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Chiral two ring compounds exhibiting antiferroelectric phases

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Novel chiral two ring compounds possessing phenylethenoate moieties were synthesized and their liquid crystalline properties determined. Some of these compounds were found to exhibit SmC^*_γ, AF and SmC^*_A phases, whereas in other compounds only SmA* and SmC* phases appear. The influence of the molecular structure on the appearance of SmC^*_γ, AF and SmC^*_A phases is discussed. The basic electro-optical properties of the homologous series of (*S*)-(*E*)-4-(1-methylheptyloxycarbonyl)phenyl 4-alkoxycinnamates, in which SmC*, SmC^*_γ, AF and SmC^*_A phases appear, were also investigated. High values of spontaneous polarization, low threshold voltages and fast switching times at room temperature were observed.

1. Introduction

In smectic phases consisting of chiral molecules a coupling between tilt angle and polarization occurs. This coupling leads to the electroclinic effect in orthogonal smectic phases and to the ferroelectricity of uniformly tilted smectic phases. Some years ago, a fundamentally novel type of smectic phase, having an alternating tilt direction from layer to layer was found [1]. When such phases are formed by chiral molecules the direction of the polarization also alternates from layer to layer thus these phases are antiferroelectric [2–5].

Since their discovery, antiferroelectric liquid crystals have attracted considerable attention from fundamental as well as practical points of view [6]. In order to understand the molecular origin for the formation of the alternating tilted structure, investigation of the relationship between molecular structure, and the occurrence as well as the stability of the alternating tilted phases, is important. During the past few years several hundred new antiferroelectric liquid crystal materials have been synthesized. However, nearly all of these compounds have a similar structure bearing a phenyl and a biphenylyl group in the mesogenic core.

Recently new antiferroelectric three ring compounds having phenylethynoate, phenylethenoate or phenylethanoate moieties in the mesogenic core have been reported [7–9]. As a comparison, the largest antiferroelectric phase ranges are obtained for the substances with the phenylethenoate group [9]. The broad antiferroelectric phase ranges in these compounds led us to assume that it should be possible to obtain antiferroelectric two ring compounds with a similar structure.

In this contribution we present novel chiral two ring compounds possessing one or two phenylethenoate groups in the mesogenic core. The basic structure of the compounds investigated is shown below.

$$\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{O{-}Ph{-}}X\mathrm{{-}COO{-}Ph{-}}Y\mathrm{{-}COO}R^*$$

with

$X, Y = {-}\mathrm{CH{=}CH}{-}$; nothing

$n = 6 \ldots 12$

$R^* = {-}\mathrm{CH(CH_3){-}C}_m\mathrm{H}_{2m+1}\ m = 4, 6, 8;$

${-}\mathrm{CH(C_2H_5){-}C_6H_{13}};\ {-}\mathrm{CH(CF_3){-}C_6H_{13}}$

Novel chiral two ring compounds exhibiting enantiotropic ferrielectric SmC^*_γ and antiferroelectric SmC^*_A phases were obtained by: (1) varying the linking groups *X*, *Y*; (2) varying the length *n* of the non-chiral alkoxy side chain; (3) varying the chiral side chain *R**; (4) introducing a lateral fluoro substituent into the phenyl ring next to the chiral side chain. In § 2 we report on the electro-optical properties of a homologous series of these new compounds. Spontaneous polarizations, optical tilt angles and switching times were determined, and the optical as well as the current response in the ferroelectric SmC*, AF, SmC^*_γ and SmC^*_A phases were studied. For information on the antiferroelectric AF phase the reader is referred to ref. [10].

