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The effect of position of (S)-2-octyloxy tail on the formation of frustrated blue phase and antiferroelectric phase in Schiff base liquid crystals[†]

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Two series of chiral salicylaldimine-based liquid crystals which differ from each other in the position of the (S)-2-octyloxy tail have been synthesized and characterized by polarizing optical microscopy, differential scanning calorimetry, and electrical switching. Compounds OH I (n = 6-7) having (S)-2-octyloxy tail close to the salicylaldimine core and compounds OH II (n = 6-11) having (S)-2-octyloxy tail far from the salicylaldimine core exhibit polymorphism of mesophases including frustrated blue phase and antiferroelectric (SmC^{*}_A) phases. Notably, as compared with structurally similar Schiff base compounds OH I (n = 7), intramolecular hydrogen bonding in antiferroelectric salicylaldimine-based compounds OH I (n = 7) induces the frustrated blue phase. However, as compared with structurally similar Schiff base compounds H I (n = 8), the lack of intramolecular hydrogen bonding in Schiff base compounds H II (n = 8) suppresses antiferroelectric properties.

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1 Introduction

Chirality and liquid crystals are both widely manifested in nature and biology. Chiral liquid crystal materials have been attracting significant attention because of the discoveries of the ferroelectric (SmC*), antiferroelectric (SmC^{*}_A), ferrielectric (SmC^{*}), twist grain boundary phase (TGB^{*}) and blue phases (BPs), and the potential for the application in electro-optical devices.¹ Both blue phases and twist grain boundary phases are two kinds of frustrated structures that can be induced by chiral groups in liquid crystals. Blue phases are usually found between the isotropic liquid and cholesteric phase of short pitches. According to the characteristic of double twist helical structure, they are classified as blue phase III (BPIII), blue phase II (BPII) and blue phase I (BPI), which appear as the temperature decreases from the isotropic liquid phase.^{2,3} The packing structures are macroscopically amorphous, simple cubic, and body-centered cubic. Blue phases are potentially useful for fast light modulators or tunable photonic crystals in applications. However, they are usually observed in a very narrow temperature range in a single molecule, which limits their practical applicability.4 Therefore, both stabilization and broadening of the temperature range of blue phase are the most important issues and attract significant attention.3,5-20 There are several different methods to broaden blue phase range.⁵⁻¹⁸ The most popular way to induce blue phase is the addition of a sufficient

amount of chiral dopant into achiral LC hosts. For synthetic chemists, it can be achieved by incorporating optically pure groups into the geometric structures of liquid crystal molecules.^{14,19-25} Consequently, chirality plays an important role in BPS.^{26,27}

The best known smectic phases are the ferroelectric chiral smectic C (SmC*) phase and the antiferroelectric chiral smectic C (SmC^{*}_A) phase. In the SmC^{*} phase the chiral molecules tilt with respect to the layers normal. In contrast, the tilting direction of the chiral molecules in the SmC^*_A phase alternates in a zig-zag mode between the layers. The antiferroelectric (SmC^{*}_A) phase in the chiral liquid crystals exhibiting a DC threshold, double hysteresis, and tristable switching properties²⁸⁻³⁰ has been demonstrated to have potential in the field technology. And the correlation between the molecular structure of the materials and the appearance of the antiferroelectric liquid crystals has been primarily successfully established.³¹⁻³³ It has been generally concluded that a rod-like molecule is made up of a three-ring core, with at least two rings that are not directly linked, and a chiral tail with a transversal disposition concerning the long molecular axis and connected to the rigid core through a carboxylate linkage. Dipole-associated functional groups such as ester or amido groups are the main types of connectors within the cores. And the formation of the SmC_A* phase in chiral liquid crystals also depends strongly on the high chirality of the molecules.

