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BILAYERED SUPER-STRUCTURES OF ANTIFERROELECTRIC MESOGENS

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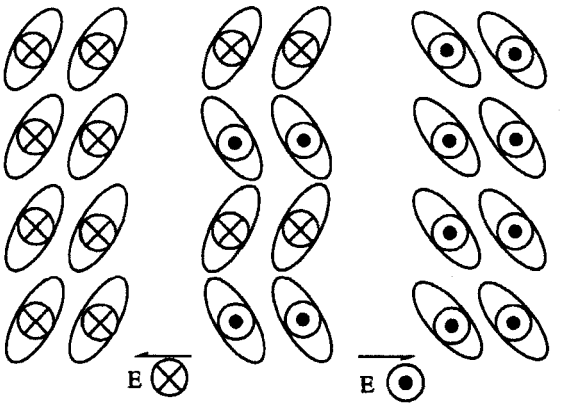
Abstract Crystal structures of two antiferroelectric mesogens, TFMHPBC and MHPBC-10, were analysed by an X-ray diffraction method. In both crystals, mesogen molecules formed a herringbone structure which was essentially the same as that proposed for the antiferroelectric liquid crystal phase. Because of the crystallographic 2_1-symmetry along the *b*-axis, only the *b*-axis component of the dipole moment remains in a smectic layer. Since the dipole moment in the next layer has the same magnitude but the opposite direction, both crystals show no dipole moment as a whole. These structural features observed in their crystal states seem to be conserved in their antiferroelectric liquid crystal phases which are just above their crystal phases.

INTRODUCTION

Antiferroelectric mesogens attract much attention not only from their application to flat-panel displays but also from the relationship between physical properties and their three-dimensional structures. After Fukuda's pioneering work,[1,2] many antiferroelectric liquid crystal (AFLC) compounds have been studied in many aspects, such as thermal behaviors, conoscopic observations, dielectric measurement and X-ray diffraction.[3] Based on these physico-chemical analyses, the structure of antiferroelectric liquid crystal phase was proposed to be one of the smectic C phases and called as antiferroelectric chiral smectic liquid crystal phase, SmCA* . In this phase, antiferroelectric molecules form either a helical structure in thick films or an unwound structure between substrates separated by several microns.[4] In the former case, dipole moments perpendicular to the helical axis are canceled within one helical pitch. On the other hand, in the latter case, the dipole moments in one layer are canceled by those in the adjacent layer in which they point to an opposite direction compared with those in the first layer because of the alternate molecular tilting from layer to layer (Figure1(b)). By applying electric field with the same direction as one of the alternate dipole moments in (b), the other dipole moment are forced to

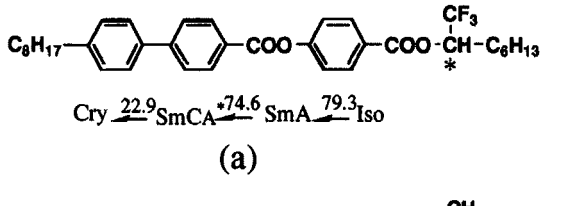
rearrange in the same direction which causes the ferroelectric liquid crystal (FLC) type arrangement (Figure1 (a)). By applying an opposite electric field, mesogen molecules will rearrange to form FLC type structure with the opposite direction of the dipole moment (Figure1 (c)). These three stable structures of AFLC mesogens can be used as a tristable electrooptic switching.



(a) (b) (c)

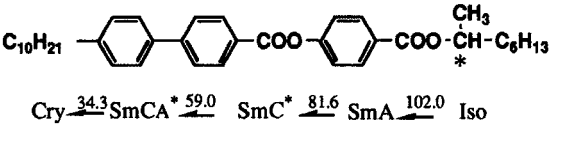
FIGURE 1 Tristable structures of antiferroelectric liquid crystal (AFLC). (a) and (c) are ferroelectric liquid crystal (FLC) state induced from (b) by applying electric field. (b) is a herringbone structure proposed for SmCA* phase in the unwound state. Ellipseuds represent mesogen molecules. The signs of a dot in a circle and a cross in a circle correspond to the direction of the net polarization going into and coming out of the plane of the figure, respectively.

