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Field-induced molecular reorientation keeping a frustrated structure in an achiral bent-shaped liquid crystal

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The layer and molecular orientational structures have been investigated by X-ray microbeam diffraction and optical birefringence measurements in the frustrated smectic phase of a bent-shaped molecule with two mesogens linked by an alkylene spacer. In the X-ray microbeam measurement, only one diffraction peak indicating (002) was observed in a thin homogeneous cell without an electric field, while two other peaks corresponding to (101) and (10$\underline{1}$) also appear by applying the field. Moreover, it was also found that the birefringence under an applied field is larger than that without the field. These results led to the conclusion that molecules reorient due to dielectric anisotropy keeping the frustrated structure.

1. Introduction

In liquid crystals, frustrated structures frequently appear due to competition between molecular interactions. For example, the homologous series of cyanobiphenyls with a large longitudinal dipole moment shows many kinds of SmA (SmA_1, SmA_2, SmA_d and SmÃ) phases because intra- and inter-layer dipole interactions compete with each other.[1,2] Another example is ferrielectric phases, the appearance of which is considered to be caused by competition between antiferroelectricity and ferroelectricity.[3,4]

Recently it was reported that banana-shaped molecules without asymmetric carbons exhibit (anti)ferroelectric properties in the smectic phase.[5,6] These banana-shaped molecules have attracted the attention of many scientists. In various studies on these homologous compounds, Niori *et al.* found that the smectic structure which appears in the homologous series of 1,3-bis{4-[(4-*n*-alkoxyphenyl)iminomethyl]benzoyloxy}phenylenes (P-*n*-O-PIMB), depends on the terminal alkyl chain length; *i.e.* P-*n*-O-PIMBs with short chains of $n=4$–6 form a frustrated structure.[7,8] Choi *et al.* reported similar results in bent molecules with two mesogens linked by an alkylene spacer; compounds with a long terminal chain showed a bilayer structure, and the structure changed to a single layer upon decreasing the terminal chain length.[9] Moreover, in compounds with terminal chains of intermediate length, X-ray diffraction 2D patterns suggest the existence of a frustrated layer structure.

In this paper, we investigated the layer structure in the smectic phase of a bent molecule with two mesogens. In the X-ray microbeam measurement, it was found that the frustrated structure is kept even after molecular switching by an applied electric field. Based on this X-ray result together with birefringence measurements before and during applying a field,

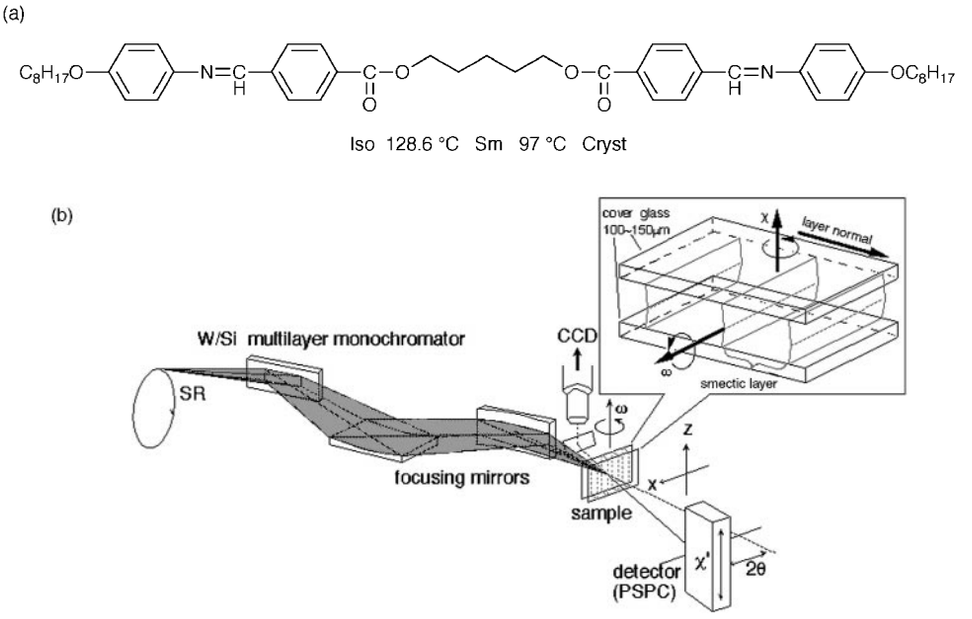

Fig. 1 Chemical structure of 8OAM5AMO8 (a) and schematic X-ray diffraction geometry (b).

