Orientational Change of the Trifluoromethyl Group at the Ferroelectric-Antiferroeletric Transition Observed by NMR Spectroscopy

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ORIENTATIONAL CHANGE OF THE TRIFLUOROMETHYL GROUP AT THE FERROELECTRIC-ANTIFERROELETRIC TRANSITION OBSERVED BY NMR SPECTROSCOPY

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Abstract   The temperature dependence of the order parameter of the $-CF_3$ group, S_{-CF_3}, at the chiral part in 4-[(1-trifluoromethylhepthyloxy)carbonyl]phenyl [(4'-octyloxy) biphenyl]-4-carboxylate (TFMHPOBC) has been investigated by NMR spectroscopy. The discontinuous change of S_{-CF_3} was observed at the ferroelectric-antiferroelectric phase transition. This suggests the importance of the conformation around the chiral center for the appearance of the antiferroelectric phase.

INTRODUCTION

Antiferroelectricity in liquid crystals was discovered in MHPOBC by Chandani *et al.* in 1989.[1] The structure that the molecules in the neighboring layers tilt in the opposite sense has been confirmed by an optical experiment at that time. Thereafter it was confirmed on the molecular scale.[2,3] The molecular orientation and macroscopic property have become clear, however, the interpretation of the appearance of the antiferroelectric herringbone structure has not been given in detail, particularly from the viewpoint of the molecular structure. Miyachi *et al.* proposed Px model, from polarized FT-IR spectroscopy since it was observed that the chiral carbonyl group has a tendency to lie on the tilt plane in SmC_A^* while upright position in SmC^*.[4] Nakai *et al.* explained from ^{13}C-NMR spectroscopy that the origin of antiferroelectricity is a strongly biased rotation due to the bent molecular structure.[5] Both results insist on the importance of the microscopic behavior at the phase transition from ferroelectric to antiferroelectric.

We report here ^{13}C- and ^{19}F-NMR investigation with static samples to analyze the conformation at the chiral part of the antiferroelectric liquid crystal molecule and the molecular orientation under a high magnetic field.

EXPERIMENT

The NMR experiments were carried out with the high resolution solid state NMR spectrometer CMX-300 (Chemagnetics), the resonance frequency being 300 MHz for proton (7.0 T). Compounds used were a racemic and an optically active MHPOBC ($R{:}S$=8:2) for ^{13}C-NMR, and a deuterated racemic TFMHPOBC (d_{43}-TFMHPOBC) for ^{19}F-NMR with the aim of removing the H-F dipolar coupling. The subphases in MHPOBC disappear by decreasing of the optical purity.[1] The samples was stuffed into zirconia tube with the diameter 7 mm and 4 mm for MHPOBC and d_{43}-TFMHPOBC, respectively. They were oriented by slowly cooling at a rate of one degree per minute from the isotropic phase to the SmA phase in the superconductive magnet. In this process, the molecular long axis is aligned parallel to the high magnetic field in SmA. In the ^{13}C NMR measurement the cross polarization (CP) technique was used in liquid crystal phases.[6] We measured the temperature dependences of ^{13}C- and ^{19}F-NMR spectra of the oriented samples.

RESULTS

^{13}C-NMR

Figure 1 shows the spectra of MHPOBC at various temperatures. On entering into the SmA phase from the isotropic phase, the peaks broadened and shifted considerably. Since CP was not applied for the isotropic sample, the background peak appeared at 112 ppm. The peaks between zero and 70 ppm, and between 130 and 240 ppm are assigned to the aliphatic carbons and the aromatic and ester carbons in liquid crystal phases, respectively. Because each of the sp^2 carbons, such as keto, ester and aromatic group, have a large chemical shift anisotropy, the carbons belonging to the core part exhibit a downfield shift.[7] At the phase transitions from SmA to SmC(*) and from SmC(*) to SmC$_A$(*), the peaks of the aliphatic carbons little moved. This indicates that the orientations of the aliphatic chains scarcely changed. On the other hand, the chemical shifts of the aromatic and ester carbons moved remarkably. These shifts reflect the orientational change of the molecule. Although the chemical shifts of aromatic and ester carbons exhibit an upfield shift at the transition from SmA to SmC* in the $R{:}S$=8:2 sample, they little shifted at the SmC*-SmC$_A$* transition. In the racemic mixture, however, the sp^2 carbons show a little downfield shift at the phase transition from SmA to SmC, and a remarkable upfield shift at the phase transition from SmC to SmC$_A$.