For better understanding of SmCA* phase, single crystal structure analyses of several antiferroelectric mesogens have been performed.[5,6] However, no structural details about SmCA* phase were obtained. One of the reasons for this is the existence of the additional liquid crystal phase between the crystal phase and the SmCA* phase. Therefore, X-ray structural analyses of mesogens whose crystal phases are just below their SmCA* phases are most important for the structural study of the SmCA* phase from crystal structure analyses.



Cry $\overset{22.9}{\rightleftharpoons}$ SmCA* $\overset{74.6}{\rightleftharpoons}$ SmA $\overset{79.3}{\rightleftharpoons}$ Iso

(a)



Cry $\overset{34.3}{\rightleftharpoons}$ SmCA* $\overset{59.0}{\rightleftharpoons}$ SmC* $\overset{81.6}{\rightleftharpoons}$ SmA $\overset{102.0}{\rightleftharpoons}$ Iso

(b)

FIGURE 2 Chemical structures and their phase sequences of (a) TFMHPBC and (b) MHPBC-10. The values on arrows represent phase transition temperature(°C).

Recently, we succeeded crystallization of 4-(1-trifluoromethylheptyloxycarbonyl) phenyl 4'-octylbiphenyl-4-carboxylate (TFMHPBC) and 4-(1-methylheptyloxycarbonyl) phenyl 4'-dodecylbiphenyl-4-carboxylate (MHPBC-10) which have the SmCA* phase just above their crystal phases.[7] The packing structures of these compounds clearly showed geometrical features similar to those of the proposed structure for SmCA* phase. This is the first paper to clarify the three-dimensional

TABLE I Crystal data and details of experiment and analysis

	TFMHPBC	MHPBC-10
Empirical formula	$C_{36}H_{43}O_4F_3$	$C_{38}H_{50}O_4$
Formula weight	596.73	570.81
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a /Å	57.846(8)	70.9(2)
b /Å	5.5935(6)	5.75(2)
c /Å	10.227(1)	16.87(3)
Cell volume/Å^3	3309.0(6)	6880(36)
Z	4	8
Dx/g cm^{-3}	1.198	1.103
Dm/g cm^{-3}	1.18	1.10
Radiation	CuKα	CuKα
μ(calcd)/cm^{-1}	6.9	5.0
F(000)	1272.0	2480.0
Crystal dimensions/mm^3	0.1 x 0.2 x 0.8	0.01 x 0.5 x 0.7
Scan mode	2θ–ω	ω
Scan speed/°(in ω) min^{-1}	4.0	4.0
Scan width/°(in ω)	1.05 + 0.30 tanθ	1.45+0.30 tanθ
2θ range/°	2.5 - 120.2	1.2 - 120.1
No. of observed unique reflections	2,967	5,601
No. of reflections for R	1,537 (I>3σ(I))	3,526 (Fo>4σ(Fo))
R	0.053	0.089
Rw	0.076	-

structure closely related to the SmCA* phase at an atomic resolution.

EXPERIMENTAL

The chemical formulas of (R)-(+)-4-(1-trifluoromethylheptyloxycarbonyl) phenyl 4'-octylbiphenyl-4-carboxylate (hereafter abbreviated as TFMHPBC) and (R)-(+)-4-(1-methylheptyloxycarbonyl) phenyl 4'-dodecylbiphenyl-4-carboxylate (hereafter abbreviated as MHPBC-10) are shown in Figure 2 together with their phase sequences. Procedures for the preparation of analogous compounds were described elsewhere.[8]

The TFMHPBC (10 mg) was dissolved in a solution of ethanol (3 ml) and one drop of water (about 50 μl). The same amount of MHPBC-10 was dissolved in a solution of acetone (3ml) and two drops of water. In both cases, colorless platelet crystals were grown from the solution by the solvent-evaporation methods for about 2 weeks in a refrigerator at about 5°C. The density of this crystal was measured by a floatation method

