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## Liquid Crystals

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### Physical properties of two systems with induced antiferroelectric phase

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## Physical properties of two systems with induced antiferroelectric phase

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Two ferroelectric three-ring chiral esters, one with a partially fluorinated alkyl chain and another with a cyano terminal group, were mixed with a structurally similar compound having an alkyl terminal chain. In their mixtures an antiferroelectric phase was induced. The phase behaviour, spontaneous polarisation, tilt angle, smectic layer spacing and helical pitch of both systems were determined. The mechanism of the induction of an antiferroelectric phase is different in both cases, with highly tilted phases in former system and less tilted phases in the latter.

**Keywords:** antiferroelectric phase; phase induction; physical properties

### 1. Introduction

Since the discovery of antiferroelectricity in liquid crystals (*I*) a large number of diffident structures exhibiting the antiferroelectric chiral smectic C ( $\text{SmC}^*_A$ ) phase have been prepared (2–7). In some mixtures, an antiferroelectric phase was observed although components of these mixtures do not possess an antiferroelectric phase. Several such systems have been described recently (8–10). The reason for such behaviour is the induction of an antiferroelectric phase, which occurs in mixtures of two compounds having differing polarity, e.g. one with an alkyl terminal chain and another with a fluorinated alkyl chain (*II*) or cyano group (*I2*). Both systems are characterised and compared here by means of spontaneous polarisation, tilt angle, layer spacing and helical pitch measurements.

### 2. Experimental

Phase transitions were investigated using a polarising optical microscope (Biolar-PZO) connected with a Linkam THMS-600 heating stage and by differential scanning calorimetry (DSC, Setaram 141). Measurements of helical pitch were based on the phenomenon of selective light reflection. A Varian Cary 3E UV–visible spectrophotometer was used for such measurements. The temperature was controlled by Peltier element with an accuracy of 0.1°C. The sample was placed on a glass plate with a homeotropic aligning layer without covering with another glass plate. To obtain the value of helical pitch the

experimental value of maximum wavelength of selectively reflected light was divided by 1.5, the value of the average refractive index for this class of materials (*I3*). Temperature characteristics of the smectic layer thickness were studied using the X-ray diffraction (XRD) method. Some of measurements were made using an X'Pert (Philips) powder diffractometer system (with Cu source, Ni filter, proportional counter) with temperature controller (Unipan 660) driven hot-stage, and others on curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer driven by a homemade temperature controller with an accuracy of  $\pm 0.05^\circ\text{C}$ . Spontaneous polarisation was measured by means of the Diamant bridge method and pulse technique (STRA generator (HP 33120A, Hewlett Packard), a digital oscilloscope (HP 54501B, Hewlett Packard)). Tilt angles were determined by means of optical switching angle measurements.

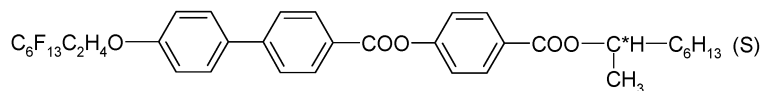
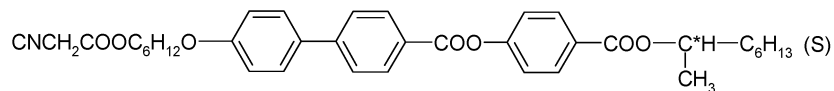
The compounds that enabled induction of an antiferroelectric phase have the structures and phase sequences shown in Scheme 1.

They were mixed with one of the members of the homologous series **2** (Scheme 2).

### 3. Results

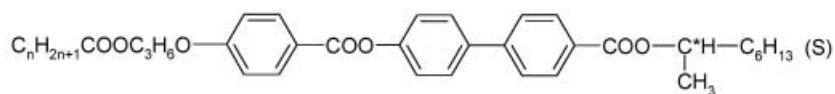
Two bicomponent systems in which an antiferroelectric ( $\text{SmC}^*_A$ ) phase is induced were compared: the first comprising a fluoro-terminated compound and a protonated compound (**1a–2b**) and the other comprising a cyano-terminated compound and the same

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**1a**Cr<sub>1</sub> 80.7 Cr<sub>2</sub> 98.1 SmC\* 138.0 SmC\*<sub>α</sub> 148.1 SmA 183.6 I (14)**1b**

Cr 62.2 SmC\* 90.5 SmA 97.6 I (15)

Scheme 1. Structures and phase sequences of compounds used to induce an antiferroelectric phase (Cr=crystalline; I=isotropic liquid; other phases as defined in text).