The possibility of getting both frustrated BP and antiferroelectric SmC_A^* phase in a rod-like molecule turned out to be difficult. It is probably due to both the frustrated BP and the nematic phase possessing long-range order of the mean orientations, but lacking any long-range translational order. In

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contrast, the antiferroelectric SmC_A^* phase demands an exceptionally long-range of translational order along the smectic layer normal. Consequently, only a few single chiral rod-like materials possessing both frustrated BP and SmC_A^* phases have been reported. In 1998, Li *et al.* synthesized a cyclohexane-based trimesogen, the first oligomeric antiferroelectric liquid crystal that exhibits a fairly rich polymorphism of mesophases including frustrated blue phase.³⁴ Lagerwall *et al.* have presented a chiral twin dimer with a change of the molecular conformation from the rod to bent shape on cooling, possessing the smectic blue phase and antiferroelectric property.³⁵ Moreover, Wu and Hsieh have reported two antiferroelectric rod-like molecules with two asymmetric carbons, representing another two frustrated phases – BP and TGBA*.^{36,37}

Schiff base (azomethine) has been widely employed as a linking group in the synthesis of many forms of liquid crystals.1 Its analogues, salicylaldimine[N-(2-hydroxy-4-alkoxybenzylidene) aniline] compounds are more stable to heat and moisture due to the presence of intramolecular hydrogen bonding between the hydroxy group and the imine group. In addition, with their synthetic versatility and ability to coordinate metals, they have been also employed in the synthesis of metallomesogens.³⁸ In general, rod-like Schiff base liquid crystals exhibited nematic and/or smectic mesophases.^{1,38} With the introduction of asymmetric carbons centers in the form of a chiral alkyl tail or present within the molecule, frustrated mesophases and new phase sequences have been discovered in Schiff base compounds, such as a monosubstituted ferrocenebased Schiff base derivative tethering a (S)-2-methylbutoxy tail, the first chiral metallomesogen³⁹ exhibited two frustrated phases, BP and TGBA* phases. Moreover, a Schiff base pro-mesogenic unit could also be an electron rich moiety that links a cholesteryl ester unit through a flexible polymethylene spacer to obtain unsymmetrical dimesogen compounds possessing frustrated BP and TGBA* phases.5 On the other hand, a few chiral Schiff base liquid crystals consisting of a three-ring mesogenic core have been employed in the design of antiferroelectric liquid crystals. Serrano and his coworkers have synthesized three such Schiff base liquid crystals through a carboxylate linkage with a terminal (R)-2-octyloxy tail exhibiting SmC* and SmA* phases and antiferroelectric behavior.40 It can be seen that the mesophase interval of the salicylaldimine-based compound is wider than that of its analogue, the Schiff base molecule, on account of the rigidity of the mesogenic nucleus and its polarizability enhanced by intramolecular hydrogen bonding between the hydroxy group and the imine group.^{41,42} In addition, the intramolecular hydrogen bonding not only forces the molecule to arrange itself in a coplanar manner, but also enhances the intermolecular attraction to make it easy for molecules to array parallel and form a layer structure. This situation was also found in another series of Schiff base compounds, the first ferroelectric SmC* liquid crystal DOBAMBC, reported by Meyer⁴³ and its derivative HDOBAMBC, prepared by Takao.44

Recently, we also reported a novel homologous series of chiral salicylaldimine-based liquid crystals in connection with a linear alkynyl chain and (S)-2-octyloxy tail possessing N*,

TGBA*, SmA* and SmC_A* phases.⁴⁵ Nevertheless, no chiral Schiff-based liquid crystal with rod-like molecules possessing both frustrated BP and antiferroelectric SmC_A^{*} phase has been reported until now. In addition, the correlation of chiral Schiff base molecular structure with the appearance of frustrated BP and antiferroelectric (SmC_A^*) phases is still not established. In order to shed light on the molecular factors of the resulting mesophases in this type of Schiff base compounds, we report two series of chiral salicylaldimine-based liquid crystals with an (S)-2-octyloxy tail to investigate the effect of the position of the (S)-2-octyloxy tail and the length of achiral alkoxy tail on the mesomorphic formation. To best of our knowledge, these simple rod-like and chiral salicylaldimine-based liquid crystals that possess frustrated blue phase and antiferroelectric behaviors have not been reported before. In addition, in order to assess the effect of the intramolecular hydrogen bond on mesomorphic behavior, corresponding Schiff base compounds **H** I (n = 7) and **H** II (n = 8) without hydroxy group were additionally prepared. We also examine the electro-optic behaviors of the materials under the appropriate applied electric field to prove the antiferroelectric properties of the molecules.

