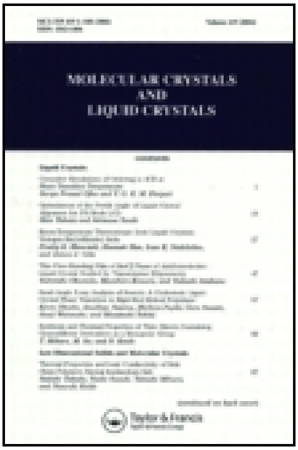

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The Synthesis of Fluorine Containing Phenyl Benzoates and Their Properties as Liquid Crystals

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The Synthesis of Fluorine Containing Phenyl Benzoates and Their Properties as Liquid Crystals

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A new series of fluorine containing phenyl benzoates has been synthesized and the transition temperatures of these compounds have been determined. A series of 4-trifluoromethylphenyl 4-*n*-alkylbenzoates showed no liquid crystalline behaviour, but the 4-trifluoromethylphenyl 4-*n*-alkoxybenzoates series, with six carbons or more in alkoxy chain, was mesomorphic. The 4-cyanophenyl 4-perfluoroalkylbenzoates showed smectic liquid crystalline properties.

INTRODUCTION

The 4-cyanophenyl 4-*n*-alkyl- or alkoxy-benzoates are well known as liquid crystals and are used widely for electro-optical displays. The cyano group which is strongly electron withdrawing plays an important role in the behaviour of these compounds as liquid crystals. Whereas nitro, trifluoromethyl and perfluoroalkyl groups all act as strongly electron withdrawing groups, the latter two fluoroalkyl groups are stable in chemical reactions.

Recently A. C. Griffin *et al.*[1] have reported a series of Schiff's bases containing the trifluoromethyl group which showed enantiotropic smectic phases.

The introduction of fluorine into compounds that might be expected to

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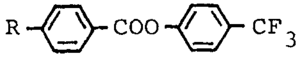
exhibit liquid crystal properties is not common, and so their syntheses and the determination of their properties are rare. The new series of fluorine containing phenyl benzoates and the examination of their properties as liquid crystals are therefore of interest.

1



R : C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}

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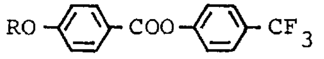

R : C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}

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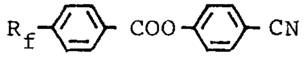

R_f : CF_3, $(CF_3)_2CF(CF_2)_2$, $(CF_3)_2CF(CF_2)_4$, $(CF_3)_2CF(CF_2)_6$

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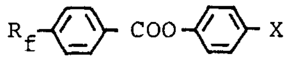


R_f : C_8F_{17}, $(CF_3)_2CF(CF_2)_2$,

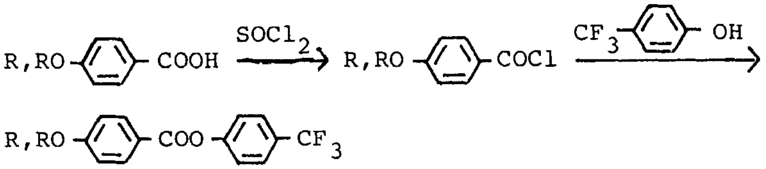
X : C_5H_{11}, CF_3, NO_2, CH_3

EXPERIMENTAL

The infra-red spectra were recorded on a Shimadzu IR-440 Spectrometer. Both ^1H and ^{19}F NMR spectra were obtained on a Hitachi R-42 High Resolution NMR Spectrometer. The textures of the mesophases were examined using a Nikon Polarizing Microscope equipped with a programmable heating and cooling stage (Mettler FP 5 and FP 52). The mesomorphic ranges were determined on a Perkin-Elmer DSC-2 Differential Scanning Calorimeter. Dielectric measurements were carried out with a transformer bridge in the frequency range 1 KHz to 100 KHz.[2]

The methods of synthesis of fluorine containing phenyl benzoates are presented below.