**2a** (n = 1) Cr 72.3 SmA 104.3 I (17)**2b** (n = 5) Cr 71.3 SmC\*<sub>FI</sub> 75.2 SmA 101.1 I (14)

Scheme 2. Homologous series (2) in which an antiferroelectric phase was induced.

protonated compound (**1b–2b**). The phase diagrams of these systems are presented in Figures 1a (11) and b (12), respectively. The temperature stability of liquid crystalline phases is higher for the fluoro-terminated

compound (clearing point around 180°C). The cyano-terminated compound can support liquid crystalline ordering only up to around 100°C. Thus the thermal stability of the induced antiferroelectric phase is higher

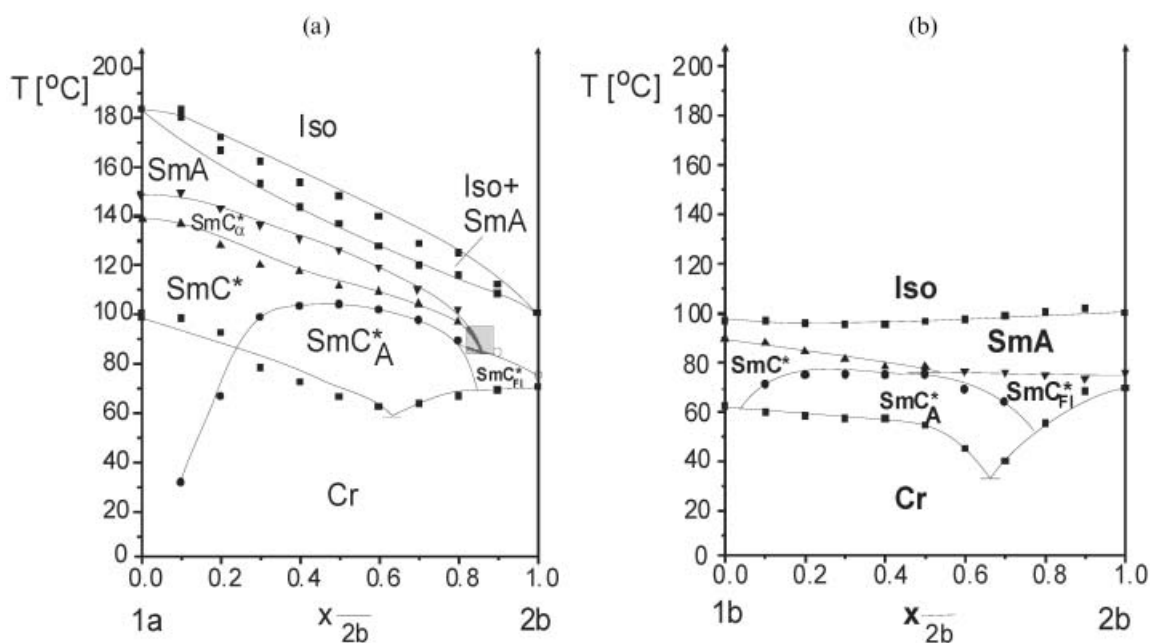


Figure 1. The phase diagrams of the systems **1a–2b** (the region marked with a grey square was not tested carefully) (a) and **1b–2b** (b).

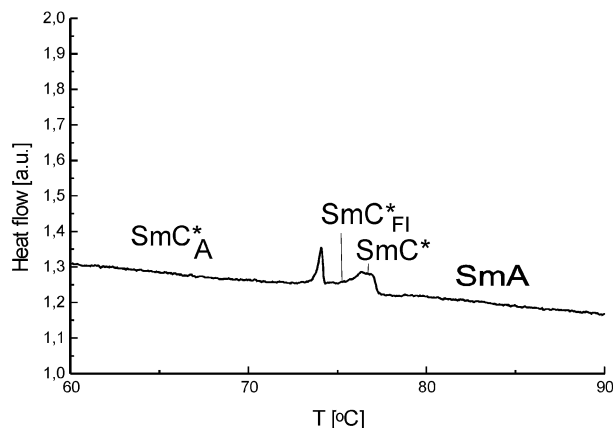


Figure 2. The heat flow vs. temperature for the mixture **1b–2b** comprising 0.5 mole ratio of compound **2b**.

in the former case. In addition to a smectic A (SmA) phase, the fluoro-terminated compound also exhibits smectic C ( $\text{SmC}^*_\alpha$  and  $\text{SmC}^*$ ) phases (14), the cyano-terminated compound has only  $\text{SmC}^*$  phases (15), but the protonated compound exhibits only a ferroelectric  $\text{SmC}^*_{\text{FI}}$  phase (16). These phases disappear in mixtures for excess of second component, but for medium concentrations all phases that are present in

the pure compounds are still observed in mixtures. This is exemplified by the results of DSC measurements of **1b–2b** compositions with 0.5 mole ratio of protonated compound mixed with the cyano-terminated compound (Figure 2). The transitions  $\text{SmC}^*_A$ – $\text{SmC}^*_{\text{FI}}$ – $\text{SmC}^*$ – $\text{SmA}$  were found. The region marked with a grey square in figure 1a was not tested carefully, because it was not the subject of this work. It was found that the sequence of phases for concentrations of 0.8 and 0.9 was as follows:  $\text{SmC}^*_A$ – $\text{SmC}^*$ – $\text{SmC}^*_\alpha$ – $\text{SmA}$  and  $\text{SmC}^*_{\text{FI}}$ – $\text{SmA}$ , respectively.

