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Mesogenic Compounds with two Chiral Lateral Groups: New Chiral Dopants for Ferroelectric Liquid Crystals

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Abstract New dopants for ferroelectric liquid crystals containing two chiral lateral groups have been synthesized. For 10 mol% doped mixtures of a non chiral SmC compound spontaneous polarization values up to 75 nC/cm² have been observed. Furthermore, one of the compounds exhibiting a smectic C* phase itself has been used to study the concentration dependence of the spontaneous polarization. A simple quadratic dependence was found which allowed to extrapolate a value of 750 nC/cm² for the pure compound.

INTRODUCTION

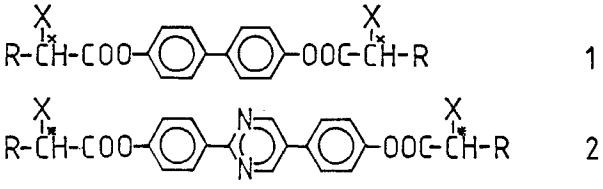
It is well known that a SmC phase containing chiral molecules shows ferroelectric properties. Most of the ferroelectric compounds consist of a mesogenic core with chiral centres in one of the side chains only. For enhancing the value of the spontaneous polarization as well as for studying the relationship between structure and ferroelectric properties it should be promising to

introduce chirality into the second side chain too, however only a few examples have been presented so far.[1,2,3]

Since the first report[4,5] optically active 2-halogenocarboxylic acids have been proved to be favourite groups to obtain liquid crystalline compounds with high values of the spontaneous polarization.

In this paper new mesogenic compounds with two chiral side chains are presented, which have been synthesized by esterification of 2-halogenocarboxylic acids with 4,4'-dihydroxybiphenyl and 2,5-bis-(4-hydroxyphenyl)-pyrimidine respectively. The spontaneous polarization has been measured for binary mixtures obtained by doping 4,4'-diheptyloxyazoxybenzene (**HOAB**) with 10 mol% of the compounds. Furthermore, for one of the compound exhibiting a SmC* phase itself the temperature dependence of the spontaneous polarization and of the optical tilt angle have been determined for different concentrations.

SYNTHESIS



1

2

R= a: $-CH_3$ b: $-C_2H_5$ c: $-C_3H_7$ d: $-C_4H_9$

e: $-CH(CH_3)_2$ f: $-CH_2-CH(CH_3)_2$ g: $-C^*H(C_2H_5)CH_3$

X=Cl, F

Two series (**1,2**) of mesogenic diesters have been prepared by esterification of 2-halogenocarboxylic acids with 4,4'-dihydroxybiphenyl and 2,5-bis-(4-hydroxyphenyl)-pyrimidine respectively. The 2-halogenocarboxylic acids were obtained from the corresponding 2-aminocarboxylic acids.[6,7] The 2,5-bis-(4-hydroxyphenyl)-pyrimidine was synthesized according to the method described previously.[8]

TRANSITION TEMPERATURES

Table I and table II show the polymorphy and transition temperatures of the pure compounds, which were determined by microscopic observations using a Mettler FP82 microheating stage and by DSC measurements (DSC7 Perkin Elmer).

TABLE I Polymorphy and transition temperatures (°C) of series **1**

Substance	Cr		Sm2		Sm1		I
1a (x=Cl)	o	132.7	o	162.4	o	163.3	o
1b (x=Cl)	o	82.8	o	83.0	o	102.2	■
1b (x=F)	o	a)	o	162.1	o	167.0	o
1c (x=Cl)	o	65.6		-		-	o
1c (x=F)	o	102.4		-	o	131.5	o
1d (x=Cl)	o	67.8		-		-	o
1e (x=Cl)	o	90.2		-		-	o
1e (x=F)	o	149.7		-		-	o
1f (x=Cl)	o	67.4		-		-	o
1g (x=Cl)	o	47.6		-		-	o
1g (x=F)	o	103.1		-		-	o

Sm1 and Sm2 are unidentified high ordered tilted smectic phases

a) A melting temperature could not be determined

TABLE II Polymorphy and transition temperatures (°C) of series **2**

Substance	Cr		SmC*		SmA		I
2b (x=Cl)	o	160.5	o	178.4	o	201.6	o
2c (x=Cl)	o	123.1	o	(118.5)		-	o
2c (x=F)	o	186.2	o	204.8	o	242.8	o
2d (x=Cl)	o	117.6	o	134.0		-	o
2d (x=F)	o	172.6	o	183.7	o	223.7	o
2e (x=Cl)	o	160.6		-		-	o
2g (x=Cl)	o	117.5		-		-	o
2g (x=F)	o	156.9		-		-	o

