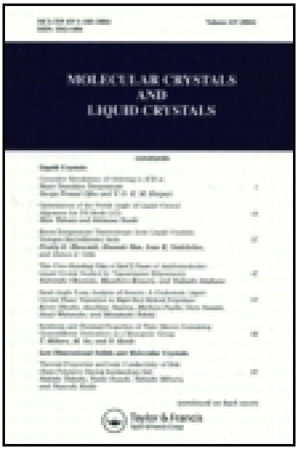

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Synthesis and Mesomorphic Properties of m-Cyano-or m-Halogeno-Benzoate Derivatives

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Synthesis and Mesomorphic Properties of *m*-Cyano-or *m*-Halogeno-Benzoate Derivatives

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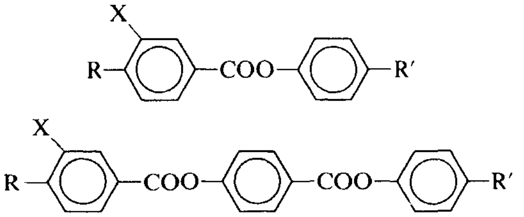
Thirty four benzoate derivatives were prepared. They belong to the two following series: the 4-*n*-alkylphenyl 3-cyano-or 3-fluoro-4-*n*-alkoxybenzoates and the 4-*n*-alkylphenyl 4-(3-cyano-or 3-bromo-4-*n*-alkoxy-or 4-*n*-alkylbenzoyloxy-)benzoates. In the latter series all the compounds are mesomorphic; in the former one, only 3-cyano compounds with long alkoxy chain, exhibit a small mesomorphic range. All the cyano compounds exhibit very high negative dielectric anisotropies.

1 INTRODUCTION

During the last few years, a great number of liquid crystals with high positive dielectric anisotropy were synthesized. Highly negative compounds, with large ranges of mesomorphism and chemical stability, are much more rare. α-cyano-stilbenes[1] exhibit a dielectric anisotropy equal to minus five. Some are nematic from fifty to eighty degrees Celsius; but they are not photochemically stable. Some phenylbenzoates[2] substituted by chlorine in 3- or in 2′-positions are negative but have very short liquid crystalline range. Phenylbenzoyloxybenzoates which are chloro-substituted in the same positions[3,4,5] are negative, or slightly positive, and exhibit much more mesomorphism.

We synthesized two new series of 3-substituted (cyano- and halogeno-) esters; their general formulas are:



with R, R' = C_nH_{2n+1}—, $C_nH_{2n+1}O$—
X = H, F, Br, CN

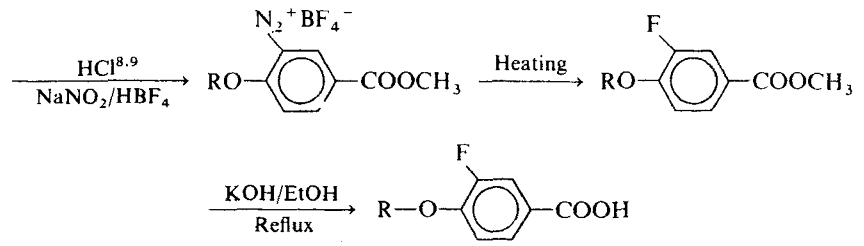
2 EXPERIMENTAL†

The synthesis of 3-fluoro compounds is quite different from that of 3-bromo and 3-cyano compounds. The two procedures are presented below.

2.1 Phenyl 3-fluorobenzoates†

3-fluoro-4-alkoxy-benzoic acids were first prepared; then the corresponding acid chlorides were condensed with the para-substituted phenols.

Steps for the preparation of 3-fluoro-4-alkoxybenzoic acids were successively:



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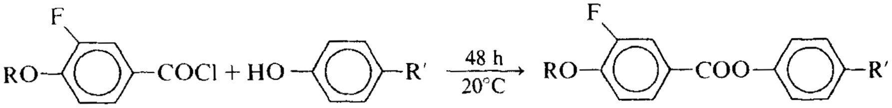
† The phenyl 3-fluoro- and 3-cyanobenzoates were first prepared by M. A. Abert-Mellah for her thesis.[6]

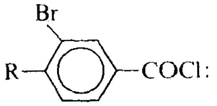
Then the obtained acid was chlorinated by means of refluxing $SOCl_2$ and the condensation with the suitable phenol was done in pyridine at room temperature:



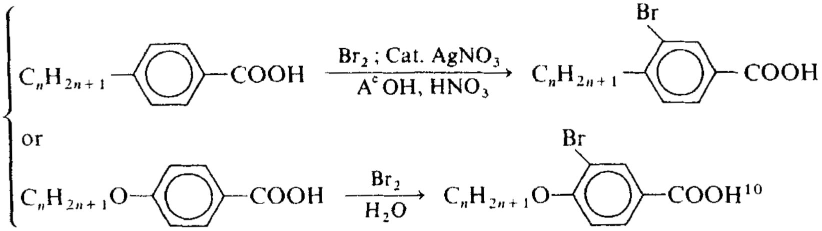
2.2 Phenyl 4-(3-bromo-or 3-cyanobenzoyloxy) benzoates

The 4-alkyl-or 4-alkoxy-3-bromobenzoic acid chlorides were first prepared, and then the 4-pentylphenyl 4-hydroxybenzoate. These compounds were condensed to form the 3-bromo-diester and then the bromine was replaced by the cyano-group by means of nucleophilic substitution. The steps in the synthesis were the following:

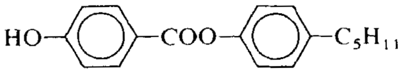
1)

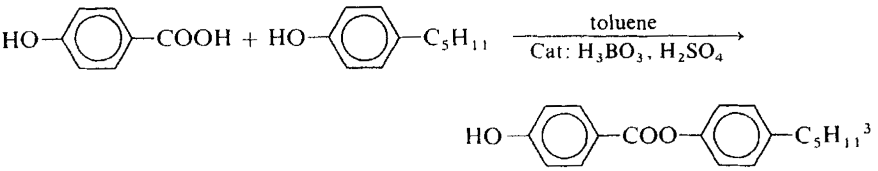


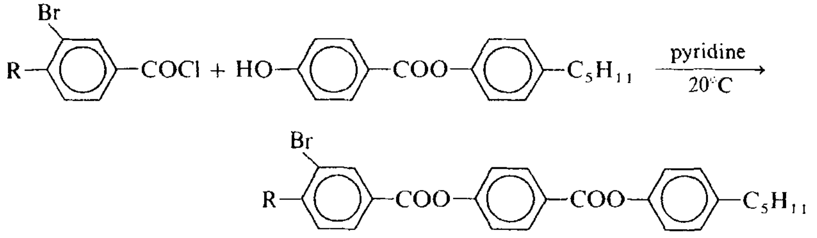
: with R = C_nH_{2n+1} or $C_nH_{2n+1}O$

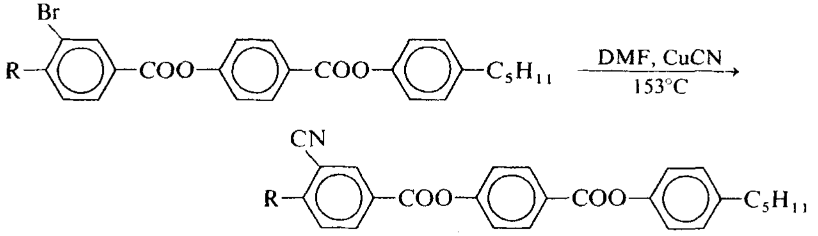


2)





3)


4)


2.3 Purification and identification

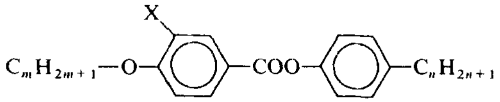
Each compound was purified by means of liquid chromatography on a silica gel column. The eluant was most generally a mixture of *n*-hexane: benzene 30:70. Then one or more recrystallizations were done from ethanol. The tests of purity were classical: thin layer chromatography, gas chromatography, thermal analysis (DSC 1 B Perkin–Elmer). Other means of identification were I.R. Spectroscopy (Perkin–Elmer 720) and U.V. Spectroscopy (Perkin–Elmer 550).

3 CHARACTERIZATION OF MESOPHASES

The temperatures and enthalpies of transitions were determined by means of differential scanning calorimetry. The results are listed in Tables I, II and III. Textures of mesophases were examined through a polarizing microscope equipped with a programmable heating and cooling stage (Mettler FP 5). The structures of the smectic phases were identified by isomorphism with a known reference compound (contact method[11]). An example of a miscibility diagram is given in Figure 1a: the unknown smectic phase of 4-heptylphenyl 4-octyloxy-3-cyanobenzoate (Table I) is isomorphic with the smectic A phase of a *p*-*p*′-disubstituted dihydrophenanthrene.[15] Therefore this smectic phase is S_A too. In Figure 1b we give another example of a miscibility diagram; the smectic phases of 4-pentylphenyl 4-(4-octyloxy-3-cyanobenzoyloxy) benzoate are isomorphic successively with the smectic