The results of spontaneous polarisation measurements of both systems, **1a–2b** and **1b–2b**, are presented in Figure 3. The temperature characteristics are presented in Figures 3a and 3c and the dependence on the concentration for set temperature  $T - T_{C-A} = -10^\circ\text{C}$  are presented in Figures 3b and 3d. The reduced temperature equal to  $-10^\circ\text{C}$  was chosen because for this value all physical parameters announced in this work are available. Graphs obtained for reduced temperature show the dependence of different parameters on the concentration and it was found that the same change characteristic was observed for other reduced temperatures, e.g.  $-20$  or  $-30^\circ\text{C}$ , regardless of the formulated phases.

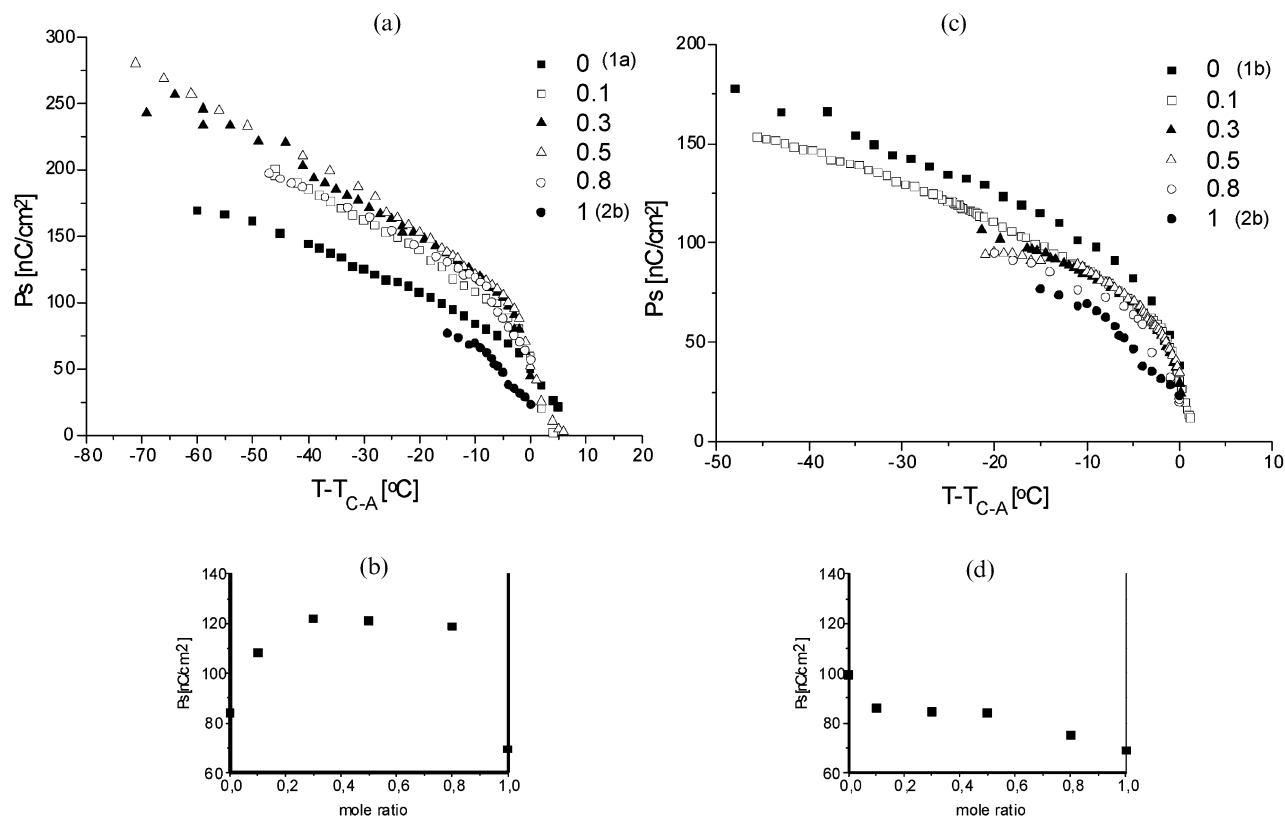


Figure 3. The spontaneous polarisation vs. temperature and concentration for set temperature  $T - T_{C-A} = -10^\circ\text{C}$  for the systems **1a–2b** (a, b) and **1b–2b** (c, d).