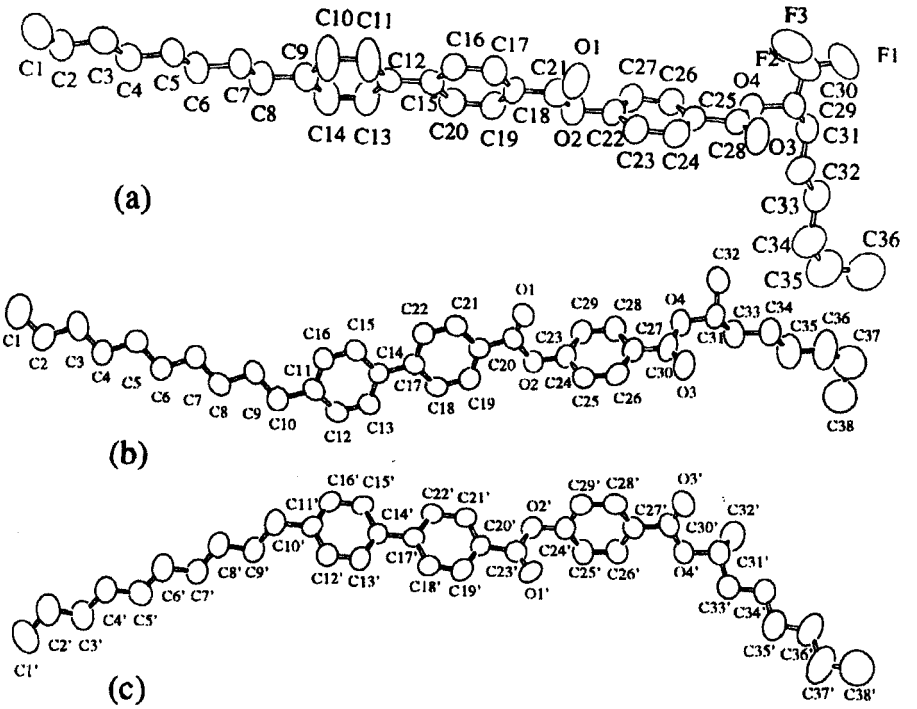


FIGURE 3 Molecular structures of TFMHPBC (a) and molecules A (b) and B (c) of MHPBC-10 with 50% probability thermal ellipsoids. Molecular structure of TFMHPBC was further analyzed by assuming statistical conformation for one of biphenyl benzene rings.

in an aqueous sodium chloride solution.

Lattice parameters and diffraction intensities were measured on a four-circle diffractometer (RASA 5RII, Rigaku Co.) with graphite monochromatized CuKα radiation (1.5418Å) from an X-ray generator (ROTA FLEX RU-200, Rigaku Co.). The lattice parameters were refined by the least-squares fit using 25 reflections in the 2θ range of 38.7°- 48.4° for TFMHPBC and 18 reflections in the 2θ range of 36.7°- 47.0° for MHPBC-10. Crystal data and experimental details are given in Table I. In both cases, three standard reflections, which were measured every 100 reflections, indicated no crystal decay. All intensities were corrected for the Lorentz and polarization effects.

Structure Determination and Refinement

Both structures were solved by direct methods[9] and expanded using Fourier techniques.[10] Non-hydrogen atoms were refined anisotropically and hydrogen atoms located at the calculated positions were refined isotropically. The quantity minimized in the refinement was

$\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$.

After several cycles of full-matrix least-squares refinement[11] of TFMHPBC, bond lengths and angles of one benzene ring in the biphenyl moiety showed unfavorable values. Furthermore, anisotropic temperature factors perpendicular to the benzene plane were fairly large compared with those in the plane (Figure 3(a)). The difference Fourier map calculated by using non-hydrogen atoms excluding six carbon atoms (C9, C10, C11, C12, C13, C14) in question showed eight peaks on the both sides of the previously occupied positions (C10, C11, C13, C14) and two peaks at C9 and C12 positions. Therefore, a statistical benzene model with two different orientation was considered. In this model, bond lengths and angles of benzene were fixed to the ideal values and only the gravimetric center position and orientation angles were refined. At the final refinement calculation, the unweighted and weighted agreement factors,

$$R = \sum \| Fo| - |Fc| \| / \sum |Fo| = 0.053$$

$$R_w = \sqrt{\sum w(|F_o| - |F_c|)^2 \ / \sum w F_o^2} = 0.076$$

were obtained. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.16 and -0.13 e/Å^3, respectively.

