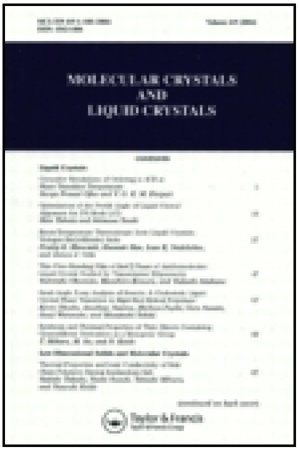

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Smectic C Compounds with Bicyclo[2,2,2]Octane Ring

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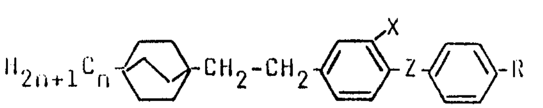
Homologous series of 4-[2-(4-alkylbicyclo[2,2,2]octyl)ethyl]phenyl 4-alkoxybenzoates were synthetized and their mesomorphic properties were investigated. These compounds exhibit smectic C phase and are useful as components of mixtures with ferroelectric properties. The influence of dopants on the tilt of the molecules in the smectic C layer of the mixtures containing mentioned compounds were studied.

Keywords: liquid crystals, smectic C, ferroelectric liquid mixtures, tilt of molecules in smectic C layer

INTRODUCTION

In our preceding report we have shown that alkylbicyclo[2,2,2]octylethylphenyl alkoxybenzoates (formula **1**, Z = —COO—, R = OC_mH_{2m+1}) are mesogenes with the S_C phase which may be considered as components of ferroelectric mixtures.[1]

