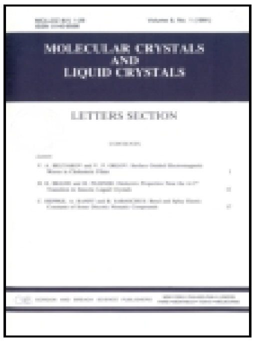

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Photo- or Electrically-induced Molecular Organizations Observed in Dichiral Azobenzene Liquid-crystalline Compounds

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Azobenzene liquid crystals, possessing two chiral moieties at both of the peripheral ends of the molecular structure, show characteristic chirality-originated liquid-crystalline and physical properties: emergence of stable smectic Q phases, a photoinduced phase transition between 3D liquid crystal phases, and induction of birefringence in the "liquid" phase. A dichiral compound, of which rigidity of the core is reduced by the introduction of ester groups, showed no smectic Q phases, but exhibited the antiferroelectric smectic C phase. The "liquid" phase of the less-rigid azo-compound was found to show electrically induced birefringence.

Keywords liquid crystal; photoinduced phase transition; smectic Q; molecular flexibility

Introduction

For common liquid crystal displays (LCDs), the precise control of the initial alignment of LC molecules is needed so that a good dark state, thus a high contrast ratio, can be obtained. If the optically isotropic LC phase is utilized, there is no need for concern about the initial alignment, which is a great advantage for the LCD production. Representative examples of such kinds of LC phases are blue phases, which are optically isotropic without the application of electric field [1, 2]. Another optically isotropic phase is a liquid phase which intrinsically shows no birefringence. Therefore, if the birefringence can be induced in the liquid phase by the application of electric field [3], it is of great use as a material for the LCD application. So far, one of our interests has been focused on the evaluation of physical properties of dichiral azobenzene mesogenic compounds. In this paper, the anomalous liquid-crystalline properties observed for dichiral azobenzene compounds are reviewed, and then the electric-field-induced birefringence in the "liquid" phase described and the correlation between molecular structures and properties discussed.

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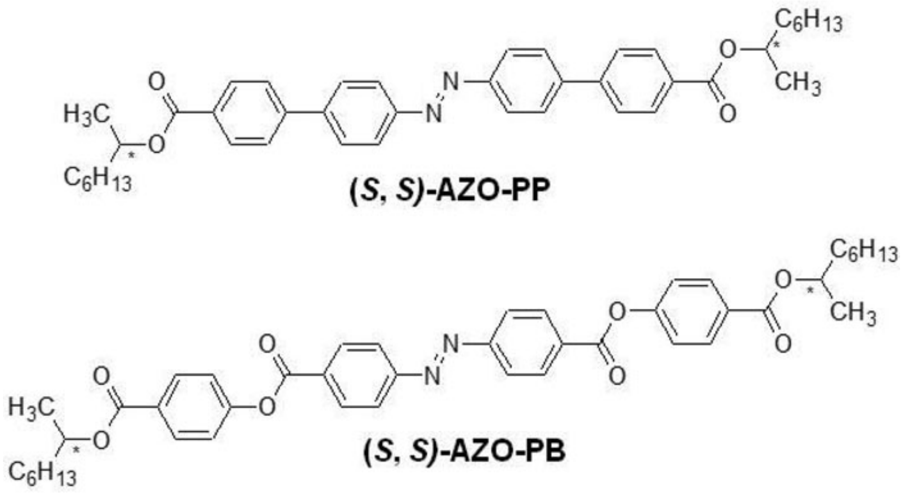

Figure 1. Structures of dichiral azobenzene derivatives studied: (a) **(*S, S*)-AZO-PP**, and (b) **(*S, S*)-AZO-PB**