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2. Experimental

The starting materials for the synthesis were 4-hydroxybenzoic acid and 4-hydroxycinnamic acid, as well as the chiral alcohols (*S*)-2-hexanol, (*S*)-2-octanol, (*S*)-2-decanol, (*S*)-3-nonanol and (*S*)-1,1,1-trifluoro-2-octanol. With the exception of (*S*)-1,1,1-trifluoro-2-octanol, all these compounds are commercially available. The (*S*)-1,1,1-trifluor-2-octanol was synthesized according to the procedure given in ref. [11]; thereby an optical purity of 89% ee was achieved. The synthesis scheme for the mesogenic compounds is outlined in figure 1. 4-Nonyloxybenzoic acid and 4-alkoxycinnamic acid were obtained by esterification of either 4-hydroxybenzoic acid or 4-hydroxycinnamic acid with methanol, followed by alkylation with the appropriate alkyl bromide and finally hydrolysis of the methyl ester using an ethanolic solution of KOH. For the esterification of 4-hydroxybenzoic acid with the chiral alcohols, a benzyloxy group, and for the esterification of 4-hydroxycinnamic acid with chiral 2-octanol, a methoxycarbonyloxy group was used to protect the hydroxy group of the acids. The final products were obtained by esterification with DCC. Purification was achieved first by column chromatography over silica gel using CH_2Cl_2 as eluent and then by crystallization from ethanol until the transition temperatures remained constant.

Transition temperatures were determined optically using a polarizing microscope (Leitz Lux 12 POL S) equipped with a hot stage (Mettler FP 80 and FP 82) and confirmed by DSC measurements (Perkin Elmer DSC 7). The classification of the liquid crystalline phases was based upon miscibility studies with the reference compounds MHPOBC [3] and MHPBC [12] using the contact method. The spontaneous polarization was measured by the triangular wave method. Optical tilt angles were obtained by an extrapolation of the switching angles to zero field. Switching times were determined by measuring the half width of the current response peak to a rectangular wave at a field strength of ±10 V μm^{-1}. For these measurements commercially available cells (E.H.C.) with a layer spacing of 10 μm were used.

3. Liquid crystalline properties

3.1. *Variation of the mesogenic core*

For studying the effects of variation of the mesogenic core, the chiral chain ($R^* = -CH(CH_3)-C_6H_{13}$), which is part of many antiferroelectric liquid crystal materials, and a length of the non-chiral alkoxy chain of $n = 9$ were chosen. In table 1, mesophase types and phase transition temperatures of three compounds having one or two phenylethenoate groups in the mesogenic core are shown. The broadest liquid crystalline temperature range is observed for the compound with one ethenoate group placed between the two phenyl rings. This compound exhibits five smectic modifications. On the basis of miscibility studies with MHPOBC and MHPBC, these phases were classified as SmA*, SmC*, AF, SmC_γ^* and SmC_A^*. Note, that the SmC_γ^*, AF and

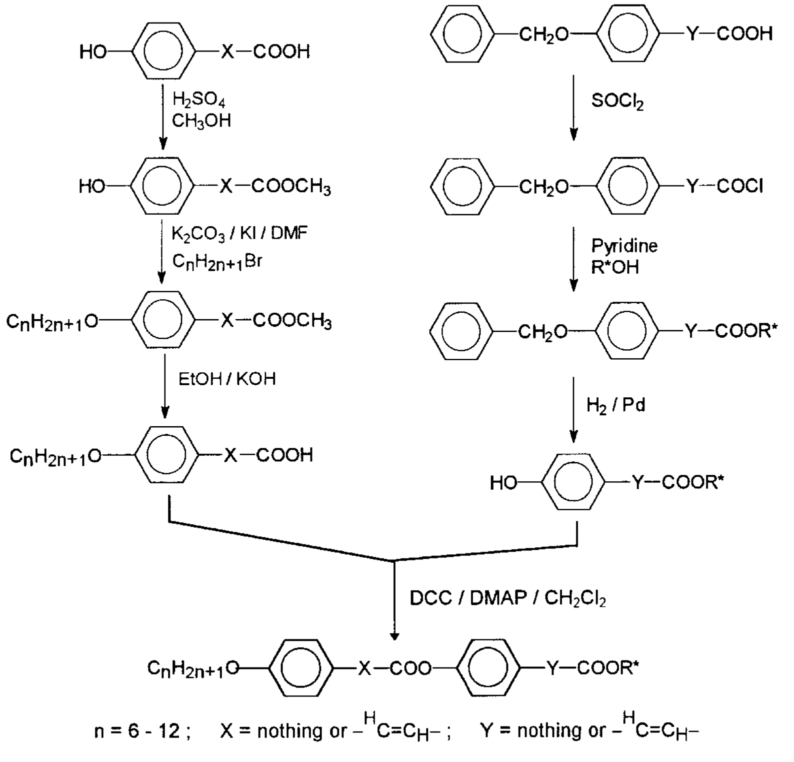
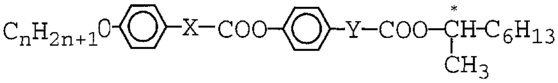