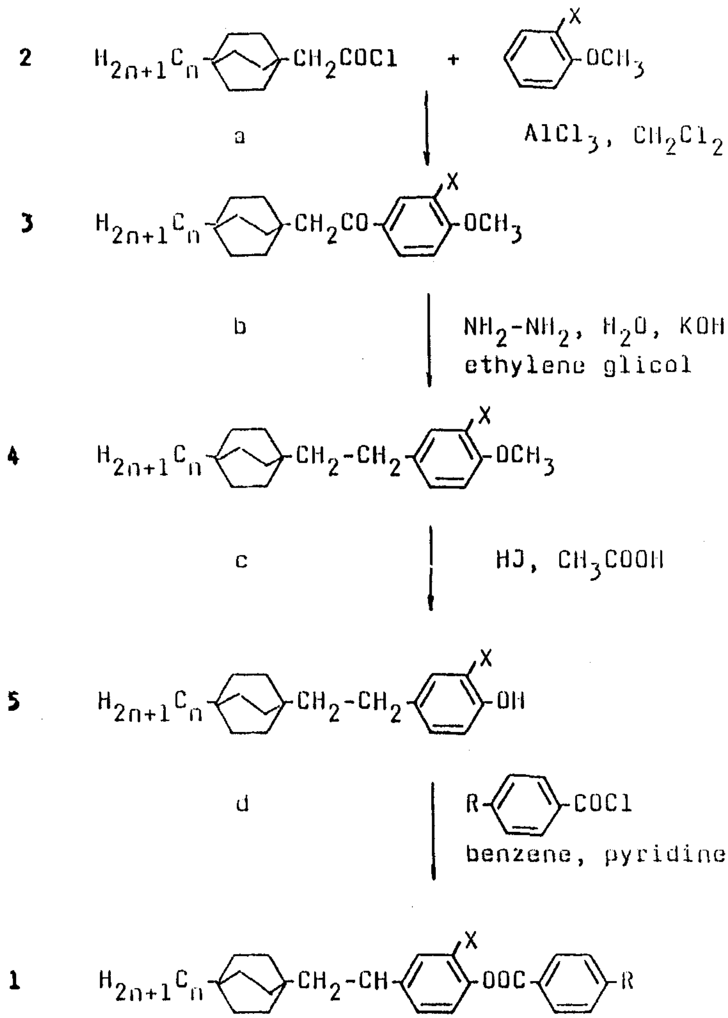


1

Compounds **1** mixed with alkoxyphenyl alkoxybenzoates yield mixtures with a wide range of the S_C phase and the phase sequence $S_C \rightarrow N$ or when suitable chiral dopants are used also $S_C^* \rightarrow Ch$ or $S_C^* \rightarrow S_A \rightarrow Ch \rightarrow I$ or else $S_C^* \rightarrow S_A \rightarrow I$. We synthesized therefore a larger number of compounds **1** to allow a better knowledge of their mesogenic properties. We also studied the effect of dopants on the tilt of the molecules in the smectic C layer of mixtures containing compound **1**.

SYNTHESIS

The compounds of formula **1**, in which Z is the —OCO— group, have been synthesized according to following scheme:



SCHEME I. The route of synthesis compounds **1**.

Compound of formula **1**, in which Z is the —COO— group, was synthesized in a similar way, however, in step (a) benzene was the second substrate and the hydrocarbon obtained after hydrazine reduction was acetylated, upon which the obtained ketone was converted into alkylbicyclo[2,2,2]octylethylbenzoic acid in the holoformic reaction.

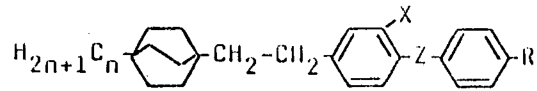
RESULTS

Mesomorphic Properties

