Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Smectic A and smectic C materials: partially deuteriated chiral liquid crystals (S)-($^{-}$)-2-methylbuty 4-(4-(d_{13})-hexyloxyphenyl)benzoate and (S)-($^{-}$)-2-methylbutyl 4-(4-(d_{17})-octyloxyphenyl)benzoate

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To cite this Article Yeap, Guan-Yeow , Nakata, Michi , Takanishi, Yoichi , Ishikawa, Ken and Takezoe, Hideo(2000) 'Smectic A and smectic C materials: partially deuteriated chiral liquid crystals (S)-($^{-}$)-2-methylbuty 4-(4-(d_{13})-hexyloxyphenyl)benzoate and (S)-($^{-}$)-2-methylbutyl 4-(4-(d_{17})-octyloxyphenyl)benzoate', Liquid Crystals, 27: 11, 1437 — 1443

To link to this Article: DOI: 10.1080/026782900750018582

URL: http://dx.doi.org/10.1080/026782900750018582

LIQUID CRYSTALS, 2000, VOL. 27, NO. 11, 1437–1443

Smectic A and smectic C materials: partially deuteriated chiral liquid crystals (*S*)-(−)-2-methylbutyl 4-(4-(d_{13})-hexyloxyphenyl)benzoate and (*S*)-(−)-2-methylbutyl 4-(4-(d_{17})-octyloxyphenyl)benzoate

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(*Received 1 October 1999; in final form 4 April 2000; accepted 7 April 2000*)

In order to study the difference in microscopic orientation of ferro- and antiferroelectric liquid crystalline molecules, we synthesized the partially deuteriated chiral compounds, (*S*)-(−)-2-methylbutyl 4-(4-(d_{13})-hexyloxy- and (*S*)-(−)-2-methylbutyl 4-(4-(d_{17})-octyloxy-phenyl)benzoates. Fundamental physical properties such as phase transition temperatures, spontaneous polarization and tilt angle were determined. Polarized FTIR measurements were also made to provide information on molecular structure and orientation.

1. Introduction

Ferroelectric liquid crystals (FLCs) are being claimed as the first of recent ferroelectric materials with fluid properties [1]. This ferroelectricity has generally been ascribed to the presence of a tilted smectic phase comprising chiral molecules which reduce the overall symmetry of the liquid crystal [2]. In fact, these chiral compounds with liquid crystalline properties have already been used for numerous practical applications in various fields [3]. As such, there has been continuous interest in developing new materials or in modifying existing ferroelectric liquid crystals.

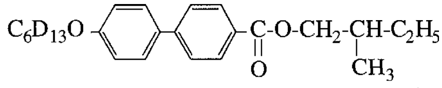
Meanwhile, the antiferroelectric phase was first observed in MHPOBC [4]. Since this discovery, the origin of the antiferroelectric phase, and subphases appearing between the ferroelectric and antiferroelectric phases, has been studied from various viewpoints [5]. In these studies, spectroscopic measurement is a powerful technique, particularly for elucidating molecular structure and intermolecular interaction.

In this work, partially deuteriated compounds for polarized FTIR measurements were synthesized and their fundamental properties were measured. The purpose of this study was to measure polarized FTIR spectra and analyse the degree of hindered rotation of the carbonyl group. Since these compounds have a simpler core structure than MHPOBC, it will be easier to determine the hindrance of the carbonyl group. Moreover, we can discuss the orientation of the chiral chain. From our results, we compare the structure of the present ferroelectric liquid crystals with that of an antiferroelectric MHPOBC with similar structure.

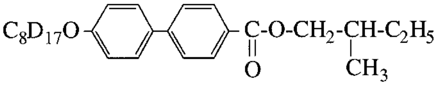
2. Experimental

2.1. *Synthesis*

The chemical structures of the target compounds are shown in figure 1. They have similar structures to MHPOBC, but simpler. Therefore it is relatively easy to determine the direction and the degree of hindered rotation. Moreover, by comparing the compounds with MHPOBC, the difference in conformation of the chiral chain can be examined. Deuteriated (d_{13})-1-bromohexane and (d_{17})-1-bromooctane were obtained from Japan TCI Chemical Company. All reagents were used directly without further purification. Details of synthetic methods were described in an earlier paper [6]. The final products were purified by column chromatography on silica gel and by recrystallization from a solvent



(S)-MB-d_{13}-HOB : Cr 35(33) SmA 59(61) I



(S)-MB-d_{17}-OOB : Cr (33) SmC* 46(39) SmA 64(62) I

Figure 1. Chemical structures and phase sequences of synthesized compounds.

