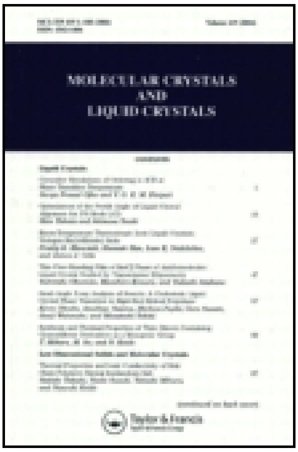

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Ferro-, Ferri- and Antiferroelectric Phases of an Optically Active Benzoate

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FERRO-, FERRI- AND ANTIFERROELECTRIC PHASES OF AN OPTICALLY ACTIVE BENZOATE

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Abstract Ferro, ferri and antiferroelectric phases of an optically active benzoate, *(R)*-1-methylheptyl 4'-(4"-n-decyloxybenzoyloxy)biphenyl-4-carboxylate, have been investigated by means of solid-state C-13 NMR and FTIR spectroscopy. Results obtained by C-13 NMR on the chemical shifts, T_1 values and shapes of peaks have been reported. The shapes and intensities for the peaks corresponding to two ester groups, obtained by FTIR measurement, have also been compared between smectic phases.

Since the new class of smectic phases, i.e., alternately tilted smectic phases, was found in some chiral liquid-crystalline materials[1-5], this behaviour has been investigated in detail and the existence of antiferroelectricity[6] and ferrielectricity[7] discovered. The origin of these properties has also been studied[8-11]. We report here C-13 NMR and FTIR investigation of molecules in the ferroelectric, ferrielectric and antiferroelectric phases, which is expected to provide useful information on the microscopic organization of molecules. To our knowledge, this is the first report of C-13 NMR and FTIR observation of the ferrielectric phase. The compound under investigation was an optically active benzoate, *(R)*-1-methylheptyl 4'-(4"-n-decyloxybenzoyloxy)biphenyl-4-carboxylate (**10B1M7**) (see figure 1), which had been already reported to exhibit ferroelectric (S_C*), ferrielectric and antiferroelectric phases[12].

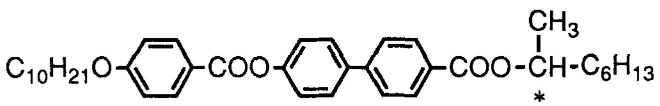

FIGURE 1 Structure of the material studied (**10B1M7**).

10B1M7 was synthesized according to the literature procedure[12]. The transition temperatures of **10B1M7**, determined by optical microscopy, are as follows:

Iso 122 °C S_A 104 ferro (S_C*) 78 ferri 73 anti 47 S_J*.

All C-13 NMR spectra were obtained by using a JEOL GSX-270 spectrometer at the magnetic field of 6.34 T. The sample was aligned macroscopically by slow cooling from the isotropic into the S_A phase in the magnet. The cooling rate was about 1 °C 15 min^{-1}. The measurements of C-13 spin-lattice relaxation time in the laboratory frame (T_1) were performed using 180° - τ - 90° pulse sequence. Infrared spectra were recorded by a JASCO Micro FTIR-100 spectrometer with a 4 cm^{-1} resolution. The sample was placed in a cell consisting of two CaF_2 windows without any surface treatments. The temperature change of the spectra was obtained using the cell equipped in a slightly modified Mettler FP82 microfurnace with a Mettler FP80 control unit.

Figures 2 (a)-(e) show static C-13 NMR spectra of **10B1M7** in the isotropic liquid, S_A, ferroelectric (S_C*), ferrielectric and antiferroelectric phases, respectively. Figure 3 shows the temperature dependence of chemical shift values of the ortho aromatic carbon (C12), the asymmetric carbon (C25) and the methylene carbon (C27) adjacent to C25. The peaks corresponding to aromatic and ester carbons show line broadening in the ferroelectric (S_C*) and antiferroelectric phases (see peaks at chemical shift values of 100-200 ppm in figures 2 (c) and (e)), whereas sharp peaks were obtained for the ferrielectric phase (see figure 2(d)). The line broadening can be related to the chemical shift anisotropy, which depends on the helical structure, as well as the characteristic motion related to the director fluctuation[13]. Thus, the helical structure of the ferrielectric phase may be different from the ferro and antiferroelectric phases, which is consistent with the result that the first ferrielectric material, 4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (**MHPOBC**), shows substantially longer helical pitch values in ferrielectric phase than in ferroelectric and antiferroelectric phases[14].

