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Orthoconic antiferroelectric liquid crystals containing biphenyl, terphenyl, or naphthyl mesogenic unit

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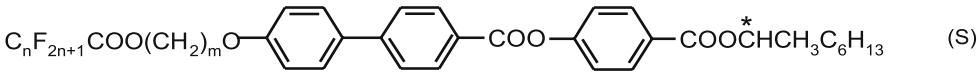
Three homologous series of orthoconic (45 degree tilt) antiferroelectric liquid crystals containing either naphthyl or terphenyl groups as mesogenic unit have been synthesized and their mesomorphic behaviour investigated by DSC and polarized light microscopy, and their properties discussed. X-ray diffraction studies have shown the presence of a de Vries-type smectic A phase which does not exhibit a layer shrinkage on transition to the ferroelectric smectic C phase. Mixtures of the new materials have been formulated and their electro-optical properties investigated for their use in surface stabilized orthoconic antiferroelectric liquid crystal (SSOAFLC) devices

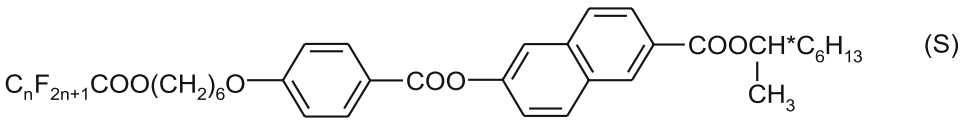
Keywords: orthoconic, antiferroelectric, liquid crystal, de Vries SmA.

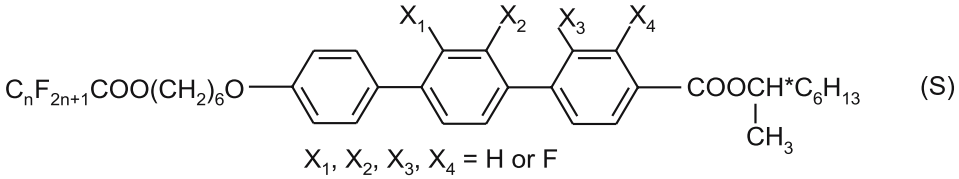
1. Introduction

Recently our group reported several new series of orthoconic antiferroelectric liquid crystalline materials, as shown by structure 1 [1,2]. These materials, and mixtures of them, exhibit a SmC^*_A phase with high tilt angles, approaching 45°, over a broad temperature range.



Molecules in the orthoconic SmC^*_A phase have a tilt angle of 45°, resulting in a switching angle of 90°. Compared to conventional antiferroelectric materials, orthoconics have only an extremely small pretransitional effect. In SSOAF cell at zero-field, the material is uniformly isotropic, even if surface defects are present resulting in a truely dark state. The bright state is excellent and contrast is limited only by the quality of the polarizers [1–5]. Here, we report the synthesis and phase characterization of several new series and related compounds, show by structures 2 and 3 below. The new materials have also been used in mixtures to investigate their electro-optical properties as orthoconic antiferroelectric materials.





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2. Experimental

The methods used for the nF6BN series are similar to those for the (4-methylheptyloxycarbonyl)phenyl biphenylates [1] shown by structures 1. All methods proceeded well with good yields.

The methods used for synthesis of the terphenyl derivatives shown by structure 3 were based on methods described in Ref. 7.

The structures of intermediates were confirmed by mass spectrometry (Agilent MSD 5973N). The purity was determined by gas chromatography (Agilent 6890N equipped with FID detector, capillary column type ultra-2, 30-m length and 0.3 mm diameter were used, 20 m and 0.3 mm in case of the MS detector) and by thin layer chromatography (silica gel plates).

Transition temperatures and enthalpies of transition were measured by DSC (SETARAM 141) calorimetry. Mesophases were determined by polarizing light microscopy (Biolar-PZO connected with Linkam THMS-600 heating stage).

The electrooptic measurements were done as described in Ref. 8.