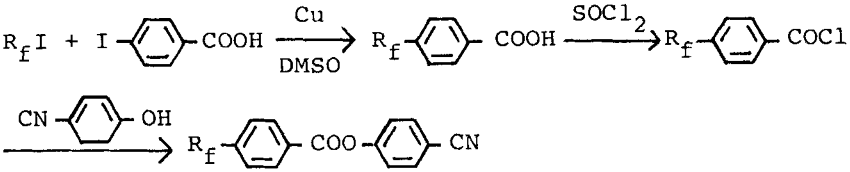
1) 4-Trifluoromethylphenyl 4-*n*-alkyl, 4-*n*-alkoxy-benzoates



The 4-alkyl- and 4-alkoxy-benzoyl chlorides, prepared by heating the appropriate benzoic acids under reflux with an excess of thionyl chloride, were reacted with 4-trifluoromethylphenol under dry N_2 and in dry benzene containing dry pyridine. The crude products thus obtained were crystallized from ethanol and further purified by means of chromatography (activated alumina column).

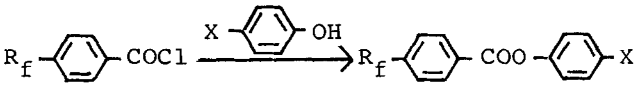
The eluent was benzene and the products were recrystallized twice from methanol. Yields of pure material ranged from 40 to 50%.

2) 4-Cyanophenyl 4-perfluoroalkylbenzoates



A mixture of perfluoroalkyl iodide, 4-iodobenzoic acid, activated copper and dried dimethyl sulfoxide was stirred at 130°C in an autoclave or a glass reactor for 14 hours. After cooling, the reaction mixture was poured into water and the precipitate was filtered off and dried. The solid was extracted with ethanol and the extract concentrated to yield crude 4-perfluoroalkylbenzoic acid which was recrystallized from ethanol-water. The 4-perfluoroalkylbenzoyl chloride was prepared as described for the 4-alkylbenzoyl chlorides. The benzoyl chloride was then reacted with 4-cyanophenol as described in 1.

3) 4-Methyl-, pentyl-, nitro-phenyl 4-perfluoroalkylbenzoates



The above esters were prepared as described in 1. Yields of the pure compounds ranged from 10 to 30%. All the new compounds gave satisfactory IR, and NMR spectra and elemental analyses. Some examples are shown below.

4-Trifluoromethylphenyl 4-butoxybenzoate

IR (KBr) cm^{-1}: 2980, 2880, 1740, 1730, 1605, 1508, 1475, 1330, 1260, 1225, 1165, 1155, 1120, 1060, 850.
^1H NMR (CD_3OCD_3): δ 0.94 (t, 3H, CH_3, J = 6.8 Hz), 1.2–1.9 (broad, m, 4H, CH_2), 4.04 (t, 2H, $ArOCH_2$, J = 6 Hz), 7.05 (d, 2H, ArCOO, J = 8.9 Hz), 7.47 (d, 2H, $ArCF_3$, J = 8.3 Hz), 7.78 (d, 2H, $ArCF_3$, J = 8.3 Hz), 8.08 (d, 2H, ArCOO, J = 8.9 Hz).
^{19}F NMR (CD_3OCD_3) ext. CF_3COOH: δ −15.5 (s).
Anal. Calcd. for $C_{18}H_{17}F_3O_3$: C, 63.91: H, 5.03: F, 16.86.
Found: C, 63.83: H, 5.19: F, 16.78.

4-Trifluoromethylphenyl 4-butylbenzoate

IR (KBr) cm^{-1}: 2950, 2880, 1750, 1740, 1608, 1520, 1470, 1420, 1335, 1275, 1225, 1175, 1135, 1065, 1020, 885.
^1H NMR (CD_3OCD_3): δ 0.87 (t, 3H, CH_3, J = 6.1 Hz), 1.10–1.73 (broad, m, 4H, CH_2), 2.62 (t, 2H, CH_2, J = 7.3 Hz), 7.32 (d, 2H, ArCOO, 8.9 Hz), 7.42 (d, 2H, $ArCF_3$, J = 8.5 Hz), 7.72 (d, 2H, $ArCF_3$, J = 8.5 Hz), 8.00 (d, 2H, ArCOO, 8.9 Hz).
^{19}F NMR (CD_3OCD_3) ext. CF_3COOH: δ − 15.5 (s).
Anal. Calcd. for $C_{18}H_{17}F_3O_2$: C, 67.08: H, 5.28: F, 17.70.
Found: C, 67.13: H, 5.04: F, 17.69.