The chemical shift values of the aromatic carbon (C12), which position at the core part, were found to decrease at the transition from S_A to ferroelectric S_C* phase (see figure 3). If the director is along to the magnetic field in the S_A phase, this result indicates that, in the ferroelectric S_C* phase, the molecules align in such a way that the core part tilts from the direction of the applied magnetic field. This is because it has been reported[15] that chemical shift values for aromatic carbons decrease as the director of the material shifts from the direction of the applied magnetic field. The chemical shift values were found to be continuous and to show gradual change through ferro, ferri and antiferroelectric phases, suggesting that there is no substantial change in molecular tilting between these phases. These results are consistent with the proposed model for ferro, ferri and antiferroelectric phases, where these phases are considered to be the subphases of the S_C* phase[16].

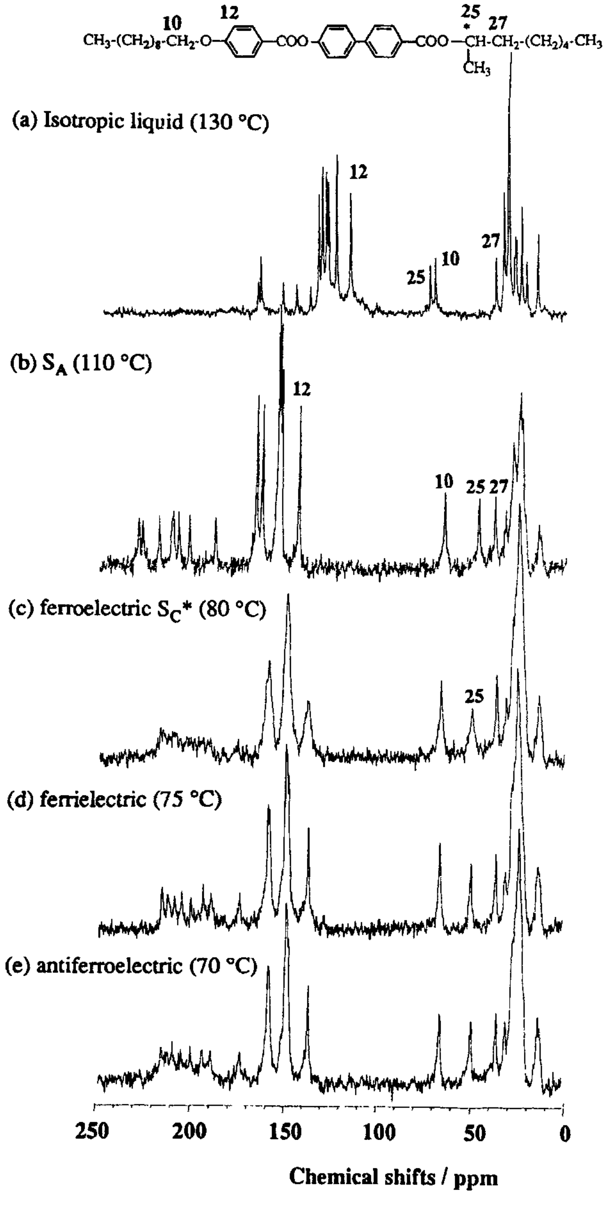

FIGURE 2 C-13 NMR spectra of **10B1M7** in (a) the isotropic liquid, (b) S_A, (c) ferroelectric (S_C*), (d) ferrielectric and (e) antiferroelectric phases.