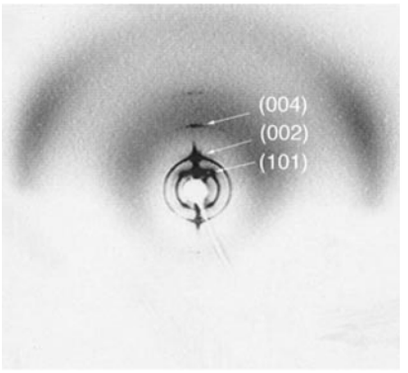

Fig. 2 Macroscopic 2D X-ray pattern in the frustrated smectic phase of 8OAM5AMO8 at 107 °C. The sample was partially oriented in a capillary tube. The indices of each spot are indicated in the figure.

the molecular orientational change by the field in a frustrated layer structure was discussed.

2. Experimental

The sample used was a twin dimer molecule, α,ω-bis{4-[(4-*n*-octyloxyphenyl)iminomethyl]benzoyloxy}pentane (8OAM5AMO8),[8] whose chemical structure and phase sequence on cooling are as shown in Fig. 1(a). The purities of the intermediates and final products were checked by thin-layer chromatography. Homogeneously aligned cells were prepared using glass plates with indium tin oxide (ITO). The glass surface was not coated with any polymer alignment layer nor rubbed. Sample cell gaps were 2.5 and 3.4 μm, and the thicknesses of the glass substrates were 150 μm and 1 mm for

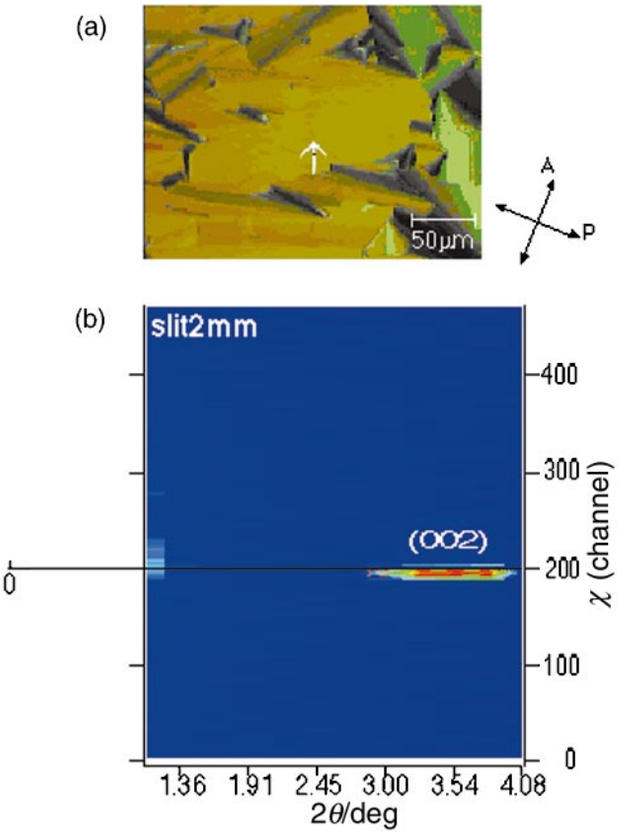

Fig. 3 (a) Microphotograph of an irradiated area and (b) 2D X-ray diffraction pattern in a 2.5 μm thick homogeneous cell before applying an electric field.

