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Synthesis and mesomorphic properties of achiral swallow-tailed liquid crystals derived from diethylaminoalkanols

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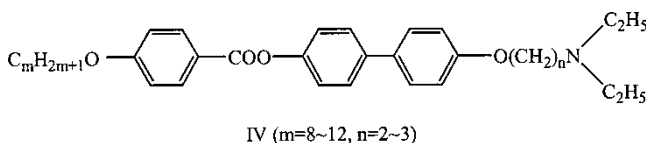
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A homologous series of achiral swallow-tailed compounds derived from diethylaminoalkanols was designed and synthesized for the investigation of mesomorphism. Spectral analyses were in accord with the expected structures. Polarizing microscopy showed that all the compounds exhibit SmA and SmC_{alt} phases. The existence of the SmC_{alt} phase was confirmed by a significant first-order SmA–SmC_{alt} phase transition in the DSC traces, and by the appearance of a schlieren texture with a large number of four-brush and a small number of two-brush singularities under microscopy.

1. Introduction

Achiral compounds with swallow-tailed moieties have already been demonstrated to possess the SmC_{alt} phase with antiferroelectric-like structure [1–3]. This type of compound has shown its potential for use as a host to be doped with antiferroelectric or ferroelectric liquid crystals to produce antiferroelectric mixtures. Terminal modification is very important in molecular design because the peripheral parts are close to the interfaces between the smectic layers, so that the structures are expected to have a significant effect on interlayer interaction. The introduction of a heteroatom such as nitrogen at the branching of the swallowtail is expected to give interesting molecular ordering due to change in hybridization and polarity. In addition, recent reports indicate that binary mixtures of achiral swallow-tailed compounds with antiferroelectric or ferroelectric liquid crystals could result in thresholdless, V-shaped switching in the electro-optical responses of the antiferroelectric or ferroelectric phase [4, 5].

As a continuation of previous investigations, the present work deals with the design and synthesis of a new series of achiral swallow-tailed materials (compounds IV), derived from diethylaminoalkanols as the swallow-tailed group, for the investigation of structure–property relationships of the mesophases. The structure of the target compounds is as shown:



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2. Experimental

2.1. Characterization

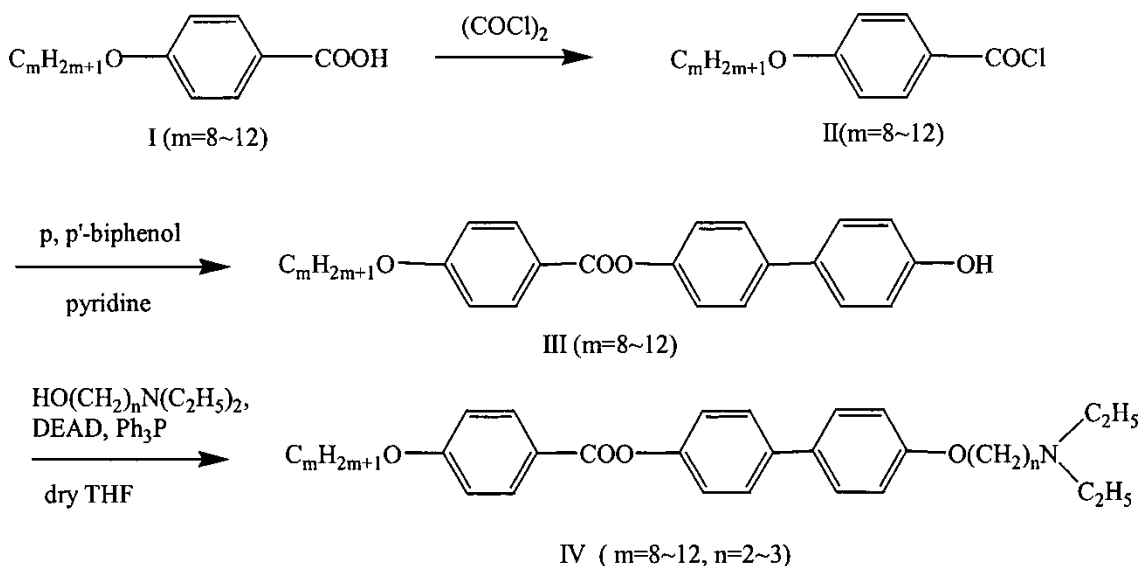
The chemical structures of the materials were analysed by nuclear magnetic resonance using a Jeol EX-400 FTNMR spectrometer. The purity of the achiral material was checked by thin-layer chromatography and further confirmed by elemental analysis.