The phase transition points and enthalpies of melting of the synthesized compounds **1** are summarized in Table I. 4-[2-(4-alkylbicyclo[2,2,2]octyl)ethyl]phenyl 4-alk-

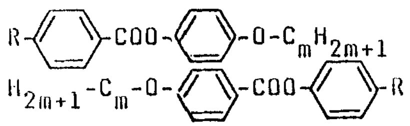
TABLE I

Transition temperatures (°C) and enthalpies (kJ mole^{-1}) for compounds **1**



n	m	X	Z	Cr_1	Cr_2	S_G	S_B	S_C	S_A	N	I
	R = OC_mH_{2m+1}										
3	10	H	OCO		· 91	· (66)	—	· (73.7)	—	· 193.5	
					29.8						
6	4	H	OCO		· 80	—				· 220.5	·
6	5	H	OCO		· 99.5	—				· 212.8	·
					32.7						
6	6	H	OCO	· 69.5	· 89.5	—				· 200	·
				7.7	13.8						
6	7	H	OCO		· 86	—				· 201.8	·
					30.8						
6	8	H	OCO		· 75.5	· (70)	—	· 90	—	· 196	·
					23.4			0.4			
6	9	H	OCO		· 74.5	· (67.5)	—	· 105.3	—	· 192.2	·
					· 25.1			1.1			
6	10	H	OCO	· 56.5	· 68	· (65.6)	—	· 118	—	· 189	·
				9.8	9.2			0.15			
6	8	Br	OCO		· 62.5	—				· 155	·
					26.5					1.6	
6	10	Br	OCO		· 61.5	—				· 148	·
					24.1					1.4	
6	10	F	OCO		· 66.5	—		· 70	—	· 177.5	·
					24.8			0.32			
6	8	H	COO		· 70.5	—	· 129		· 183	· 197	·
					17.0		7.0				
	R = C_mH_{2m+1}										
6	10	H	OCO		· 73.3	—	· 122.5	·	· 132	· 171.3	·
					14.1		5.2		0.6		
	R = —(S)—O—$\overset{*}{C}H(CH_3)$—C_2H_5										
6	—	H	OCO		· 101.5	—	· (76.5)	·		· 187	·
					28.0						
6	—	Br	OCO		· 107	—				· 141	·
	R = —(S)—O—$\overset{*}{C}H(CH_3)C_6H_{13}$										
6	—	H	OCO		· 53.5	—	· 61.5	·		· 127.5	·