For compounds derived from the branched aminocarboxylic acids (**e-g**) no liquid crystalline properties were observed, whereas for linear side chains in most cases smectic phases occur. Compound **1c**(x=F) exhibits one and compounds **1a**(x=Cl) and **1b**(x=F, Cl) two high ordered tilted smectic phases yet to be identified. The three-ring compounds **2b**(x=Cl), **2c**(x=F, Cl) and **2d**(x=F, Cl) exhibit SmC* and in some cases SmA phases additionally.

RESULTS

The spontaneous polarization of 10 mol% mixtures with 4,4'-di-heptyloxyazoxybenzene (**HOAB**) were measured in 4 µm cells using a Diamant bridge (table III). The values of the spontaneous polarization obtained 10K below the SmC*/N* transition temperature are in the range of 20 to 45 nC/cm^2. These values are approximately twice as high as the values observed for corresponding compounds with only one chiral side chain[2], as expected on the basis of a simple additivity law.

TABLE III SmC*/N* transition temperatures and spontaneous polarization of 10 mol% mixtures in **HOAB**

chiral dopant	T (°C)	P_S (nC/cm²)
1b (x=Cl)	83.8	21.2
1c (x=Cl)	80.6	24.8
1c (x=F)	82.7	25.0
1d (x=Cl)	81.0	25.8
1e (x=Cl)	80.0	36.8
1f (x=Cl)	76.0	19.8
1g (x=Cl)	77.6	26.4
1g (x=F)	77.7	45.1
2c (x=Cl)	103.3	20.0
2d (x=Cl)	102.3	21.0
2e (x=Cl)	102.5	29.8
2g (x=Cl)	100.6	31.1
2g (x=F)	100.3	45.3

P_S has been measured 10K below the SmC*/N* transition temperature

As shown in figure 1 for the fluor containing dopant **2g**(x=F) a spontaneous polarization of about 75 nC/cm² is observed 40k below the SmC*/N* transition temperature, being of the same order as the highest value reported so far for a 10 mol% doped mixture.[9]

Usually the ferroelectric properties of chiral dopants are characterized by a linear extrapolation of the spontaneous polarization values obtained at low concentration to the pure compound. However besides a chiral-racemic mixture[10] no system is known to follow exactly this simple behaviour.

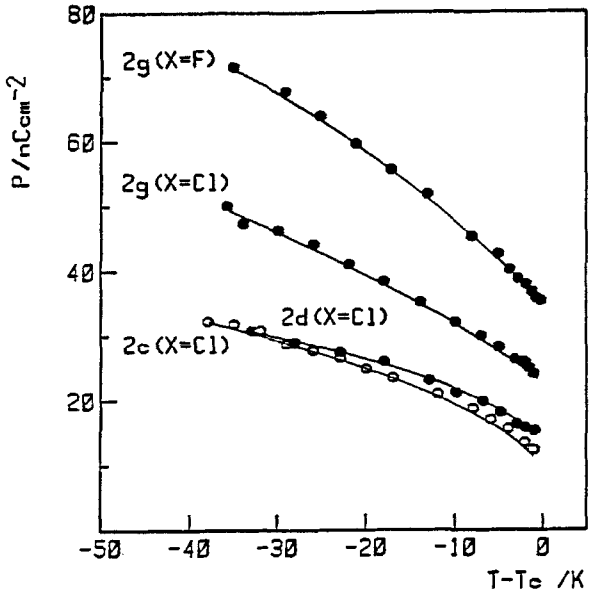


Figure 1. Temperature dependence of the spontaneous polarization of **HOAB** doped with 10 mol% chiral dopant

Recently, using dopants with rather low spontaneous polarization, a linear concentration dependence of $P_S/\sin\Theta$ has been obtained.[11] Compound **2d**(x=Cl), which exhibits a SmC* phase itself, was chosen to carry out the respective investigation for a dopant with high spontaneous polarization.

The miscibility diagram for **HOAB** and compound **2d** shows total mixing of the SmC phases (figure 2). For concentrations between 30 and 90 mol% **2d** a SmA phase is induced.

