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Evidence of the smectic antiphase $\tilde{C}$ in 4-decyloxybiphenyl ester imide derivatives

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The series of liquid crystalline 4-[(4′-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide alkane acid methyl esters has been synthesized and studied by DSC, polarized optical microscopy and X-ray diffraction methods. All compounds form a monolayer smectic A phase. It was found that 2-{4-[(4′-decyloxybiphenyl-4-yl)oxycarbonyl]-phthalimido}propanoic acid methyl ester and 4-[(4′-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimidoacetic acid methyl ester also form a ribbon $S_{\tilde{C}}$ phase. It was shown clearly that in the former compound, transition from the S_{A_1} to $S_{\tilde{C}}$ phase occurs *via* an intermediate S_{C_1} phase. The 6-{4-[(4′-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimido}-hexanoic acid methyl ester exhibits smectic A_1 and C_1 phases only.

Since the first observation in 1979 of phase transitions between two optically identical smectic A phases,[1] the study of thermotropic liquid crystals has revealed a considerable variety of smectic phases with liquid-like in-plane order.[2]

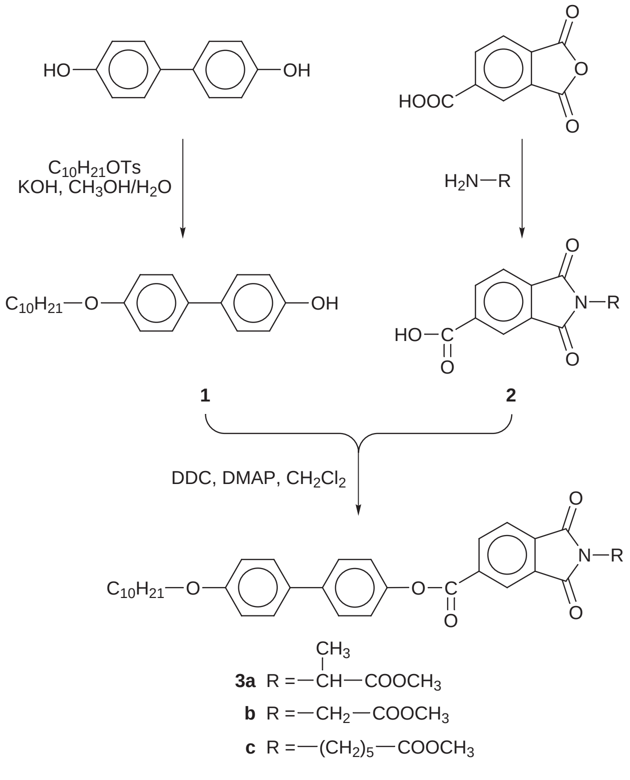
In a conventional smectic A_1 phase, rod-like molecules are randomly oriented up and down within each layer. The order can be described by one-dimensional mass density modulation in the direction of the layer normal. Smectic A polymorphism is typically observed in molecules with long (three ring) aromatic cores and a polar head which introduces longitudinal molecular dipoles. In such a system, the formation of antiferroelectric pairs becomes energetically favourable and this can induce a one-dimensional polarization modulation. Thus there are two competing lengths L and L' simultaneously present at the molecular level: the steric length of a molecule L and a favourable dipole–dipole nearest-neighbour pair interaction length L' ($L \leqslant L' \leqslant 2L$). The frustration arising from two preferred length scales leads to three kinds of smectic A phases: a monolayer smectic A_1 with layer thickness $d = L$, a bilayer smectic A_2 with $d = 2L$ and a partial bilayer smectic A_d with $L \leqslant d \leqslant 2L$.

An alternative compromise between these competing periodicities is to form one of the two dimensional modulated phases such as antiphase $S_{\tilde{A}}$ and ribbon phase $S_{\tilde{C}}$. Locally they are very similar to bilayer or partial bilayer S_A phases, but the location of the polar heads undulates with respect to the monolayers. The structure of the ribbon $S_{\tilde{C}}$ phase possesses a local bilayer arrangement, but the planes of equal dipolar density form an angle with those of equal mass density. Furthermore, molecules are tilted with respect to both patterns. Prost and co-workers[3] have developed a phenomenological Landau model for frustrated smectic phases. This model very successfully explains the smectic polymorphism.