With respect to aliphatic carbons, the chemical shift value for the asymmetric carbon (C25) decreased suddenly at the Iso-SA transition and increased slightly at the S_A-S_C* transition, whereas the methylene carbon (C27) showed continuous and slight decrease at the transitions. These results suggest that the asymmetric carbon may be included in the core part of the molecule, because it has also been reported[15] that chemical shift values for aliphatic carbons increase as the director shifts from the direction of the applied magnetic field. Furthermore, the peak associated with C25 shows line broadening in the S_C* phase (see figure 2 (c)), which is also similar to the behaviour observed for the carbons at the core part. Note that these line broadening and chemical shift behaviours were not observed for the asymmetric carbon of an analogous compound possessing a 2-methylalkanoyl group as the chiral part[13,17]. Therefore, the asymmetric carbon of **10B1M7** is expected to be quite different in nature from the other aliphatic carbons in the flexible tail part, e.g. C27, and hence to have close relation to the mesophasic helical structure.

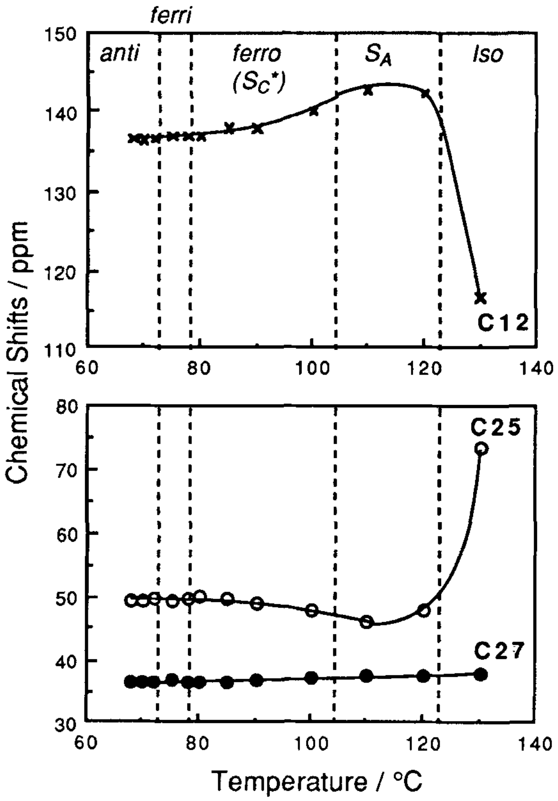

FIGURE 3 Temperature dependence of chemical shift values of the ortho aromatic carbon (C12), the asymmetric carbon (C25) and the methylene carbon (C27) which is adjacent to C25.

Figure 4 shows the temperature dependence of C-13 T_1 values of the ortho aromatic carbon (C12), the asymmetric carbon (C25) and the methylene carbon (C27). Sudden increase for C-13 T_1 values of C12 and C25 was observed in the S_C* phase, near to the S_A-S_C* transition. The increase in C-13 T_1 has been proposed to result from the dynamic molecular deformation, i.e., the appearance of a twist or bend structure, for the core part[13]. Sudden jumps of C-13 T_1 values for C12 and C25 were also observed round the ferroelectric-ferrielectric transition, suggesting that the occurrence of the ferroelectric-ferrielectric transition is also closely related to the structural changes for the molecules.

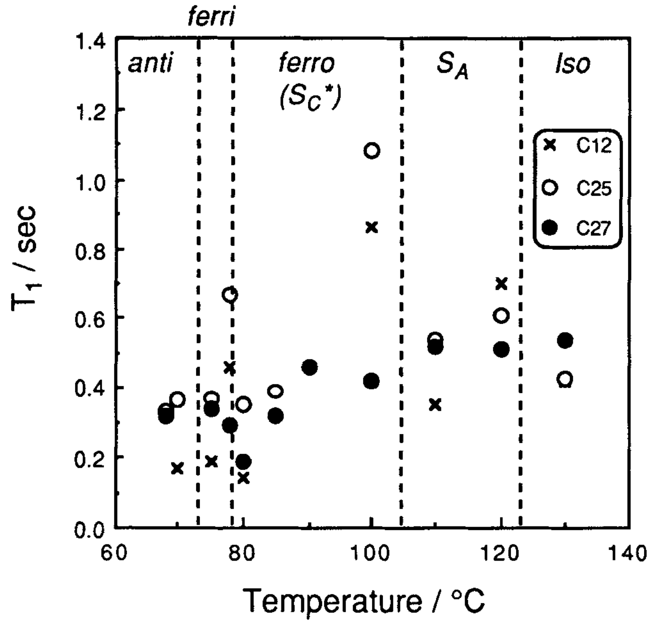

FIGURE 4 Temperature dependence of C-13 T1 values of the ortho aromatic carbon (C12), the asymmetric carbon (C25) and the methylene carbon (C27) which is adjacent to C25.