Experimental Section

(*S, S*)-AZO-PP (see **Figure 1 (a)**) was prepared from *p*-bromoaniline by four steps, as described in the previous paper [4]. **(*S, S*)-AZO-PB** (see **Figure 1 (b)**) was synthesized by a simple esterification, using N,N′-Dicyclohexylcarbodiimide (0.61 mg, 3.0 mmol) and N,N-dimethyl-4-aminopyridine in dry dichloromethane (10 ml), between 4,4′-azodibenzoic acid (Tokyo Chemical Industry Co., Ltd. Japan) (0.27 mg, 1.0 mmol) and [(1R)-1-methylheptyl] 4-hydroxybenzoate (0.55 mg, 2.2 mmol) prepared according to the standard procedures. The crude product was purified by column chromatography using dichloromethane as the eluent, and recrystallized from ethanol (50 ml), giving a light orange solid. Yield = 0.33 g (46%). The structure was confirmed by ^{1}H NMR and elemental analysis: Elemental analysis found (%): C 72.0, H 6.9, N 3.8; calculated for C44H50N2O8 (%): C 72.0, H 6.9, N 3.8. δH (400 MHz, CDCl3, TMS); 8.39 (m, 4H, Ar–H), 8.15 (m, 4H, Ar–H), 8.08 (m, 4H, Ar–H), 7.33 (m, 4H, Ar–H), 5.18 (m, 2H,–COO–CH(–CH3)–CH2–), 1.74 (t, 4H, –COO–CH(–CH3)–CH2–), 1.40 (m, 22H, –COO–CH(–CH3)–CH2–CH2–CH2–CH3, –COO–CH(–CH3)–CH2–), 0.89 (t, 6H, –CH3).

Liquid-crystalline properties were studied on the basis of polarizing optical microscopy (Olympus, BX51), and differential scanning calorimetry (Mac Science, DSC 3100S + MTC 1000S + CU 9440) under the similar conditions reported previously [4]. The electro-optical measurements were conducted in commercially available sandwich cells (E.H.C. Corp.) by the application of ac fields at frequency of 100 Hz. The cell gap was 3 μm. The glass substrates were treated with no alignment layers.

Results and Discussion

Emergence of Stable Smectic Q Phases

(*S, S*)-AZO-PP (see **Figure 1 (a)**) was found to show two kinds of stable smectic Q (SmQ) phases, the SmQ$_H$ and SmQ$_L$ phases [4]. The phase sequence, the transition temperatures,

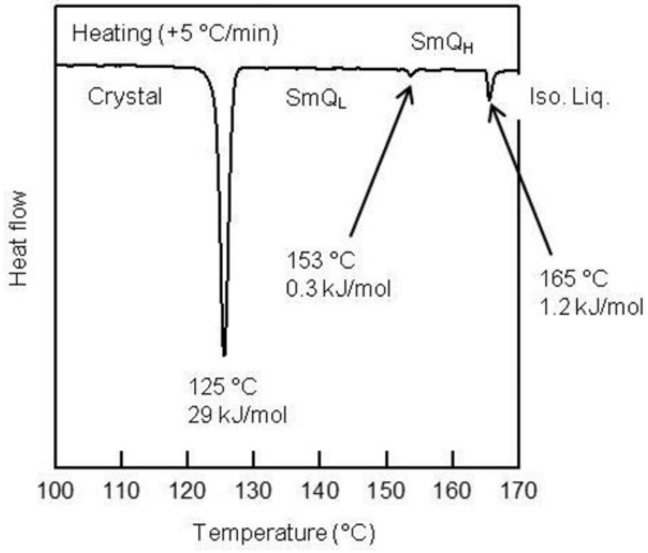

Figure 2. The phase sequence, the transition temperatures, and the DSC thermogram of ***(S, S)*-AZO-PP**.

and the DSC thermogram are summarized in Figure 2. Relatively small enthalpy change of 1.2 kJ/mol was obtained for the transition between the $\mathrm{SmQ_H}$ and the isotropic liquid phases.

The SmQ phase has so far been observed for the liquid-crystalline compounds possessing two chiral centres at each peripheral end of the molecular structure [5], The SmQ phase appears only for the compound with high optical purity, thus is considered to be one of the chirality-induced liquid-crystalline phases. As similar chirality-induced liquid-crystalline phases, the blue phases [1] and the twist grain boundary (TGB) [7] have been widely studied by many researchers. The blue and TGB phases are so-called frustrated liquid crystal phases. Frustration between desires for the molecules to produce helical structures around all directions of the molecular axis and to fill the space results in the production of the double twist structure. The blue phase is a special case where the double twist structure can fill a large volume of the space if the occurrence of the defects at regular points between the cylinders is allowed. The TGB phase is the other frustrated liquid crystal phase, formed as a result of the competition of the formation between the layered and helical structures. This competition can result in frustrated structures containing a regular lattice of grain boundary, thus the dislocation-driven twist grain boundary (TGB) phase can be obtained. The existence of the defects at the regular points is essential for the stabilization of the frustrated structures of both blue and TGB phases. It has so far, however, not yet been clarified whether the SmQ phase is a frustrated liquid crystal phase stabilized by the regularly formed "intrinsic" defects.