On the other hand, all benzene rings and bond lengths in several alkyl parts of MHPBC-10 molecule were found to deviate from the standard geometry after several refinement cycles. Therefore, all benzene rings were fixed to the standard geometry and alkyl parts in question were restrained to the desired values in the further refinement. At the final calculation R=0.089 was obtained. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and -0.41 e/Å^3, respectively.

Neutral atomic scattering factors were taken from International Tables for X-ray Crystallography.[12] All calculations were performed using the teXsan[13] crystallographic software package of Molecular Structure Corporation.

RESULTS AND DISCUSSION[14]

Molecular Conformation of TFMHPBC

The molecular structure and atom numbering scheme are given in Figure 3(a). All the bond lengths and angles are compatible with those of the related mesogens.[5] Alkyl chains in both ends have *trans* conformation with one exception of *gauche* for C33-C34-C35-C36. As mentioned already, one of the benzene rings in the biphenyl moiety had a statistical structure. That is, two benzene rings with half occupancies were found with twist angles

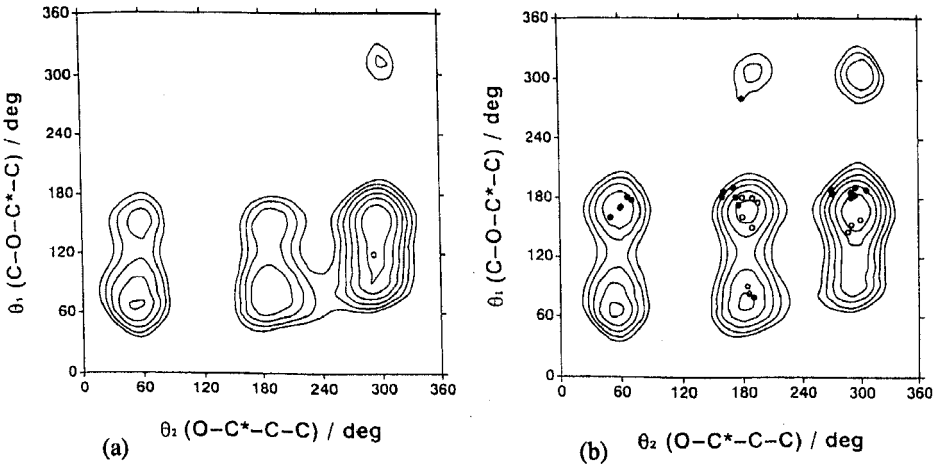


FIGURE 4 Conformational energy maps of (a) trifluoromethylheptylbenzoate and (b) methylheptylbenzoate. Contours drawn every 0.5kcal/mol show energy levels calculated by MM2. Filled and open circles in (b) represent methylethylbenzoate and methylheptylbenzoate moieties, respectively.

of ±10° from the other ring plane of the biphenyl moiety.