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mixture of ethyl acetate and *n*-hexane (1 : 10). The phase sequences and transition temperatures of (*S*)-MB-d_{17}-OOB were almost the same as those of the undeuteriated compound.

2.2. *Characterization of materials*

The qualitative characterization of the liquid crystalline behaviours of these materials was carried out by measurement of phase transition temperatures by differential scanning calorimetry (DSC), spontaneous polarization, and apparent tilt angle, and by observation of texture by polarizing microscopy.

The initial phase assignments together with corresponding transition temperatures for the final products were made by thermal optical microscopy using a Nikon OPTIPHOTO-POL polarizing microscope which was attached to a Mettler FP82 hot stage. Transition temperatures were measured by DSC using a Seiko DSC-10 calorimeter. The materials were studied at a scanning rate of 5°C min^{-1} for heating and cooling cycles. The sample was encapsulated in aluminum pans and alumina was used as a reference.

The magnitude of helical pitch was determined by measuring the distance of the dechiralization lines observed in thick homogeneously aligned cells. The spontaneous polarization of (*S*)-MB-d_{17}-OOB was measured for a 2.7 μm thick homogeneously aligned rubbed cell by using a triangular wave method [7]. The $\mathbf{P}_S$ value was determined at 30 Hz with an applied voltage of 20 V_{pp}. The tilt angle was measured on a similar cell by applying a 20 V_{pp}/2.7 μm triangular wave field at 1.0 Hz.

2.3. *Polarized FTIR measurement*

The polarized infrared absorption spectra were recorded on a JEOL WINSPEC50 FTIR spectrophotometer equipped with an MCT detector, as a function of polarizer rotation angle. A wire grid polarizer (Cambridge Physical Science IGP227) was employed to obtain polarized IR radiation. All the spectra were recorded at a 10 cm^{-1} resolution and 50 scans were accumulated. The sample analysed was inserted between two SrF_2 plates covered with a thin ITO electrode and also coated with polyimide which was one-side-rubbed along one direction. For (*S*)-MB-d_{17}-OOB, the cell thickness used was 2.48 μm. The sample cells, filled by capillary action, were prepared by heating the material to the isotropic liquid state and then slowly cooling to the SmA and SmC* phases. The temperature was controlled by a CHINO DB controller. All manipulations on the spectra and calculations were performed with the software supplied by JEOL.

3. Results and discussion

3.1. *Liquid crystalline phase characteristics*

The transition temperatures observed on both heating and cooling processes by DSC for the target compounds are shown in figure 1. Texture observations by polarizing microscopy for the smectic phases of (*S*)-MB-d_{13}-HOB and (*S*)-MB-d_{17}-OOB are shown in figures 2 and 3, respectively. (*S*)-MB-d_{13}-HOB shows SmA texture, i.e. fan-shaped textures, at 50°C on cooling. A similar texture, characteristic of the SmA phase on cooling from the isotropic phase, was also observed for (*S*)-MB-d_{17}-OOB. Upon cooling, periodical disclination lines parallel to the smectic layer were clearly observed in the temperature range 40–36°C, indicating the SmC* phase where the molecules are tilted with respect to the layer plane and form a helix.

3.2. *Spontaneous polarization, tilt angle and helical pitch*

The temperature dependence of spontaneous polarization in the SmC* phase for (*S*)-MB-d_{17}-OOB is shown in figure 4. The $\mathbf{P}_S$ value was found to be very small, and the behaviour is typical for a compound exhibiting a second order SmA–SmC* transition. No induced polarization was observed in the SmA phase. The temperature dependence of the tilt angle for (*S*)-MB-d_{17}-OOB in the SmC* phase is also shown in figure 4, and is similar to that of $\mathbf{P}_S$.

The helical pitch obtained by measuring the distance of disclination lines observed in the texture of (*S*)-MB-d_{17}-OOB, figure 3 (*b*) was found to be 50 μm.