Although the frustrated smectic phases have been most thoroughly studied in strongly polar mesogens, and these effects have been discussed in terms of antiparallel pairing of dipolar molecules, modulated phases were also detected for non-polar polymeric mesogens[4,5] and mesogens with a fluorinated terminal chain.[6] In fact, both the polar and steric asymmetry of the constituent molecules prove to be important.

In our previous paper,[7] it was found that ester imide rings connected with cholesteric groups show a tendency to form chiral nematic phases. Studies of the liquid crystalline properties of dimeric[8] and monomeric[9] compounds comprising a cholesteryl ester imide group reveal that the compounds form chiral nematic and smectic A or C phases. It has been found that cholesteryl ester imides with oxyethylene tails form chiral nematic N* phases and bilayer chiral smectic C_2* phases. Such bimolecular arrangement for compounds without strong polar (cyano or nitro) terminal groups seems to be a consequence of the fine balance between repulsive steric forces and attractive forces from localized or distributed dipoles of the ester imide group and oxyethylene tail.

In the present study, the cholesteryl group has been replaced



Scheme 1 Synthesis of 4-[(4′-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide alkane acid methyl esters.

by a mesogenic biphenyl one and a series of 4-[(4′-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide alkane acid methyl esters has been synthesized (see Scheme 1). In order to introduce chirality into the mesogenic molecule, an L-alanine methyl ester moiety was used in **3a**. Racemic compound **3a** was studied as well. Our X-ray investigation revealed the occurrence of a modulated smectic $S_{\tilde{C}}$ phase for both the enantiomer and racemate. To clarify the role of chirality in the formation of the frustrated smectic $\tilde{C}$ phase, a glycine methyl ester moiety was used in **3b**.

Additionally, compound **3c**, in which the polar ester group was separated from the polar imide group by a $(CH_2)_5$ nonpolar fragment, was synthesized.

Experimental

Instrumentation

The structures of products were confirmed by elemental analysis and ^{1}H NMR spectroscopy. The NMR spectra were obtained on a Varian Gemini 200 MHz spectrometer. Thermal studies were made by differential scanning calorimetry (DSC). DSC measurements were carried out at a rate of 5 °C min^{-1} using a Perkin-Elmer 7 calorimeter. The transition temperatures, taken from DSC heating traces, were taken as corresponding to the onset points of enthalpic peaks. The textures of the mesophases were studied using a polarizing microscope BIOLAR PI equipped with a hot stage. The X-ray diffraction patterns were obtained from samples oriented in a magnetic field of *ca.* 1.5 T with an X-ray beam perpendicular to the field direction using a flat camera with monochromatic Cu-Kα radiation. The interlayer smectic distances were measured using a Guinier camera equipped with a bent quartz monochromator (Co-Kα).

Synthesis

All chemicals used were analytical grade commercial products (Aldrich) and were used without further purification.

Synthesis of 4-decyloxy- 4′-hydroxybiphenyl 1

4-Decyloxy-4′-hydroxybiphenyl was obtained from 4,4′-dihydroxybiphenyl and decyl tosylate according to the synthesis of 4-(10-undecenyloxy)-4′-hydroxybiphenyl described by Perček and Heck.[10] The crude product was crystallized twice from methanol and then from toluene. The structure checked by IR and ^{1}H NMR spectroscopy was in agreement with those postulated for the product. Yield 25%, mp 151 °C (lit., [11]149 °C).

Synthesis of 2a–c

Stoichiometric amounts (0.05 mol) of benzene-1,2,4-tricarboxylic anhydride (trimellitic anhydride), pyridine and L- or DL-alanine methyl ester hydrochloride (compound **2a**), glycine methyl ester hydrochloride (compound **2b**) or 6-aminohexanoic acid methyl ester hydrochloride (compound **2c**) were dissolved in 50 ml of DMF and refluxed for 4 h. The mixtures were then diluted with 5% HCl and cooled. In the case of **2a** the crude products were purified by column chromatography (SiO_2) using $CHCl_3$–MeOH (5 : 1) as eluent. Yield 2.5 g (20%); mp 138–140 °C for the L-enantiomer and racemate.