In the case of the system with fluorinated compound (**1a**) strongly non-additive behaviour is observed. The values of spontaneous polarisation ( $P_s$ ) are the lowest for pure compounds (**1a** and **2b**), and they increase for mixtures of these compounds (Figures 3a and 3b). The highest value of  $P_s$  is about  $280 \text{ nC cm}^{-2}$  for the mixture with 0.5 mole ratio of compound **2b**. The same behaviour was found in a previously described system also containing a fluoro-terminated compound (**14**). In the case of the system containing the cyano-terminated compound (**1b**), the value of the spontaneous polarisation changes linearly with the concentrations of compounds **1b** and **2b** (Figures 3c–3d). The maximum value of  $P_s$  is around  $180 \text{ nC cm}^{-2}$  for the pure cyano-terminated compound. These results indicate that the mechanism of the induction of an antiferroelectric phase is different in both systems.

Similar results were observed for tilt angle measurements (Figure 4). The addition of a small amount of protonated compound **2b** (0.1 mole ratio) drastically increases the tilt angle from  $35^\circ$  to  $40^\circ$  in the system with fluoro-terminated compound (Figure 4a), whereas in the system with cyano-terminated compound only a monotonous decrease

of the tilt with the increase of compound **2b** is observed (Figure 4c). Unfortunately, we were unable to measure the tilt angle of pure compound **2b** because of sample crystallization, but from the extrapolation of the results for the mixture with cyano-terminated compound, in which the dependence of the tilt versus concentration is linear, it can be estimated as around  $15^\circ$ .

The results of XRD measurements (Figure 5) show that the order of the fluorinated compound (**1a**) dominates in the mixture **1a–2b** and the fluorinated compound forces the protonated compound to adopt the layer spacing characteristic for it. The layer spacing is constant up to 0.7 mole ratio of protonated compound (Figure 5b). In the system containing the cyano-terminated compound (**1b**) the smectic layer spacing changes linearly with the concentration of both compounds (**1b** and **2b**), as shown in Figure 5d.

The results of selective light reflection measurements on the two tested systems, **1a–2b** and **1b–2b**, did not provide the information about the influence of the concentration on the pitch in both phases (antiferroelectric  $\text{SmC}^*_A$  and ferroelectric  $\text{SmC}^*$ ). Thus, additional mixtures were prepared. These mixtures contained, instead of compound **2b**, a

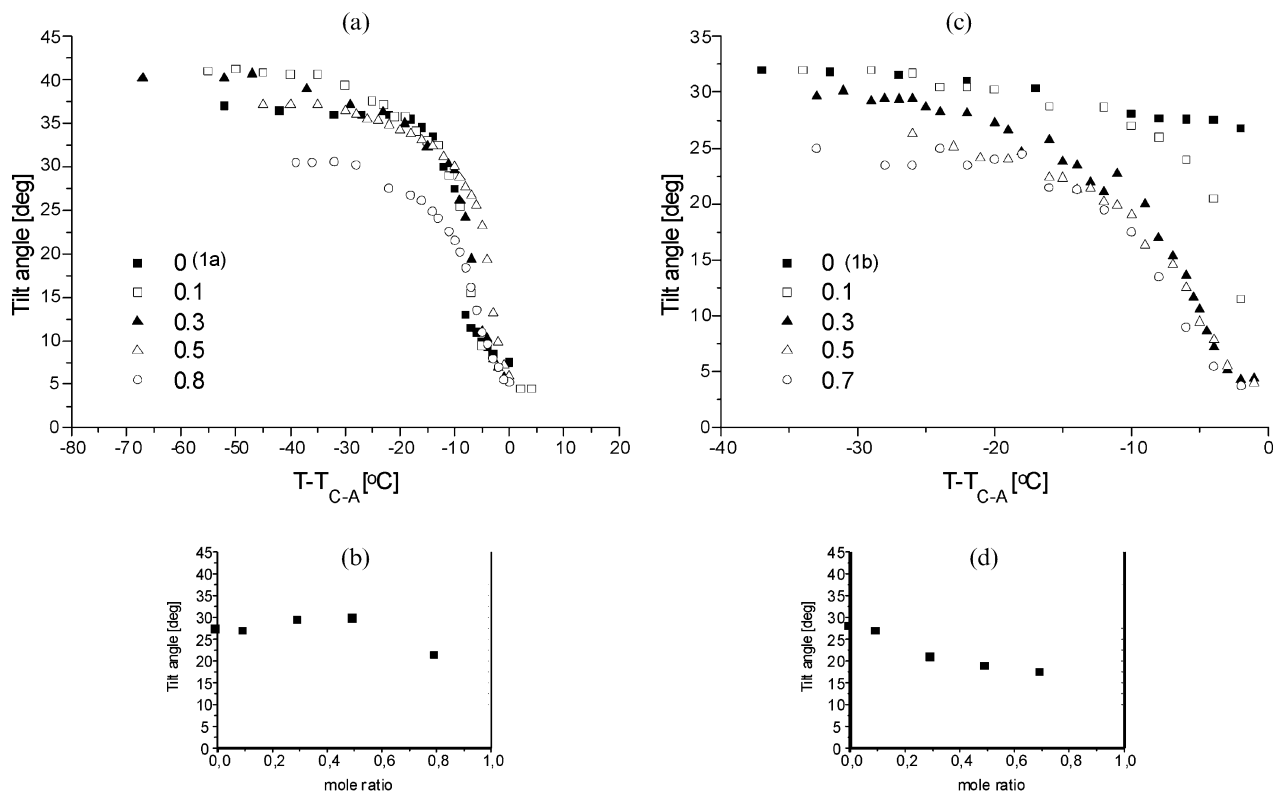


Figure 4. The tilt angle vs. temperature and concentration for set temperature  $T - T_{C-A} = -10^\circ\text{C}$  for the systems **1a–2b** (a, b) and **1b–2b** (c, d).