Next, let us consider the effect of central linking group and the stability of the SmQ phase. **M7BBM7** [7], which is a standard SmQ compound (for the structure, see Figure 3), possesses an ester central linkage group instead of the azo linkage of **AZO-PP**, as shown in Figure 3. Replacing the ester group by the azo group dramatically increases the stability of the SmQ phase, i.e., **AZO-PP** shows substantially high temperature for the transition between the SmQ and isotropic liquid phases. The azo group produces the conjugated

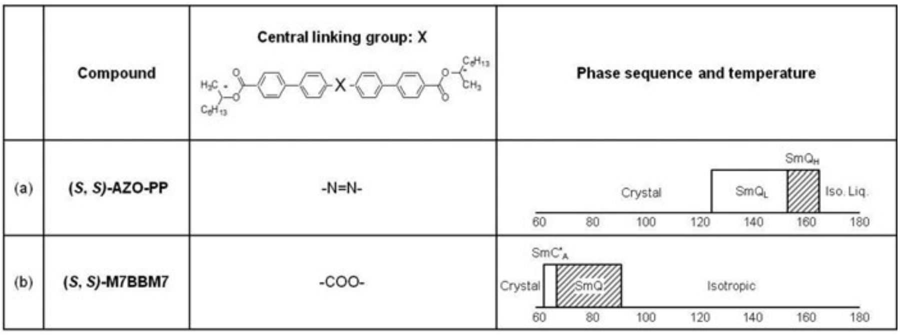

Figure 3. Phase sequences and transition temperatures: (a) ***(S, S)*-AZO-PP** and (b) ***(S, S)*-M7BBM7**.

structure among the adjacent aromatic rings, thus increases the rigidity and the planar structure of the core part. The rigidity of the core is important to stabilize the SmQ phase.

Photoinduced Transition Between Two 3D Liquid-Crystalline Phases

The SmQ phase shows the “mosaic texture” as shown in Figure 4 (a), indicating a relatively strong long-range order. However, the x-ray diffraction result exhibits that the SmQ phase showed a broad scattering in the wide angle region of the x-ray diffraction profile, which is similar to that obtained in the liquid phase, indicating that the SmQ phase possesses no short range order between the molecules [8]. Due to the strong long range order, the molecular orientations of the SmQ phase are not so sensitive to the external electric field. The mosaic texture is not changed by applying the strong electric field (70 V/3 μm). The molecular order, however, is sensitive to the internal molecular structural change, induced by the *trans-cis* isomerization of the ***(S, S)*-AZO-PP** molecules by the UV-irradiation. Figure 4 shows the photoinduced phase transition between two SmQ phases, in which the irradiated area shows the texture of the UV-induced SmQ$_H$ phase whereas the non-irradiated region remains as the original SmQ$_L$ phase.

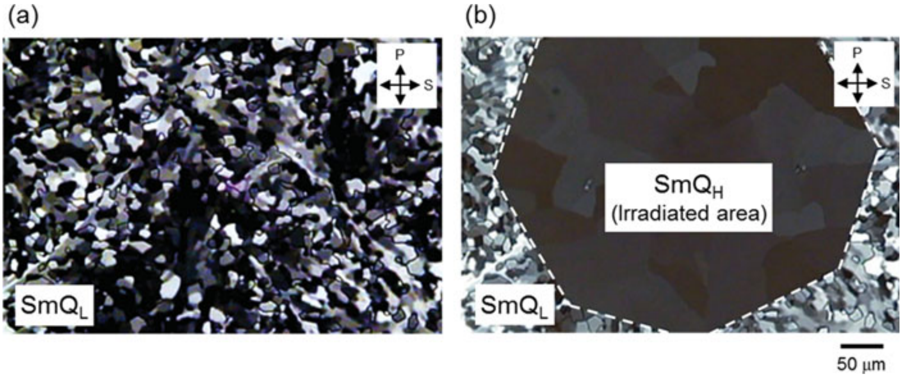

Figure 4. Photo-induced phase transitions from SmQ$_L$ phase to SmQ$_H$ phase observed for ***(S, S)*-AZO-PP**: (a) and (b) are before and during irradiation at 144 °C, respectively.