3.3. *Polarized FTIR*

In order to elucidate the molecular structure which exists in the mesophases of (*S*)-MB-d_{17}-OOB, the polarized FTIR absorption spectra were recorded at both 50°C

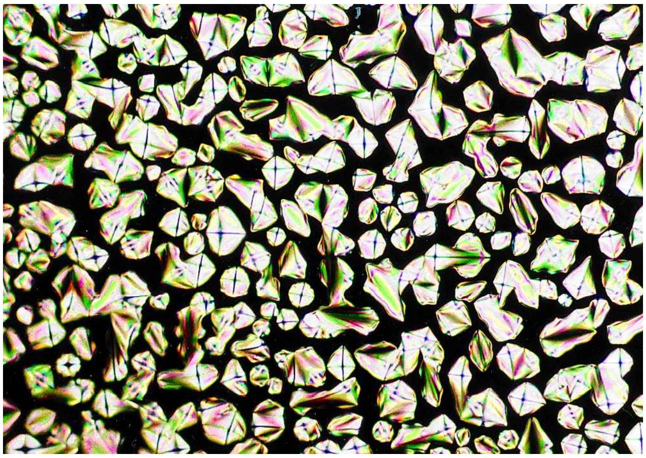

Figure 2. Photomicrograph of (*S*)-MB-d_{13}-HOB at the phase transition from the isotropic phase to SmA phase.

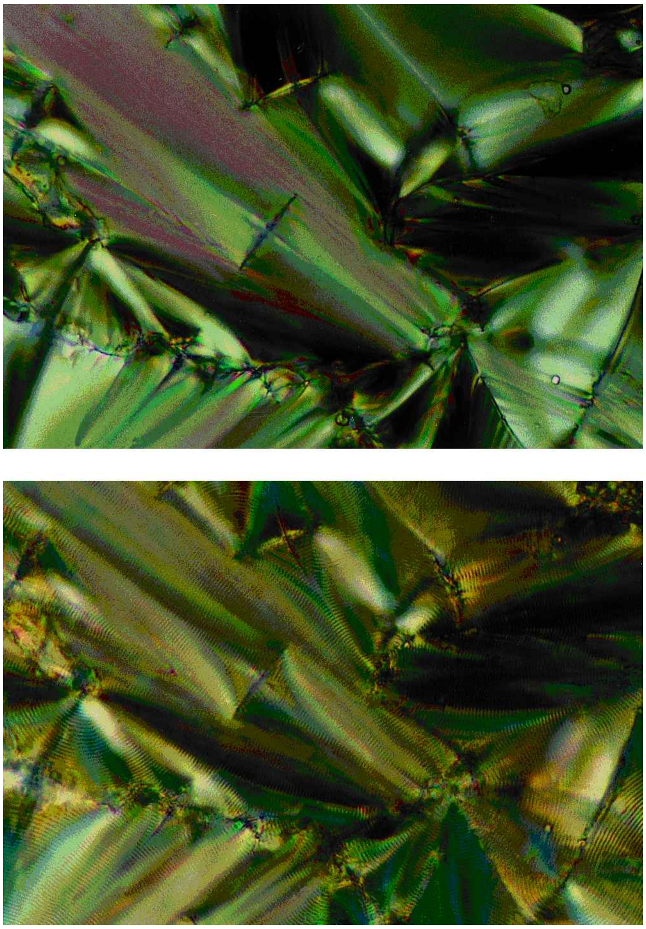

Figure 3. Polarized optical micrographs observed on cooling (*S*)-MB-d_{17}-OOB from the isotropic melt: (*a*) 50°C, SmA and fan-shaped textures; (*b*) 39°C SmC* helical structure.

(SmA) and 37°C (SmC*). A representative absorption spectrum of (*S*)-MB-d_{17}-OOB at 50°C is shown in figure 5. Both the symmetric and asymmetric stretching peaks assigned to CD_2 and CD_3 groups were clearly observed, as listed in the table. The resolution of bands associated with CD_2 and CD_3 is more tangible in comparison with that for CH_2 and CH_3. The band peaking at 2160 cm^{-1} can be ascribed to the presence of CO_2 in the air.

