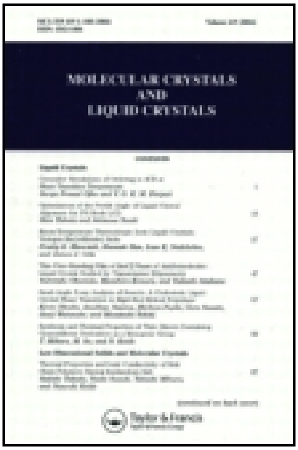

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Study of Some Achiral Liquid Crystalline Ester Derivatives

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Study of Some Achiral Liquid Crystalline Ester Derivatives

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Ferroelectric properties of a perfluoroalkyl substituted two-ring benzoate doped with a chiral additive have been studied and compared with those of well-known alkyl substituted benzoate. A study of weakly polar three-ring ester derivatives has revealed their applicability as the components of ferroelectric liquid crystal materials for display applications. The results of this work are discussed in terms of the structure-property relationships.

Keywords: perfluoroalkyl groups; ferroelectric properties; ester derivatives; liquid crystals

1. INTRODUCTION

An ester group is one of the most important linkages as constituents of the liquid crystalline core.(1–15) The introduction of the ester group increases the flexibility and polarity of the molecular core. It has been shown that the dissymetrical structure of the ester group significantly affects the thermal efficiency of both substituents attached to the group.(1–15) In other words, the replacement of the substituents, for example alkyl groups by perfluoroalkyl ones, leads to a sufficient change in the molecular structure of ester derivatives with the corresponding significant change in liquid crystalline properties.(17–24)

Over the past two decades there has been shown much interest in the design and synthesis of liquid crystalline perfluoroalkyl substituted ester derivatives owing to their promising physico-chemical and electro-optical properties.(17–24)

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As a part of our systematic study of the structure-property relations in liquid crystals {see, for example our previous publications which discuss the effects of perfluoroalkylation in one-ring ester derivatives(19–23)}, we present here our results on the study of the ferroelectric properties of a perfluoroalkyl substituted two-ring benzoate doped with a chiral additive. These results have been compared with those of well-known alkyl substituted benzoate. Also, three-ring ester alkyl-alkoxy derivatives have been studied for the estimation of their applicability as the components of ferroelectric liquid crystal materials for display applications.

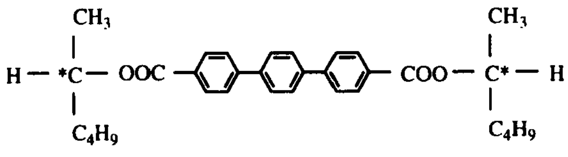
2. PHYSICO - CHEMICAL AND ELECTRO-OPTICAL PROPERTIES

The phase transition temperatures of two-ring perfluoroalkyl substituted benzoate, alkyl substituted reference compounds and three-ring ester derivatives are summarized in table I, where Cr, SmA, SmC, N and I are the crystalline, smectic A, smectic C, nematic and isotropic phase, respectively.

It is evident from table I that the perfluoroalkylation of two-ring benzoate lowers the melting point (crystal – smectic A phase transition), introduces an additional smectic C phase and increases the clearing point (smectic A – isotropic phase transition) {compounds **1** and **2**}.

In order to estimate the tilt angle Θ and the rotational viscosity(27,28) γ_φ of compound **1** and reference compound **3**, each of them was doped with 10 wt % of a chiral dopant(29):

Chiral dopant



Cr 79 I

which does not change these parameters.(30) The tilt angle (of the mixture based on perfluoroalkyl derivative) and the rotational viscosity of these two binary mixtures have been measured according to the methods described in references.(27,28) The temperature dependence of Θ and γ_φ of compound **1** doped with a chiral additive on cooling from the isotropic phase are shown in figure 1. The rotational viscosity shows decreasing behavior with increasing the temperature. This is a usual situation which has been observed for many other ferroelectric liquid crystals.(31,32) While the tilt angle is almost independent on the temperature {which is very important for ferroelectric display applications(31,32)} and exhibits a jump near the smectic A-smectic C phase transition. These indicate the first order of the SmA – SmC phase transition. It is rather seldom seen for this type of phase transitions: usually the smectic A -smectic C phase transition is the second order one.(31,32) As can be seen in figure 2, the mixture based on compound **1** is more viscous than the corresponding mixture based on compound **3**.