Crude products **2b** and **2c** were crystallized from methanol–water. **2b** (71%), mp 176–8 °C; **2c** (65%), mp 125 °C.

Synthesis of 3a–c

To 0.001 mol of *N*-substituted trimellitimides **2a**, **2b** or **2c**, 0.310 g (0.001 mol) of **1** in 25 cm^3 of dry CH_2Cl_2, 0.230 g (0.0011 mol) of *N*,*N*-dicyclohexylcarbodiimide and a catalytic amount of 4-dimethylaminopyridine were added. The reaction mixture was stirred for 24 h, then *N*,*N*-dicyclohexylurea was filtered off and, after removal of the solvent, crude products were crystallized from methanol and next purified by column chromatography (SiO_2) using $CHCl_3$–ethyl acetate (3 : 1) as eluent. Yields *ca.* 20%; $[\alpha]_D^{20}$ −10.03 for L-**3a**.

For **3a**: δ_H 0.88 (t, CH_3), 1.28 [m, $(CH_2)_7$], 1.74 (d, CH_3), 1.80 (m, CH_2), 3.77 (s, OCH_3), 4.00 (t, OCH_2), 5.03 (q, CH), 6.95–8.70 (m, ArH).

For **3b**: δ_H 0.88 (t, CH_3), 1.28 [m, $(CH_2)_7$], 1.80 (m, CH_2), 3.79 (s, OCH_3), 4.00 (t, OCH_2), 4.50 (s, NCH_2), 6.95–8.70 (m, ArH).

For **3c**: δ_H 0.88 (t, CH_3), 1.28–1.85 [m, $(CH_2)_8$, $(CH_2)_3$], 2.32 (t, $CH_2C{=}O$) 3.66 (s, OCH_3), 3.73 (t, NCH_2), 4.00 (t, OCH_2), 6.95–8.70 (m, ArH).

Results and discussion

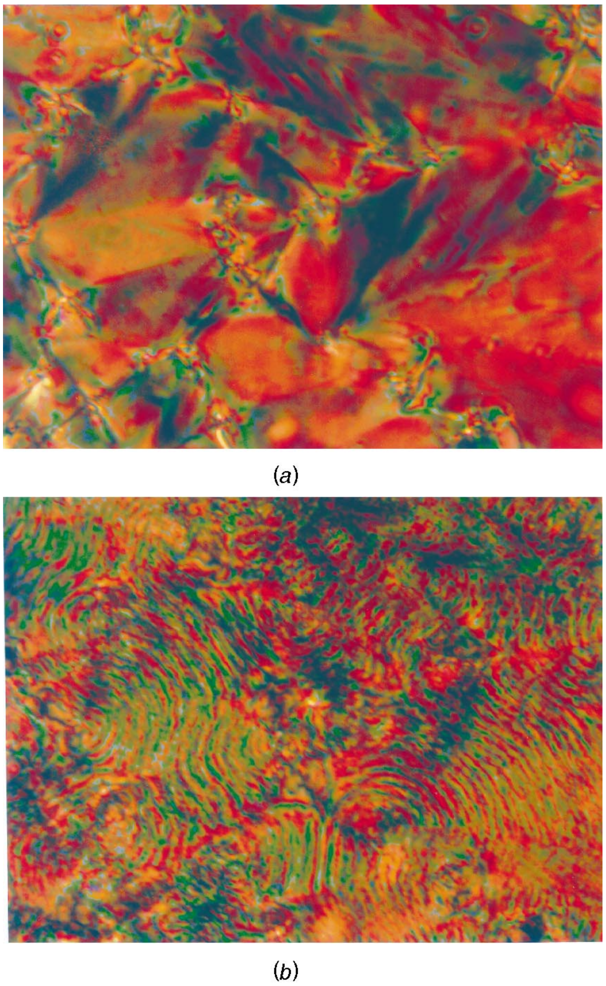
The phase sequence and phase transition temperatures, as well as relevant heat effects, for compounds **3a–c** are given in Table 1. Our microscopic observations reveal that all compounds form a smectic A phase. On cooling from the isotropic melt, a focal conic texture typical of a smectic A phase was observed [Fig. 1(*a*)]. The smectic A phase was assigned as A_1 for all compounds from its characteristic X-ray pattern which exhibits, in the reciprocal space, a sharp peak $q_0 = 2\pi/d_1$ ($d_1 \approx L$) along the layer normal and a diffuse halo in the perpendicular direction at $q_\perp \approx 2\pi/4.5$ Å. On cooling from the smectic A phase, the schlieren texture characteristic of a smectic C phase was observed for all investigated compounds (Fig. 2). Moreover, the L-enantiomer of compound **3a** also exhibits a striated focal conic texture typical of a chiral smectic C* phase [Fig. 1(*b*)]. It was found from the X-ray measurements of the interlayer distance that the smectic C phase obtained on cooling compounds **3a** and **3c** from the S_{A_1} phase is a monolayer C_1 one. The thickness of the smectic layers in **3a** and **3c** decreases with decreasing temperature, which corresponds to an increase in the tilt angle of the director with respect to the smectic layer plane. The tilt angle for racemate of **3a** is equal to 18° at 100 °C.