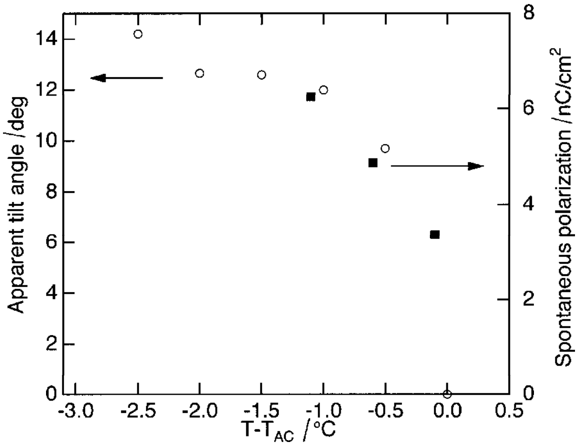

Figure 4. Temperature dependences of spontaneous polarization and apparent tilt angle.

Figure 6 shows the absorbance as a function of polarizer rotation angle ω in SmA, where 0° is the angle parallel to the layer normal. Absorption due to the phenyl ring C–C stretching appears at 1601 cm^{-1} which has generally been used to determine the average direction of the molecular long axis [8–11]. In particular, since the core part of this compound is composed of only two phenyl rings and an ester group, and is hence very simple, the anisotropy of the C–C stretching unambiguously defines the molecular long core axis. Profiles were fitted using the following equations,

$$D = (A_{\max} - A_{\min})/(A_{\max} + A_{\min}) = 3S/(S+2) \tag{1}$$

$$A(\beta, \omega) = k\left[\frac{1}{2}S(2 - 3\sin^2\beta)\cos^2\omega + \frac{1}{2}S\sin^2\beta + \frac{1}{3}(1 - S)\right] \tag{2}$$

Table. Wavenumber and assignment of each transition moment of (*S*)-MB-d_{17}-OOB. Polarizer rotation angles showing the maximum absorption are also shown in the SmA and SmC* phases under a positive field.

Wavenumber/cm^{-1}	Assignment	$\omega_{\max}$(SmA)/°	$\omega_{\max}$(SmC*)/°
2966	CH_3 asymmetric stretching	− 0.90	− 7.50
2937	CH_2 asymmetric stretching	− 2.23	22.07
2877	CH_3 symmetric stretching	3.57	51.43
2861	CH_2 symmetric stretching	87.21	74.27
2215	CD_3, CD_2 asymmetric stretching	89.16	79.69
2100	CD_3, CD_2 symmetric streching	88.91	81.28
1718	Ester C=O streching	90.07	90.25
1601	Phenyl ring C–C stretching	− 0.83	− 10.85

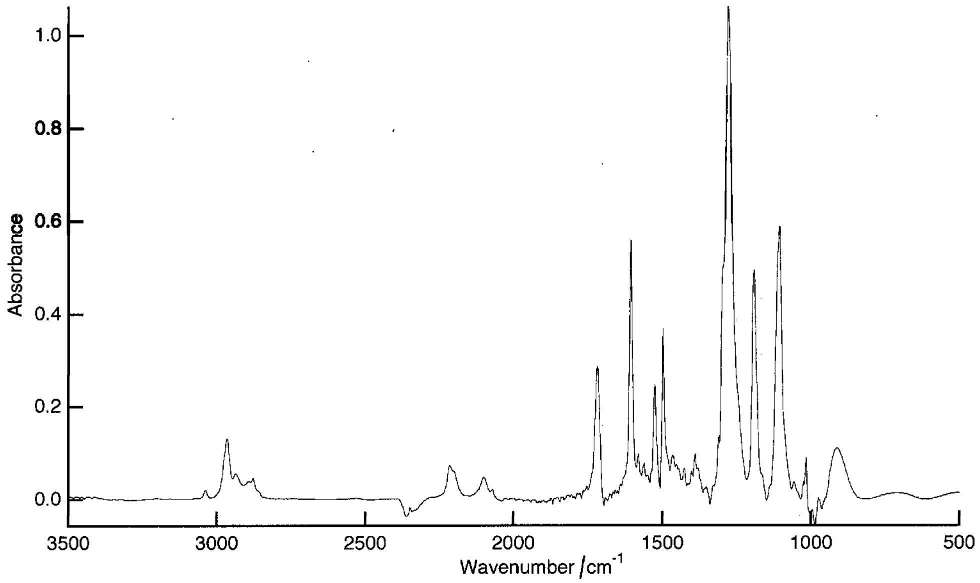

Figure 5. Typical FTIR spectrum for (*S*)-MB-d_{17}-OOB at 50°C (SmA).