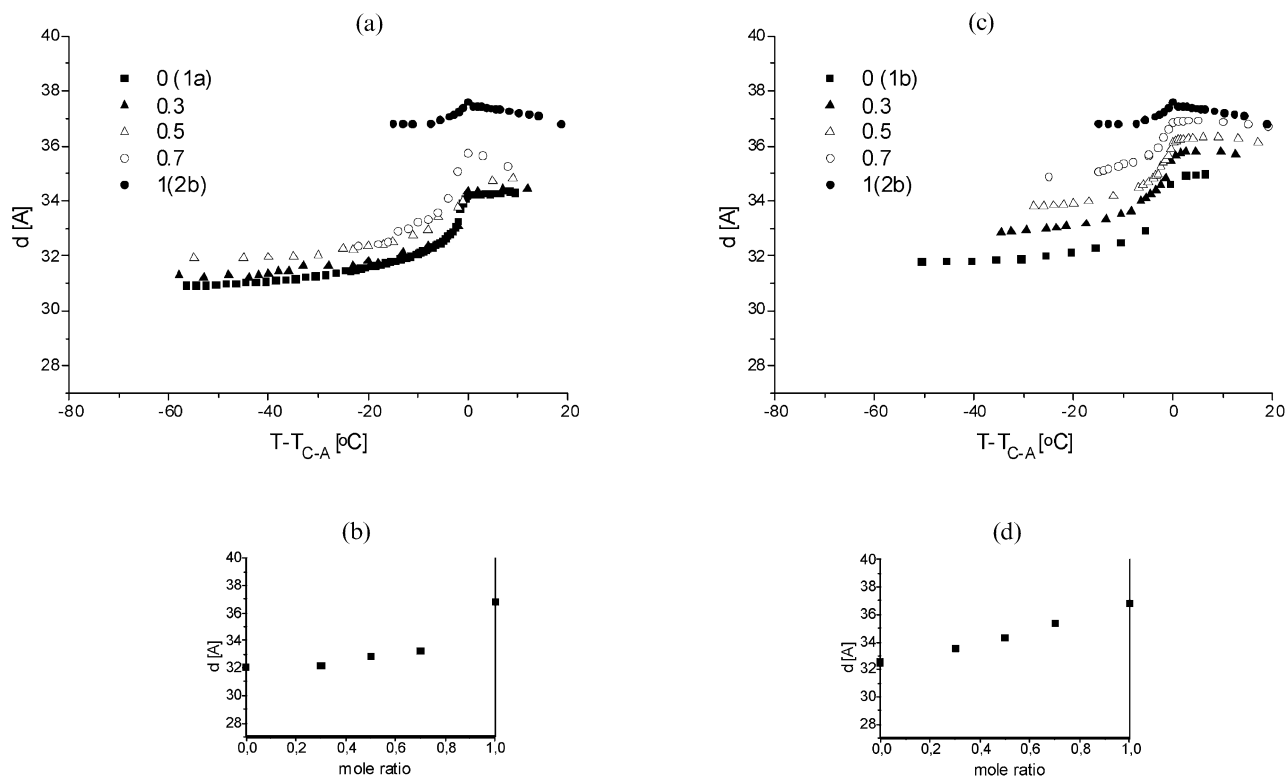


Figure 5. The smectic layer spacing vs. temperature and concentration for set temperature  $T - T_{C-A} = -10^\circ\text{C}$  for the systems **1a-2b** (a, b) and **1b-2b** (c, d).

shorter homologue having only one carbon atom in its terminal alkyl chain (**2a**). The temperature characteristics of the maximum wavelength of selectively reflected light in both phases ( $\text{SmC}_A^*$  and  $\text{SmC}^*$ ) were significantly different for the two systems. The results shown in Figure 6 indicate that, in the antiferroelectric phase, the helical pitch decreases in the system **1a-2b** and increases in the system **1b-2a** with an increase of temperature. In the ferroelectric phase, the helical pitch increases in the system **1a-2b** and decreases in the system **1b-2b** with an increase of temperature. An increase of the concentration of protonated compound causes a decrease of the helical pitch in both systems and in both phases.

#### 4. Discussion

The mechanism of the induction of an antiferroelectric phase is different in both tested systems, i.e. those comprising a fluoro-terminated compound (**1a**) or a cyano-terminated compound (**1b**).