oxybenzoates in which R = OC_mH_{2m+1} is a normal alkoxy group have only the nematic phase, if the total number of carbon atoms in both alkyl and alkoxy terminals fulfils the condition n + m < 13, or the nematic and smectic C and G phases if n + m ≥ 13. The branching of the alkoxy chain in position α with respect to the oxygen atom (R = —O—CH(CH_3)—C_6H_{13}) or β (R = —O—CH_2—CH(CH_3)—C_2H_5) results in the appearance of the smectic B phase. The orthogonal phases are also observed only when R = C_mH_{2m+1}. The change of orientation of the ester group in the molecule, i.e., the change of the group —OCO— to —COO— leads to the disappearance of the tilted phases. In 4-octyloxyphenyl 4-[2-(4-n-hexylbicyclo[2,2,2]octyl)ethyl]benzoate the phase sequence: $S_B \rightarrow S_A \rightarrow N$ was observed. The mesomorphic properties of esters **1** are different from those that could have been expected by analogy to the binuclear compounds **6** and **7**.



6

7

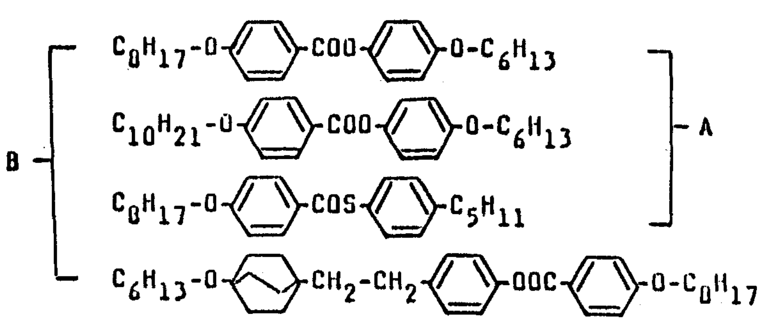
In the esters of formula **6** in which R = C_nH_{2n+1} is a normal alkyl group (analog of compound **1** for Z = —COO—) the smectic C phase is often observed, whereas in esters of formula **7** (analog of compound **1** for Z = —OCO—) the smectic A phase is preferred.[2]

Substitution of the hydrogen atom by a bromine atom in the central benzene ring in the ortho position to the —OCO— bridge produces a decay of the tilted C and G phases whereas substitution by a fluorine atom results in the preservation of the C phase.

The mesogenic properties of compound **1** are similar to those observed by Kelly[3,4,5] in 4-[2-(4-trans-n-alkylcyclohexyl)ethyl]-phenylbenzoates. The main difference consisted in that compounds **1** have a higher clearing point (30–50°C) and higher $S_C \rightarrow N$ phase transition point on the average by about 10°C.

Properties of Compounds 1 in the Multicomponent Mixtures

The four component eutectic mixture **B** was obtained by combining compound **1** (n = 6, m = 8, Z = —OCO—) and three binuclear esters:



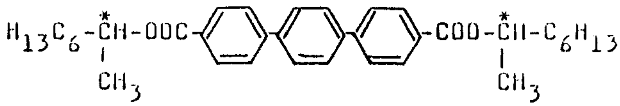
23.35 wt.%

10.00 wt.%

25.41 wt.%

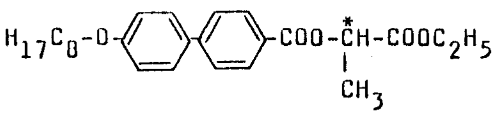
32.44 wt.%

This mixture had the following phase transition sequence: Cr 8 S_C 58.8 N 119.5 I. Addition of the compound **1** lowered the viscosity of mixture containing only two ring benzoates (mixture **A**, Figure 1), for example at 40°C the viscosities of mixtures **B** and **A** were 536 and 783 mPa · s respectively. Next chiral compounds **8, 9, 10** and the achiral compound **11** were added to the mixture **B**:



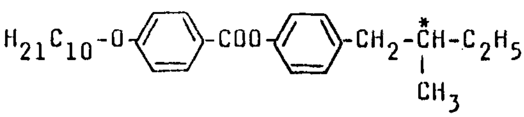
8

Cr 70 I Ps (+), p (-) Ref.(6)



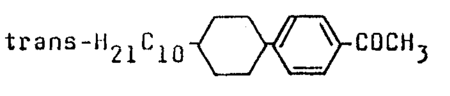
9

Cr 45 (S_A 43) I Ps (+), p (-) Ref.(7)



10

Cr 42.5 S_A 44 Ch 47 I Ps (+), p (+) Ref.(8)



11

Cr 76 I Ref.(9)

The admixtures were selected so as to lower the high clearing points of mixture **B**, to induce phase S_A, and to change the tilt angle of molecules in the smectic C layer and also to introduce chirality.

In Figure 2a, 2b, 2c and 2d fragments of phase diagrams are presented obtained by adding to the base mixture **B** compounds **8, 9, 10** and **11**, respectively. These compounds lower the clearing point of mixture **B** but also effect the stability of the S_C phase; the maximal $S_C \rightarrow$ Ch phase transition point is observed at an approximately 20% content of compound **8** in **B**; a similar observation was made by Rabinovich *et al.* for this compound in other mixtures.[6] Compound **9** lowers the $S_C \rightarrow$ N phase transition points almost proportionally to its concentration, compound **10** when added in an amount below 20 wt.% it has no practical effect on the $S_C \rightarrow$ Ch transition point; above this concentration the S_A phase is induced what is accompanied by the lowering of the $S_C \rightarrow S_A$ phase transition temperatures. Compound **11** when added in quantities exceeding 8 wt.% strongly destabilizes the S_C phase and strongly induces the S_A phase. In Figure 3 the dependence of the tilt

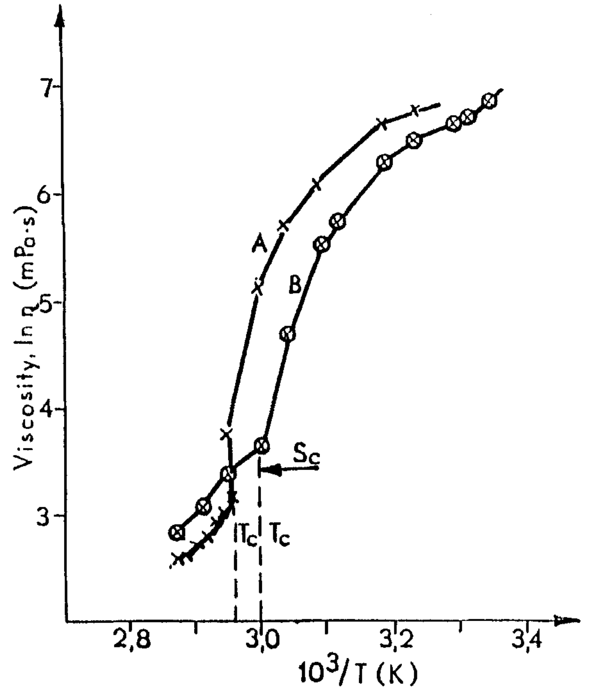


FIGURE 1 Viscosity of the mixture **A** and **B** versus temperature.

angle of the molecule in the smectic C phase on temperature is presented for mixture **B** and mixture **B** doped with **8, 9, 10** and **11** respectively. The tilt θ was measured by X-ray method for achiral mixtures: **B** and **B** + **11**, for the rest mixtures with chiral dopants by electrooptical methods.[10]

The mixture **B** and **B** with compound **8** show a high value of the tilt angle θ, compounds **9** and especially **10** and **11** strongly lower the value of θ, and in the case of the two latter this lowering correlates with the induction of the S_A phase.

Compound **8** seems to be the most advantageous among the chiral compounds used as an dopant for inducing spontaneous polarization. Addition of two compounds, i.e., **8** and **10** or **8** and **11** allows us to obtain mixture simultaneously with the phase sequence $S_C \rightarrow S_A \rightarrow$ Ch and the more optimal temperature range of S_A and Ch phases and tilt angle θ. It is shown on the following Figures 4, 5 and 6.

