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Synthesis of Tfmhpncbc with Deuterated Achiral Chain and Study of Extremely Bent Chiral Chain in Antiferroelectric Smectic-I_A*

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SYNTHESIS OF TFMHPNCBC WITH DEUTERATED ACHIRAL CHAIN AND STUDY OF EXTREMELY BENT CHIRAL CHAIN IN ANTIFERRO-ELECTRIC SMECTIC-I_A*

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Abstract We have synthesized 4-(1-trifluoromethylheptyloxycarbonyl)phenyl-4'-nonylcarbonyloxybiphenyl-4-caboxylate with deuterated achiral chain (TFMHPNCBC-d_{19}), which enantiotropically exhibits the antiferroelectric hexatic SI_A* phase, and studied the orientational structure of the alkyl chains by polarized IR spectroscopy. The extremely bent chiral alkyl chain structure that was already observed in SC* and SA is confirmed even in SI_A*. Hence, contrary to the previous conclusion by Neundorf *et al.* [J. Mater. Chem., 4, 997 (1995)], the antiferroelectricity both in SC_A* and SI_A* results from the same type of intermolecular interactions among dipole moments near the smectic layer boundaries.

INTRODUCTION

Intermolecular interactions among dipole moments near the smectic layer boundaries are considered to play an essential role for the emergence of antiferroelectricity in liquid crystals.[1-4] Takanishi *et al.*[3] proposed the pairing model, in which permanent dipoles form pairs in adjacent layers, Miyachi *et al.*[4] suggested the P_X model, where the biased/hindered rotation of permanent dipoles about the long molecular axes tends to produce in-layer spontaneous polarizations parallel to the tilt plane, P_X's, at the smectic layer boundaries; the emergence of P_X's themselves together with their interaction among the boundaries through the fluctuation force[5,6] results in the stablization of antiferrolectricity in the chiral smectic-C_A(SC_A*) phase. If only the chiral chain is actually bent extremely as observed in crystals by Hori *et al.*,[7,8] the Coulomb interaction among permanent dipoles may become strong enough to stabilize the SC_A* antiferroelectricity. In fact, quite recently, Jin *et al.*,[9] Nakai *et al.*[10], and Ouchi *et al.*[11] proved unambiguously that the chiral chain projected obliquely at an angle of about the magic angle (54.7°) from the molecular core long axis even in the smectic-A (SA) phase.

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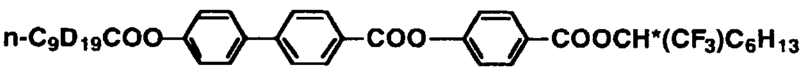
The chiral smectic $\mathrm{I_A}$ ($\mathrm{SI_A}$*) phase is interesting because of its hexatic and antiferroelectric properties. In a previous paper, Neundorf *et al.*[12] clarified the following three facts experimentally: (1) Ferroelectric SI* but not antiferroelectric $\mathrm{SI_A}$* may emerge below antiferroelectric $\mathrm{SC_A}$*; (2) A temperature-induced phase transition from $\mathrm{SI_A}$* to SI* is sometimes observed on cooling and (3) The layer spacing is larger in both $\mathrm{SI_A}$* and SI* than that in $\mathrm{SC_A}$*. They concluded that molecules are more elongated and local positional ordering is higher in $\mathrm{SI_A}$* than in $\mathrm{SC_A}$*; hence the pairing of transverse dipoles in adjacent layers, which was at that time accepted as the orgin of antiferroelectricity in $\mathrm{SC_A}$*, was not considered to cause the $\mathrm{SI_A}$* antiferroelectricity. Neundorf *et al.*[12] speculated that a group of transverse dipoles interacting with one another across adjacent layers stabilizes the $\mathrm{SI_A}$* antiferroelectricity, insisting the difference in origin between the $\mathrm{SC_A}$* and $\mathrm{SI_A}$* antiferroelectricity.

Motivated by Jin *et al.* s proof of the bent molecular structure[9-11] and by Neundorf *et al.*'s speculation about the orgin of antiferroelectricity,[12] we intended to determine unambiguously whether the molecular structure in $\mathrm{SI_A}$* is bent or straight by polarized IR spectroscopy using a sample with deuterated achiral chain. The results obtained clearly indicate that the molecules are extremely bent even in $\mathrm{SI_A}$*. The details are reported in the following.

EXPERIMENTAL

Synthesis

So far only a few materials enantiotropically exhibit antiferroelectric hexatic $\mathrm{SI_A}$*. One of such candidates is 4-(1-trifluoromethylheptyloxycarbonyl)phenyl 4'-nonylcarbonyloxy biphenyl-4-carboxylate (TFMHPNCBC). We have synthesized TFMHPNCBC-d_{19}, with achiral alkyl chain deuterated, in which the chiral and achiral chain can be observed seperately by polarized IR spectroscopy. The molecular structural formula together with the phase sequence is given in Figure 1. The synthetic route of TFMHPNCBC-d_{19} is illustrated in Figure 2. The intermediates were structurally identified by ^{1}H NMR and IR, while the target compound was confirmed by ^{1}H, ^{13}C NMR, IR, MS, OR and elemental analysis.