As can be seen in Fig. 3, in both the racemate and L-enantiomer of **3a** below the smectic C_1 phase, a small enthalpy peak is observed which indicates the existence of an additional liquid crystalline phase. The X-ray measurements of the powder sample of compound **3a** using a Guinier camera reveals (at 89 °C for the racemate), two quasi-Bragg peaks with $q_0 = 2\pi/d_1$ ($d_1 = 31.1$ Å) and $q_1 = 2\pi/L'$ ($L' = 46.3$ Å, $L' = 1.4\ L$). The existence of two sharp diffraction peaks at q_0 and q_1 (the ratio q_0/q_1 being irrational) may be indicative of a one-dimensional incommensurate A_{inc} phase for the asymmetric molecules. Moreover, Prost and Barois[3] have predicted the commensurate antiphases ($\tilde{A}$ and $\tilde{C}$) identified by appearance of off-longitudinal axis reflections, indicative of additional translational order in the plane of the layers. The X-ray diffraction pattern obtained for the magnetically oriented racemic sample of compound **3a** shows such off-axis reflections. In the centre of the region of the S_{A_1} phase at 116 °C, the condensed quasi-Bragg peak was located at $\boldsymbol{q}_0 = (0,\ 0,\ 0.190)$ Å^{-1} [Fig. 4(*a*)], which corresponds to $L = 33.1$ Å and is comparable to the calculated (Hyperchem program) length of the molecule in its most extended conformation (33.3 Å). When the temperature was decreased, the peak $\boldsymbol{q}_0$ changed its position to off-axis [$\boldsymbol{q}_0 = (0.05,\ 0,\ 0.190)$ Å^{-1} at 98 °C] [Fig. 4(*b*)]. Below 95 °C, the smectic layer undulations became evident as two off-axis $\boldsymbol{q}_1{}'$ and $\boldsymbol{q}_2{}'$ peaks. They are equal to $(\pm 0.08,\ 0,\ 0.118)$ Å^{-1} at 85 °C [Fig. 4(*c*)]. This fact, together with the microscopic observation of schlieren-like texture [see Fig. 2(*b*)] leads to the conclusion that compound **3a** forms a ribbon phase $\tilde{C}$. The projections of the incommensurate wave vector $\boldsymbol{q}_1{}'$ parallel and perpendicular to the smectic layer normal were $q_1{}'\cos\alpha$ and $q_1{}'\sin\alpha$ respectively, where α is the

Table 1 Phase transition temperatures (°C) and enthalpies (kJ mol^{-1}) (in italic) for 4-[(4′-decyloxybiphenyl-4-yl)oxycarbonyl]phthalimide alkane acid methyl esters^a