Figure 1. The general synthesis scheme for the mesogenic compounds. In the right hand part, where $Y = CH{=}CH$, the phenolic $-OH$ group was protected by a methoxycarbonyloxy group.

Table 1. Polymorphism and transition temperatures of two ring compounds with one or two phenylethanoate groups in the mesogenic core; $n=9$.



X	Y	Cr		SmC$_A^*$		SmC$_\gamma^*$		AF		SmC*		SmA*		I
CH=CH	nothing	•	26.4	(•	10.2	•	12.5	•	26.1)	•	49.4	•	55.9	•
nothing	CH=CH	•	53.9	—		—		—		—		•	54.0	•
CH=CH	CH=CH	•	84.2	—		—		—		•	84.3	•	93.6	•

SmC$_A^*$ phases are monotropic phases. The compound can be supercooled down to about -5°C at a cooling rate of 1 K min^{-1} (30 K below the melting point) before recrystallization takes place.

Thus the AF phase of this compound can be obtained in a metastable state at room temperature. If the ethenoate group is placed between the mesogenic core and the chiral end chain, the melting point increases strongly and only a narrow SmA* phase remains. The compound with two ethenoate groups exhibits a 40 K higher clearing temperature, but also a much higher melting point. For this compound the polymorphism Cr–SmC*–SmA*–I was found. Additionally, by using fast cooling rates, the appearance of the SmC$_\gamma^*$ phase was observed just before recrystallization. However, no transition temperature could be determined in this case. As a consequence of this investigation the core structure of the (S)-(E)-4-(1-methylheptyloxycarbonyl)phenyl 4-nonyloxycinnamate was used in studies of the effects of variation of both end chains.

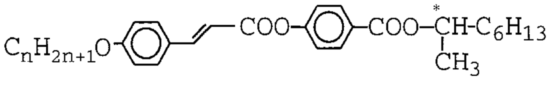
3.2. *Variation of the length of the non-chiral end chain*

In order to optimize the phase range of the SmC$_A^*$ phase, the length of the non-chiral alkoxy chain was varied. The liquid crystalline properties of the homologous series of (S)-(E)-4-(1-methylheptyloxycarbonyl)phenyl 4-alkoxycinnamates are shown in table 2 and depicted graphically in figure 2 (higher homologues of this series were described earlier in the literature [11]). As can be seen, the AF, SmC$_\gamma^*$ and SmC$_A^*$ phases occur for alkyl chain lengths $n=9$ and 10. The compound with $n=8$ shows only the SmC$_\gamma^*$ and the SmC$_A^*$ phase. Higher as well as lower homologous exhibit SmC* and SmA* phases only. The melting point shows a minimum for the nonyl derivative.