2 Results and discussion

2.1 Synthesis and molecular structure characterization

The target chiral Schiff base compounds and their intermediates were synthesized as outlined in Fig. 1. The key amines, 4alkoxyaniline and 4-[(1S)-1-methylheptyloxy]aniline were obtained in quantitative yields by catalytic hydrogenation of 4alkoxynitrobenzene and 4-[1-(1S)-methylheptyloxy]nitrobenzene, respectively. The 4-alkoxynitrobenzene was prepared by known etherification of 4-nitrobenzene with bromoalkane in the presence of K_2CO_3 (process A). 4-[1-(1S)-Methylheptyloxy] nitrobenzene was prepared by the Mitsunobu reaction of 4nitrobenzene with (R)-2-octanol (process B). The other key intermediates, 4-formyl-3-hydroxyphenyl 4'-[(1S)-(1-methylheptyl)oxy]benzoate, 4-formyl-3-hydroxyphenyl 4-(alkyloxy) benzoate were synthesized by the selective O-alkylation of 2,4dihydroxybenzaldehyde with (S)-4-(1-methylheptyloxy)benzoic acid and 4-(alkyloxy)benzoic acid, respectively. 4-Formylphenyl 4'-[(1S)-(1-methylheptyl)oxy]benzoate and 4-formylphenyl 4-(alkyloxy)benzoate were prepared by a similar method starting from 4-hydroxybenzaldehyde. In the final step, the amines and aldehydes were refluxed in alcohol to perform Schiff base condensation to give the target molecules. The molecular structures of the target products and the intermediates were confirmed by spectroscopic analysis and microanalytical data, as described in ESI.†

2.2 Mesophase characterizations and calorimetric studies

The mesophases and transition temperatures and enthalpies for all Schiff base liquid crystals were determined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). These results are presented in Table 1 and 2. Compounds **OH I** (n = 6, 7) in which the (*S*)-2-octyloxy tail far from the salicylaldimine core exhibits fairly rich polymorphic



Fig. 1 Chemical structures of compounds OH I (n = 6-12), OH II (n = 6-12), H I (n = 7) and H II (n = 8).

sequence including frustrated blue phase (BPI) and antiferroelectric SmC^{*}_A phase that were determined by observation of characteristic textural patterns. Compound OH I (n = 7), on slow cooling (0.2 °C min⁻¹) from their isotropic phase, displays the grazed platelet textural pattern as shown in Fig. 2a, indicating the presence of blue phase (BPI). On further cooling, the paramorphotic defect texture also grows; in addition and concomitantly, the characteristic of chiral nematic (N*) threadlike texture in which dark lines connect two $s = \pm 1/2$ point defects or from closed loops appears as shown in Fig. 2a and in full texture shown in ESI.[†] As the temperature continued to cool down from the nematic (N*) phase, the focal-conic texture appeared, indicating the characteristic of SmA* phase. On further cooling, the red petal texture started growing and other color petal textures appeared as temperature declined, as shown in Fig. 2a. The antiferroelectric SmCA* phase appeared as a petal texture and the colors of texture changed with temperature caused by the variation of helical pitches with changing temperature in the visible region of the spectrum.46,47 Compounds **OH I** (n = 6, 7) show a phase transition sequence of

Iso.-BPI-N*-SmA*-SmC_A*-Cr. When the achiral alkoxy chain length is extended, the higher homologues **OH I** (n = 8-12) show the absence of the frustrated blue phase. This suggests that extending the terminal alkoxy chain length could increase the intermolecular interaction such that it diminishes the formation of the blue phase in this series of Schiff base liquid crystals.