Iso.116.7℃ SmA 95.3℃ $\mathrm{SmC_A}$* 43.9℃ $\mathrm{SmI_A}$* 29.9℃ Cryst.

FIGURE 1 Molecular structural fomula and phase sequence of TFMHPOCBC-d_{19}

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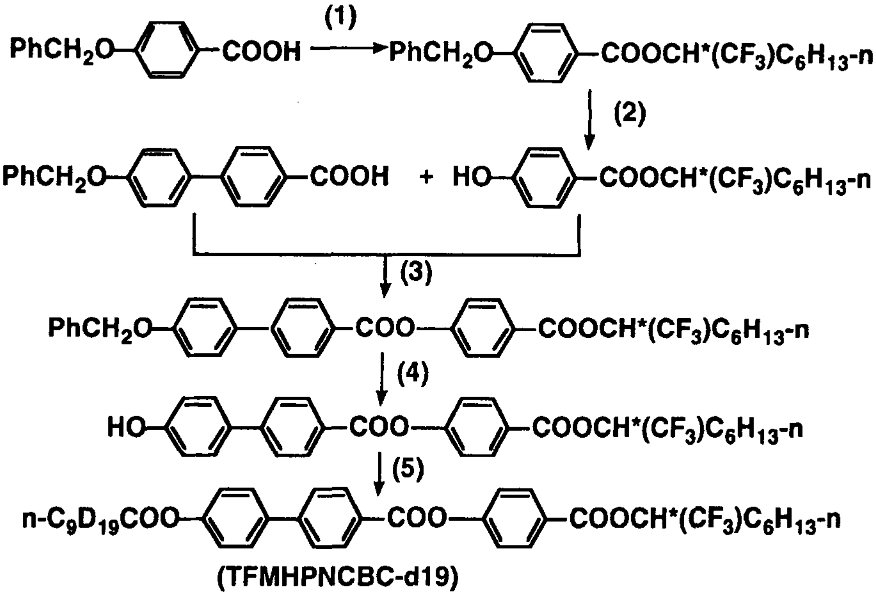

(1) DCC, DMAP, CH_2ClCH_2Cl, (*R*)-$HOCH^*(CF_3)C_6H_{13}$ (2) Pd-C(10%), H_2, CH_3CH_2OH (3) DCC, DMAP, CH_2ClCH_2Cl (4) Pd-C(10%), H_2, CH_3CH_2OH (5) DCC, DMAP, n-$C_9D_{19}COOH$, CH_2ClCH_2Cl

FIGURE 2 Synthetic route of TFMHPNCBC-d_{19}

Polarized IR Absorption Measurement

As described previously,[9] homogeneously aligned samples were prepared between two SrF_2 substrates with indium oxide (ITO) electrode, which are transparent in the visible and IR region. These plates were spin coated with polyimide (Toray 510), one of which was rubbed unidirectionally. The cell thickness was estimated from the interference pattern measured before the sample introduction. The prepared cell was placed in a temperature-controlling oven with a fluctuation less than 0.02℃. The texture observation under an optical microscope was made to check the alignment quality and to identify the phase sequence. The polarized IR absorption as a function of polarizer rotation angle was obtained by a JEOL Winspec FT-IR spectrophotometer; a wire-grid polarizer (Cambridge Physical Science IGP 227) was used.

RESULTS AND DISCUSSION

Figure 3 illustrates the absorption spectrum with peaks of CH_3, CH_2, CD_3, CD_2 and phenyl ring stretching vibrations. Asymmetric stretching peaks of CH_2 and CD_2 are rather well seperated from those in CH_3 and CD_3, respectively. Symmetric stretching, on

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the other hand, does not show any good seperation, particularly in CD$_2$. Consequently, the results obtained from the asymmetric stretching peaks of CH$_2$ and CD$_2$ are more reliable than those obtained from the symmetric stretching peaks. The phenyl ring stretching peak at 1604 cm^{-1} was used to determine the average direction of the molecular long axis.[9]