3.3. *Variation of the chiral end chain*

Slight variations in the structure of the chiral end group were made in order to study the influences on the liquid crystalline properties of these novel compounds. The results are shown in table 3. The structures of the first three compounds differ only in the length of the 2-alkyl group. For the 2-hexyl and 2-octyl derivatives the same enantiotropic polymorphism, and, with the exception of the melting points, nearly the same transition temperatures were found. In contrast no mono- or enantiotropic ferri- or antiferro-electric phase occurs in the 2-decyl derivative. An exchange of the methyl group of the chiral centre by an ethyl or trifluoromethyl group leads to a pronounced decrease of the clearing temperature. The ethyl derivative (3-nonyl) exhibits monotropic SmA* and SmC$_A^*$ phases and the trifluoromethyl derivative a monotropic SmA* phase only.

Table 2. Polymorphism and transition temperatures of the homologous series of (S)-(E)-4-(1-methylheptyloxycarbonyl)phenyl 4-alkoxycinnamates.



n	Cr		SmC$_A^*$		SmC$_\gamma^*$		AF		SmC*		SmA*		I
6	•	55.1	—		—		—		(•	32.6)	•	61.8	•
7	•	50.9	—		—		—		(•	39.9)	•	55.2	•
8	•	40.1	(•	30.9	•	33.4)	—		•	46.4	•	57.8	•
9	•	26.4	(•	10.2	•	12.5	•	26.1)	•	49.4	•	55.9	•
10	•	36.8	(•	27.9	•	29.8	•	36.4)	•	52.6	•	57.8	•
11	•	42.3	—		—		—		•	53.6	•	56.9	•
12	•	53.3	—		—		—		•	55.3	•	57.8	•

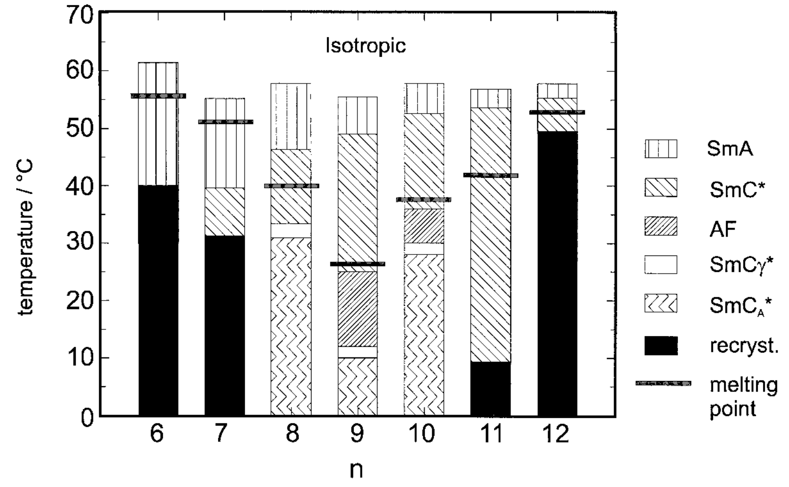
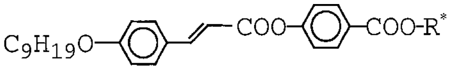


Figure 2. Phase sequences of the homologous series of (*S*)-(*E*)-4-(1-methylheptyloxycarbonyl)phenyl 4-alkoxycinnamates (vs. the achiral chain length *n*).

Table 3. Polymorphism and transition temperatures of the homologous series of (*S*)-(*E*)-4-(1-alkoxycarbonyl)phenyl 4-nonyloxycinnamates (variation of the chiral end group).



*R**	Cr		SmC$_A^*$		SmC$_\gamma^*$		AF		SmC*		SmA*		I
2-hexyl	•	36.3	(•	34.0)	•	37.3		—	•	52.3	•	63.3	•
2-octyl	•	26.4	(•	10.2	•	12.5	•	26.1)	•	49.4	•	55.9	•
2-decyl	•	27.1		—		—		—	•	45.1	•	54.0	•
3-nonyl	•	39.9	(•	17.2		—		—		—	•	19.8)	•
trifluoro-2-octyl	•	43.2		—		—		—		—	(•	20.5)	•

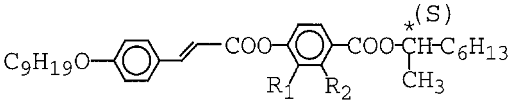
3.4. *Fluoro substituted derivatives*

In table 4, the polymorphism and phase transition temperatures of two compounds with a fluoro substituent in the phenyl ring are shown. Depending on the position of the fluoro substituent very different phase sequences are observed. Whereas for the compound with the fluoro substituent at the 2-position, the ferri- as well as the antiferro-electric phase is shifted to higher temperatures, none of these phases remains if the fluorine is placed at the 3-position.