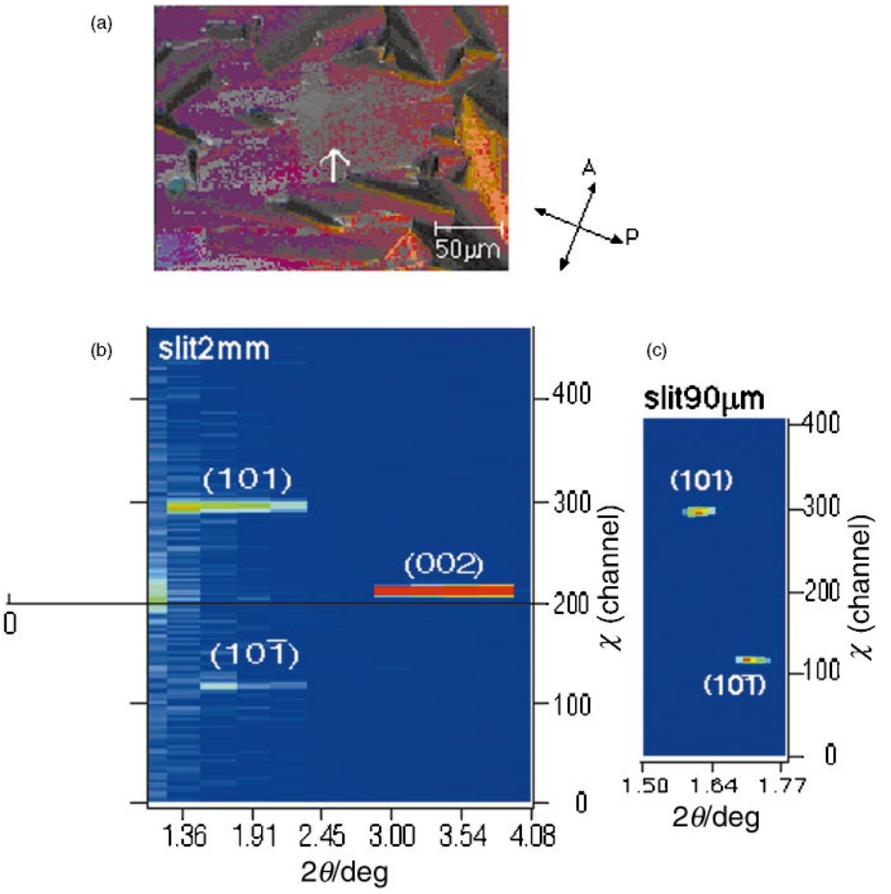

Fig. 4 (a) Microphotograph of an irradiated area and (b) 2D X-ray diffraction pattern under 6 V μm^{-1} DC field at 107 °C (smectic phase). (c) Details of X-ray pattern around (101) peaks obtained using narrow receiving slit conditions.

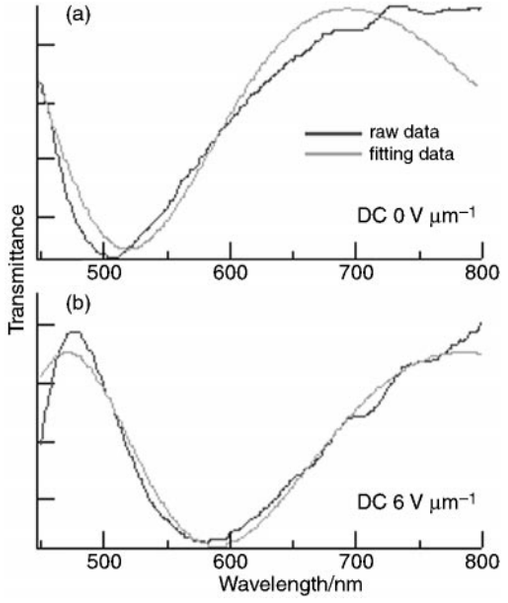

Fig. 5 Visible light transmittance spectra of a 3.4 μm thick homogeneous cell in the absence (a) and presence (b) of the DC field. Broken lines are curves fitted to eqn. (1).

X-ray and optical measurements, respectively. We could obtain relatively large uniform domains by gradual cooling from the isotropic liquid.

X-Ray microbeam measurements[10,11] were performed at the Photon Factory on the beam line 4A (Tsukuba). The X-ray energy was monochromated to 8 keV ($\lambda = 1.54$ Å). The incident beam was collimated using a Si/W multilayer mirror with an angular divergence of 0.5 mrad, and the spatial resolution was 2.5×3 μm^2. The details of the optical geometry are shown in Fig. 1. By fixing the sample rotation angle to the diffraction conditions and changing the position of the position sensitive proportional counter (PSPC) detector, we could obtain a 2D diffraction pattern. The accumulation time was 100 s per point.