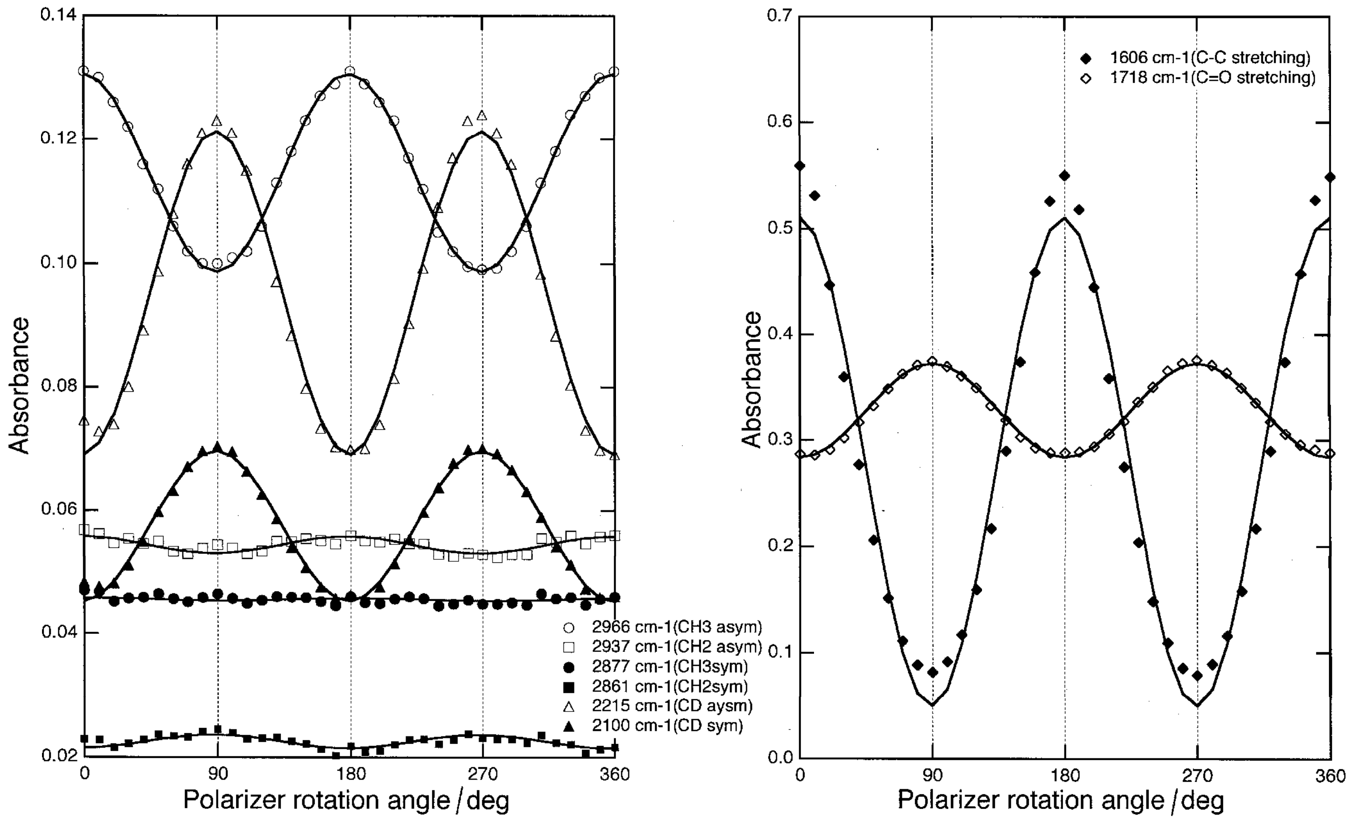

Figure 6. Absorbance as a function of polarizer rotation angle of (*S*)-MB-d_{17}-OOB at 50°C (SmA).

where $A_{\max(\min)}$ is the maximum (minimum) absorbance, S is the orientational order parameter, k the absorption coefficient, and β the angle between the molecular long axis and the transition moment. This C–C stretching band shows an absorption maximum at $-0.83°$, i.e. almost parallel to the layer normal. The dichroic ratio D of this band was determined to be 0.818 and S was 0.75 in SmA, which is almost the same as that of other compounds reported previously [9]. Other peaks show the absorption maxima at about 0° or 90°, as shown in the table, which indicates that the molecular rotation along the long axis parallel to the core axis is isotropic in SmA. The angular dependence of the C=O stretching absorption peak was also well fitted by equation (2) with $\beta = 59.8°$ and $S = 0.75$.