3. Results and discussion

3.1. nF6BN series

The transition temperatures and phase properties for the nF6BN series are shown in Fig. 1. The first member of the series $n = 1$, exhibits a monotropic SmA phase. On increasing n, both SmC^*_A and SmC* phases are observed, with the SmA phase reappearing for $n \geq 5$. An odd-even effect is seen in the SmC^*_A-SmC* transition temperatures, but this is not observed in the SmC*-SmA and clearing temperatures, which both increase on increasing n.

Figure 1 also shows the transition temperatures of another recently reported naphthyl-containing series [6] along with the related biphenyl and benzyl series for comparison [1,2]. Comparing the nF6BN series to the nF6BiN series, it can be seen that replacing the biphenyl group by a phenyl group has reduced the melting points by ~50 degrees and that there has been the greater reduction in the liquid crystal transition and clearing points; the phase range of the liquid crystalline region has been dramatically reduced, becoming monotropic for $n = 1$. This can be explained by the reduction in length of the mesogenic core and increase in the length/breadth ratio. Comparing the nF6BN series to the nF6B series it is observed that substituting the naphthyl group for the biphenyl as little effect on the melting points but that the clearing temperature and mesophase transition temperatures have been suppressed, especially the range of the SmC^*_A phase. This destabilization of the phase stability can again be explained by the reduction of the mesogenic unit length/breadth ratio.

3.2. nF6T(nF) series

Compounds from the nF6T series have a mesophase region between 110°C and 160°C with a SmC_A^*-SmC*-SmA sequence, 4F6T exhibits a direct SmC_A^*- SmA transition, see Fig. 2.

When a fluorine atom is introduced in 2 position, nF6T(2F) series, a drop in melting point is observed (Fig. 3). The range of mesophase is very similar to the previous series but it starts about 20°C lower. When two fluorine atoms are introduced in 2 and 3 positions, nF6T(2,3F) series, a further decrease in melting point is observed, see Fig. 2. When the two fluorine atoms are introduced to the central ring in 2', 3' positions, nF6T(2',3'F) series, a lower melting point is observed in comparison with nF6T(2,3F). The range of smectic phases is also broader.

The change of phase sequence for different lengths of fluorinated chain is similar for all the series apart of the biphenyl analogues, nF6BPh which do not exhibit any enantiotropic LC phases at all. For all terphenyl derivatives mentioned above we notice that on increasing n a strong destabilization of the SmC^* phase is observed, opposite to the nF6Bi. For 4F6T compound and SmC^* phase it is not observed.