In order to investigate the correlation of the position of (S)-2octyloxy tail on the formation of frustrated phases, we prepared compounds **OH II** (n = 6-12) in which the position of (S)-2octyloxy tail is closer to the salicylaldimine core. These materials also exhibited more rich polymorphic sequences than compounds **OH II** (n = 6-12). When slow cooling from their isotropic phase, the BPII appeared as an iridescent platelet texture as shown in Fig. 2b and Fig. S2 in ESI[†] for compound **OH II** (n = 8) as a representative case. On further cooling, the BPI was confirmed by the formation of the grazed plane texture. The colors of both BPII and BPI textures changed with the temperatures mainly because of the variation of the helical pitches with temperatures. Compound **OH II** (n = 8) exhibits chiral nematic (N*) phase with fan-liked texture, indicating the characteristic of strongly twisted material. On further cooling, the homeotropic (dark) texture of smectic A* phase and a petal texture similar to compounds OH I (n = 7), indicating the characteristic of antiferroelectric SmCA phase are shown in Fig. 2b. Antiferroelectric SmC^{*}_A phases for compounds OH I and OH II were further characterized by the Schlieren texture. Two brush and a few of four brush singularities can be observed in the Schlieren texture for compound **OH I** (n = 7) as shown in Fig. 3a, and mostly two brush singularities for compound OH II (n = 9) as shown in Fig. 3b.^{36,48,49}

In addition, in order to study the effect of the intramolecular hydrogen bonding between the hydroxyl group and the imine group on the formation of blue phases and SmC^*_A phases, we also prepared Schiff base compounds **H I** (*n* = 7) and **H II** (*n* = 8)

Table 1 Mesophases, transition temperatures (°C) and enthalpies ΔH (in brackets, kJ mol⁻¹) of compounds OH I (n = 6-12) recorded from DSC thermograms at heating/cooling rate of 3 °C min⁻¹

Compound	Iso		BPI		N*		SmA*		$\mathrm{SmC}^*_{\mathrm{A}}$		Cr. ^a	Mp ^b
OH I $(n = 6)$		147 7	•	146.6^{c}	•	90.1	•	70.0^{c}	•	58.8	•	89.9
0111(// 0)		[1.1]		d		[0.6]		e		[19.6]		[22.6]
OH I $(n = 7)$	•	149.6	•	146.0^{c}	•	95.1	•	87.0 ^c	•	60.0	•	87.2
		[1.6]		d		[0.6]		е		[28.9]		[26.5]
OH I $(n = 8)$	•	149.0^{c}	_		•	107.6	•	91.0	•	62.5	•	92.2
		[0.75]				[0.8]		е		[19.6]		[22.6]
OH I $(n = 9)$	•	144.7^{c}	_		•	113.2	•	87.0 ^c	•	55.6	•	88.4
		[0.7]				[1.0]		е		[11.4]		[19.7]
OH I $(n = 10)$	•	143.4^{c}	—		•	118.6	•	83.0 ^c	•	46.7	·	80.0
		[1.0]				[1.3]		е		[20.3]		[25.5]
OH I $(n = 11)$	·	140.4^{c}	_		·	121.3	•	76.0 ^c	•	42.7	•	67.9
		[0.8]				[1.5]		е		[18.4]		[21.8]
OH I $(n = 12)$	•	138.1^{c}	—		•	122.6	•	76.0^{c}	•	44.2	•	67.2
		[1.1]				[1.7]		е		[19.8]		[23.4]

^{*a*} Cr. refers to crystal. ^{*b*} Mp refers to melting point taken from DSC thermograms recorded at heating rates of 3 °C min⁻¹. ^{*c*} The phase transition temperature was determined by optical microscopy at cooling rate of $0.1 \degree C \min^{-1}$. ^{*d*} The enthalpy of BPI-N* transition was added into that of Iso-BPI transition. ^{*e*} The enthalpy of phase transition was too small to be determined at a cooling rate of 3 °C min⁻¹.