4-Cyanophenyl 4-perfluoro(5′-trifluoromethyl)hexylbenzoate

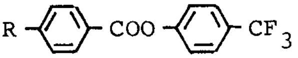
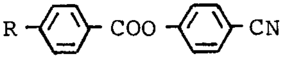
IR (KBr) cm^{-1}: 2250, 1745, 1600, 1503, 1410, 1267, 1245, 1210, 1170, 1150, 1090, 980.
^1H NMR ($CDCl_3$, CD_3OD): δ 7.4–8.4 (broad, m, ArCOO, $ArCF_3$).
^{19}F NMR ($CDCl_3$, CD_3OD) ext. CF_3COOH: δ −5.6 (d, d, t, 6F, $(CF_3)_2CF$, J = 11.9, 8.1, 6.0 Hz), 33.1 (m, 2F, CF_2), 37.1 (m, 2F, CF_2), 42.3 (m, 2F, CF_2), 43.5 (m, 2F, CF_2), 108.3 (m, 1F, CF).
Anal. Calcd. for $C_{21}H_8F_{15}NO_2$: C, 42.64: H, 1.35: F, 48.22.
Found: C, 42.63: H, 1.08: F, 48.12.

RESULTS AND DISCUSSION

Table I shows the effect on the mesomorphic properties of introducing the trifluoromethyl and cyano groups into the phenylbenzoates.

The 4-cyanophenyl 4-*n*-alkyl- and 4-*n*-alkoxy-benzoates are both strongly positive in dielectric anisotropy with high nematic thermal stabilities. Whereas the 4-trifluoromethyl 4-*n*-alkylbenzoates are not mesomorphic, the alkoxy analogues show smectic liquid crystalline properties when the alkoxy chain contains six carbon atoms or more. Terminal substituents are important in

TABLE I
Comparison of transition temperatures

R						
	C→I	C→S	S→I	C→I	C→N	N→I
C_4H_9	68.7			66.5		
C_5H_{11}	66.8			64.0		
C_6H_{13}	58.8				44.0	47.0
C_7H_{15}	61.0				44.0	56.0
C_8H_{17}	58.5				46.0	55.0
C_4H_9O	93.4			110.0		
$C_5H_{11}O$	78.5				87.0	96.0
$C_6H_{13}O$		60.0	74.7		70.0	81.0
$C_7H_{15}O$		62.9	74.3		71.5	80.0
$C_8H_{17}O$		62.5	72.5		75.0	83.0

their effect on the dielectric anisotropies of liquid crystalline materials and it is known that the cyano group is useful as it produces materials of strongly positive dielectric anisotropy.[3] The trifluoromethyl group gives the same effect in the series of alkoxyphenyl benzoates. Dielectric measurements for the 4-trifluoromethylphenyl 4-hexyloxybenzoate are shown in Figure 1 and 2. The compound shows a smectic phase on cooling and its texture is given in Figure 3. Instead of the alkyl groups in 4-cyanophenyl 4-*n*-alkylbenzoates, perfluoroalkyl groups were introduced to establish their effect. The perfluoroalkyl groups were normal and branched, and the results are shown in Table II and Figure 4. These compounds exhibit smectic phases and the materials with a *n*-perfluoroalkyl chain show wider mesomorphic ranges than those with branched chains. The effect of the terminal group upon the m.p.s. and transition temperatures of the 4-perfluoroalkylphenyl 4-X-benzoates is illustrated in Table III. Cyano and nitro group give rise to mesomorphic properties in the benzoates, but the trifluoromethyl group and *n*-alkyl