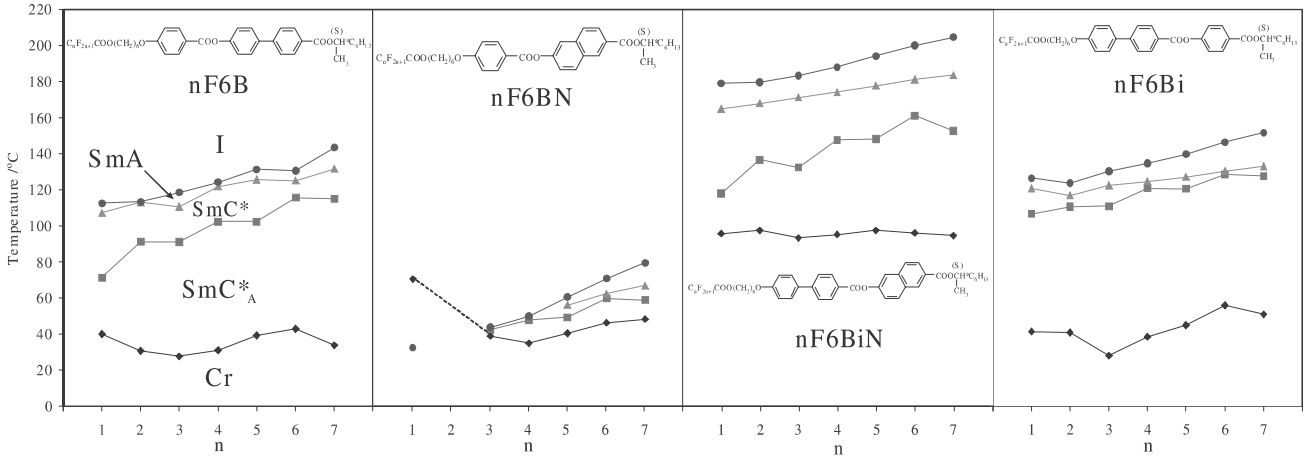

Fig. 1. Transition temperatures of the nF6BN series (second data set) together with the NF6B, NF6BiN and nF6Bi series for comparison. ◆ melting point, ■ SmC^*_A-SmC*, ▲ SmC*-SmA, ● SmA-I.

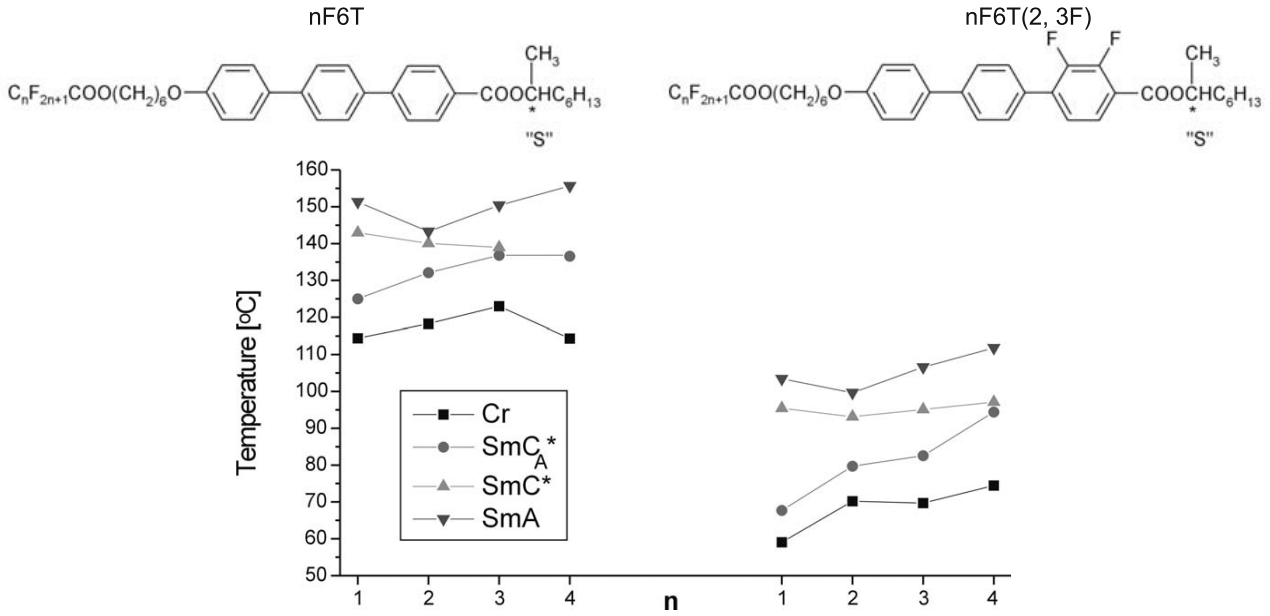

Fig. 2. Comparison of phase transition temperatures of two series (nF6T-left, nF6T(2,3F)-right) for different lengths of perfluorinated terminal chains.