Table 2	Mesophases, transition temperatures (°C) and enthalpies ΔH (in brackets, kJ mol	$^{-1}$) of compounds OH II ($n=6-12$) recorded from DSC
thermog	grams at heating/cooling rate of 3 $^{\circ}$ C min $^{-1}$	

Compound	Iso		BPII		BPI		N*		SmA*		$\mathrm{SmC}^*_\mathrm{A}$		Cr. ^a	Mp ^b
OH II $(n = 6)$	•	146.4 [0.9]	•	${145.6}^{c}_{\scriptstyle d}$		$^{145.2}_{_{d}}$	•	83.7 [1.2]		$_{e}^{76.0^{c}}$		45.1 [19.1]	•	93.1 [28.2]
OH II $(n = 7)$	•	146.1 [1.0]	•	${\displaystyle {145.7}^{c} \atop {}_{d}}$	•	$^{145.2}_{d}$	•	97.0 [1.9]	•	$^{84.3}_{e}$	•	39.3 [18.7]	·	80.7 [27.2]
OH II $(n = 8)$	•	147.6 [0.9]	•	${\displaystyle \mathop{147.2^{c}}\limits_{d}}$	•	146.6	•	105.6 [1.9]	·	71.6^{c}	·	56.8 [22.1]	·	80.8 [23.7]
OH II $(n = 9)$	•	143.5 [0.9]	•	${\substack{143.0^c\\ d}}$	•	$_{d}^{142.2}$	•	111.4 [1.9]	·	$_e^{68.1^c}$	·	57.1 [23.3]	·	86.0 [29.3]
OH II $(n = 10)$	•	142.0 [0.9]	•	${\displaystyle \mathop{141.4^{c}}\limits_{d}}$	·	$_{d}^{141.1}$	•	114.4 [2.1]	·	$_e^{63.1^c}$	·	55.6 [23.1]	·	90.0 [28.2]
OH II (<i>n</i> = 11)	•	139.0 [1.3]	•	137.7^c	•	137.1 _d	•	118.1 [3.2]	•	48.3^{c}_{e}	•	47.4 [24.7]	·	79.3 [32.2]
OH II $(n = 12)$	•	136.9 [1.6]	•	136.3^{c}_{d}	•	136.1	•	118.5 [2.8]	•		—	41.5 [23.2]	•	65.6 [26.5]

^{*a*} Cr. refers to crystal. ^{*b*} Mp refers to melting point taken from DSC thermograms recorded at heating rates of 3 °C min⁻¹. ^{*c*} The phase transition temperature was determined by optical microscopy at cooling rate of 0.1 °C min⁻¹. ^{*d*} The enthalpy of BP-N* transition was added to that of Iso-BPII transition. ^{*e*} The enthalpy of phase transition was too small to be determined at a cooling rate of 3 °C min⁻¹.







Fig. 2 Microphotographic textures of the mesomorphic phases obtained from (a): OH I (n = 7), (b) OH II (n = 8), (c) H I (n = 7), (d) H II (n = 8) at various mesogenic phase temperatures (magnification \times 400).

that are in the absence of intramolecular hydrogen bonding and structurally similar to compound **OH I** (n = 7) and compound **OH II** (n = 8), respectively (Table 3). Schiff base compound **H I** (n = 7) exhibits mesomorphic behavior similar to compound **OH I** (n = 7) except that the blue phase gets eliminated, as shown in Fig. 2c. This SmC^{*}_A phase was further characterized by Schlieren texture with mostly two-brush singularities, as shown in Fig. 3c.

The temperature range of antiferroelectric SmC_A^{*} phase for compound I (n = 7) exists from 87.6 °C to the crystallization point 59.2 °C, and is similar to that of compound **OH I** (n = 7). On the other hand, we repeated DSC measurements to examine the stability of Schiff base compound **H I** (n = 7). The DSC thermograms of the 2nd and 3rd heating-cooling cycles exhibited traces similar to those of 1st heating-cooling cycles, as shown in

Table 3 Mesophases, transition temperatures (°C) and enthalpies ΔH (in brackets, kJ mol⁻¹) of compounds I and II recorded from DSC thermograms at heating/cooling rate of 3 °C min⁻¹

