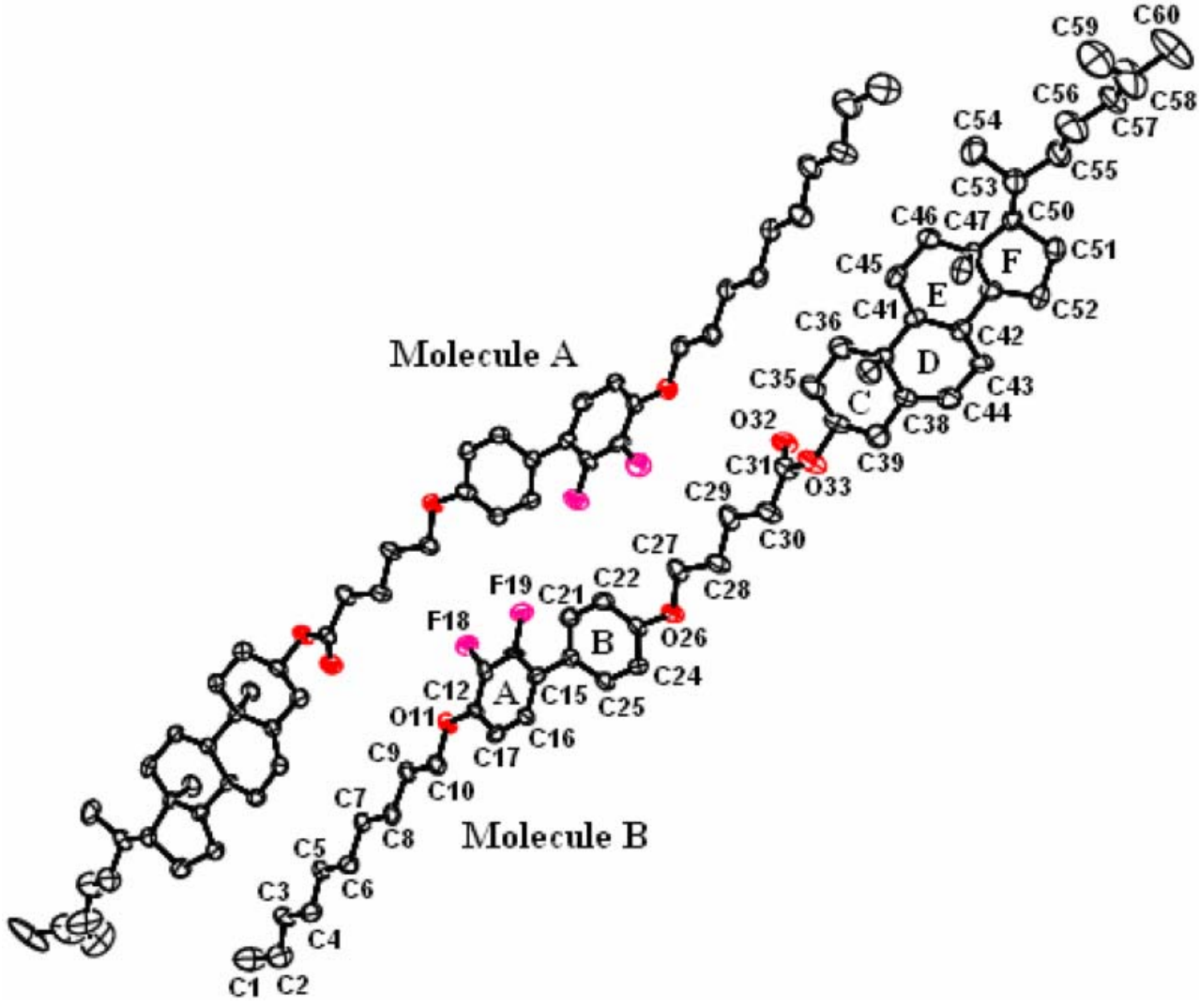

Figure 2. A view of the two independent molecules, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity.

