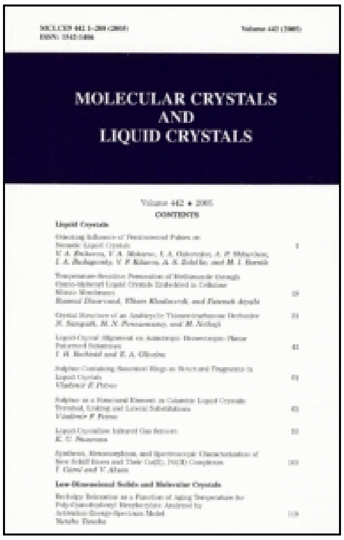

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Comparison of Racemic and Enantiomeric 4'-(1-Methylheptyloxycarbonyl)Biphenyl-4-yl 4-[3-(2,2,3,3,4,4,4-Heptafluorobutoxy)Prop-1-Oxy]Benzoates

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Comparison of Racemic and Enantiomeric 4′-(1-Methylheptyloxycarbonyl)Biphenyl-4-yl 4-[3-(2,2,3,3,4,4,4-Heptafluorobutoxy) Prop-1-Oxy]Benzoates

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Four racemic compounds (R, S)-4′-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-[3-(2,2,3,3,4,4,4-heptafluorobutoxy)prop-1-oxy]benzoates were synthesized and characterized. Their mesomorphic properties, such as phase transitions temperatures and enthalpies were measured by polarizing optical microscope and differential scanning calorimetry. The example of mixture containing racemic components and its properties is presented.

Keywords Anticlinic smectic mixture; enthalpies; helical pitch; orthoconic antiferroelectrics chiral compounds; phase transitions; synthesis

1. Introduction

Since few years we have been intensively searching for new orthoconic antiferroelectric liquid crystals with improved properties [1], because they produce perfect dark state and in the consequence very high contrast is obtained [2]. They are very perspective for many applications. Since known orthoconic antiferroelectric LC compositions, for example W-193B [1,3], are showing very short helical pitch at room temperature. To obtain well oriented smectic layer a very thin cell should be used in this case. To prepare a mixture with longer pitch we are in search of for compounds with stable a chiral anticlinic smectic layer. It was found recently that (S)-(+)-4′-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-[3-(2,2,3,3,4,4,4-heptafluorobutoxy)prop-1-oxy]benzoates (formula I) exhibit very stable SmC_A^* phase with direct transition to the isotropic phase (SmC_A^*-Iso) [4]. Therefore we were to believe, that also their racemates should exist in anticlinic order.

Four racemic structurally similar esters expressed by general formula II, wherein $X_1 = X_2 = H$ (a), $X_1 = H$, $X_2 = F$ (b), $X_1 = F$, $X_2 = H$ (c) and $X_1 = X_2 = F$ (d), were obtained and their properties were compared with early prepared enantiomers

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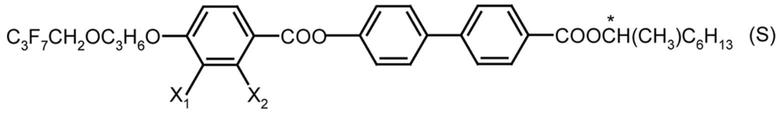
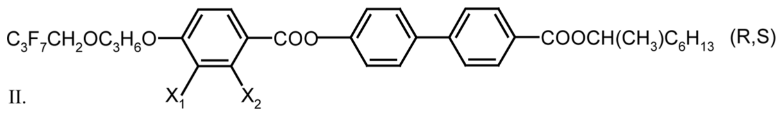
(formula I). The usefulness of racemates for the formulation of mixture with longer pitch was tested.



I.



II.

2. Synthesis

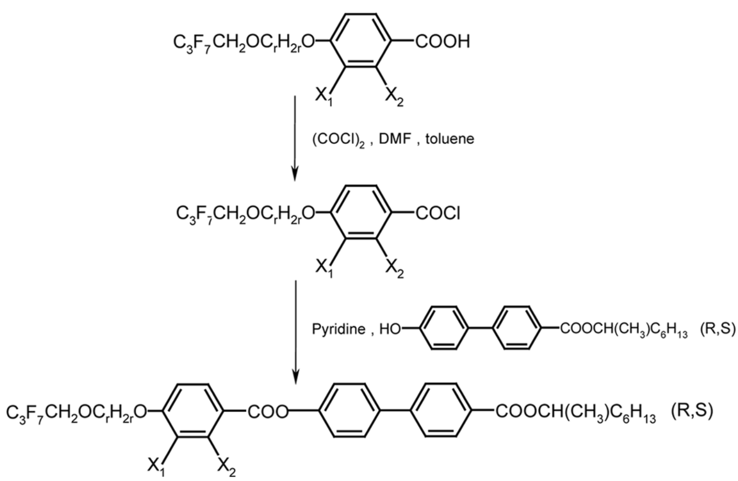
Racemic esters were prepared and purificated in the same condition way by treating 4′-(1-methylheptyloxycarbonyl)biphenol with benzoic acid chloride, see on Scheme 1, as was recently described in detail for chiral analogues [5].