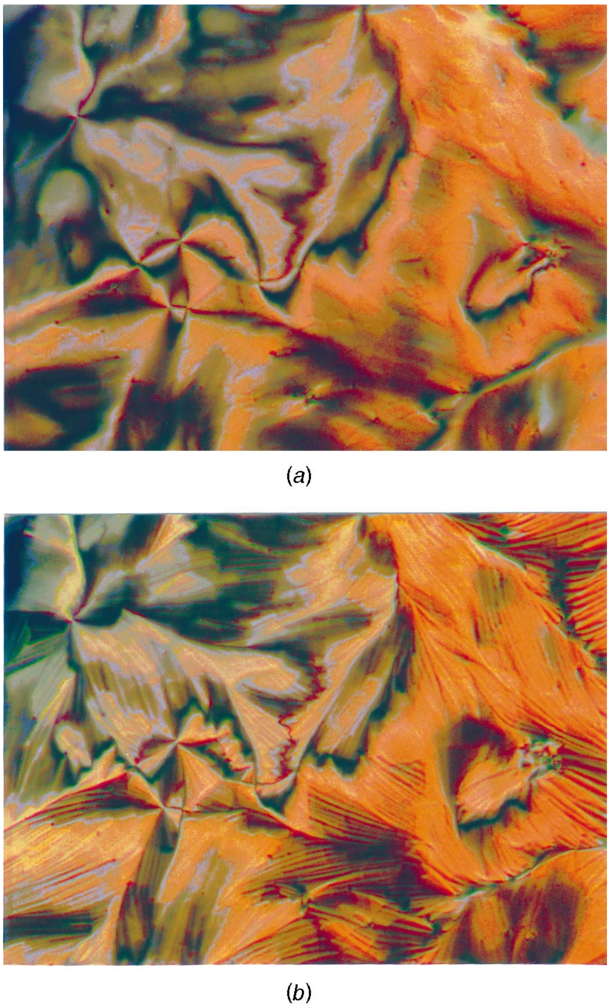
Compound	Cr 1		Cr 2		$\tilde{C}$		C_1		A_1		Iso
3a (L-isomer)	•	66.3 *15.56*	•	89.2 *7.48*	•	[84.5] *0.15*	•	103.5 *0.28*	•	120.2 *4.53*	•
3a (racemate)	•	71.6 *16.26*	•	100.7 *5.06*	•	[95.2] *0.07*	•	105.0 *0.55*	•	120.7 *4.58*	•
3b	•	63.5 *10.25*	•	114.0 *22.23*	•	[90.1] *14.3*	—		•	155.4 *4.92*	•
3c	•	130.3 *51.39*	—		—		•	136.6 *0.17*	•	154.5 *6.03*	•

^{a}Square brackets indicate a monotropic transition.


(*a*)

(*b*)

Fig. 1 Microphotographs of compound **3a** (enantiomer): (*a*) the focal-conic fan texture of the smectic A phase at 118 °C and (*b*) the chiral smectic C* texture at 94 °C [same area as (*a*)].


(*a*)

(*b*)

Fig. 2 Microphotographs of compound **3a** (enantiomer): (*a*) the schlieren texture of the smectic C_1 phase at 98 °C and (*b*) the schlieren like texture of the smectic $\tilde{C}$ phase at 82 °C [same area as (*a*)].

angle between the $\boldsymbol{q}_0$ and $\boldsymbol{q}_1'$ vectors. At 95 °C, $\alpha = 23°$ and the period of the antiphase modulation in the smectic plane was $2\pi/(q'_1 \sin\alpha) = 113$ Å, which increases with decreasing temperature.

The effect of the degree of optical purity on the liquid crystal transition temperatures can be seen in Table 1 and the differential scanning thermograms (Fig. 3). The C_1–A_1 and A_1–Iso phase transition temperatures do not differ meaningfully when the optical purity is raised from zero for the racemate to about 100% for the L-enantiomer (commercially available L-alanine methyl ester had optical purity of about 100%). However, the temperature of the C_1–$\tilde{C}$ phase transition for the racemate is *ca.* 10 °C higher than for the L-enantiomer. Such an effect may be evidence of pronounced chiral discrimination.[12]

The modulated smectic $\tilde{A}$ and $\tilde{C}$ phases in low molar systems have been observed mainly in compounds with NO_2 or CN terminal groups (see ref. 13–16 for examples). In such compounds (or their mixtures) the ribbon $\tilde{C}$ phase has been formed upon cooling from the smectic A_1 phase. The existence of the smectic C phase between the S_{A_1} and $S_{\tilde{C}}$ phase was deduced for DB_9ONO_2 compound[14] from X-ray scattering measurements. Our X-ray, calorimetric and microscopic observations have shown clearly that, in compound **3a** with an asymmetric carbon atom, transition from the S_{A_1} to $S_{\tilde{C}}$ phase occurs *via* an intermediate S_{C_1} phase.