4. Electro-optical properties

The temperature dependence of the spontaneous polarization and optical tilt angle of the (*S*)-(*E*)-4-(1-methylheptyloxycarbonyl)phenyl 4-alkoxycinnamates are shown in figures 3 and 4, respectively. Maximum spontaneous polarization values between about 150 and 210 nC cm^{-2} and maximum optical tilt angles θ between about 26° and 32° were measured. A plot of spontaneous polarization and optical tilt angle against the alkoxy chain length, at two constant temperature differences below the respective SmA*–SmC* transition temperatures (figure 5), clearly shows that the optical tilt angle increases monotonously with increasing chain length, whereas the spontaneous polarization shows a maximum for the nonyloxy derivative. It is interesting to note that the highest spontaneous polarization values were observed for those compounds for which the ferri- and the antiferro-electric phases

Table 4. Polymorphism and transition temperatures of two fluoro substituted compounds.



R$_1$	*R*$_2$	Cr		SmC$_A^*$		SmC$_\gamma^*$		SmC*		SmA*		I
H	F	•	42.5	•	44.1	•	45.1	•	47.5	•	51.2	•
F	H	•	45.0		—		—		—	(•	31.8)	•

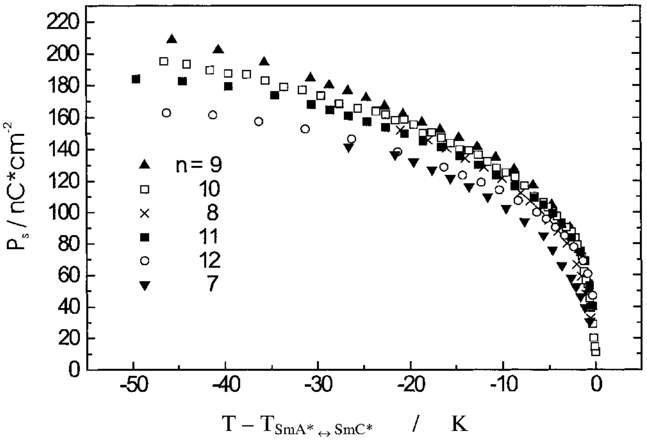


Figure 3. The spontaneous polarization of the (*S*)-(*E*)-4-(1-methylheptyloxycarbonyl)phenyl 4-alkoxycinnamates vs. the reduced temperature.

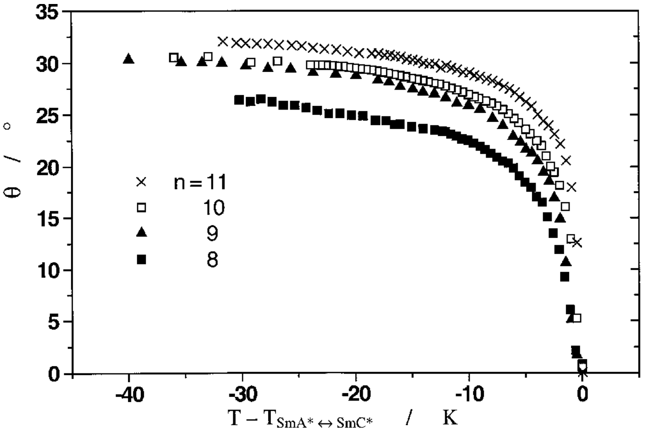


Figure 4. The optical tilt angle for the (*S*)-(*E*)-4-(1-methylheptyloxycarbonyl)phenyl 4-alkoxycinnamates vs. the reduced temperature.