Mesophases of the achiral compounds were principally identified by microscopic texture of samples sandwiched between two glass plates under a crossed polarizing microscope (Nikon Microphot-FXA) in conjunction with an Instec HS1 hot stage. Phase transition temperatures and their corresponding transition enthalpies were determined by differential scanning calorimetry using a Perkin-Elmer DSC7 calorimeter at heating/cooling rates of 5°C min⁻¹.

2.2. Synthesis

The starting achiral compounds, 2-diethylaminoethanol and 3-diethylamino-1-propanol, were purchased from Aldrich with purity greater than 99%. Thin-layer chromatography was performed with TLC sheets coated with silica, and spots were detected by UV irradiation. Silica gel (MN Kieselgel 60, 70–230 mesh) was used for column chromatography.

Organic solvents, dichloromethane (CH₂Cl₂) and tetrahydrofuran (THF), were purified by treatment with CaH₂ and LiAlH₄, respectively, and distilled before use. The syntheses of the target materials were carried out as outlined in the scheme.



Scheme. Synthetic procedures for the target compounds, IV ($m=8\sim 12, n=2\sim 3$).

2.2.1. Syntheses of 4-alkoxyphenylbenzoyl chlorides, II ($m=8\sim 12$)

The acid I ($m=8\sim 12$) (5 mmol), was dispersed in dry dichloromethane (15 ml) with stirring under nitrogen. Oxalyl chloride (12.6 mmol) was added drop wise to the mixture, the stirring continued for 1 h, and the mixture then heated to gentle reflux for a further 2 h. The reaction mixture became homogeneous; the solvent and excess oxalyl chloride were then removed under reduced pressure. The precipitate obtained was used immediately without further purification.

2.2.2. Synthesis of 4'-hydroxybiphenyl 4-alkoxybenzoates, III ($m=8\sim 12$)

Compound II ($m=8\sim 12$) (5 mmol) dissolved in dry dichloromethane was added dropwise to a mixture of 4,4'-biphenol (25 mmol), dry pyridine (5 ml) and THF (30 ml). The reaction mixture was kept in freezer for 2 days. Silica gel (5 g) was added to the mixture, which was then dried and powdered. The product was purified by passing through a silica gel column (70–230 mesh) using dichloromethane as eluant, and crystallized from ethanol; yield 40–50%. ^1H NMR data of representative compound III ($m=10$) in δ (ppm): 0.85–1.82 (m, 19H, RCH_2 ; CH_3), 4.98 (s, 1H, OH), 4.01–4.08 (t, 2H, ArOCH_2) 6.88–8.19 (m, 12H, ArH).

2.2.3. Synthesis of 4'-(2-diethylamino-ethoxy)-biphenyl 4-alkoxybenzoates, IV ($m=8\sim 12, n=2$)

A solution of diethyl azodicarboxylate (1.6 mmol) and compound III ($m=8\sim 12$) (1.08 mmol) in anhydrous THF (7 ml) was added dropwise to a solution of triphenylphosphine (1.6 mmol) and 2-diethylaminoethanol

(1.6 mmol) in anhydrous THF (7 ml) at room temperature with vigorous stirring. The mixture was held overnight at room temperature; the triphenylphosphine oxide thus formed removed by filtration and THF was removed under vacuum. After a work-up procedure, the products were isolated by column chromatography over silica gel (70–230 mesh) using a dichloromethane/ethyl acetate mixture as eluant. The product was crystallized from absolute ethanol; yield 60–70%. ^1H NMR data of representative compound IV ($m=10, n=2$) in δ (ppm) 0.85–1.81 (m, 25H, RCH_2 ; CH_3), 2.63–2.74 (m, 4H, NCH_2), 2.89–2.95 (t, 2H, $\text{OCH}_2\text{CH}_2\text{N}$), 3.98–4.12 (m, 4H, OCH_2), 6.94–8.24 (m, 12H, ArH).

2.2.4. Synthesis of 4'-(3-diethylaminopropoxy)-biphenyl 4-alkoxybenzoates, IV ($m=8\sim 12, n=3$)

A similar synthetic procedure to that used for compounds III was used to obtain the title compound using the appropriate starting materials. ^1H NMR data for representative compound IV ($m=10, n=3$) in δ (ppm) 0.85–2.20 (m, 27H, RCH_2 ; CH_3), 2.88–3.01 (m, 6H, NCH_2), 4.02–4.12 (m, 4H, OCH_2), 6.94–8.18 (m, 12H, ArH).