In Figure 4a we see a fragment of the phase diagram of a mixture consisting of 70 wt.% of **B** and 30 wt.% of compound **10** revealing the following phase transitions: S_C^* 50 S_A 62 Ch 97 I, into which subsequently compound **8** was added. In Figure 4b we see an analogous relationship for a mixture consisting of 91.4 wt.% of **B** and 8.6 wt.% of compound **11**. In the former mixture the S_C phase shows maximal stability when the concentration of compound **8** is about 30 wt.%, and in the latter mixture a monotonous increase of the S_C phase stability was observed in the whole investigated range of concentrations of compound **8**.

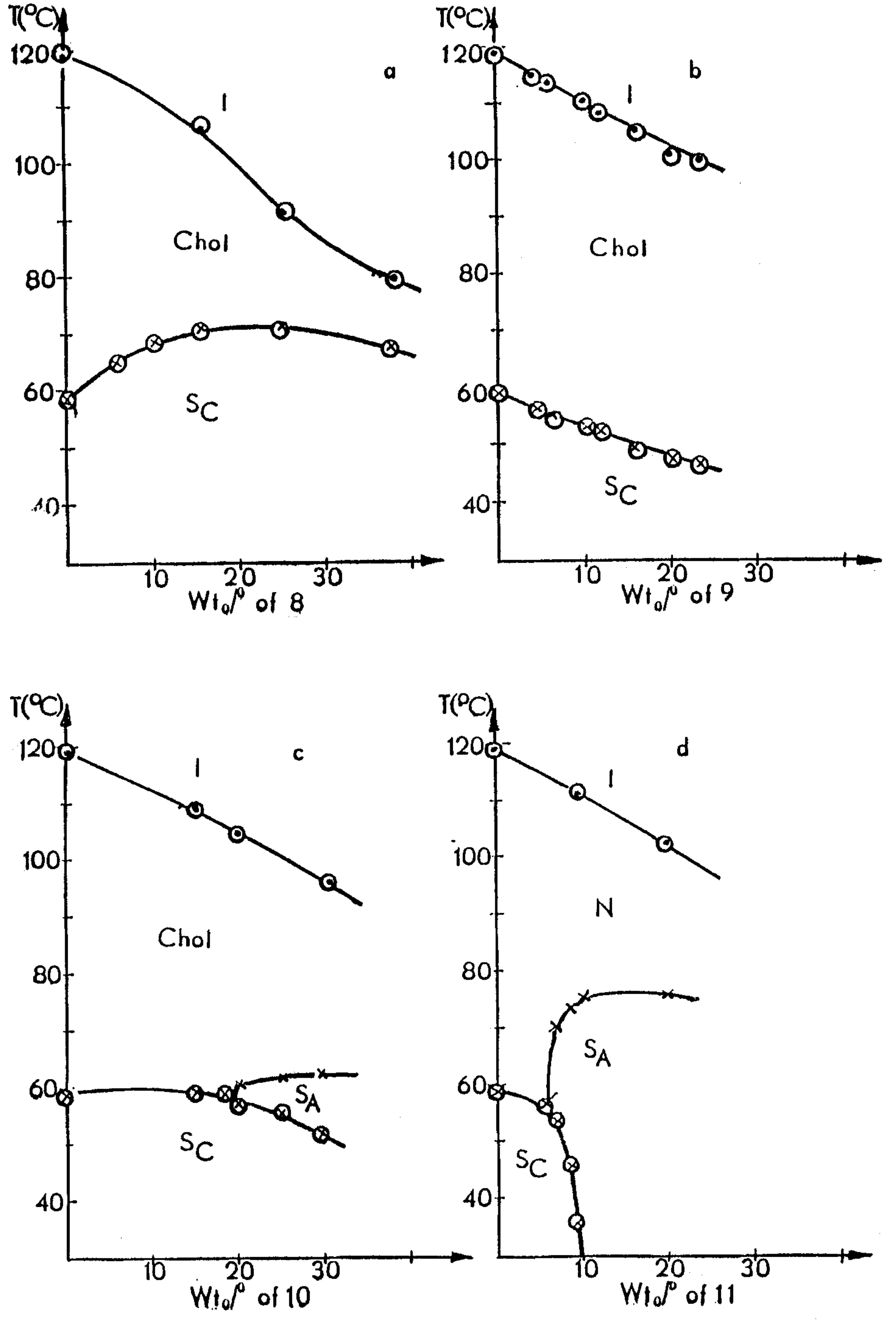


FIGURE 2 Phase transition temperature of the mixture **B** versus concentration of the dopant: a = compound **8**, b = compound **9**, c = compound **10** and d = compound **11**.

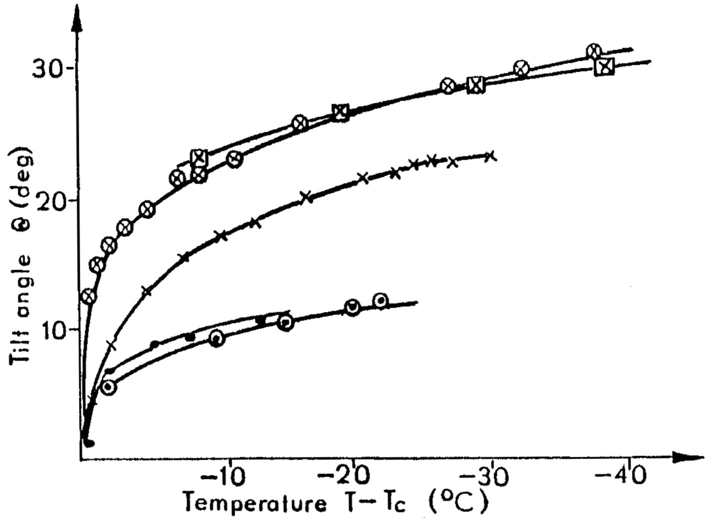


FIGURE 3 Tilt angle θ of molecules in smectic C layer versus temperature: ⊠ = mixture **B**, ⊗ = mixture **B** doped with 20 wt.% of **8**, or 20 wt.% of **9** = ×, or 20 wt.% of **10** = •, or 8.6 wt.% of **11** = ⊙.