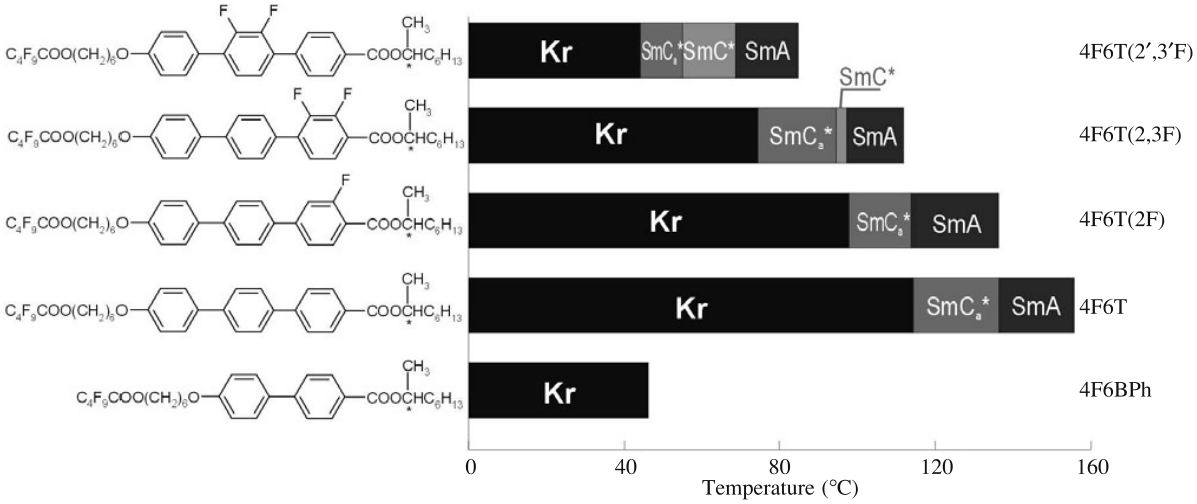

Fig. 3. Comparison of phase transition temperatures of different terphenyl rigid cores and biphenyl analogues.

The results of tilt angles of 4F6T(2,3F) compound, determined by SAXS measurements are shown in Fig. 4. The huge difference in values of tilt angle calculated from d/d_A ratio and d/l ratio (see grey squares in Fig. 4) suggests that the orthogonal SmA phase is of the de Vries type with angle of diffuse cone about 25 degrees.

3.3. Electro-optical results

W-214 and W-216 mixtures were calculated according to CSL equations to formulate eutectic mixtures of compounds from the nF6BN with nF6B series, W-214 mixture, and from the nF6B with nF6T, nF6T(2,3F) series, W-216 mixture. Electrooptic results are shown in Figs. 5 and 6, respectively. The orthoconic state in both cases is not observed in the thicker cell [Figs. 5(a) and 6(a)] due to the short helical pitch of the mixture. These two mixtures show

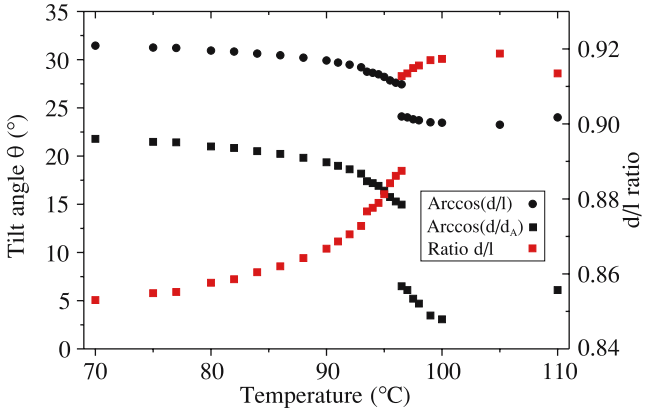

Fig. 4. Temperature dependence of tilt angles for 4F6T(2,3F) calculated from SAXS measurements, and temperature dependence of d/l ratio (d-layer spacing; d_A-layer spacing in SmA phase; l-calculated length of molecule by PM3 method).

similar behaviour. Very good contrast ratio is observed, especially in the 0.8-μm cell which is thin enough to observe orthoconic condition [Fig. 5(b) and 6(b)]. The dynamic range is also good, although the response times, especially fall time, are rather large. For W-216 mixture, the hysteresis loops are more asymmetric than for W-214 mixture.