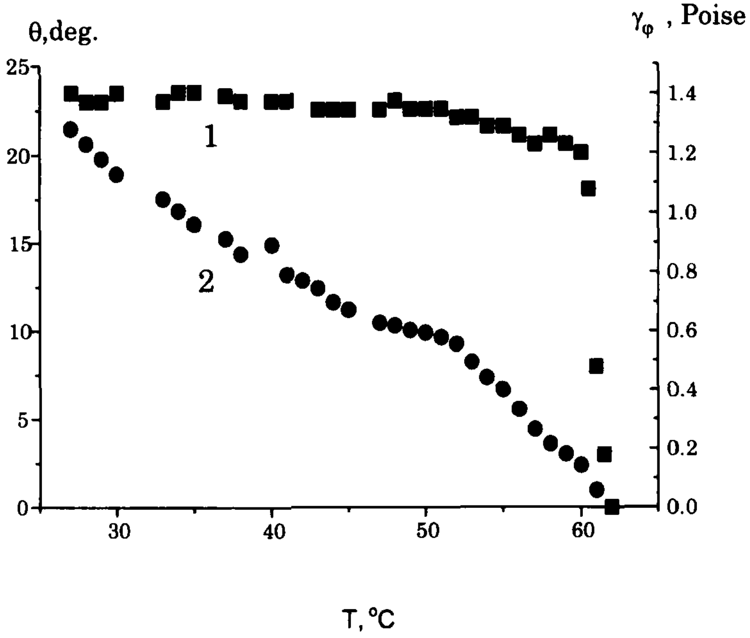
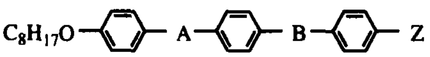


FIGURE 1 Temperature dependence of the tilt angle Θ (curve 1) and the rotational viscosity γ_φ (curve 2) in the smectic C* phase of compound **1** doped with a chiral additive on cooling from the isotropic phase

The thermal data collated in table I reveals that the hexyloxy homologue of three-ring ester derivative exhibits higher phase transition temperatures in comparison with those of the corresponding two-ring derivative (compounds **3** and **4**). While changing the orientation of ester groups significantly affects the mesomorphic properties of the ester derivatives (considering compounds with the same terminal substituents, compounds **4, 6, 8, 10; 5, 7, 9, 11**, table I). It is convenient to express the influence of the orientation of ester linking groups (A-B) on the mesomorphic properties of three-ring derivatives by the following orders of increasing the clearing point (T_{cl}) {nematic – isotropic phase transition temperature}, smectic A thermostability (T_{SmA}) {smectic A – nematic phase transition temperature}, smectic C thermostability (T_{SmC}) {smectic C – smectic A or smectic C – nematic phase transition temperature}, smectic C range (ΔT), and melting point (T_m) {crystal – smectic C phase phase transition temperature}:

List of systems



$Z = OC_6H_{13}$

T_{cl} ⇨ A-B: COO-OOC < COO-COO < OOC-OOC < OOC-COO

T_{SmA} ⇨ A-B: OOC-OOC < COO-COO < OOC-COO

T_{SmC} ⇨ A-B: COO-OOC < OOC-OOC < COO-COO < OOC-COO

ΔT ⇨ A-B: COO-OOC < OOC-COO < COO-COO < OOC-COO

T_m ⇨ A-B: COO-COO < OOC-OOC < COO-OOC < OOC-COO

d / L ⇨ A-B: OOC-COO < COO-COO < OOC-OOC

$Z = C_6H_{13}$

T_{cl} ⇨ A-B: COO-COO = OOC-COO < OOC-OOC < COO-OOC

T_{SmA} ⇨ A-B: COO-COO < OOC-COO

T_{SmC} ⇨ A-B: OOC-OOC < COO-COO < COO-OOC < OOC-COO

ΔT ⇨ A-B: COO-OOC < OOC-OOC < COO-COO < OOC-COO

T_m ⇨ A-B: COO-COO < OOC-OOC < COO-OOC < OOC-COO

d / L ⇨ A-B: OOC-COO < COO-COO < OOC-OOC

These results and the phase transition temperatures of compounds **4–11** reveal that the following combination of two ester groups A-B: OOC-COO, which are introduced into the core, gives the highest clearing point, smectic A and smectic C thermostabilities, melting point and broadest smectic C range among the hexyloxy substituted derivatives. While COO-OOC combination results in the lowest clearing temperature, smectic A and C thermostabilities and narrowest smectic C range. The lowest melting temperature is achieved in the COO-COO combination. These changes in the mesomorphic properties correspond to the changes of the ratio d / L and the character of the temperature dependence of the parameter d(33) (where d is the layer spacing obtained from X-ray diffraction measurements and L is the molecular length, see table 1 and list of systems), with the lowest and highest values observed for the liquid crystals which have OOC-COO and OOC-OOC combinations of linking groups, respectively. It is important to note that three-ring hexyloxy substituted ester derivatives **4**, **6**, **8** exhibit the ratios d / L < 1 which mean the monolayer arrangements of their smectic phases.

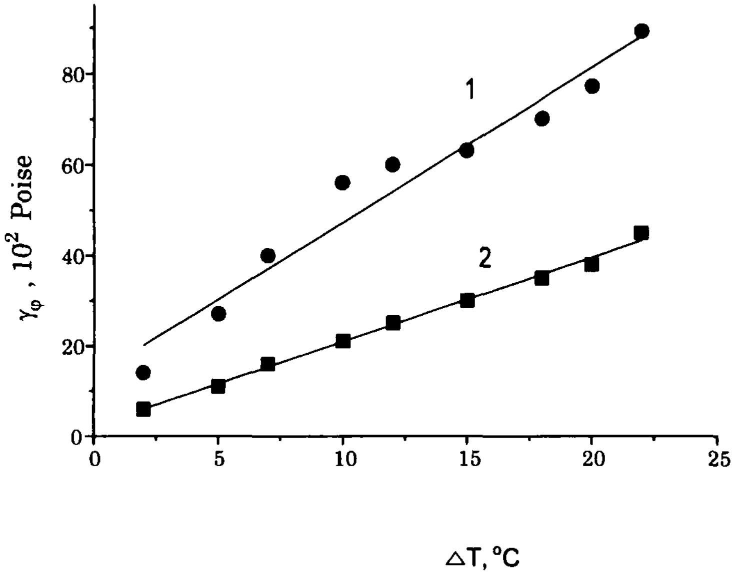
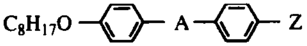
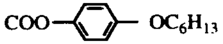
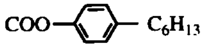
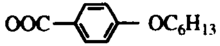
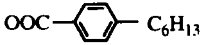
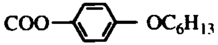
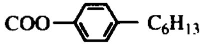
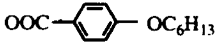
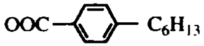


FIGURE 2 Rotational viscosity of the mixtures based on compound **1** (curve 1) and compound **3** (curve 2) in dependence on the distance from the phase transition temperature SmA-SmC: $\Delta T = T_{SmA\text{-}SmC} - T_{meas}$

The replacement of the hexyloxy group by a hexyl group significantly lowers the phase transition temperatures of three-ring ester derivatives (compounds **4** and **5**, **6** and **7**, **8** and **9**, **10** and **11**) and leads to the different orders of increasing T_{cl}, T_{SmA}, T_{SmC} and maintains the same orders of increasing ΔT and T_m. It is evident from table I and list of systems that the influence of the orientation of ester groups on the clearing points (nematic-isotropic phase transition temperatures) of the hexyl substituted derivatives is less pronounced in comparison with that of the corresponding hexyloxy substituted derivatives.