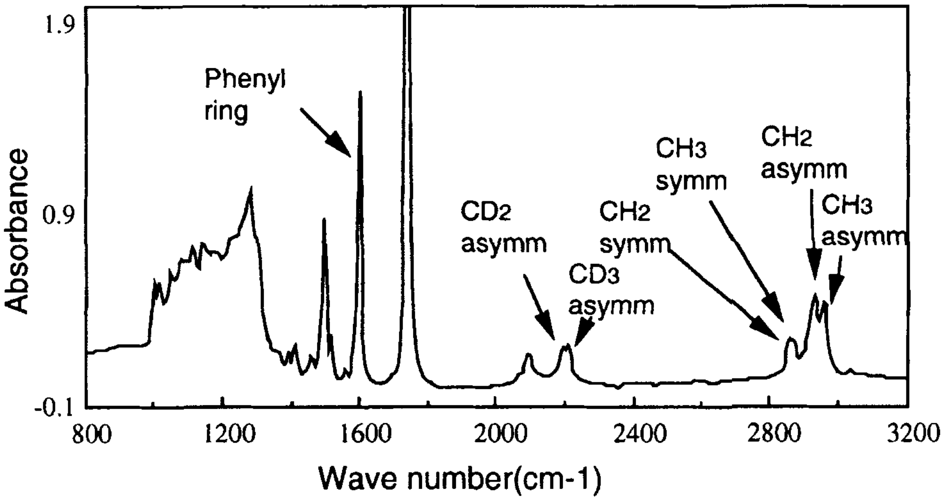

FIGURE 3 Absorption spectrum showing CH$_3$, CH$_2$, CD$_3$, CD$_2$ and phenyl ring stretching peaks.

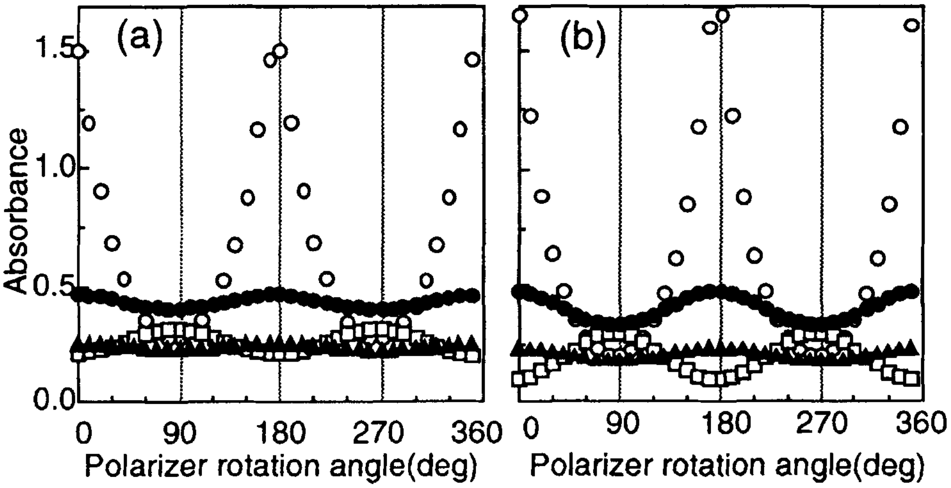

FIGURE 4 Absorbance vs polarizer rotation angle for (a)phenyl ring stretching (○) CH$_2$ asymmetric stretchings(●) and symmetric stretching (▲), CD$_2$ asymmetric stretching(□) in (a) SA and (b) helicoidal SI$_A$* obtained using 5μ m thick homogeneously aligned cell.

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Figures 4(a) and 4(b) show the absorbance vs polarizer rotation angle observed in SA and helicoidal SI_A* of TFMHPNCBC-d_{19}, respectively. Because of partial deuteration, we can obtain information about the chiral and the achiral chains seperately. In SA, as seen in Figure 4(a), the angular dependance of CH_2 asymmetric stretching peak in the chiral chain is in-phase with that of the phenyl ring stretching peaks, whereas that of CD_2 asymmetric stretching peak in the achiral chain is out-of-phase. Comparing with the same results observed in MHPOBC, [9] we can firmly conclude that the chiral chain of TFMHPNCBC-d_{19} is projecting obliquely with an angle between the molecular long axis and the average chiral chain axis larger than the so-called magic angle (54.7°), whereas the achiral chain is rather parallel to the molecular long axis.

In helicoidal SI_A*, as clearly seen in Figure 4(b), the similiar in-phase and out-of-phase results were obtained. Since the helicoidal structure does not destroy the in-phase angular dependence, we can safely conclude that, even in SI_A*, the chiral chain of TFMHPNCBC-d_{19} is bent and that the angle between the molecular long axis and the average chiral chain axis is larger than the magic angle (54.7°). Two additional facts that are worth noticing in Figure 4 are: (1) The degree of polarization of the stretching peaks, especially that of CD_2, in helicoidal SI_A* is larger than that in SA; and (2) The absorbance of the phenyl ring stretching in SI_A* is almost the same as or slightly larger than that in SA, despite of the tilted structure of molecules in SI_A*. These facts clearly indicate that the orientational order of molecules must be higher in SI_A* than that in SA and SC_A*. We are in the process of detailed investigations.

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