The most remarkable feature of this molecule is that the molecular chain bends at the chiral carbon atom by about 90°. This type of bend structure was also found in crystal structures of several antiferroelectric mesogens.[5,6,7] Since this bend structure is based on the *skew* and *-gauche* conformation of the dihedral angles at both sides of an asymmetric carbon atom (θ_1(C-O-C*-C) and θ_2(O-C*-C-C)), respectively, the conformational energy for trifluoromethylheptylbenzoate was calculated by changing θ_1 and θ_2 stepwisely with the step width of 5°. The obtained energy map was shown in Figure 4 (a). The θ_1 and θ_2 of TFMHPBC (θ_1=119°, θ_2=-68°) locate in the most stable and wide region in the map. The other two local minima have higher energy values by about 1 kcal/mole. Especially, the region corresponded to the *trans* conformation (θ_1=θ_2=180°) is 1.5 kcal higher than the bend structure. There are no other structure analyses for mesogens with trifluoromethylbenzoate moiety. Figure 4 (b) shows the conformational energy map of methylheptylbenzoate. In this case, five local minimums were observed with similar conformational energies. Crystal structures of mesogens with this chemical structure showed that they belongs to four different local minimums (open circles in Figure 4 (b)). Mesogens with related chemical structure (methylethylbenzoate) showed similar distribution in the map (filled circle). These results suggest that the bulkyness of the trifluoromethyl moiety favors the bend structure rather than the extended structure.

Molecular Structure of MHPBC-10

There are two molecules A and B in an asymmetric unit of MHPBC-10 crystal. The

molecular structures and atom numbering schemes are given in Figure 3 ((b) and (c)). Alkyl chains took *trans* conformation in both molecules with one exception of *-gauche* for C35-C36-C37-C38 in molecule A. The conformations at the chiral carbon atoms were different from that of TFMHPBC. The values of θ_1 and θ_2 are 93° and -175° in molecule A, and 153° and -170° in molecule B, respectively (Figure 4 (b)). Biphenyl moieties in molecules A and B are almost planar structures and twisted about ±70° from the phenyl moiety in the same molecule.

Packing Structures

Figure 5 shows stereo views of smectic layer structures of (a) TFMHPBC and (b) MHPBC-10. In the former crystal, molecules are inclined by about 50° to the smectic layer surface and in the latter, about 75°. The direction of inclination are alternately changed from layer to layer. Two such neighboring layers form one repeating unit along the *a*-direction. In a smectic layer molecules are arranged in an antiparallel fashion by the 2_1-symmetry along the *b*-axis. Because of the bend structure cited above, trifluoromethyl moieties are located on the surface of the smectic layer and close to those from the next layer.

In TFMHPBC crystal, some short atomic contacts were observed between adjacent molecules. These were F3---C36 3.32(2), O1---C27 3.48(1), O3---C31 3.33(1), O3---C32 3.40(1), C15---C14 3.49(1), C11'---C13' 3.36(1), C11'---C14' 3.38(1) and C10'---C14' 3.36(1)Å. Because of the statistical structure, there are two benzene rings with half-occupancies, (C9, C10, C11, C12,C13 and C14) and (C9', C10', C11', C12',C13' and C14'). Compared with the van der Waals distance of 3.55Å between aromatic carbon atoms, the latter four contacts are very short. Since these contacts occured between carbon atoms belonged to one of the statistical benzene rings in the adjacent molecule, they can be avoided if molecules are packed along the *c*-axis so that two statistical benzene rings are arranged alternately. This might be the reason for the statistical structure of benzene ring in the biphenyl moiety of this compound.

No short atomic contacts were observed in MHPBC-10 crystal. One of the structural features in this crystal is that A and B molecules in an asymmetric unit has a slightly different conformations (Figure 3 (b) and (c)) and make a pair in a parallel fashion. These pairs make a smectic layer by the 2_1-symmetry along the *b*-axis.

The dipole moment (D) of TFMHPBC and MHPBC-10 molecules were calculated by MM3 for the obtained molecular conformations (D=4.24 for TFMHPBC and 3.01 for A and B molecules of MHPBC-10). Because of the crystallographic 2_1-symmetry at the center of a smectic layer, only one component of the dipole moment along the *b*-axis (Db) remains and the other two components perpendicular to this axis become zero (Figure 6). Since the adjacent smectic layers are related by the other 2_1-symmetry along the *a*- or *c*-