3. Results and discussion

The mesophases were identified principally by microscopic texture observations; all the compounds exhibited enantiotropic mesophases. The mesophases were characterized by the microscopic textures of sample, homeotropically aligned between two glass substrates. The SmA phase was identified by the appearance of a focal-conic texture; the SmC_{alt} phase was characterized by a broken focal-conic texture in the

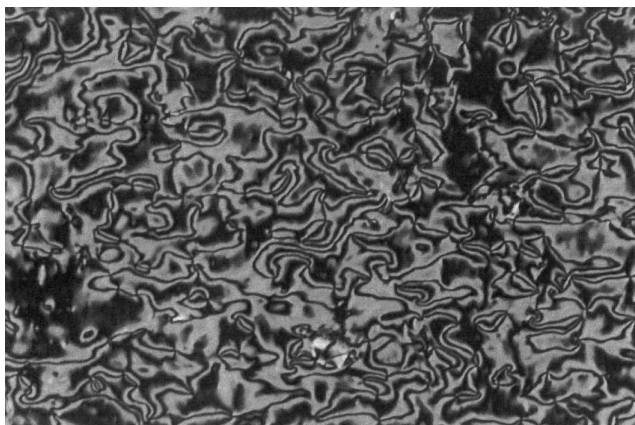


Figure 1. The schlieren texture of the SmC_{alt} phase showing two- and four-brush singularities obtained from $\text{IV}(m=10, n=2)$ (105.5°C ; magnification $\times 200$).

thicker region and in the thinner region, by the formation of a schlieren texture with the presence of large number of four-brush and a small number of two-brush singularities (see figure 1) [4, 5]. Two-brush declinations in the SmC_{alt} phase have previously been observed in other antiferroelectric phases [1, 6, 7] and indicate the existence of antiferroelectric-like structure. Further confirmation of the mesophases was conducted by observation of samples in parallel-aligned cells. The SmA phase appeared like an isotropic phase (in the plane of the substrates), and the SmC_{alt} phase appeared like a SmA phase.

Mesophase transition temperatures were determined

Table. Transition temperatures ($^\circ\text{C}$) and associated enthalpy data (in square brackets, J g^{-1}) for the compounds $\text{IV}(m=8-12, n=2-3)$.

m	n	I	SmA	SmC_{alt}	Cr	m.p. ^a	
8	2	•	142.0 [1.872]	•	109.7 [4.542]	•	70.7 [15.02]
9	2	•	149.4 [1.825]	•	117.3 [4.497]	•	77.7 [15.816]
10	2	•	142.6 [1.587]	•	119.6 [3.164]	•	85.9 [15.08]
11	2	•	132.9 [2.223]	•	115.6 [4.827]	•	78.8 [19.99]
12	2	•	134.8 [2.214]	•	119.6 [4.776]	•	92.4 [21.38]
8	3	•	151.2 [2.212]	•	121.3 [5.618]	•	85.4 [15.451]
9	3	•	145.3 [1.958]	•	122.5 [5.01]	•	80.3 [14.05]
10	3	•	143.3 [1.492]	•	123.5 [4.667]	•	75.1 [14.37]
11	3	•	138.5 [2.042]	•	124.3 [5.206]	•	76.4 [17.484]
12	3	•	137.7 [2.405]	•	126.7 [5.588]	•	78.8 [14.961]

^aTaken from DSC thermograms recorded at heating rates of 5°C min^{-1} .

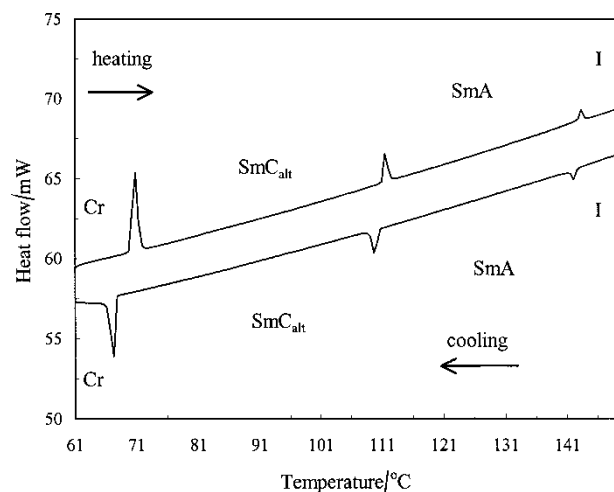


Figure 2. Heating and cooling thermograms for compound $\text{IV}(m=8, n=2)$; heating and cooling rates were 5°C min^{-1} .

by DSC with heating and cooling rates of 5°C min^{-1} . A representative DSC thermogram obtained from compound $\text{IV}(m=8, n=2)$ is shown in figure 2. The results indicate that the SmA and SmC_{alt} phases are enantiotropic; moreover, all the SmA – SmC_{alt} transitions show strong first-order characteristics, further supporting the existence of the SmC_{alt} phase [1, 2]. The mesophases, phase transition temperatures and corresponding transition enthalpies for all the compounds are summarized in the table.