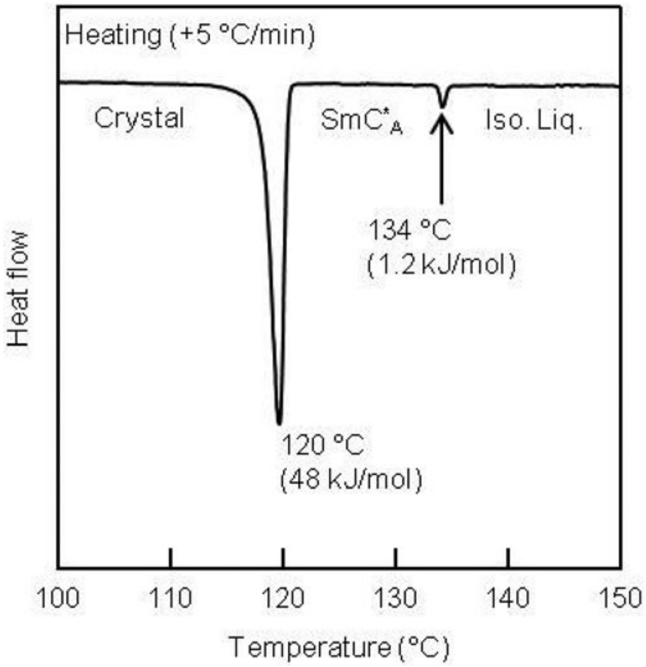

Figure 5. The phase sequence, the transition temperatures, and the DSC thermogram of ***(S, S)*-AZO-PB**.

Rigidity of the Core Part on the Stability of SmQ Phase

The effect of the rigidity on the stability of the SmQ phase was studied by introducing an ester group at the middle of each biphenyl moiety of **(*S, S*)-AZO-PP** producing a less rigid azobenzene liquid crystal, **(*S, S*)-AZO-PB** (see **Figure 1 (b)**). **(*S, S*)-AZO-PB** was found to only show the antiferroelectric phase. The phase sequence, the transition temperatures, and the DSC thermogram are summarized in Figure 5. Relatively small enthalpy change of 1.2 kJ/mol was obtained for the transition between the $\mathrm{SmQ_H}$ and the isotropic liquid phases.

A similar effect of the rigidity of the core part is also observed for the other non-azobenzene compounds (Figure 6 (c) and (d)) [8]. **Compound 1** possesses a five-ring core part, whereas **Compound 2** a four-ring. Thus, **Compound 2** is considered to possess less rigid structure than **Compound 1**. In this case, the SmQ phase again disappears by reducing the rigidity of the core part, i.e, **Compound 2** only shows the antiferroelectric phase as ***(S, S)*-AZO-PB** does.

Electrically-induced Birefringence in the "Liquid" Phase

It has been well known that the optically isotropic phases, such as liquid phases or gas phases, look dark under the polarized light microscope, because the isotropic media do not produce birefringence thus exhibit just a dark texture under such optical configuration. In the isotropic phase of ***(S, S)*-AZO-PB**, a totally dark texture was observed under the crossed polarized light microscope (Figure 7 (a)), as the phase is optically isotropic. Birefringence was, however, induced by the application of the ac electric field (35 $\mathrm{V_{0\text{-}p}}/\mu$m, 100 Hz) in the

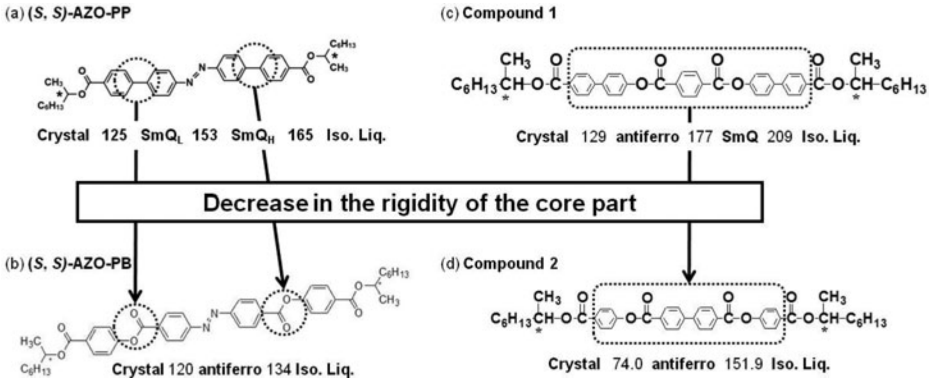

Figure 6. Effect of decreasing the rigidity of the core part, by introducing ester groups or by the reduction of the number of phenyl rings on the stability of the smectic Q phase.