The efficient preparation of (R, S) 4′-(1-methylheptyloxycarbonyl)biphenol was described recently in Ref. [6].

3. Experimental Part

The purity of the prepared final liquid crystalline esters was checked by using Shimadzu HPLC prominence chromatograph with MS (API-ESI) detector 2010EV and starting 4-(3-heptafluorobutoxy)propoxy benzoic acids by using Hewlett-Packard HP-6890N chromatograph with MS detector HP5973N.

An "Olimpus" polarizing microscope in conjuction with a "Linkam" TMS-93 hot stage and temperature controller were used to test phase transitions temperatures. The phase sequence and the phase character were established by observation of microscopic



Scheme 1. Synthetic route of esters IIa-IId, $r = 3$.

patterns. The temperatures and enthalpies of phase transitions were recorded parallel by DSC "Setaram" 141 microcalorimeter in heating and cooling cycles.

The helical pitch p for orthoconic antiferroelectric mixture W-252 was estimated based on selective reflection method. The pitch p was calculated for antiferroelectric and ferroelectric phase from dependence; $\lambda_{max} = n \cdot p$ and $\lambda_{max} = 2n \cdot p$ respectively, where n is the average refractive index. The value: $n = 1.5$ was taken to calculation [7]. Wavelength λ_{max} was determinated from minimum of transmitted light through the sample. Light transmission spectrum was recorded during cooling cycle using Peltier cells by Shimadzu UV-3600 spectrophotometer in the range of 360–3000 nm.

The optical tilt angle Θ of mixture W-252 was measured by standard optical methods [8] using 1.6 [μm] thick cells with ITO electrodes. Both cell surfaces were spin coated by RN 1199 (Nippon Chem.) polyimide. For the uniform orientation, anti-parallel rubbing was applied. The cells were filled with the investigated material by capillary actions at the isotropic phase. The uniform quasi-bookshelf structures were finally obtained upon several slow melting-cooling cycles. All measurements were done upon cooling from the isotropic phase.

4. Mesomorphism of Prepared Esters

Phase transitions temperatures and enthalpies of racemic esters II and their pure enantiomers from DSC measurement (onset points) are compared in Table 1 and visualized on Diagram 1. All four racemates exhibit anticlinic smectic C_A phase in broad temperature range and synlinic smectic C phase in short range (about $2 \div 3$ degree), while pure enantiomers show only SmC_A^* phase.

It is quite different from observed early for other families of orthoconic esters, wherein the anticlinic order was strongly depressed in range 1 deg or even totally disappeared [9]. Clearing points of enantiomers and their racemates are similar while clearing enthalpy of IIa and IIb are much lower than Ia and Ib even if $SmC_A|SmC$ transition enthalpy is added. $SmC_A|Iso + SmC_A|SmC$ of IIc and IId are similar to $SmC_A^*|Iso$ of Ic and Id. Melting points in series I and II are changed in irregular way and any correlate between them are not observed.

Table 1. Phase transitions temperatures [°C], enthalpies [$kJ \cdot mol^{-1}$] and chromatographic purity [%] of esters Ia–Id [5] and IIa-IId

No.	X_1	X_2	Cr		$SmC_A^{(*)}$		$SmC^{(*)}$		Iso	Purity
Ia	H	H	*	54.5; 78.9 *3.5; 21.6*	*		–	116.2 *7.1*	*	99.9
IIa	H	H	*	70.3 *19.5*	*	(110.0) *0.54*	*	(111.5) *2.4*	*	99.9
Ib	H	F	*	39.1 *20.3*	*		–	87.8 *5.9*	*	99.9
IIb	H	F	*	60.4 *20.9*	*	(86.8) *0.75*	*	(88.8) *2.85*	*	99.9
Ic	F	H	*	51.2 *24.7*	*		–	98.9 *6.0*	*	99.9
IIc	F	H	*	64.3 *19.9*	*	93.9 *0.05*	*	98.3 *5.8*	*	99.02
Id	F	F	*	74.0 *21.5*	*		–	97.0 *5.5*	*	99.9
IId	F	F	*	48.3 *20.3*	*	95.6 *0.04*	*	98.1 *5.2*	*	99.87

Upper row – temperatures from DSC observations obtained in heating cycle; down row – enthalpies; () – temperatures from DSC observations obtained during cooling cycle.