Note that the polarizer angle dependences of the symmetric and asymmetric CD_2 peaks were out of phase with respect to the C–C stretching. This result was the same as that in MHPOBC [11], i.e. the average long axis of the achiral chain is parallel to the core axis. One noticeable feature is the angular dependence of CH_2 bands in the chiral chain. The angular dependences of the asymmetric stretching vibrations of CH_2 and CH_3 groups are in-phase with respect to the C–C stretching, while that of symmetric CH_2 bands is out-of-phase. Considering the cylindrical distribution of the chiral chain along the molecular long axis due to the macroscopic uniaxial symmetry of the SmA phase, these profiles suggest that the chiral chain of this compound largely tilts with respect to the core axis as in MHPOBC [11]. Since the angular dependence of the CH_2 symmetric stretching is different from that of MHPOBC, however, the detailed microscopic structure around the chiral chain is different. If the internal rotation around the chiral chain axis is isotropic, the angular dependence of CH_2 symmetric vibration is isotropic, or in-phase with respect to that of the phenyl ring C–C stretching. Therefore because the angular dependence of CH_2 symmetric vibration is out-of-phase, the rotation of the chiral chain may be hindered because the chiral chain is short; asymmetric carbon may strongly suppress the internal rotation of the chiral chain even in SmA. Hindered internal rotation of the chiral chain in MHPOBC was also reported by Yoshida *et al.* using D-NMR [12]. Because of many unknown parameters such as the bending angle between chain axis and core axis, the hindered direction and the degree of hindrance of the chiral chain axis, it is difficult to determine molecular structure quantitatively. This analysis will be a subject for future study. The qualitative schematic molecular structure is illustrated in figure 7.

Figure 8 shows the absorbance under the application of a positive d.c. electric field at 37°C (in SmC*). The polarizer rotation angles giving rise to the maximum absorption are shown in the table. By applying an electric field stronger than the threshold, the maximum absorption direction of the phenyl ring C–C stretching was tilted by $-10.9°$, which is smaller than the apparent optical tilt angle (14°). The polarizer rotation angles (ω_{max}) showing the maximum absorption of CD_2(asym) and CD_2(sym) are 79.7° and 81.3°, respectively, and the profiles are almost symmetric and out of phase with respect to that of C–C stretching. In contrast, CH_2(asym) and CH_2(sym) are less anisotropic and ω_{max} is $+22.1°$ and $+74.3°$, respectively. These results are not symmetric with respect to the C–C stretching, suggesting that the chiral chain rotation is hindered as in SmA.

Another remarkable feature observed in figures 6 and 8 is that the angle of the maximum absorbance corresponding to the stretching of the carbonyl (C=O) group remains almost unaltered despite the temperature change from 50°C (SmA) to 37°C (SmC*). In other words, the maximum absorption of the C=O peak in the present compound stays parallel to the smectic layer, though the director is tilted in SmC*. This effect can be ascribed to hindered rotation, as reported for the C=O group of the core part in MHPOBC [9]. According to Kim *et al.* [9], the distribution function of the transition

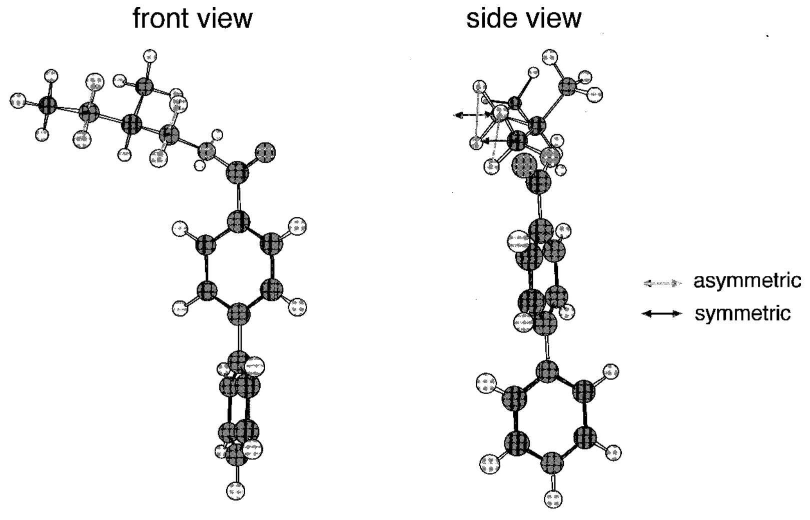

Figure 7. Qualitative schematic structure of MB-d_{17}-OOB inferred from polarized FTIR absorption.