This obsevation indicates that the molecule begins to tilt with respect to the field at the SmA to SmC* transition in the optically active mixture, and remains parallel to the field in the racemic mixture even in SmC.[8] A little downfield shift at the phase

transition from SmA to SmC in the racemic mixture indicates an increase of the order parameter. Nevertheless, the molecule tilts in the SmC$_A$ in the racemic mixture as well as in the optically active one. In the optically active mixture, the helical structure is formed with its helicoidal axis parallel to the layer normal in the tilted smectic phase, while there is no helical structure in the racemic mixture. The layer prefers to align perpendicular to the high magnetic field in SmC* because of the helix. On the other hand, the molecule is parallel to the high magnetic field in SmC of the racemic mixture without helical structure. In SmC$_A$ and SmC$_A$*, since the molecules in neighboring layers tilt in the opposite sense, the average axis of the least diamagnetic susceptibity anisotropy is parallel to the layer normal. Therefore, the layer orients perpendicular to the high magnetic field irrespective of the presence of the helix.
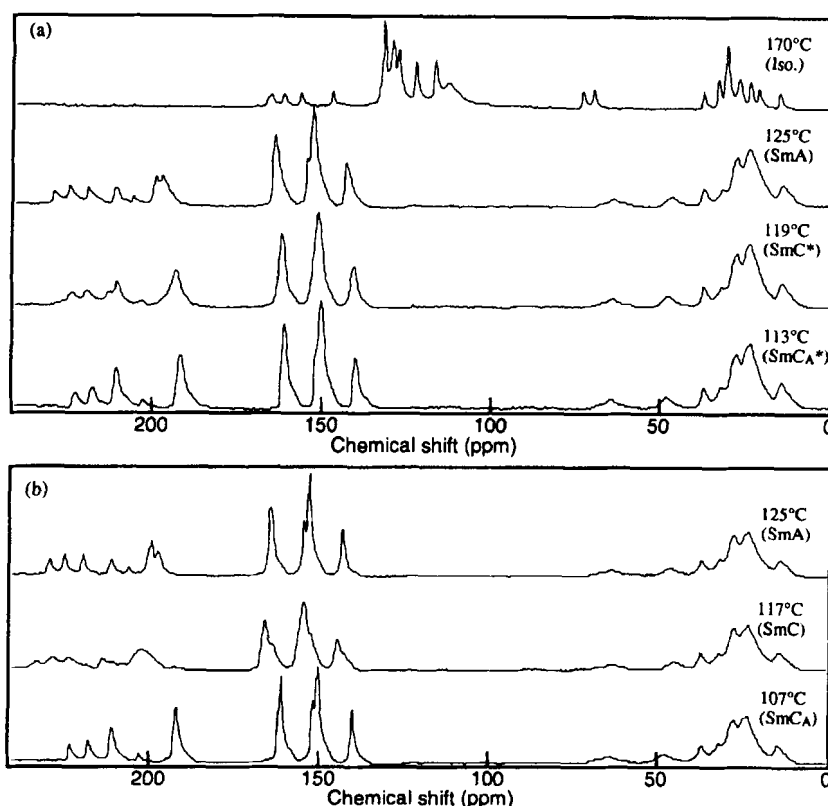