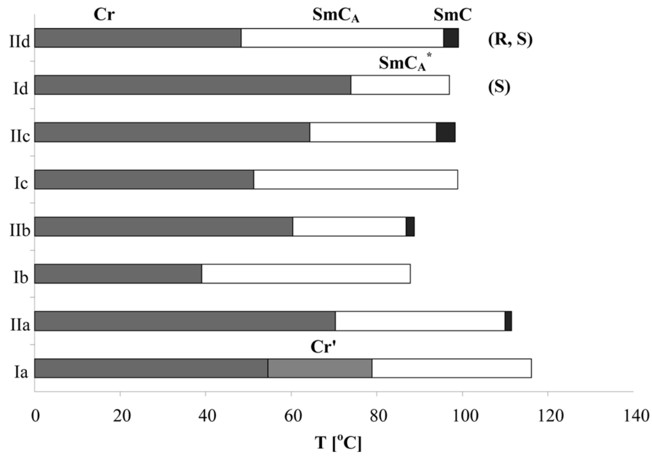


Diagram 1. Comparison of phase transitions temperatures from DSC measurement for enantiomeric (S) and racemic (R, S) esters.

5. Properties of Mixture W-252

Five component eutectic marked as mixture W-252 composed of two racemic esters and three chiral esters prepared early with longer methylene spacer with the composition listed in [5] (Table 2) was formulated.

Its phase transitions temperatures are listed in Table 3; temperature dependence of selective reflection and optical tilt Θ are given in Figures 1 and 2 respectively.

Table 2. Components of mixture W-252

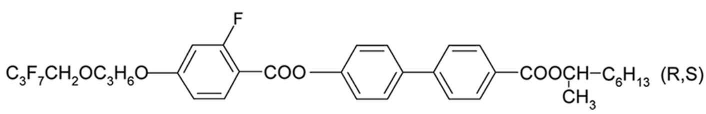
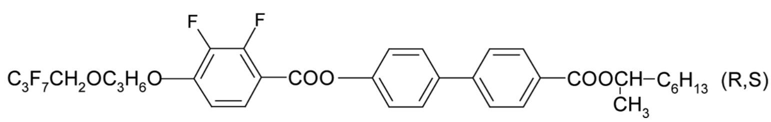
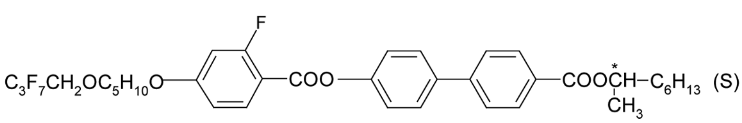
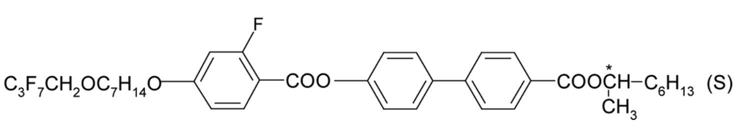
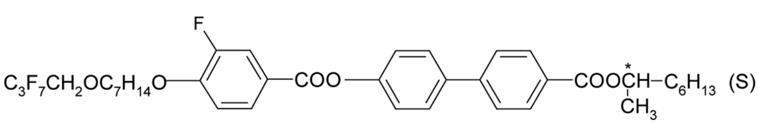
		Weight ratio [%]
1.		11.181
2.		16.059
3.		10.722
4.		47.210
5.		14.830

Table 3. Phase transition temperatures [°C] from polarizing microscope measurements of mixture W-252

Melting point	−13.2
SmC_A^*-SmC^*	95.6
SmC^*-SmA	98.8
SmA-Iso	100.6

Temperatures obtained during heating cycle.

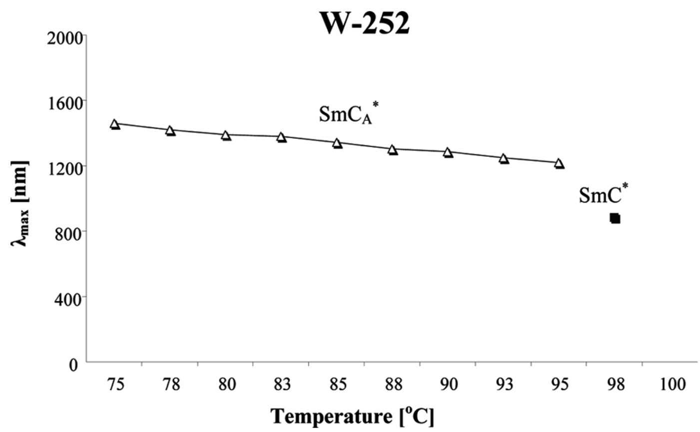


Figure 1. Temperature dependence of maximum selective reflection in mixture W-252.