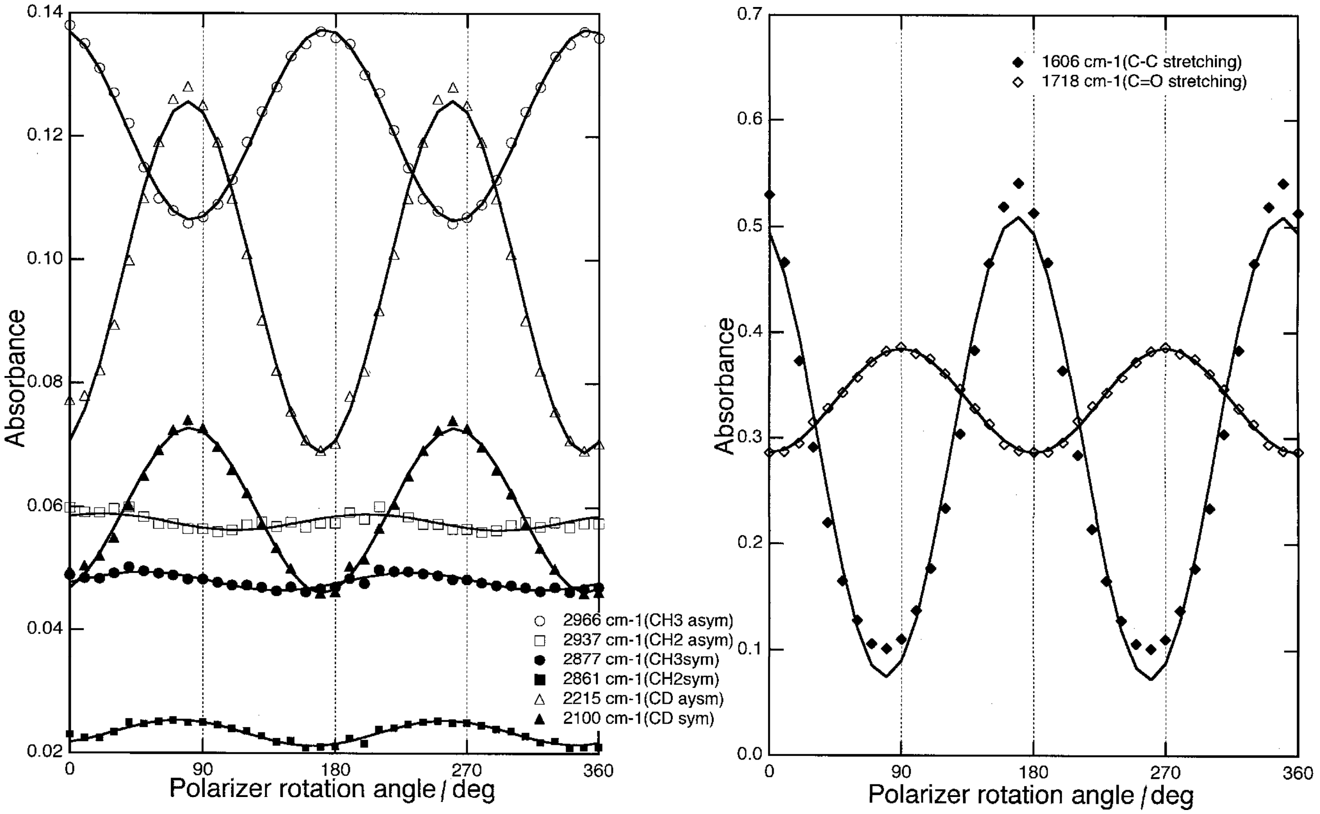

Figure 8. Absorbance as a function of polarizer rotation angle of (*S*)-MB-d_{17}-OOB at 37°C (SmC*) under the application of + 10 V.