Optical birefringences of the homogeneous cells were determined from the transmittance spectra under crossed polarizers using a microscopic spectrometer (TFM-120AFT-PC, OAK). The angle between the layer normal (extinction direction) and one of the crossed polarizers was set to be 45 degrees. By fitting the obtained spectra $T(\lambda)$ between 500 nm and 800 nm of λ to eqn. (1),

$$T(\lambda) \propto \sin^2(\pi \Delta n d/\lambda) \quad (1)$$

the anisotropy of refractive indices Δn's were determined. Here λ is the light wavelength, and d, cell thickness. The measurement area was 20×20 μm^2.

3. Results and discussion

In the small angle macroscopic 2D X-ray imaging plate (IP) measurement using a partially oriented sample, two diffraction rings corresponding to 36.04 and 22.62 Å were observed in the smectic phase, as shown in Fig. 2. Two rings contained some spots which were attributed to the diffractions of the reciprocal planes (101) and (002), indicating a frustrated layer structure. Now we show the result of the X-ray microbeam diffraction from a monodomain shown by an arrow in Fig. 3(a). Fig. 3(b) shows the 2D X-ray diffraction pattern of a 2.5 μm thick cell before applying an electric field. Only one spot peak was observed at $2\theta = 3.95°$ (22.34 Å), contrary to the results of IP measurement. Since this spot was observed in the direction of the smectic layer normal, it is considered to correspond to (002). Since the lattice constant obtained by the microbeam measurement was not corrected using the proper reference

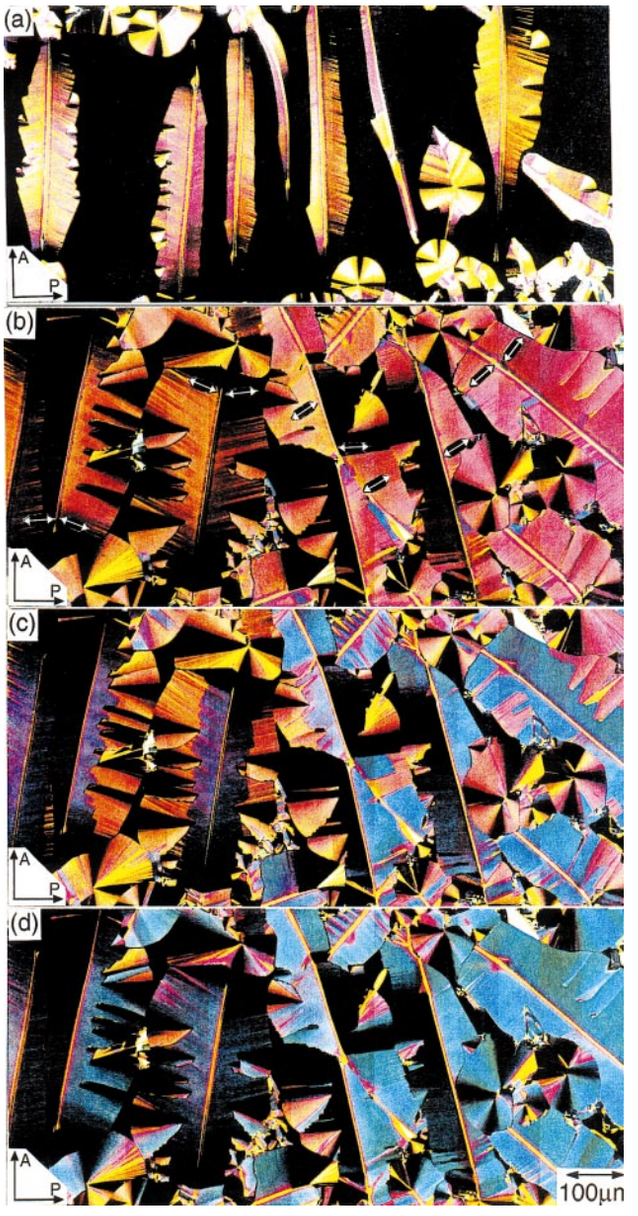

Fig. 6 Microphotographs of the planar cell of 8OAM5AMO8: at the phase transition from the isotropic to the smectic phase (a), at 107 °C (smectic phase) without a field (b), with +DC 5.6 V μm^{-1} (c) and with +DC 6 V μm^{-1} (d). White arrows indicate layer normal directions of each domain.