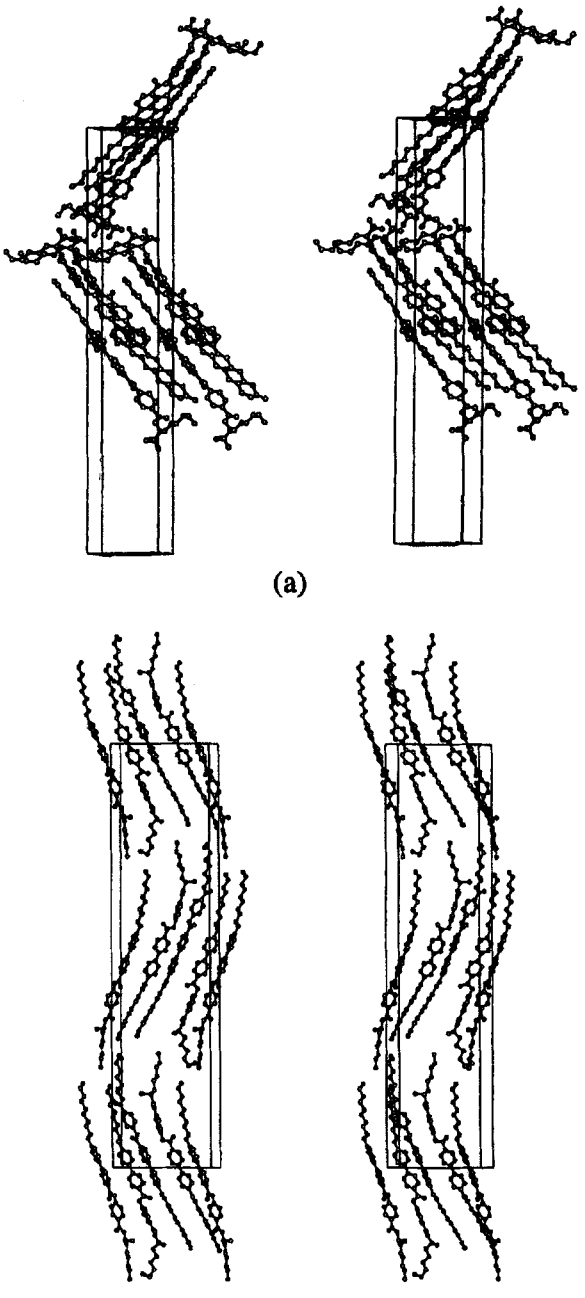


FIGURE 5 Stereoscopic views[15] of (a) TFMHPBC and (b) MHPBC. Two statistical benzene rings were drawn in (a).

axis, the dipole moment in the neighboring layer has the same value but the opposite direction. As a whole, both crystals show no dipole moment. These structural features in

crystal state seem to be conserved in SmCA* phase.

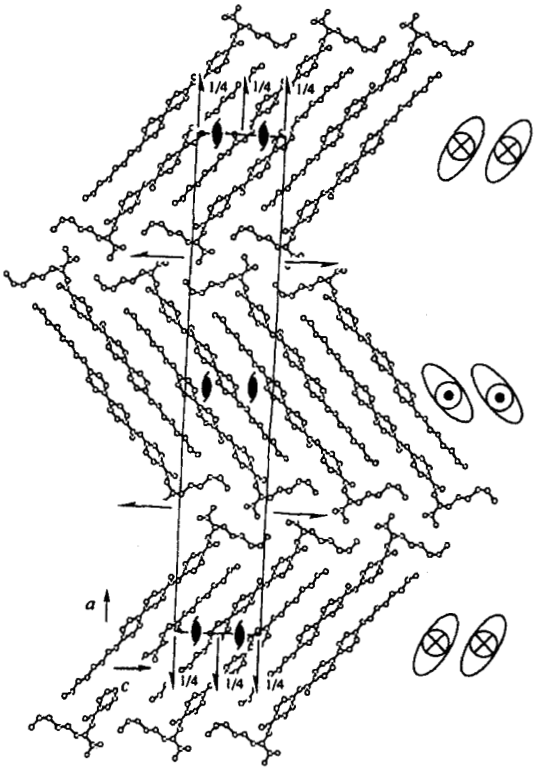


FIGURE 6 Herringbone structure of TFMHPBC, together with schematic illustration of bilayered super-structure.

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