4. Conclusions

Several homologous series and related analogous compounds exhibiting an orthoconic antiferroelectric smectic C phase (SmC^*_A) have been synthesized and characterized. Mixtures have been formulated which, in thin cells, exhibit the orthoconic condition; behave like an optically isotropic medium which allows the generation of a huge contrast ratio. Unfortunately, the response times are rather high and asymmetric.

Further work is now underway to further investigate the smectic phase layer spacings and tilt angles, as well as into the electro-optic responses, in both pure compounds and mixtures. Work is continued to synthesis new materials with the larger helical pitch and faster rise and fall times.

Acknowledgements

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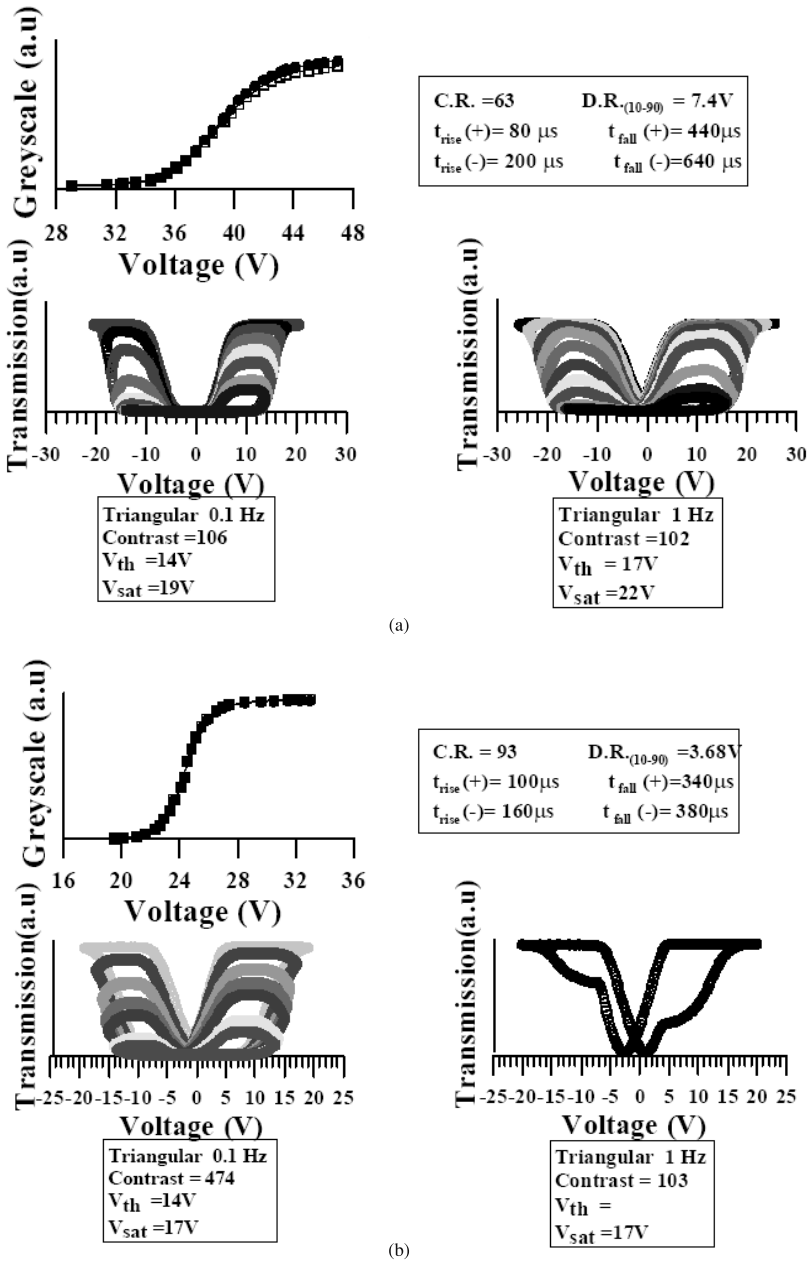

Fig. 5. Electrooptical results for W-214 mixture in (a) 1.5 μm cell, SiO_2-nylon with parallel rubbing. Tilt angle 39°, temperature 35°C, and (b) in 0.8-μm cell, SiO_2-nylon with cross rubbing on top plate. Tilt angle 45°, temperature 35°C.