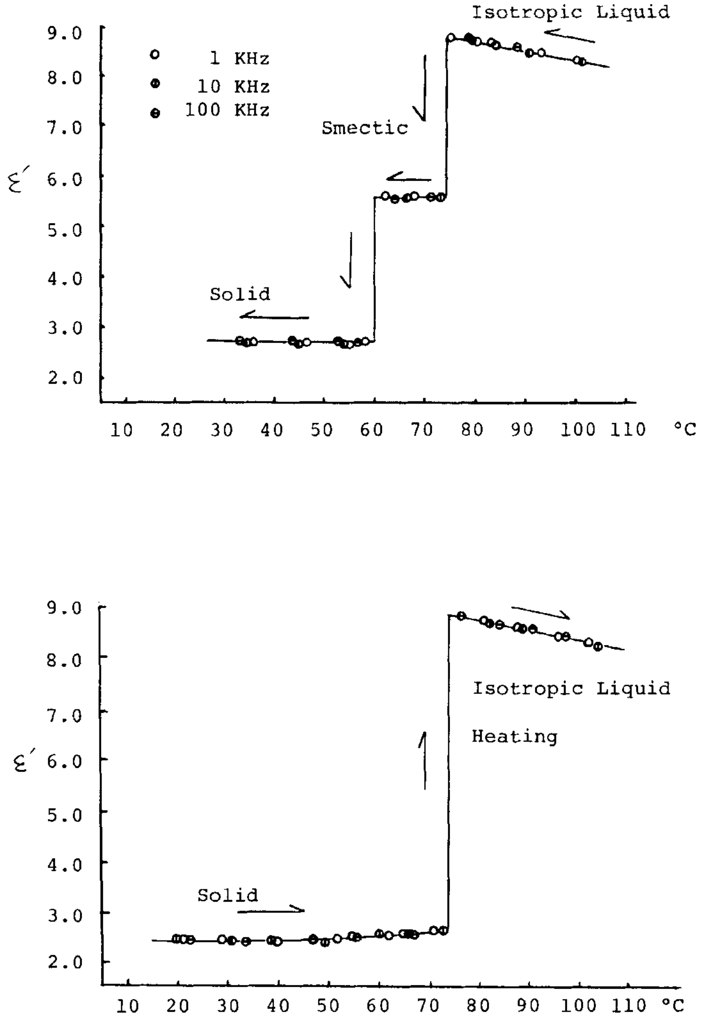


FIGURE 1 Dielectric properties of 4-trifluoromethylphenyl 4-hexyloxybenzoate.

groups give no such effects. G. W. Gray *et al.*[3] reported similar results for series of Schiff's base compounds.

Trifluoromethyl and perfluoroalkyl groups were introduced into phenyl benzoates. Their properties as liquid crystal materials were considerably

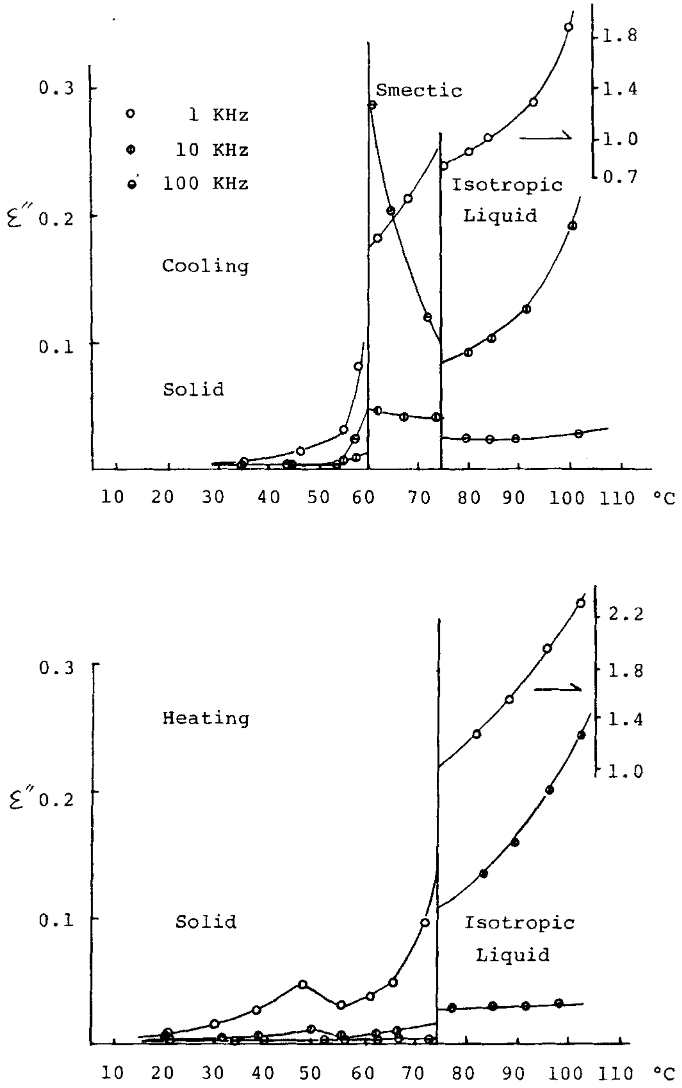


FIGURE 2 Dielectric properties of 4-trifluoromethylphenyl 4-hexyloxybenzoate.

different from those of the hydrocarbon analogues. Fluoroalkyl groups are chemically stable and their use in liquid crystal materials for many applications may be interesting.