sample, there were small differences between the lattice constants obtained by the two methods (IP and microbeam). Fig. 4(a) shows a microphotograph of the cell under the application of a +6 V μm^{-1} DC field. By applying the field, the color changes but the extinction direction does not change. In this state, two spot peaks in addition to the (002) peak appear, as shown in Fig. 4(b). These spots are tilted by ±43° with respect to the layer normal and they correspond to the lattice constant of *ca.* 35 Å. Therefore, this result clearly indicates that (10 ± 1) reciprocal planes satisfying the Bragg condition appear due to molecular switching in the presence of the field.

In order to determine the molecular orientation, the optical birefringence of the homogeneous cell was also measured. From the optical transmittance spectra shown in Fig. 5, the birefringences are determined to be 0.297 and 0.337 in the absence and presence of a DC field, respectively. Optical micrographs of the cell used are shown in Fig. 6. At the phase transition from the isotropic to the smectic phase, pinkish smectic domains grew from defect-like lines, and they became

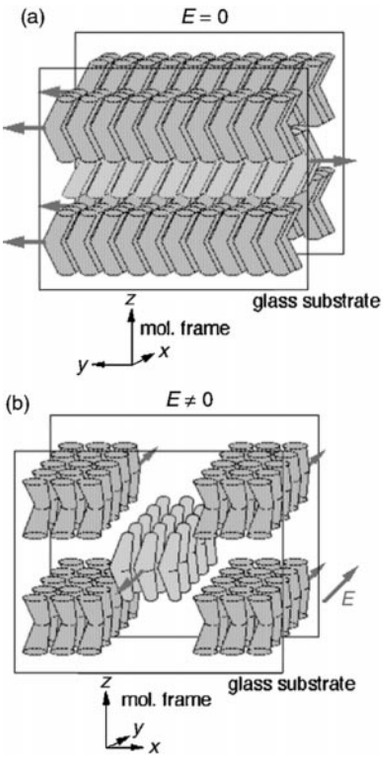

Fig. 7 Molecular arrangement of a thin homogeneous cell in the frustrated smectic phase of 8OAM5AMO8 (a) without a field and (b) under a sufficiently high field for the molecular orientation.

like banana leaves, as shown in Fig. 6(a). In the smectic phase without a field, the extinction direction was parallel to the layer normal (the direction of arrows in Fig. 6(b)). On increasing the applied field, bluish domains grew normal to the smectic layer (see Fig. 6(c)), but the extinction direction does not change. Since the texture did not change on reversing the sense of the field, molecules switch due to dielectric anisotropy, but not due to polarization switching.

From these results, we can conclude the molecular orientation before and during application of the field, as shown in Fig. 7. From the extinction direction parallel to the layer normal and the small birefringence, the molecular bending plane is parallel to the substrate plane before applying a field (see Fig. 7(a)). The increase of the birefringence on applying the field suggests that molecules reorient so that their bending plane becomes normal to the substrate. Moreover the appearance of the (101) spots in this state indicates that the frustrated layer structure is formed in the normal direction of the molecular bending plane (see Fig. 7(b)). Considering the (101) diffraction observed using the IP in the absence of a field, to our surprise, it was found that molecules reorient keeping the frustrated structure on applying the field. This behavior is also supported by the observation that the switching domain grows along the layer normal.

4. Conclusion

The layer structure and the molecular orientation in the frustrated smectic phase of bent-shaped molecules were investigated. From the results of the X-ray microbeam diffraction pattern and the optical birefringence with and without a field, it was concluded that dimer molecules switch due to dielectric anisotropy, retaining the frustrated structure.

Acknowledgements

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