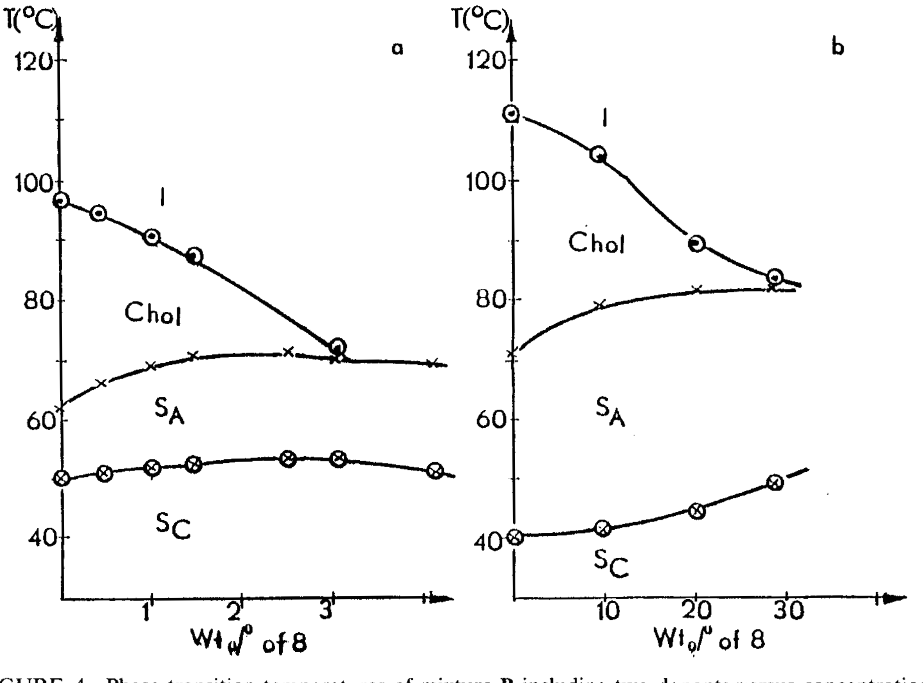


FIGURE 4 Phase transition temperatures of mixture **B** including two dopants versus concentration of the first dopant: a = mixture **B** containing 30 wt.% of compound **10** into which compound **8** is added, b = mixture **8** containing 8.6 wt.% of **11** into which compound **8** is added.

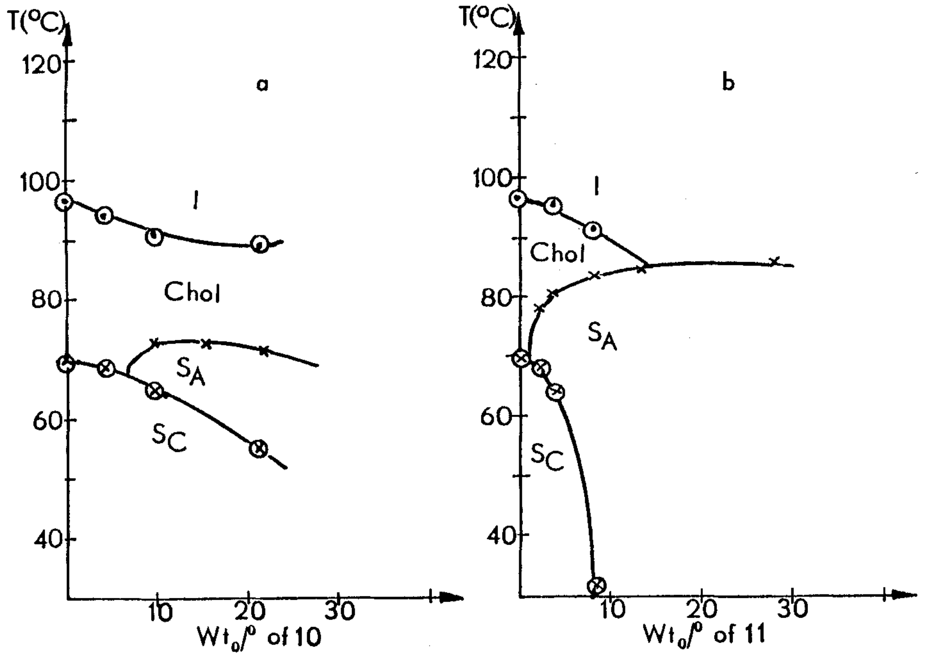


FIGURE 5 Phase transition temperatures of mixture **B** including two dopants versus concentration of the second dopant: a = mixture **B** containing 20 wt.% of compound **8** into which compound **10** is added, b = the same mixture into which compound **11** is added.