In the case of the system with a fluoro-terminated compound the physical properties change non-additively with the concentration of components and in the case of the cyano-terminated compound the change is linear with the concentration.

In general, the tilt angle of molecules in the majority of compounds, both in ferroelectric as well as in antiferroelectric phases, is low, although a high tilt (about  $45^\circ$ ) can also be observed in these phases [see Inukai *et al.* (18) and Dąbrowski (19), respectively]. Similar behaviour was observed here for mixtures in which an antiferroelectric phase was induced. Highly tilted phases were formed in mixtures consisting of fluorinated compound (**1a**) and protonated compound **2b**, whereas less tilted phases were formed in mixtures consisting of cyano-terminated compound (**1b**) and protonated compound **2b**, even though the pure fluoro-terminated (**1a**) and cyano-terminated (**1b**) compounds have similar tilt angles of  $35^\circ$  and  $32^\circ$ , respectively.

Between molecules of fluorinated and protonated compounds strong intermolecular interactions must occur, which cause the nonlinear change of physical parameters. For example, a small amount (0.1 mole ratio) of protonated compound **2b** increases the tilt angle from  $35^\circ$  (for fluorinated compound) to  $40^\circ$ . In the mixture the layer spacing remains as low as that for the fluorinated compound up to 0.3 mole ratio of compound **2b** and only slightly increases for concentration up to 0.7 mole ratio of compound **2b**. The spontaneous polarisation increases from

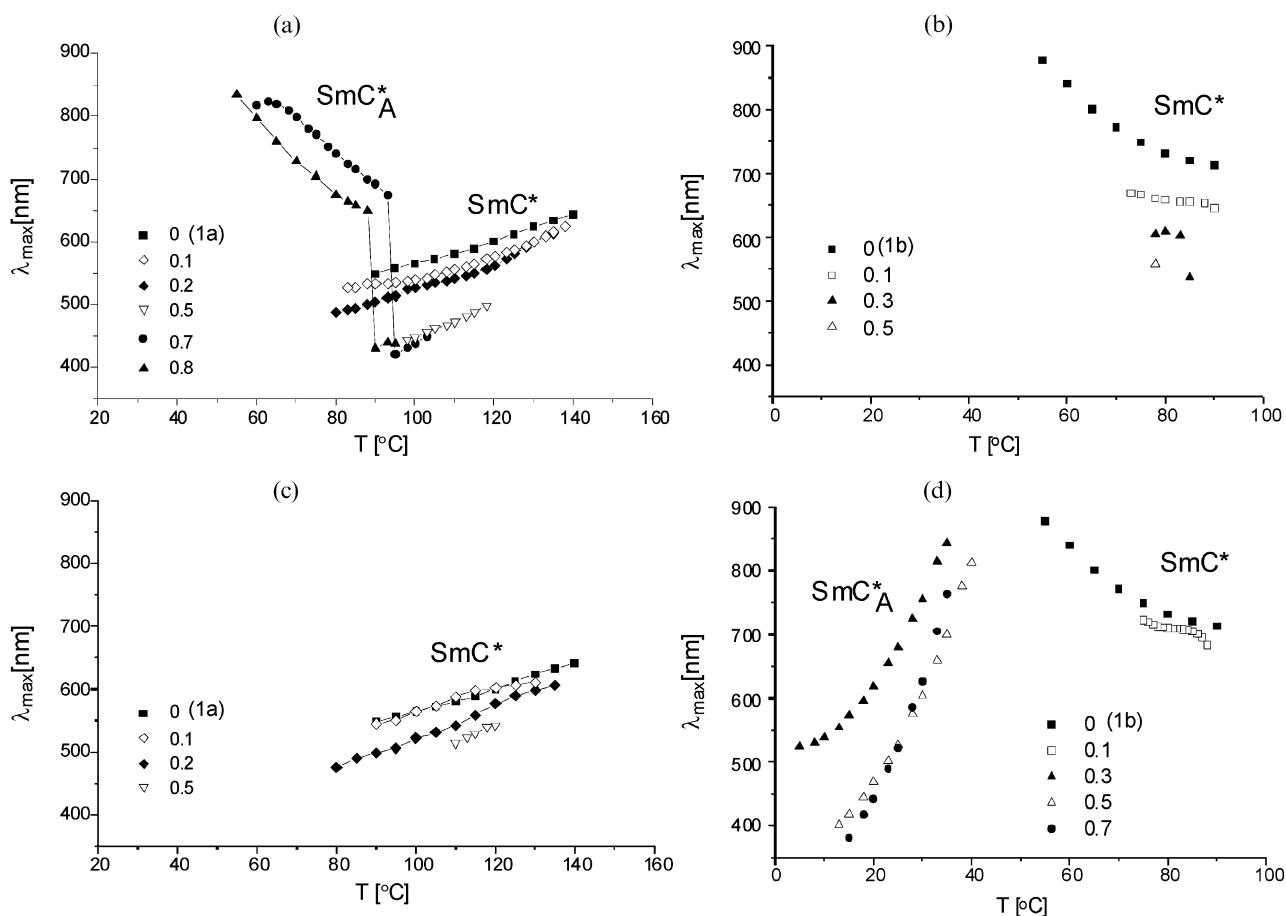


Figure 6. The maximum wavelength of selectively reflected light vs. temperature for the systems **1a–2b** (a), **1b–2b** (b), **1a–2a** (c) and **1b–2a** (d).