Compound	Iso		BPII		N*		SmA*		$\mathrm{SmC}^*_\mathrm{A}$		Cr. ^a	Mp ^b
$\mathbf{I}(n=7)$	•	138.9 [1.8]	—		•	90.7 [2.1]		$_{e}^{87.6^{c}}$		59.2 [33.1]	·	77.0 [26.9]
II $(n = 8)$	•	144.4 $[1.1]$	·	${\displaystyle \mathop{143.8^{c}}\limits_{d}}$	•	121.0 [0.6]	·		—	65.1 [38.3]	•	86.6 [37.6]

^{*a*} Cr. refers to crystal. ^{*b*} Mp refers to melting point taken from DSC thermograms recorded at heating rates of 3 °C min⁻¹. ^{*c*} The phase transition temperature was determined by optical microscopy at cooling rate of 1 °C min⁻¹. ^{*d*} The enthalpy of BPII-N* transition was added to that of Iso-BPII transition. ^{*e*} The enthalpy of phase transition was too small to be determined at a cooling rate of 3 °C min⁻¹.



Fig. 3 Microphotomorphic textures: (a) Schlieren texture displaying both two- and four-brush singularities of the SmC^{*}_A phase obtained from compound **OHI** (n = 7) at 82.2 °C. (b) Schlieren texture displaying mostly two-brush singularities of the SmC^{*}_A phase obtained from compound **HI** (n = 7) at 66.4 °C. (c) Schlieren texture displaying mostly two-brush singularities of the SmC^{*}_A phase obtained from compound **OHI** (n = 7) at 66.4 °C. (c) Schlieren texture displaying mostly two-brush singularities of the SmC^{*}_A phase obtained from compound **OHII** (n = 9) at 60.5 °C (magnification × 400).

ESI.[†] It can be seen that Schiff base compound **H** I (n = 7) is stable under repeated heating condition. However, Schiff base compound **H II** (n = 8) displays BPII, N* and SmA* without an antiferroelectric SmCA* phase. Comparison of mesomorphic behaviors of two Schiff base compounds and their respective structurally similar salicylaldimine-based compounds shows that the mesomorphic interval increases when the rigidity and polarity of mesogenic nucleus are enhanced by intramolecular hydrogen bonding between the hydroxyl group and the imine linkage. Thus salicylaldimine-based compound **OH I** (n = 7)displays a higher melting point and clearing point and a wider mesophase interval (ca. 10 °C) as compared with compound H I (n = 7). In addition, a wider temperature range of smectic layers can be observed for compound **OH II** (n = 8) when compared with compound **H** II (n = 8). These results indicate that the existence of intramolecular hydrogen bonding in the molecular structure possibly enhances the rigidity and the intermolecular

attraction of mesogenic nucleus to make it easy for molecules to array parallel and form a layer structure. These tendencies are predictable and similar to mesogenic molecules derived from salicylaldimines, such as the previously mentioned ferroelectric SmC* liquid crystal HDOBAMBC ⁴⁵ as well as antiferroelectric salicylaldimine-based liquid crystals reported by Serrano.42 These salicylaldimine-based liquid crystals and each of their analogues exhibit similar mesomorphic behaviors. In addition, recently, Nandiraju has also reported that cholesterol-based dimeric Schiff base liquid crystal KI-4 exhibited frustrated blue phases, N*, TGBC* and SmC* phases.50 However, the ortho hydroxyl group in the salicylaldimine moiety of the homologue KI-5(OH) suppressed the formation of a blue phase and widened the temperature range of the SmA* phase. Interestingly, in our case, the presence of intramolecular hydrogen bonding in salicylaldimine-based compounds **OH I** (n = 6, 7)with (S)-2-octyloxy tail far from the salicylaldimine core further induces the formation of frustrated fluid structure, BPI. However, when the position of the (S)-2-octyloxy tail is closer to the salicylaldimine core, the presence of intramolecular hydrogen bonding in salicylaldimine-based compounds OH II (n = 6-12) further induces the formation of frustrated fluid structure, antiferroelectric SmC_A^{*} phase. This means that the two types of Schiff base molecular structures in conjunction with the (S)-2-octyloxy tail generates high chirality. The plot of temperature vs. the length of achiral alkoxy tail (n) (Fig. 4) shows the increasing n decreases melting point and depresses the formation of a frustrated fluid blue phase for compounds OH I with (S)-2-octyloxy tail far from the salicylaldimine core. However, Fig. 5 shows increasing n destabilizes the formation of antiferroelectric SmC^{*}_A phase for compounds OH II with (S)-2octyloxy tail close to the salicylaldimine core. Notably, compound **OH II** (n = 7) exhibits the widest temperature range of an antiferroelectric SmC^{*}_A phase (45 °C) and compound OH II (n = 12) displays lack of the antiferroelectric SmC^{*}_A phase. Therefore, it can be seen that increasing the achiral alkoxy tail (n) supports the formation of a layered structure to widen the interval of smectic mesophases, especially the SmA phase, in which molecules are parallel to the layer normal.