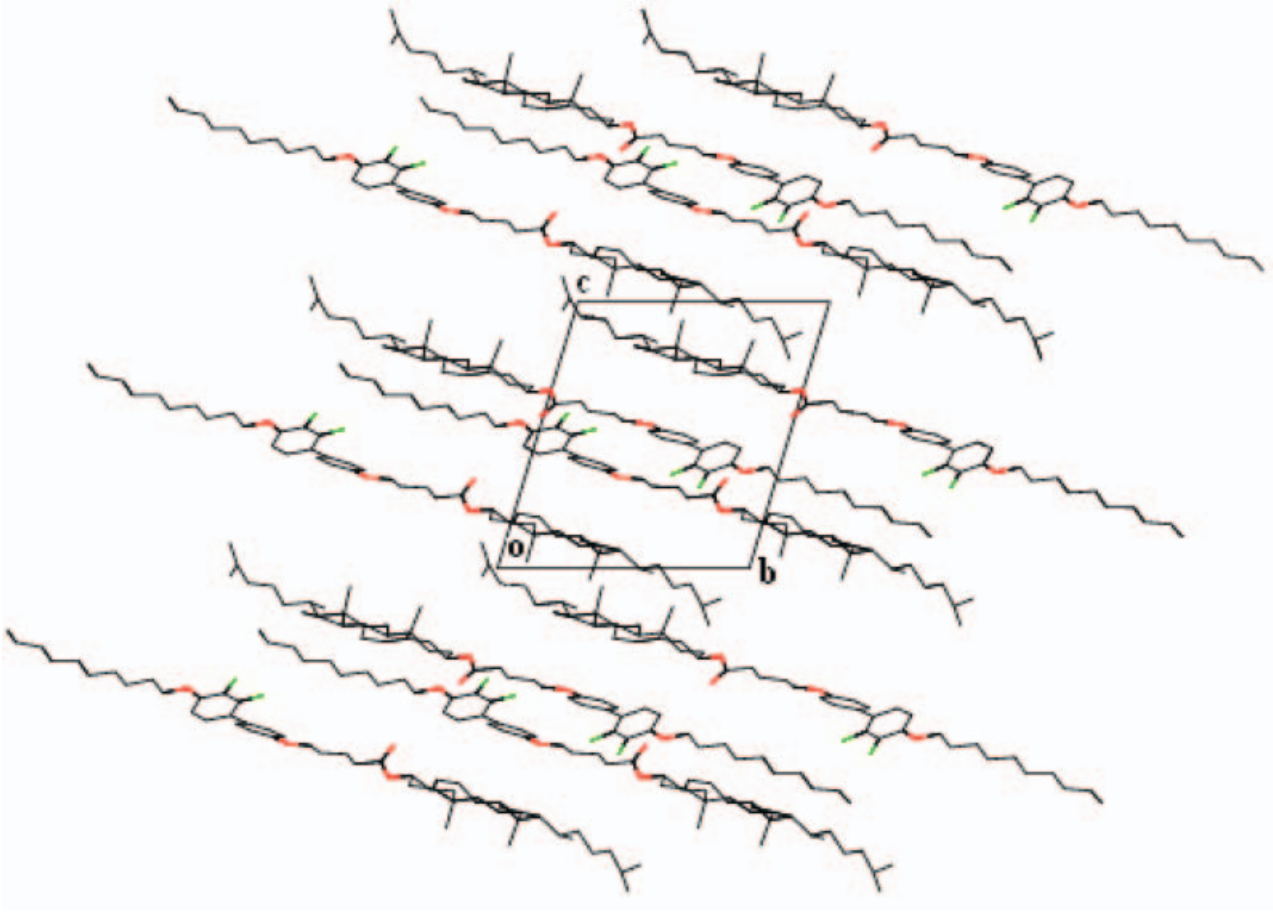

Figure 3. Packing of molecules in the unit cell.

mirror plane passes through C41 and C47, with ΔC_s(C41)=2.57. Ring F is intermediate between half-chair and envelope conformation [ΔC_s(C47)=10.67, ΔC_2(C47–C48)=8.99]. In molecule B, ring C has a chair conformation with asymmetry parameters ΔC_s (C35)=2.37, ΔC_2(C35–C36)=1.12. Ring D adopts half-chair conformation [ΔC_2(C38–C44)=3.39]. Ring E has a chair conformation [ΔC_2(C41–C45)=6.44, ΔC_s(C41)=2.04]. The five-membered ring F is in envelope conformation [ΔC_s(C47)=7.3].

The pseudo-torsion angles, C40A–C37A…C47A–C49A=−4.9° in molecule A, C40B–C37B…C47B–C49B=13.1° in molecule B, provide a quantitative measure of the twist about the length of the cholesteryl ester moiety. The pseudo-torsion angles show that the cholesteryl moiety in molecule A is not twisted to any significant degree and that the moiety is quite flat, rather than being folded, whereas in molecule B the cholesteryl moiety is slightly twisted.

Table 4. C–H…F, C–H…O and C–H…π hydrogen bonding geometry. Cg1 represents the centre of gravity of the phenyl ring (A) in molecule A and Cg2 represents the centre of gravity of the phenyl ring (A) in molecules B.

D–H…A	D–H (Å)	D…A (Å)	H…A (Å)	D–H…A (°)
C21A–H21A…F19A	0.93	2.900(10)	2.465(4)	108.7(5)
C21B–H21B…F19B	0.93	2.886(9)	2.443(4)	109.2(5)
C10A–H10A…O32A[i]	0.97	3.384(11)	2.591(7)	139.1(4)
C17B–H17B…O32B[ii]	0.93	3.402(10)	2.497(6)	164.4(5)
C35B–H35D…Cg1[iii]	0.93	3.683	2.820	148.5
C7B–H7D…Cg1[iv]	0.93	3.882	3.088	140.0
C7A–H7B…Cg2[v]	0.93	3.880	3.081	140.6
Symmetry:	(i) x+1, y−1, z	(ii) x−1, y+1, z	(iii) x−1, y, z	
	(iv) x−3, y+1, z	(v) x+3, y−1, z		

Packing of molecules in the unit cell is shown in Figure 3. Both the asymmetric molecules are extended and have almost the same molecular length (calculated lengths of molecules in the crystalline state are, for molecule A, 46.340 Å and, for molecule B, 46.015 Å). The crystal structure is stabilised by the presence of intermolecular short contact of the type C–H…O involving O32 of the ester group. Three C–H…π interactions are also observed, which serve to link the molecules in the unit cell. Details of C–H…F, C–H…O and C–H…π interactions are given in Table 4. Therefore, from this data it may be reasonable to assume that the dimers melt into a monolayered SmA phase; this presumption is supported by the general observation that the cholesterol-based non-symmetric dimers stabilise a monolayer SmA phase if the spacer length is less than the length of the terminal tail.

Supplementary material

CCDC-677850 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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