moment of the C=O group around the molecular long axis is approximated as

$$f(\Psi) = \frac{1}{2}\pi[1 + a\cos(\Psi - \Psi_0)]. \qquad (3)$$

Here Ψ is the azimuthal angle, Ψ_0 the hindered rotation angle and a the degree of hindrance. $\Psi_0 = 90°$ means that the hindered direction is perpendicular to the tilting plane. Suppose that the layer tilt with respect to the substrate surface is zero because the tilt angle θ is small, the normalized absorbance is given by [8]

$$A(\omega') = \frac{1}{2}\int f_{t+}(\Psi)(\sin\omega'\sin\beta\sin\Psi + \cos\omega'\cos\beta)^2\,d\phi$$

$$+ \text{ a corresponding term with } f_{b+}(\Psi). \qquad (4)$$

Here ω' is equal to $\omega - \theta$. In order to take into account the head and tail equivalence, two molecular orientations with the C=O group at the top (t) and bottom (b) in a layer were considered. Only the molecular tilting sense under the positive (+) field was considered. Since the core part of this compound is very simple, as mentioned above, it is natural that β is 60°. Actually the profile in SmC* was well fitted to equation (4) with $\beta = 54.2°$, $a = 0.22$ and $\Psi_0 = 156.5°$. Ψ_0 is far from 90° or 270°, and hence it is considered that the transverse dipole moment may contribute weakly to the spontaneous polarization.

4. Conclusion

In order to study the difference of microscopic orientation of ferro- and antiferro-electric liquid crystalline molecules, we synthesized partially deuteriated chiral compounds. Their fundamental physical properties such as phase transition temperatures, textures, spontaneous polarization and tilt angle were determined. The results of polarized FTIR measurement indicate that the chiral chain of the ferroelectric liquid crystal is bent as observed in MHPOBC; hindrance of the internal rotation of the chiral chain was also observed, even in the SmA phase.

The authors thank the Japanese Society for the Promotion of Science for financial support. One of the authors (Y. G.-Y.) also thanks the Universiti Sains Malaysia for granting long-term research leave.

References

[1] Goodby, J. W., Blinc, R., Clark, N. A., Lagerwall, S. T., Osipov, M. A., Pikin, S. A., Sakurai, T., Yoshino, K., and Zeks, B., 1991, *Ferroelectric Liquid Crystals: Principles, Properties and Applications* (Philadelphia: Gordon and Breach).

[2] MEYER, R. B., 1977, *Mol. Cryst. liq. Cryst.*, **40,** 33.

[3] KALLARD, T., 1973, *Liquid Crystal Devices* (New York: Optosonic Press); WILLIAMS, E. L., 1975, *Liquid Crystals for Electronic Devices* (New Jersey, London: Park Ridge).

[4] CHANDANI, A. D. L., GORECKA, E., OUCHI, Y., TAKEZOE, H., and FUKUDA, A., 1989, *Jpn. J. appl. Phys.*, **28,** L1265.

[5] FUKUDA, A., TAKANISHI, Y., ISOZAKI, T., ISHIKAWA, K., and TAKEZOE, H., 1994, *J. mat. Chem.*, **4,** 997.

[6] YEAP, G. Y., TAKANISHI, Y., and TAKEZOE, H., 1999, *Spectroscopy* (submitted).

[7] MIYASATO, K., ABE, S., TAKEZOE, H., FUKUDA, A., and KUZE, E., 1983, *Jpn. J. appl. Phys.*, **22,** L661.

[8] MIYACHI, K., MATSUSHIMA, J., TAKANISHI, Y., ISHIKAWA, K., TAKEZOE, H., and FUKUDA, A., 1995, *Phys. Rev. E*, **52,** R2153.

[9] KIM, K. H., ISHIKAWA, K., TAKEZOE, H., and FUKUDA, A., 1995, *Phys. Rev. E*, **51,** 2166.

[10] JANG, W. G., PARK, S. S., MACLENNAN, J. E., KIM, K. H., and CLARK, N. A., unpublished results.

[11] JIN, B., LING, Z., TAKANISHI, Y., ISHIKAWA, K., TAKEZOE, H., FUKUDA, A., KAKIMOTO, M., and KITAZUME, T., 1996, *Phys. Rev. E*, **53,** R4295.

[12] YOSHIDA, S., JIN, B., TAKANISHI, Y., TOKUMARU, K., ISHIKAWA, K., TAKEZOE, H., FUKUDA, A., KUSUMOTO, T., NAKAI, T., and MIYAJIMA, S., 1999, *J. phys. Soc. Jpn. Lett.*, **68,** 9.