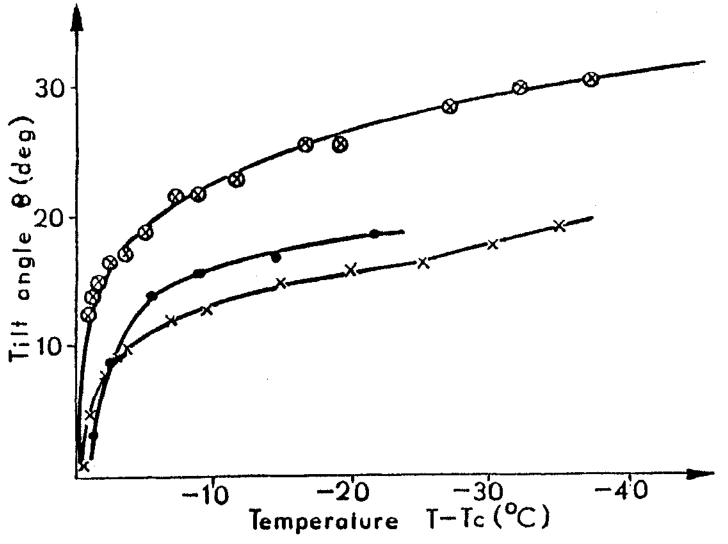


FIGURE 6 Tilt angle θ versus temperature for mixture containing 20 wt.% of compound **8** = ⊗ and the same mixture containing additively 9.7 wt.% of compound 10 = × or 6.9 wt.% of compound **11** = •.

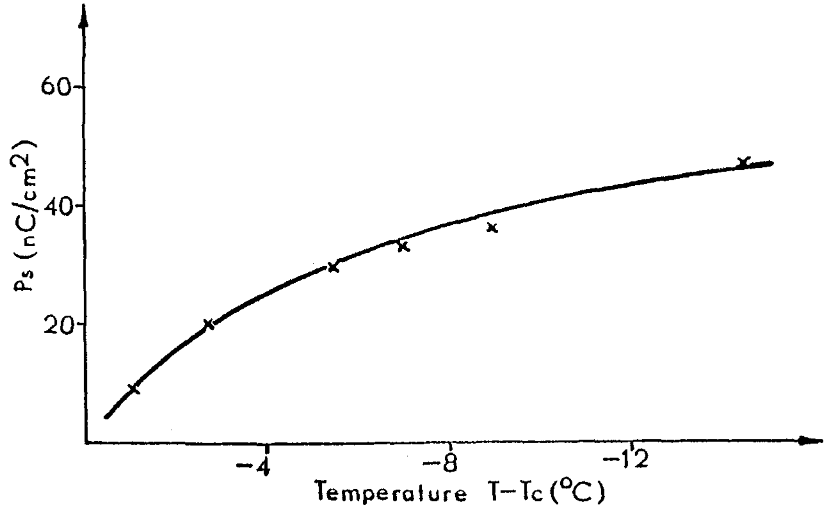


FIGURE 7 Spontaneous polarization of mixture **B** containing 20 wt.% of compound **8** and then doped with 6.9 wt.% of compound **11**.

The mixtures presented in Figures 4a and b reveal a fairly wide range of the S_A phase so the observed θ angle in this phase is small; the lowering of the concentration of compound **10** or **11** in the mixture produces an increase of the angle θ. The minimal amount of compound **10** in a mixture comprising of 80 wt.% of **B** and 20 wt.% of compound **8** that induces the S_A phase is 8 wt.%, the respective amount for compound **11** being 3 wt.% (Figure 5).

In Figure 6 decreasing is shown of the tilt angle θ of the molecules in the smectic C layer of mixture **B** containing 20 wt.% of compound **8** after adding of compound **10** or **11**. By varying the concentration of compound **10** or **11** in the mixture we can vary the angle θ in to more optimal value.

In Figure 7 temperature dependence spontaneous polarization of mixture **B** doping compound **8** and than else 6.9 wt.% of compound **11** is shown.

CONCLUSIONS

4-[2-(4-alkylbicyclo[2,2,2]octyl)ethyl]phenyl 4-alkoxybenzoates are useful components for preparing ferroelectric mixtures from two ring benzoates because they allow to decrease their viscosity. The mixtures including esters of alkoxybenzoic acids and compound **1** reveal $S_C \rightarrow N$ sequence and a large tilt angle of the molecules in the smectic C layer. This angle may be varied arbitrarily by adding to the mixture dopants which have or do not have a S_C phase. Besides, the additions allow us to induce S_A phase and to optimize in the required way the $I \rightarrow Ch \rightarrow S_A \rightarrow S_C$ phase sequence, i.e. to decrease or extend the ranges of the neighbouring phases at will.
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