FIGURE 1 ^{13}C-NMR spectra of MHPOBC without sample spinning;(a)R:S=8:2, and (b)racemate

^{19}F-NMR

For three identical nuclei that have a spin moment I=1/2 placed at the apices of an

equilateral triangle that rapidly rotates around the axis normal to the triangular plane, the dipolar interaction of the nuclei exhibits three peaks in an NMR spectrum.[9] Figure 2 shows the spectra of the -CF$_3$ group of d$_{43}$-TFMHPOBC. Because the capacitor in the probe head for ^{19}F-NMR contains grease including fluorocarbons, the spectrum of -CF$_3$ is superimposed upon a grease signal. Because the grease signal is considerably broad without sharp peaks, this scarcely influences on the spectrum of the -CF$_3$ group. The splitting width between right and left peaks, Δv_d, is expressed by[10]

$$\Delta v_d = \frac{3\mu_0}{8\pi^2}\hbar\gamma_F r^{-3} \times |P_2(\cos\eta)|,$$ (1)

where γ_F is the magnetogyric ratio of ^{19}F, r is the distance between fluorines in the -CF$_3$ group, P_2 is the second order Legendre polynomial and η is the angle between the spinning axis of -CF$_3$ and the high magnetic field. Δv_d is proportional to the absolute value of $P_2(\cos\eta)$. Thus Δv_d depends on the orientation of the -CF$_3$ group. Figure 3 shows the temperature dependence of v_d. While the peak positions change continuously at the SmA to SmC transition, they change discontinuously at the SmC to SmC$_A$ transition.
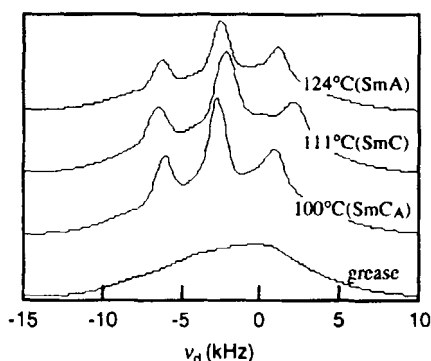

FIGURE 2   ^{19}F-NMR spectra of oriented d$_{43}$-TFMHPOBC
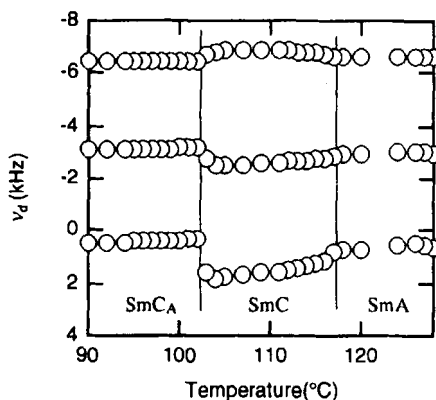
FIGURE 3   Temperature dependence of the peaks of ^{19}F-NMR spectra

From the result of electron diffraction of 1,1,1-trifluoroethane, r is 2.03 Å.[11] Thus, Δv_d is given by

$$\Delta v_d = 38.11(\text{kHz}) \times |P_2(\cos\eta)| = \Delta v_d^\circ \times |P_2(\cos\eta)|.$$ (2)

Since the molecular motion is rapid compared to NMR frequency, $P_2(\cos\eta)$ should be averaged out over the orientation of the -CF$_3$ spinning axis. Then,

$$\Delta v_{\mathrm{d}} = \Delta v_{\mathrm{d}}^{\circ} \times \left| \langle P_2(\cos\eta) \rangle \right| = \Delta v_{\mathrm{d}}^{\circ} \times |S|. \tag{3}$$

S is the orientational order parameter of the -CF$_3$ spinning axis with respect to the high magnetic field, and represented by the product of the order parameters of the long molecular axis with respect to the high magnetic field and the order parameter of the -CF$_3$ spinning axis with respect to the long molecular axis.

$$\langle P_2(\cos\eta) \rangle = \langle P_2(\cos\theta_0) \rangle \times \langle P_2(\cos\theta) \rangle \times \langle P_2(\cos\beta) \rangle$$
$$= S_{\mathrm{tilt}} \times S_0 \times S_{\mathrm{-CF_3}} \tag{4}$$

where θ_0 is the angle between the director and the high magnetic field, θ is the angle between the molecular long axis and the director, and β is the angle between the -CF$_3$ spinning axis and the molecular long axis.