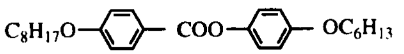
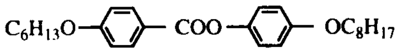
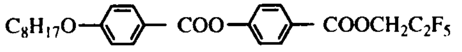
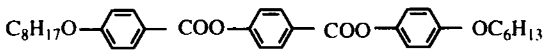
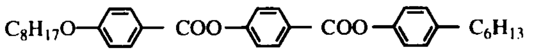
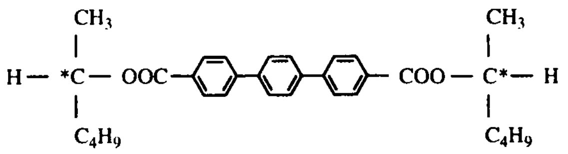
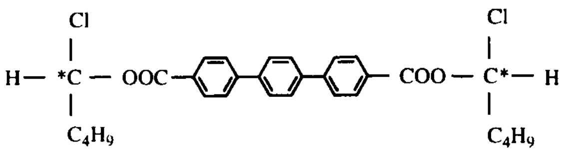
TABLE I Physico-chemical properties of liquid crystals 

No.	*A*	*Z*	*Phase transitions, °C*	d^a, Å	d^a/L	*Ref.*
1	COO	$COOCH_2C_2F_5$	Cr 48 SmC 68 SmA 84 I			(18, 19)
2	COO	$COOC_3H_7$	Cr 52.2 SmA 79.8 I			(25)
3	COO	OC_6H_{13}	Cr 55 SmC 64 N 86 I			(26)
4	COO		Cr 91 SmC 144 SmA 158 N 197 I	35.7	0.98	(33)
5	COO		Cr 84 SmC 103 SmA 156 N 179 I	35.3	1.00	(33)
6	OOC		Cr 96 SmC 132 SmA 144 N 198 I	36.4	1.00	(9, 33)
7	OOC		Cr 89 SmC 95 N 180 I	34.0	1.01	(9, 33)
8	OOC		Cr 145 SmC 177 SmA 183 N 200 I	35.2	0.96	(33)
9	OOC		Cr 129 SmC 152 SmA 163 N 179 I	34.4	0.97	(33)
10	COO		Cr 106 SmC 107 N 202 I			(34)
11	COO		Cr 103 SmC 106 N 184 I			(9)

a. $T_{meas} = T_{SmA\text{-}N}$ or $T_{SmC\text{-}N} - 10$ °C

The ratios d / L collated in table I reveal that the replacement of the hexyloxy group by a hexyl one in the three-ring ester derivatives increases the d / L values and maintains the monolayer arrangement of the smectic phases (compounds **4** and **5**, **6** and **7**, **8** and **9**). It has been shown that the character of the temperature dependence of the layer spacing d is strongly influenced by the orientation of ester linking groups of the hexyl substitued ester derivatives,(33) while the values of the ratio d / L follow the same order in the dependence on the orientation of ester groups which has been observed for the corresponding hexyloxy substituted ester derivatives (see list of systems).

These achiral three-ring ester derivatives exhibiting smectic C phase and previously discussed two-ring perfluoroalkyl substituted benzoate can be used as the components of ferroelectric liquid crystal material for display applications. Here it is an example of such material comprising compounds **1**, **3**, **4** and **5**:

Ferroelectric liquid crystal material	Content, wt %
	11.39
	11.39
	14.8
	15.94
	7.29
	7.06
	17.32
	14.81

This material exhibits the following phase transition temperatures (°C): Cr 4 SmC* 53 SmA 90 I. Low melting and wide temperature range of the chiral smectic C* phase and the values of the spontaneous polarization, rotational viscosity, tilt angle and electro-optical response time of this mixture (figures 3, 4) make it to be very suitable for display applications.(31,32)