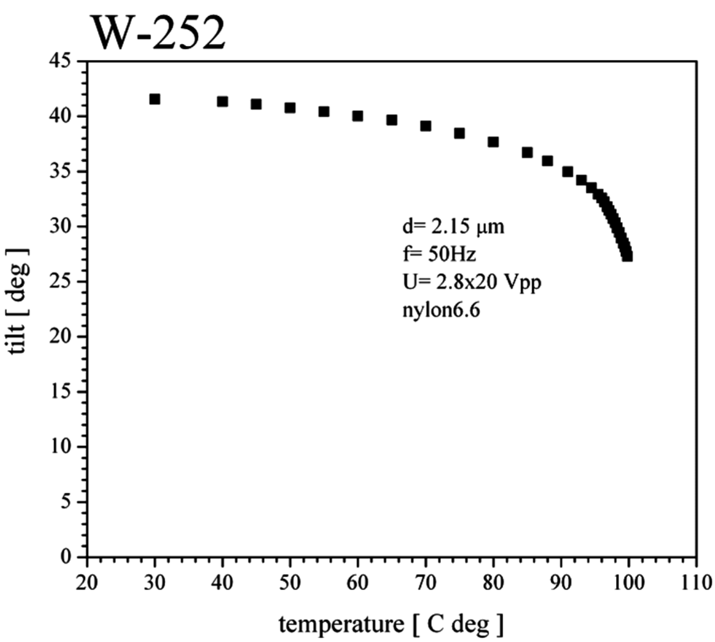


Figure 2. Optical tilt of mixture W-252.

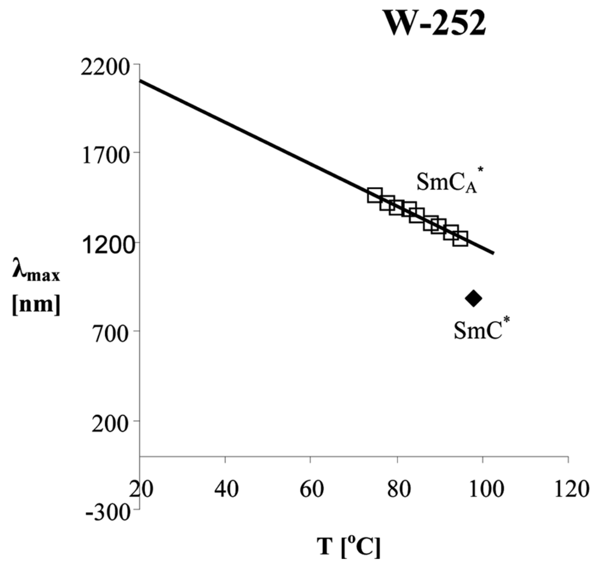


Figure 3. Extrapolation curve of selective reflection to 20°C for mixture W-252.

The mixture shows tilt above 42 degree at room temperature and the length of selective reflection maximum increasing with the decrease of temperature. The selective reflection is possible to observe only in the ferroelectric phase and in the antiferroelectric phase in the temperature range 75 ÷ 100°C. At lower temperature the bard of selective reflection becomes very broad and maximum disappeares. Extrapolation curve to room temperature (see Fig. 3) gives $\lambda_{max} \approx 2100$ nm (at 20°C), so $p \approx 1400$ nm.

6. Conclusions

The optical active enantiomeric (S) and racemic (R, S) unsubstituted, monofluoro- and difluorosubstituted 4′-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-[3-(2,2,3,3,4,4,4-heptafluoro-butoxy)prop-1-oxy]benzoates have anticlinic smectic phase in a broad temperature range. The enantiomeric esters have the direct SmC_A^*–Iso phase transition, while for racemic ones the anticlinic SmC phase is also observed in short temperature range. The racemic compounds are useful to prepare high tilted antiferroelectric mixtures with long pitch. Multicomponent eutectic mixture W-252 composed of three enantiomeric and two racemic materials was prepared. It is orthoconic antiferroelectrics at room temperature with pitch about 1500 nm.

Acknowledgments

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