170nCcm<sup>-2</sup> (for fluorinated compound) up to 280nCcm<sup>-2</sup> for a concentration of 0.5 mole ratio of compound **2b**.

Compound **1a** is a fluorinated analogue of MHPOBC; both compounds have the same rigid core, chiral terminal chain and the number of carbon atoms in non-chiral chain, but different ability for formation of antiferroelectric phase in the pure state. MHPOBC exhibits a SmC<sub>A</sub> phase but compound **1a** does not. On the other hand, compound **1a** has a very similar structure to a fluorinated compound that exhibits an antiferroelectric phase, C<sub>3</sub>F<sub>7</sub>COO(CH<sub>2</sub>)<sub>3</sub>OPhPhCOOPhCOOC\*H(CH<sub>3</sub>)C<sub>6</sub>H<sub>13</sub>, with the following phase transition temperatures: Cr 82.1 (SmI<sub>A</sub>\* 54.0) SmC<sub>A</sub>\* 122.0 SmC\* 124.5 SmA 129.9 I (4). It has the same length of the non-branched chain as in MHPOBC, the part of the chain is fluorinated as in compound **1a** and the additional ester group separating the fluorinated part of the alkyl chain from non-fluorinated one is introduced. This compound comes from the group of compounds forming orthoconic antiferroelectric phase (cone tilt angle equal to 90°)

(5, 20). As can be seen, the antiferroelectric phase is very sensitive to molecular structure. The fluorinated part of the chain (perfluoroalkyl group) is bulky and rigid. The segregation of these units appears between molecules. When part of the alkyl chain (C<sub>8</sub>H<sub>17</sub>O-) in MHPOBC is fluorinated (C<sub>6</sub>F<sub>13</sub>C<sub>2</sub>H<sub>4</sub>O-), the antiferroelectric phase disappears, with microsegregations causing different arrangement of molecules. The ester group comprises polar carbonyl group C=O, which gives the main component to the transverse dipole moment. Moreover, this group causes that the terminal chain to be nonlinear owing to steric interactions. The fluorinated part is rigid and bulky, and tends to lie in the opposite direction to which the carbonyl group is oriented, thus leading to bending of the chain. This bending together with additional dipole-induced dipole interactions introduced to the chain with an ester group (C<sub>3</sub>F<sub>7</sub>COOC<sub>3</sub>H<sub>6</sub>O-) enable formation of an antiferroelectric phase.

The placement of molecules of compound **1a**, which have a tendency to form the antiferroelectric phase but cannot fulfil all conditions, in a suitable

matrix of compound **2b** causes the appearance of an antiferroelectric phase. The fluorinated compound **1a** dominates in the mixtures with protonated compound. X-ray measurements show that the layer spacing is constant up to 0.7 mole ratio of protonated compound **2b**, thus some interaction between molecules must occur, and molecules of protonated compound **2b** are built in the layers of fluorinated compound **1a**.

The situation is quite different for the other system, **1b–2b**. Compound **1b** is more similar in structure to compounds of the same series that exhibit an antiferroelectric phase, i.e.  $\text{CH}_3\text{COO}(\text{CH}_2)_6\text{OPhPhCOOPhCOOC}^*\text{H}(\text{CH}_3)\text{C}_6\text{H}_{13}$  (phase sequence Cr 66.7 SmC\*<sub>A</sub> (48.0) SmC\* 104.9 SmA 117.3 I) and  $\text{C}_2\text{H}_5\text{COO}(\text{CH}_2)_6\text{OPhPhCOOPhCOOC}^*\text{H}(\text{CH}_3)\text{C}_6\text{H}_{13}$ , (Cr 58.1 SmC\*<sub>A</sub> 95.2 SmC\* 103.5 SmA 112.2 I), and to the compounds with a trifluoroacetate group in the terminal position, i.e.  $\text{CF}_3\text{COO}(\text{CH}_2)_6\text{OPhPhCOOPhCOOC}^*\text{H}(\text{CH}_3)\text{C}_6\text{H}_{13}$ , (Cr 39.8 SmC\*<sub>A</sub> 104.3 SmC\* 119.7 SmA 125.6 I). Introduction of a cyano group to the third structure instead of the fluoromethyl group or to the second structure instead of methyl group, or additionally to the alkyl group in the first structure, causes the lowering of phase transition temperatures. It is very probable that the antiferroelectric phase is a monotropic phase for this compound, but has not been detected. In the mixture there are not strong intermolecular interactions between cyano-terminated and protonated molecules, which induce only small additive perpendicular component of dipolar moment involving antiferroelectric coupling but still too small to cause the physical parameters to change nonlinearly with concentration.