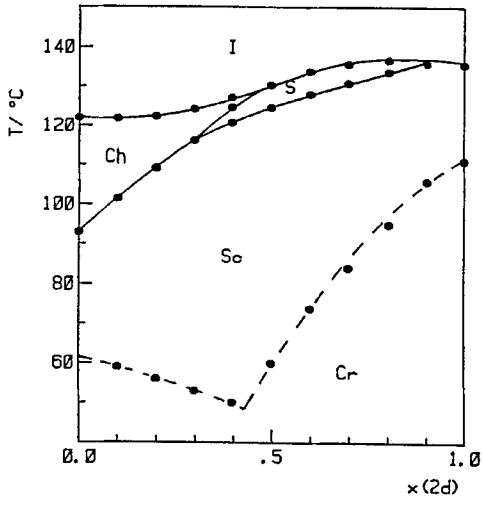


Figure 2. Diagram of state of the binary system **HOAB/2d**

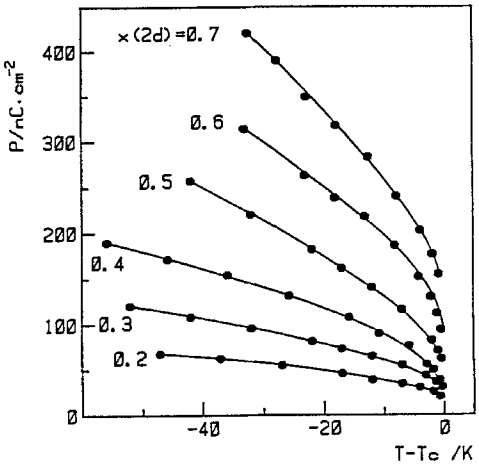


Figure 3. Temperature dependence of the spontaneous polarization for different concentrations of **2d** in **HOAB**

The temperature dependence of the spontaneous polarization is shown in figure 3 for different concentrations of the chiral dopant **2d.** For a concentration of 20 mol% **2d** a value of 60 nC/cm² is measured at a temperature 30K below the SmC*/N* transition, whereas for a concentration of 70 mol% **2d** the value increases to about 400 nC/cm² (30K below the SmC*/SmA transition) being twice as high as expected for a linear relationship. Indeed the experimental values are found to follow a simple square law ($P_S \sim x^2$).

The tilt angle which was measured optically depends only slightly on the composition (figure 4). Thus the dependence of the polarization - tilt angle coupling P_S/Θ on the mole fraction of the chiral dopant shows a square law also (figure 5).

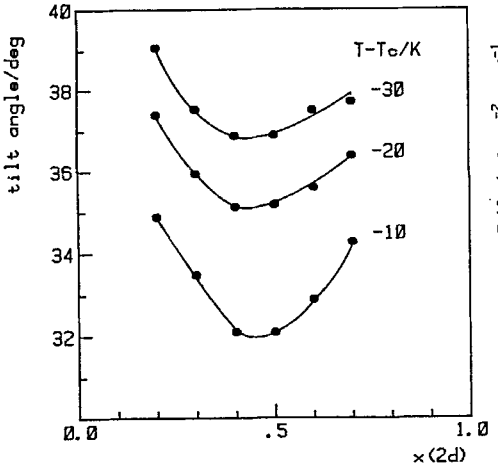


Figure 4. Concentration dependence of the optical tilt angle in the binary system **HOAB/2d**

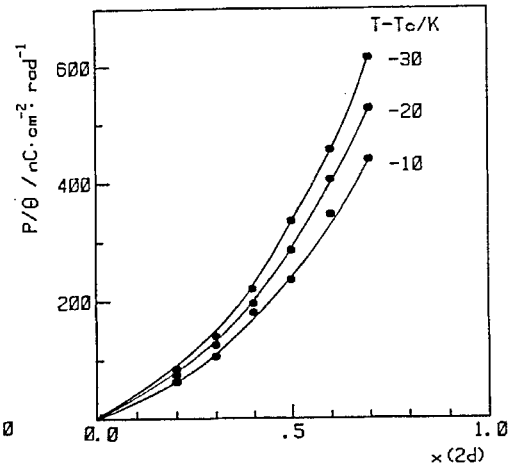


Figure 5. Concentration dependence of the polarization tilt angle ratio in the binary system **HOAB/2d**

Further investigations concerning the concentration dependence of the ferroelectric properties for chiral dopants with high spontaneous polarization are in progress.

Acknowledgement

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