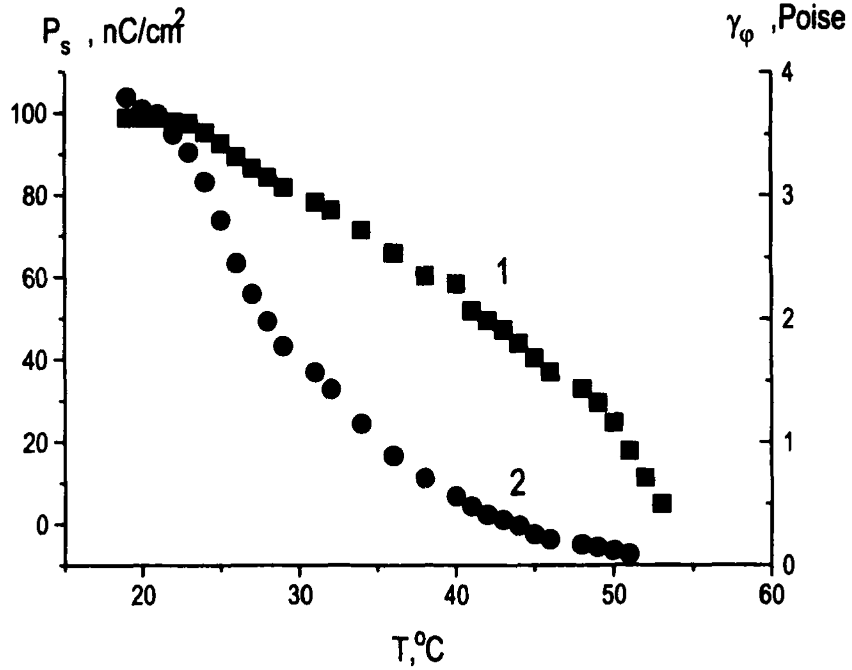


FIGURE 3 Temperature dependence of the spontaneous polarization Ps (curve 1) and the rotational viscosity γ_{φ} (curve 2) of the liquid crystal material

3. CONCLUSION

The studies of the ferroelectric properties of achiral perfluoroalkyl substituted benzoate doped with a chiral additive and the liquid crystal material comprising this benzoate derivative and three-ring achiral ester derivatives have been performed, with attempts to correlate the molecular level parameters with the observed properties. The information here presented may lead to a better understanding of the nature of liquid crystals.

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V. F. Petrov would like to thank Osaka National Research Institute and STA for providing an opportunity to work with Osaka National Research Institute under the STA Fellowship Program.

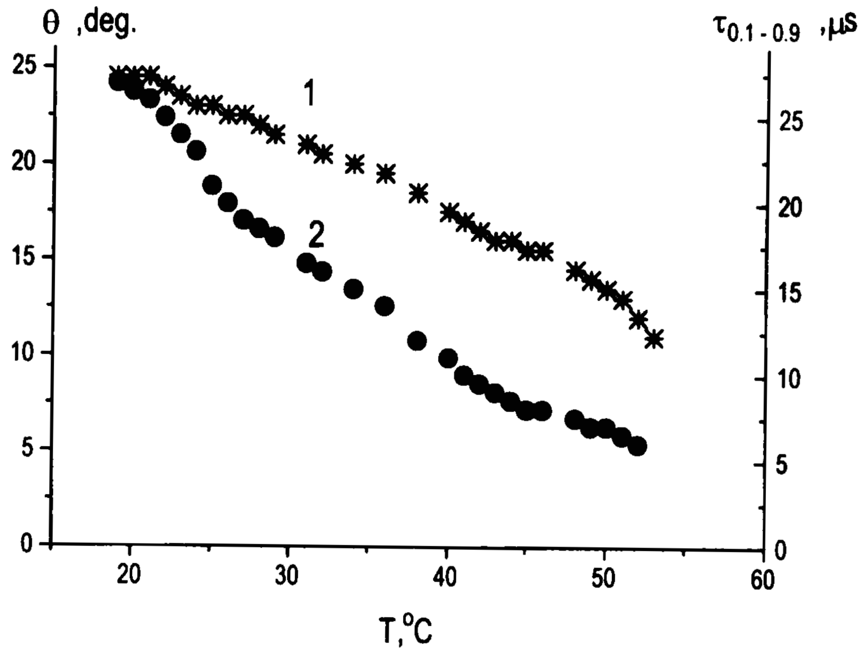

FIGURE 4 Temperature dependence of the tilt angle Θ (curve 1) and the electro-optical response time $\tau_{0.1-0.9}$ at the electric field tension 10 Vμm (curve 2) of the liquid crystal material

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