2.3 Electrical switching study

The antiferroelectric SmC_A^* phase was also further characterized from the switching current and dielectric permittivity

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Fig. 4 Plot of transition temperatures vs. achiral alkoxy tail length (n) for compounds OH I (n).



Fig. 5 Plot of transition temperatures vs. achiral alkoxy tail length (n) for compounds OH II (n).

measurements. The triangular wave is the most effective among DC, square and triangular waveforms for the alignment recovery of antiferroelectric liquid crystal molecules.⁵¹ In addition, the appearance of two switching current peaks means the instance of the transmittance changes, indicating the switchings from and to the third stable state occur at different voltages.28 We take compound OH II (n = 7) as representative material for these measurements. Their switching current behaviors were measured in a 5 µm homogeneously aligned cell, and the switching profiles are presented in Fig. 6. For compound OH II (n = 7), besides a broad current peak found close to the zero field point due to the ionic effect, it is seen that there are two switching current peaks appearing simultaneously, located approximately at opposite sides of the zero field point on applying a triangular wave and representing the antiferroelectric-ferroelectric and ferroelectric-ferroelectric switchings in the SmC_A^{*} phase, similar to that reported previously in MHPOBC.30

In clarifying the characteristic and determining the origin of the layer switching, microscopic observation of the texture upon application of the triangular wave field serves as a useful



Fig. 6 Switching current in a triangular electric field (50 Hz, 6 V_{pp}) in the SmC_A^{*} phase at 82.0 °C for compound OH II (n = 7) in 5 μ m thickness of homogeneously aligned cell.

method. Fig. 7 shows texture change of compounds **OH I** (n = 7) by turning on and off an electric field in the SmC_A^{*} phase. Before the application of an electric field, ellipse-hyperbola focal



Fig. 7 Electric-field-induced textural changes observed at 82.0 °C in a 5.0 μ m thickness of homogeneously aligned cell of compound OH I (n = 7).

conics are observed in a 5 μ m homogeneously aligned cell. With the application of the triangular wave field (50 Hz, 5 V_{pp}), the texture changes in such a way that ellipse–hyperbola focal conics gradually disappeared. When the field is turned off, microscopic striped pattern of the homogeneous texture appeared. This possibly suggests that dechiralization lines are perpendicular to the layer normal and the ferroelectric domains appear. This first change of defects is irreversible. However, the texture changes reversibly between Fig. 7b and c during the subsequent switching.⁵² In addition, Fig. 8 and 9 also show the electric-field-induced textural changes of compound **H II** (n = 7) and compound **OH II** (n = 7), respectively, indicating the switching behaviors similar to compound **OH I** (n = 7).