S_0 is estimated at 0.7 from polarized FT-IR spectroscopy.[12] The molecular tilt angle by X-ray diffraction experiments is adopted.[13] The angle between director and the high magnetic field in SmA and SmC is nearly zero. In SmC$_A$, the molecular long axis tilts with respect to the high magnetic field. Using Eqs.(3)(4), the orientational order parameter of the -CF$_3$ spinning axis, $S_{\mathrm{-CF_3}}$, with respect to the molecular long axis is determined, as shown in Figure 4. The absolute values of the order parameter are about 0.28, 0.32 and 0.25 in SmA, SmC and SmC$_A$, respectively. The value of $S_{\mathrm{-CF_3}}$ is determined by the angle between the averaged direction of the -CF$_3$ spinning axis and the molecular long axis, and also by the degree of fluctuation of the -CF$_3$ spinning axis. It is difficult to assume that the latter quantity decreases drastically at the the SmC-SmC$_A$ transition. Therefore the former quantity, i.e., the static factor is supposed to dominate the temperature dependence of the order parameter of the rotational axis of -CF$_3$ group, $S_{\mathrm{-CF_3}}$. Therefore the confomational change is supposed to occur at SmC-SmC$_A$ phase transition. If we assume that the order parameter $S_{\mathrm{-CF_3}}$ includes only the statical factor, the angle β changes from 42° to 44° or from 70° to 68° on entering from from SmC to SmC$_A$.

It is considered that the transverse dipole moment in the vicinity of the chiral center of the molecule is important to the origin of spontaneous polarization and the stability of the antiferroelectric liquid crystal phases.[4,14] Particularly in Px model, the average distance of dipoles across the layer boundary must be shorter than the distance of dipoles in the layer.[4] In this viewpoint the conformation at the chiral part and its vicinity is a significant key since the terminal chain on the chiral side obstruct s close approach of dipoles across the layer. Thus it is guessed that the conformation change at the chiral part reflects the change of inter- and intramolecular interaction, and it gives a distinction in the antiferroelectric liquid crystal phase from the other liquid crystal phases.
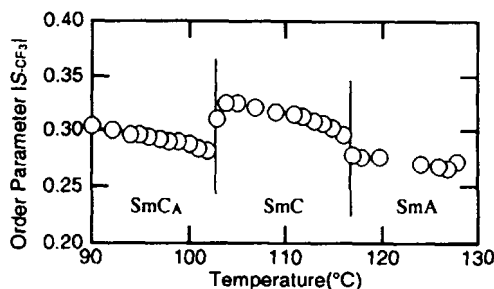
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FIGURE 4   The Orientational order parameter of the -CF$_3$ group with the respect to the molecular long axis in d$_{43}$-TFMHPOBC

CONCLUSIONS

The molecular orientation in a high magnetic field was confirmed by ^{13}C-NMR. While molecules are parallel to the high magnetic field and the layer is tilted in the SmC for the racemized sample, the layer normal is parallel to the high magnetic field in SmC$_A$ irrespective of the optical purity. From this result, we recognize that the interaction of the neighboring layers is sufficiently strong. As a result of ^{19}F-NMR the jump of the orientational order parameter of the trifluoromethyl group was observed at the phase transition between SmC and SmC$_A$. It is concluded that the antiferroelectric liquid crystal phase is distinguished from the ferroelectric phase by this conformational change at the chiral position.

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