The phase diagram as a function of alkyl chain

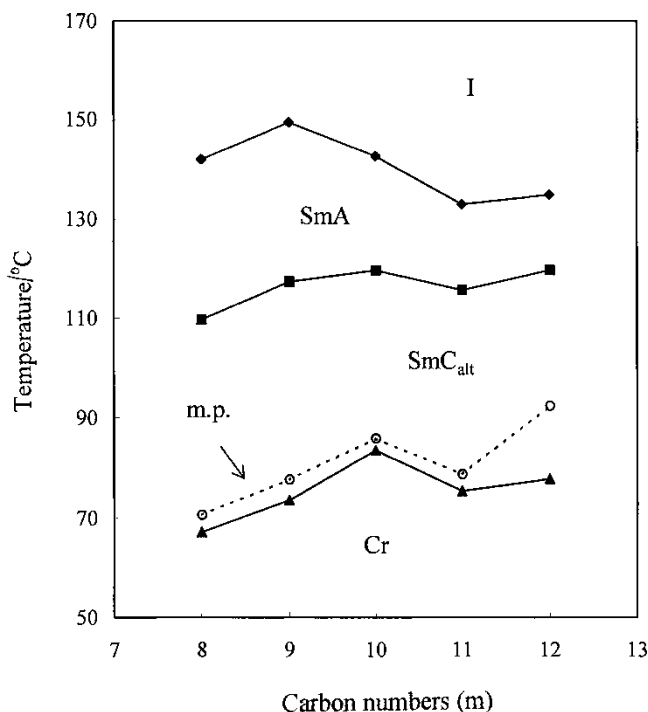


Figure 3. Plot of transition temperature as a function of terminal alkyl chain length for compound IV ($m=8-12$, $n=2$) during cooling at $5^{\circ}\text{C min}^{-1}$.

length on the achiral tail (m), for compounds IV ($m=8-12$, $n=2$) is plotted in figure 3. The thermal stabilities of the SmA phase are decreased as the alkyl chain length m increases, but the range of the SmC_{alt} phase remains almost constant. The phase diagram for compounds IV ($m=8-12$, $n=3$) is plotted in figure 4. Again, the thermal stability of the SmA phase decreases as m increases; but the SmC_{alt} phase range increases as m increases.

The comparison of these two series of achiral swallow-tailed compounds, IV ($n=2$) and IV ($n=3$), indicates that the latter series, in general, has a wider temperature range SmC_{alt} phase than the former. These results demonstrate that an additional methylene unit between the chiral tail and rigid core of the molecule helps to increase the thermal stability of the SmC_{alt} phase.

4. Conclusion

New achiral swallow-tailed compounds derived from diethylaminoalkanols have been demonstrated to exhibit the SmC_{alt} phase. It was also observed that

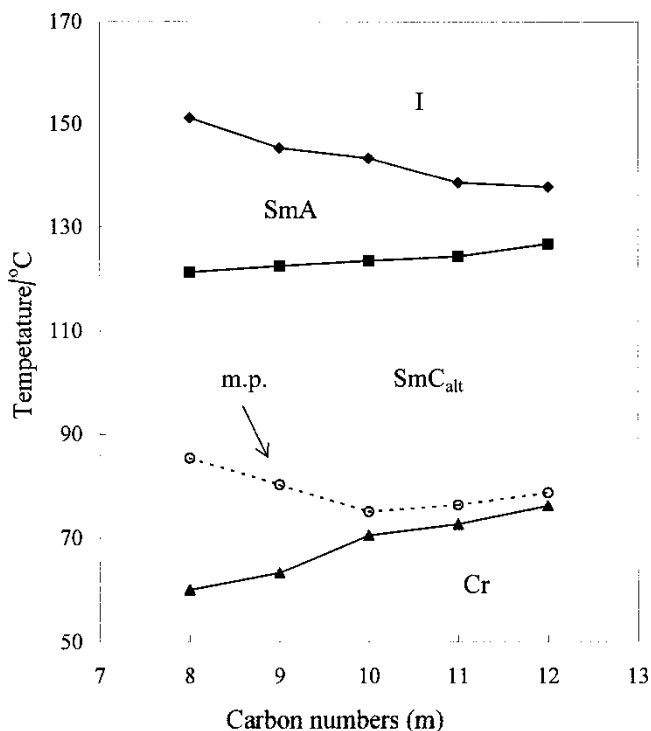


Figure 4. Plot of transition temperature as a function of terminal alkyl chain length for compound IV ($m=8-12$, $n=3$) during cooling at $5^{\circ}\text{C min}^{-1}$.

the thermal stability of the SmC_{alt} phase is increased by increasing the length of the spacer between the rigid core and the branching of the carbon chain. The feasibility of mixing these achiral swallow-tailed compounds with antiferroelectric liquid crystals or ferroelectric liquid crystals will be investigated and reported elsewhere.

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