Next, FTIR measurement was performed. The alignment of the sample under the measurement condition was checked by a polarized light microscopy. The sample showed homeotropic alignment in the S_A phase, and the direction of layers was found to be unchanged through the S_A to antiferroelectric phase, i.e., layer direction is parallel to the surfaces of CaF_2 windows. IR light travels along the layer normal. Figures 5 (a)-(e) show FTIR spectra of **10B1M7** in the isotropic liquid, S_A, ferroelectric (S_C*), ferrielectric and antiferroelectric phases, respectively. The peaks appeared at 1736 cm^{-1} and 1717 cm^{-1} can be assigned to C=O str. bands for the ester groups at the central core part and next to the asymmetric carbon, respectively. Ratio of peak height between these two C=O str. bands observed in S_C* phase is apparently different from that in the S_A phase. The peak height has close relation to the angle between the direction of travelling of IR light and that of C=O stretching. This result indicate, therefore, that the structural change of the molecules occurs at the S_A-S_C* transition, which agrees with the result obtained from the C-13 T_1 measurement. Furthermore, in the antiferroelectric phase, line broadening was observed for the peak corresponding to the C=O str. band of the ester group at the core part. Line broadening for peaks corresponding to C=O str. bands can be considered to result from the appearance of additional peaks which possess slightly different frequencies. The frequency shifts for C=O str. bands have been reported to be due to conformational changes producing various conformers which possess different torsional angles between the direction of C=O str. and the plane of the adjacent benzene ring[18,19], and to the emerge of intermolecular interaction[19,20]. Thus, the changes of the structure or the strength of intermolecular interactions at the core part may be expected to be closely related to the emerge of the antiferroelectric phase. This hypothesis is also supported by the fact that materials possessing quite limited core structures have been reported to exhibit the antiferroelectric character.

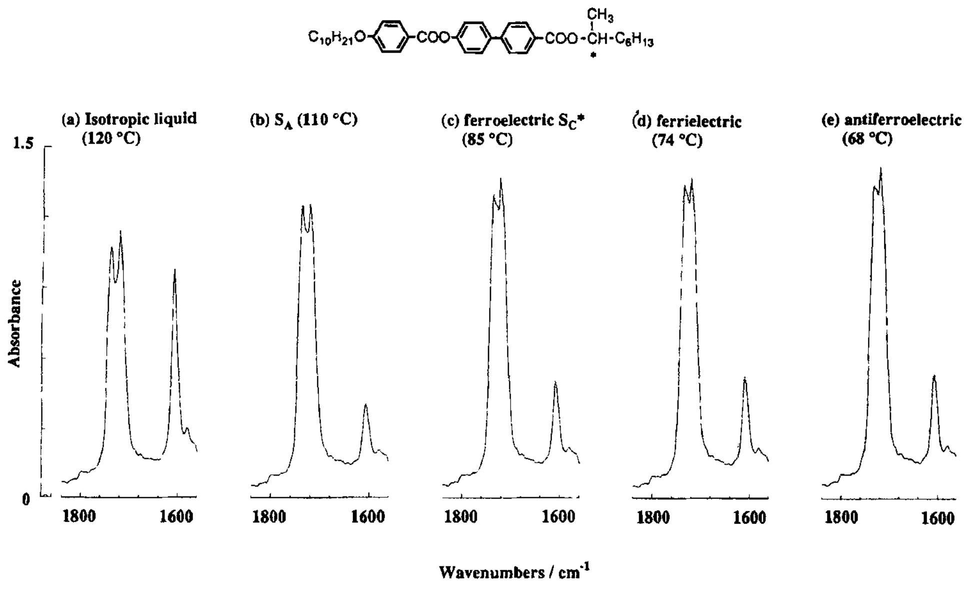

FIGURE 5 FTIR spectra of **10B1M7** in (a) the isotropic liquid, (b) S_A, (c) ferroelectric (S_C*), (d) ferrielectric and (e) antiferroelectric phases.

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