## 5. Conclusions

Differences in two systems with an induced antiferroelectric phase, i.e. those comprising a fluoro-terminated compound (**1a**) or cyano-terminated compound (**1b**) mixed with the same protonated compound (**2b**), have been demonstrated. The mechanisms for the induction of an antiferroelectric phase the two systems are different.

In the case of the system with a fluoro-terminated compound, the physical properties change non-additively with the concentration of components and strong coupling between molecules occurs, whereas in the case of the cyano-terminated compound the coupling is small and the change of physical properties is linear with the concentration. Systems with higher tilted phases in the former and lower tilted phases in the latter are the result of mixing compounds with different polarity.

Between molecules of fluorinated and protonated compounds, intermolecular interactions occur that are so strong that a small amount of protonated compound (0.1 mole ratio) increases the tilt angle from 35° to 40° and spontaneous polarisation from 170nCm<sup>-2</sup> to 280nCm<sup>-2</sup>.

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## References

- (1) Chandani A.D.L.; Górecka E.; Ouchi Y.; Takezoe H.; Fukuda A. *Jap. J. Appl. Phys.* **1989**, *29*, L1265–L1268.
- (2) Fukuda A.; Takanishi Y.; Isozaki T.; Ishikawa K.; Takezoe H. *J. Mater. Chem.* **1994**, *4*, 997–1016.
- (3) Matsumoto T.; Fukuda A.; Johno M.; Motoyama Y.; Yuki T.; Seomum S.S.; Yamashita M. *J. Mater. Chem.* **1999**, *9*, 2051–2080.
- (4) Drzewiński W.; Dąbrowski R.; Czupryński K.; Przedmojski J.; Neubert M. *Ferroelectrics* **1998**, *212*, 281–292.
- (5) Drzewiński W.; Dąbrowski R.; Czupryński K. *Polish J. Chem.* **2002**, *76*, 273–284.
- (6) Wu S.-L.; Lin C.-Y. *Liq. Cryst.* **2006**, *33*, 495–502.
- (7) Stipetic A.I.; Goodby J.W.; Hird M.; Raoul Y.M.; Gleeson H.F. *Liq. Cryst.* **2006**, *33*, 819–828.
- (8) Gauza S.; Dąbrowski R.; Czupryński K.; Drzewiński W.; Kenig K. *Ferroelectrics* **2002**, *276*, 207–217.
- (9) Gauza S.; Czupryński K.; Dąbrowski R.; Kuczyński W.; Pocięcha D. *Mol. Cryst. Liq. Cryst.* **2001**, *365*, 189–198.
- (10) Tykarska M.; Skrzypek K. *Ferroelectrics* **2006**, *343*, 193–200.
- (11) Tykarska M.; Skrzypek K.; Ścibior E.; Samsel A. *Mol. Cryst. Liq. Cryst.* **2006**, *449*, 71–77.
- (12) Skrzypek K.; Tykarska M. *Ferroelectrics* **2006**, *343*, 177–180.
- (13) Raszewski Z.; Kędziński J.; Perkowski P.; Piecek W.; Rutkowska J.; Kłosowicz S.; Zieliński J. *Ferroelectrics* **2002**, *276*, 289–300.
- (14) Mandal P.K.; Jaishi B.R.; Haase W.; Dąbrowski R.; Tykarska M.; Kula P. *Phase Transitions* **2006**, *79*, 223–235.
- (15) Dziaduszek J.; Dąbrowski R.; Czupryński K.; Bennis N. *Ferroelectrics* **2006**, *343*, 3–9.
- (16) Gąsowska J.; Drzewiński W.; Kenig K.; Tykarska M. *SPIE* **2002**, *4759*, 39–45.
- (17) Bennis N.; Spadło A.; Castillo P.L.; Tykarska M.; Piecek W.; Dąbrowski R.; Otón J.M.. In *Proceedings of 16<sup>th</sup> Conference on Liquid Crystals*, Stare, Jabłonki, Poland, 2005; Perkowski P., Raszewski Z., Zieliński J. (Eds); p. 77–82; Red.Wyd.WAT: Warsaw, 2007.
- (18) Inukai T.; Saitoh S.; Inoue H.; Miyazawa K.; Terashima K.; Furukawa K. *Mol. Cryst. Liq. Cryst.* **1986**, *141*, 251–266.
- (19) Dąbrowski R. *Ferroelectrics* **2000**, *243*, 1–18.
- (20) Dąbrowski R.; Gąsowska J.; Otón J.; Piecek W.; Przedmojski J.; Tykarska M. *Displays* **2004**, *25*, 9–19.