isotropic liquid phase 1 degree above the clearing temperature. The induced birefringence is a texture of smectic liquid crystal phase (Figure 7 (b)), thus, this is a kind of appearance of the electrically-induced smectic phase. The emergence of the birefringence in the optically isotropic medium is useful as a new type of switching device, and also as the subject for studying the dynamics between ordered and disordered phases.

In conclusion, dichiral azobenzene liquid crystals show the chirality-originated liquid-crystalline and physical properties as follows:

(i) the azobenzene compound possessing two chiral moieties at both peripheral ends of the molecular structure, **(*S, S*)-AZO-PP** (see **Figure 1 (a)**), was found to show two kinds of stable smectic Q (SmQ) phases, the $\mathrm{SmQ_H}$ and $\mathrm{SmQ_L}$ phases.
(ii) **(*S, S*)-AZO-PP shows** a photoinduced phase transition between 3D liquid crystal phases, i.e., the transition between the $\mathrm{SmQ_H}$ and $\mathrm{SmQ_L}$ phases, and also exhibits a photoinduced phase transition between the $\mathrm{SmQ_H}$ and the “liquid” phases, and
(iii) the rigidity of the core plays an important role in the stabilization of the SmQ phase. The dichiral azobenzene liquid crystal with less rigid core structure, **(*S, S*)-AZO-PB** (see **Figure 1 (b)**), shows the antiferroelectric phase instead of the

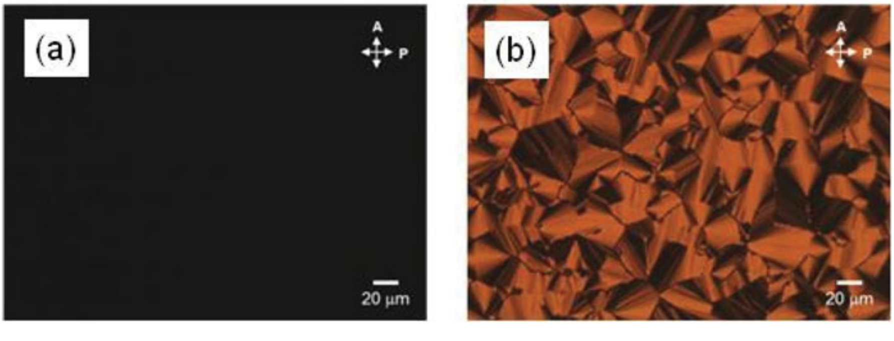

Figure 7. Polarizing optical micrographs of **(*S, S*)-AZO-PB** in optically isotropic phase: (a) without, and (b) with (35 $\mathrm{V_{0\text{-}p}}/\mu\mathrm{m}$) ac fields (frequency = 100 Hz). Temperature is 135 °C (1 °C above the clearing temperature of **(*S, S*)-AZO-PB**).

SmQ phase, and also exhibits a special "liquid" phase in which the birefringence is induced by the application of the electric field.

References

[1] Kikuchi, H. (2008). *Struct. Bonding*, *128*, 99.
[2] Yoshizawa, A. (2013). *RSC Advances*, *3*, 25475.
[3] Nishiyama, I. (2010). *Chemical Record*, *9*, 340.
[4] Yamamoto, T., Nishiyama, I., & Yokoyama, H. (2007). *Chem. Lett.*, *36*, 1108.
[5] Levelut, A.-M., Hallouin, E., Bennemann, D., Heppke, G., & Loetzsch, D. (1997). *J. Phys. II, France*, *7*, 981.
[6] Goodby, J.W., Cowling, S.J., & Goerts, V. (2009). *C.R. Chimie*, *12*, 70.
[7] Bennemann, D., Heppke, G., Levelut, A.-M., & Loetzsch, D. (1995). *Mol. Cryst. Liq. Cryst.*, *260*, 351.
[8] Nishiyama, I., Yamamoto, J., Goodby, J.W., & Yokoyama, H. (2004). *Proc. of SPIE*, *5518*, 201.