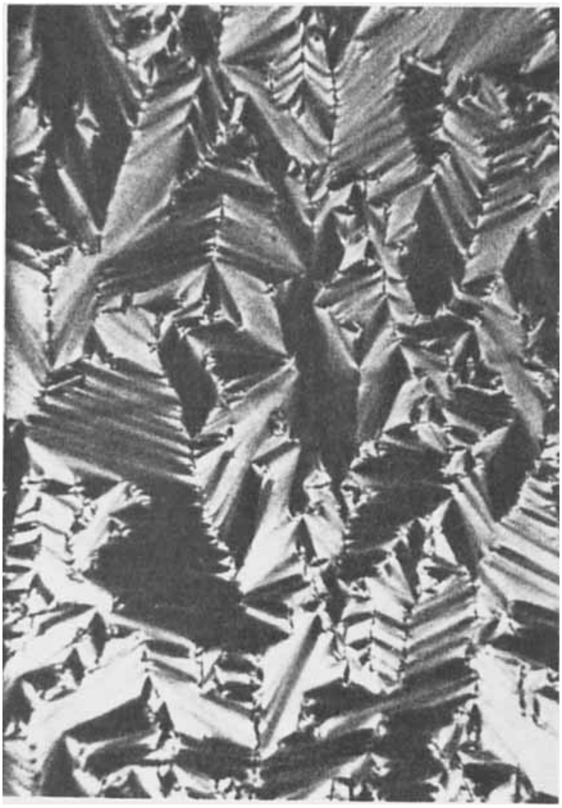


FIGURE 3 Photomicrograph of 4-trifluoromethylphenyl 4-hexyloxybenzoate in its smectic phase.

TABLE II

Transition temperatures of 4-perfluoroalkylphenyl 4-cyanobenzoates

R_f	C → S	S → I
$(CF_3)_2CF(CF_2)_2$	90.0	98.5
$(CF_3)_2CF(CF_2)_4$	109.6	121.3
$(CF_3)_2CF(CF_2)_6$	130.7	140.7
n-C_6F_{13}	99.8	123.3
n-C_8F_{17}	118.0	145.0

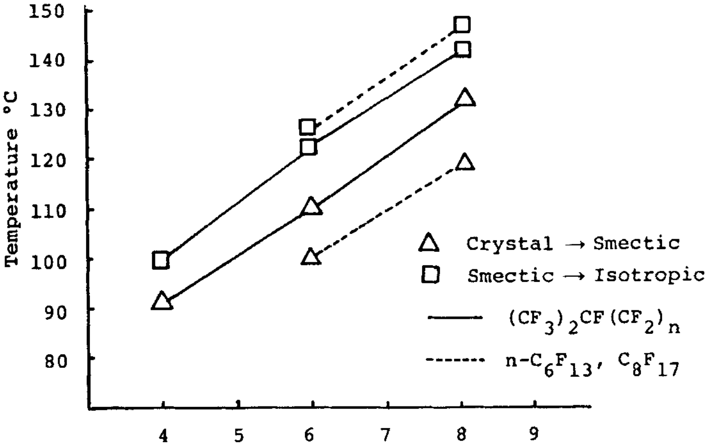


FIGURE 4 A plot of transition temperatures vs. the perfluoroalkyl chain length.

TABLE III

Comparison of transition temperatures of 4-perfluoroalkylphenyl 4-X-benzoates

Rf	X	C→I	C→S	S→I
$(CF_3)_2CF(CF_2)_2$	CN		90.0	98.5
$(CF_3)_2CF(CF_2)_2$	NO_2		68.6	79.2
$(CF_3)_2CF(CF_2)_2$	CF_3	68.0		
$(CF_3)_2CF(CF_2)_2$	C_5H_{11}	58.0		
n-C_8F_{17}	CH_3	112.0		

Acknowledgements

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