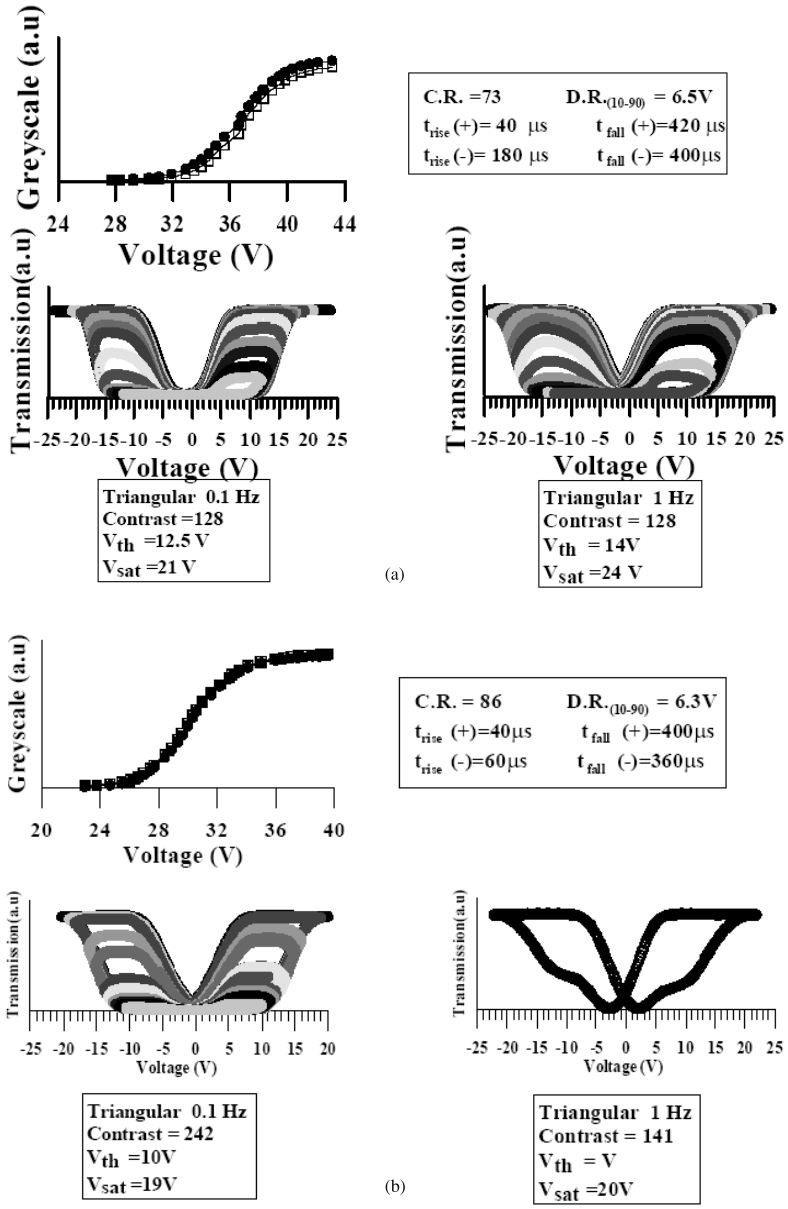

Fig. 6. Electrooptical results for W-216 mixture in (a) 1.7-μm cell, SiO_2-nylon with parallel rubbing. Tilt angle 37°, temperature 35°C, and (b) in 0.8-μm cell, SiO_2-nylon with cross rubbing on top plate. Tilt angle 45°, temperature 35°C.

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