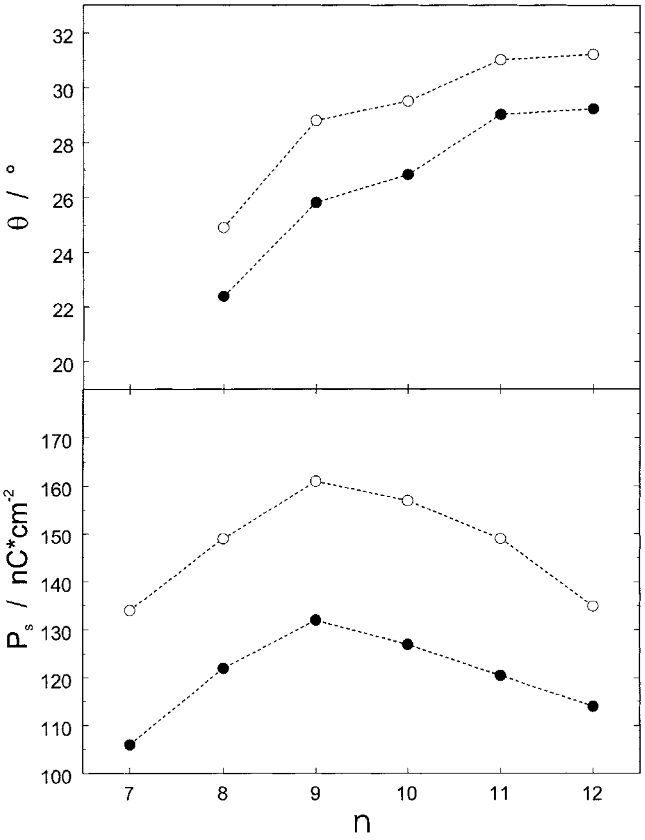


Figure 5. Spontaneous polarization and optical tilt angle for the (*S*)-(*E*)-4-(1-methylheptyloxycarbonyl)phenyl 4-alkoxycinnamates vs. the achiral alkoxy chain length n at two constant reduced temperatures (●: $T - T_{\mathrm{SmA*}\leftrightarrow\mathrm{SmC*}} = -10$ K; O: $T - T_{\mathrm{SmA*}\leftrightarrow\mathrm{SmC*}} = -20$ K).

occur. The switching times of the homologues 8–10 are depicted in figure 6. These materials show fast switching times at room temperature in comparison with ordinary antiferroelectric materials.

In the antiferroelectric phase the frequency of the applied electric field was varied in order to observe a second current peak and tristate switching, which was achieved only at frequencies lower than 0.01 Hz. The threshold voltages for the homologues 8 to 10 are approximately 2 V $\mu\mathrm{m}^{-1}$ at room temperature. The frequency dependent switching behaviour is rather complex and indicates that these compounds belong to the nearly V-shaped switching materials reported recently [14]. A detailed study of the switching behaviour of the homologues 8–10 will be reported elsewhere.

5. Discussion and concluding remarks

5.1. *Correlation between molecular structure and liquid crystalline properties*

By using phenylethenoate moieties new chiral two ring compounds exhibiting SmC*, AF, SmC^*_γ and $\mathrm{SmC}^*_\mathrm{A}$ phases were obtained. The influence of structural variations on the appearance and stability of the alternating tilted $\mathrm{SmC}^*_\mathrm{A}$ phase shows some general trends which were previously found for antiferroelectric three ring compounds.

In the homologous series of antiferroelectric liquid crystal materials, the broadest $\mathrm{SmC}^*_\mathrm{A}$ phase range is quite often observed for chain lengths between 8 and 10 carbon atoms in the achiral chain [9, 15]. This is also observed in the homologous series reported here, where the $\mathrm{SmC}^*_\mathrm{A}$ phase occurs only in this range.