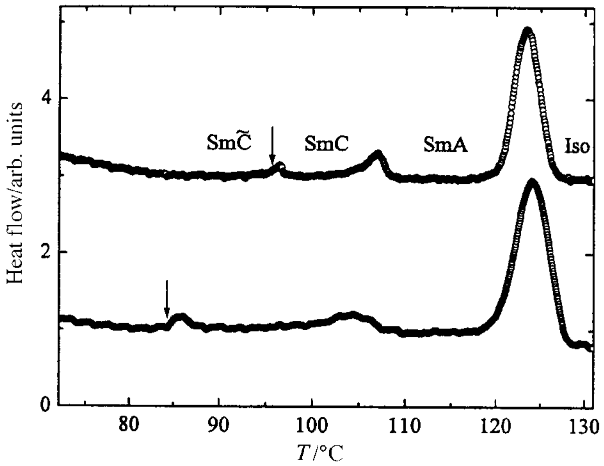


Fig. 3 Differential scanning calorimetry traces for heating scans of the racemate (upper trace) and the L-enantiomer (lower trace) of compound **3a**.

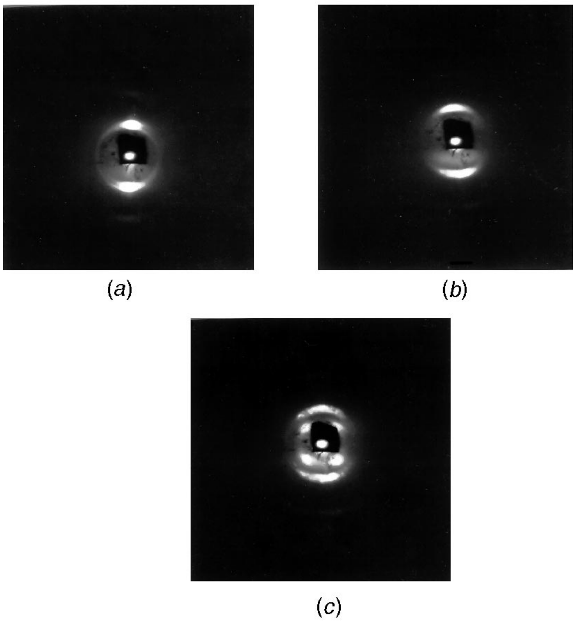

(*a*)
(*b*)
(*c*)

Fig. 4 Small angle X-ray diffraction patterns of a magnetically ordered sample of racemic compound **3a**: (*a*) the smectic A_1 phase at 118 °C, (*b*) the smectic C_1 phase at 98 °C and (*c*) the smectic $\tilde{C}$ phase at 83 °C. The direction of the magnetic field is vertical.

The intermediate smectic C_1 phase was not observed for compound **3b**, which lacks an asymmetric carbon atom. As can be seen from Table 1, the transition temperature to the isotropic phase is higher for compound **3b** than for **3a** with an asymmetric carbon atom. The X-ray investigation of a magnetically ordered sample of **3b** indicated the presence of a ribbon smectic $\tilde{C}$ phase with almost the same vectors q_0, q_1' and q_2' as were observed for compound **3a**. Thus, this is evidence that chirality has no significant influence on the formation of the modulated smectic phase.

In compound **3c**, in which the polar ester group was separated from the imide group by a nonpolar $(CH_2)_5$ fragment, only the smectic A_1 and C_1 phases have been observed.

Conclusions

The interesting result of this work is the observation of the tilted antiphase for new compounds without polar cyano or nitro terminal groups. The formation of the ribbon smectic $\tilde{C}$ phase seems to be determined by a delicate balance of the attractive forces of distributed molecular dipoles.

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