The temperature dependence of the dielectric constants ε' measured at 100 Hz in the 25 µm homogeneously aligned cell was investigated. The represented results for compound **OH II** (n = 7) from the cooling measurements are shown in Fig. 10. During cooling, the dielectric constants ε' in the SmA* phase are small and slightly increase at the SmA* to SmC^{*}_A transition. The characteristic point corresponding to the SmA* to SmC^{*}_A

transition is seen as a small peak at approximately 85 °C to 87 °C. Since the macroscopic polarization from ferroelectric contribution does not exist in the antiferroelectric phase, the contribution of the Goldstone mode (the small winding and unwinding motions of helical structure) cannot be detected by means of the dielectric measurement: thus, the enhancement of the dielectric constant in the antiferroelectric phase is considered to be the result of the antiferroelectric soft mode⁵³ and the vibration of the azimuthal molecular motion.54 Moreover, a broad peak shown in the antiferroelectric phase possibly resulted from the weaker vibration of the azimuthal molecular motion. Similar trends for other compounds such as OH I (n =7) and **H I** (n = 7) could also be observed, as shown in ESI.[†] There was no existence of Goldstone relaxation in the SmC^{*}_A phase, further demonstrating the existence of antiferroelectric property. All of the results from switching behaviors and dielectric permittivities are similar to our previously reported antiferroelectric salicylaldimine-based compounds C_m-**YCBOC**₈* (m = 6-10) having the (S)-2-octyloxy tail.



Fig. 8 Electric-field-induced textural changes observed at 78.0 $^{\circ}$ C in a 5.0 μ m thickness of homogeneously aligned cell of compound H I (n = 7).



Fig. 9 Electric-field-induced textural changes observed at 82.0 °C in a 5.0 μ m thickness of homogeneously aligned cell of compound OH II (n = 7).



Fig. 10 Temperature dependence of the dielectric constant ϵ' for compound OH II (n = 7) at 100 Hz in a cell with 25 μ m thickness under 1 °C min⁻¹ cooling process.

3 Conclusion

In this article, we have described the synthesis and thermotropic properties of two series of chiral salicylaldimine-based liquid crystals having an (S)-2-octyloxy tail with two different positions. Two homologues have been investigated with the correlation of the position of (S)-2-octyloxy tail on the frustrated blue phase and antiferroelectric (SmC^{*}_A) phase. In addition, the length of achiral alkoxy tail has been varied from a hexyloxy to a dodecyloxy tail with the intention of understanding the structure and property relationship. In general, the majority of chiral salicylaldimine-based liquid crystals exhibit an antiferroelectric (SmC_A^*) phase. For compound **OH I** (n = 6-12) in which the (S)-2octyloxy tail is far from the salicylaldimine core, frustrated blue phase destabilizes and the temperature range of SmCA* phase extends as the length of the achiral alkoxy tail (n) increases. For compound **OH II** (n = 6-12) with the (S)-2-octyloxy tail close to the salicylaldimine core, all the compounds exhibit BPII and BPI. However, increasing the length of the achiral alkoxy tail depresses the stability of the antiferroelectric SmC_A^{*} phase. Only chiral salicylaldimine-based compound **OH II** (n = 12) exhibits lack of the antiferroelectric SmC^{*}_A phase. In addition, Schiff base compounds **H** I (n = 7) without a hydroxy group also exhibits an antiferroelectric SmC_A^{*} phase but no blue phase sequence. However, Schiff base compounds **H** II (n = 8) without hydroxy group exhibits a BPII phase but no antiferroelectric property. It can be seen that the existence of the intramolecular hydrogen bonding in the chiral salicylaldimine-based compounds OH I with an achiral alkoxy tail close to the salicylaldimine core could enhance the rigidity and polarity of the mesogenic nucleus and further induce the formation of the frustrated blue phase. However, the antiferroelectric property of the chiral salicylaldimine-based compounds OH II with (S)-2-octyloxy tail close to the salicylaldimine core could result from the intermolecular attraction of mesogenic nucleus to array parallel and form a layer structure. It can be concluded that this type of Schiff base compounds in conjunction with an (*S*)-2-octyloxy tail generate high chirality to easily exhibit a BP and an antiferroelectric SmC_A^* phase. More related compounds will be studied and reported on the correlation of molecular structure to the appearance of the blue phase and the SmC_A^* phase in the nearest future.

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