The appearance and stability of antiferroelecric smectic phases strongly depends on the structure of the branched (chiral, racemic or swallow-tailed) end chain and only a small number of terminal chiral chains have been successfully used for the synthesis of antiferroelectric liquid crystals. In most cases, the chiral part is composed of

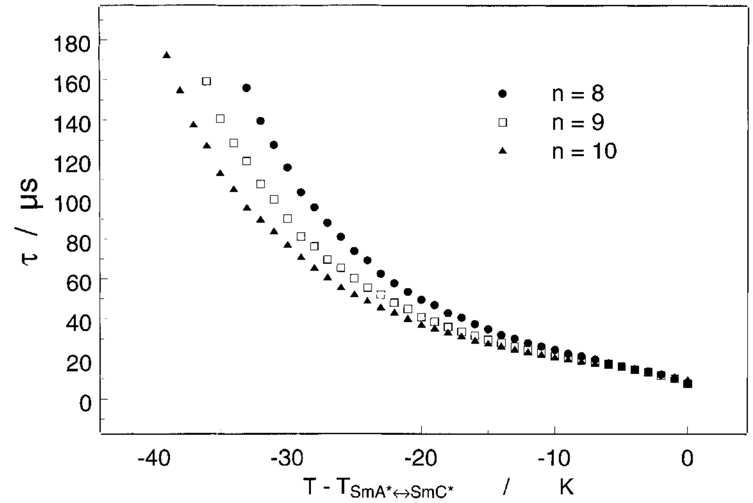


Figure 6. The switching times of the (*S*)-(*E*)-4-(1-methylheptyloxycarbonyl)phenyl 4-alkoxycinnamates with $n = 8, 9, 10$ vs. the reduced temperature.

an α-branched aliphatic chain which may be fluorinated and is linked to the mesogenic core by an ester or a ketone group. Five chiral chains of this type were used in the present study where the length of the long branch, as well as the length and size of the short branch, have been varied. An increase of the length or the size of the short branch often leads to a decrease of all transition temperatures and to a stabilization of the SmC_A^* phase relative to the SmC* phase; in this way compounds with a direct transition from the SmA* phase into the SmC_A^* phase can be obtained [16]. This tendency is also observed for the compounds presented.

Fluorination of the aromatic ring system can strongly affect the antiferroelectric phase range [17]. A fluoro substituent in the *ortho*-position to the chiral side chain often leads to a stabilization [18] and in the *meta*-position to a destabilization of the antiferroelectric phase range [19]. This effect can be clearly seen for the compounds investigated here.

5.2. *Electro-optical properties*

For all investigated compounds with mesophases at room temperature, the spontanoues polarization is in the range 100 to 200 nC cm^{-2}, the tilt angle is about 30°, switching times are in the order of 10 to 150 μs and the rotational viscosity is in the range 1 to 5 kg s^{-1} m^{-1}. At room temperature the compounds show threshold voltages less than 3 V μm^{-1} in the AF and the SmC_A^* phase which is exceptionally low in comparison with most antiferroelectric liquid crystals.

5.3. *Application aspects*

For the electro-optical application of antiferroelectric liquid crystals, wide range SmC_A room temperature mixtures with high spontaneous polarization and low viscosity are required. So far, suitable mixtures consist mainly (or totally) of antiferroelectric three ring compounds which result in high viscosity at room temperature. The addition of two ring compounds can reduce the viscosity and thus an improvement in the response time is obtained [20–22]. The liquid crystalline and especially electro-optical properties of the antiferroelectric two ring compounds presented here are promising for this application. However, the photostability of the ethene group is perhaps unsuitable for device applications. A better photostability without significantly changing the geometry of the mesogenic core should be obtainable by exchanging the ethene group for an epoxy group. It would be interesting to study the liquid crystalline and electro-optical properties of such compounds.

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