TABLE I

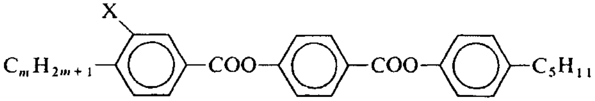
Mésomorphic properties of 4-*n*-alkylphenyl 4-*n*-alkoxy-3-substituted benzoates



m	*n*	*X*	K		S_A		N		I	ΔH_m (Kcal/Mole)	ε_a
1	3	H	.	40	–	–	(.	36	)		
1	5	H	.	32.5	–	–	.	43	.	5.7	+*0.1*
			(.	29.5	)					(4.2)	
4	5	H[12]	.	68	–	–	(.	62	)		
6	5	H[12]	.	49.5	–	–	.	62	.		
8	3	H	.	59.5	–	–	.	64	.		
8	5	H	.	56	.	56.5	.	66	.	6.25	
1	5	F	.	78	–	–	–	–	.		−0.1
1	5	CN	.	67.5	–	–	–	–	.		−0.86
1	7	F	.	80	–	–	–	–	.		
1	7	CN	.	63	–	–	–	–	.		
4	5	F	.	73	–	–	–	–	.		
4	5	CN	.	69	–	–	–	–	.		
4	7	F	.	72	–	–	–	–	.		
4	7	CN	.	58	–	–	–	–	.		
8	5	F	.	71	–	–	–	–	.		−0.2
8	5	CN	.	46	.	52	–	–	.	3.3	−1.12
8	7	F	.	69	–	–	–	–	.		
8	7	CN	.	47	.	57	–	–	.		

TABLE II

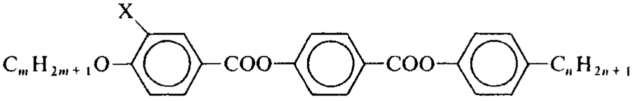
Mesomorphic properties of 4-*n*-pentylphenyl 4-(3-substituted 4-*n*-alkylbenzoyloxy-) benzoates



m	*X*	K		S_C		S_A		N		I	ΔH_m kcal/Mole	ε_a
1	Br	.	113	–	–	–		.	121	.		
1	CN	.	113	–	–	–		.	123	.	6.0	
3	H[3]	.	78	–	–	–		.	188	.		
3	Br	.	76	–	–	–		.	118	.	5.6	+*0.1*
3	CN	.	80	–	–	–		.	110	.	4.8	−1.0
		(.	70)	–	–	(.	76)	.				−2.9
6	H[3]	.	74	–	–	.	78	.	169	.		
6	Br	.	57	(.	48)	–		.	117	.	5.9	
6	CN	.	117	–	–	(.	115)	.	120.5	.	12.0	
8	H[3]	.	79	–	–	.	117	.	161	.		
8	Br	.	57	(.	48)	–	–	.	104	.	5.3	
8	CN	.	87	–	–	.	–	.	120.5	.	7.5	−1.1

TABLE III

Mesomorphic properties of 4-*n*-pentylphenyl 4-(3-substituted-4-*n*-alkoxybenzoyloxy-) benzoates



m	*n*	*X*	K		S_C		S_A		N		I	ΔH_m (kcal/Mole)	ε_a
1	5	H[3]	.	88.5	–	–	–	–	.	224	.	5.7	
1	5	Br	.	125	–	–	–	–	.	163	.	6.5	−0.6
1	5	CN	.	123	–	–	–	–	.	158	.	5.1	−1.45
2	5	Br	.	117	–	–	–	–	.	176	.		
2	5	CN	.	112	–	–	.	124	.	171	.		
4	5	H[3]	.	89	–	–	–	–	.	209.5	.		
4	5	Br	.	124	–	–	–	–	.	167	.		
4	5	CN	.	102	–	–	.	160	.	170	.	6.6	
8	2	Br	.	128	–	–	–	–	.	146	.		
8	2	CN	.	108	–	–	.	156	–	–	.		
8	5	H[3]	.	86	.	96	.	152	.	186	.		
8	5	Br	.	125	–	–	–	–	.	150	.		
8	5	CN	.	82	.	100	.	167	–	–	.	5.1	−1.7

C and A phases of an azoxy compound† (Figure 1b). The texture of the S_C phases of the diesters listed in Table II and III is generally a Schlieren texture, when heating, and a focal conic texture with smooth outlines, when cooling from the focal conic S_A phase (Figure 2).

4 DIELECTRIC ANISOTROPY MEASUREMENTS

The dielectric anisotropy ε_a was determined by classical capacity measurement of a 50 μ flat cell filled with the liquid crystal. The molecules were orientated by a magnetic field of 10 kGauss, either parallel ($\varepsilon_{\parallel}$) or perpendicular ($\varepsilon_{\perp}$) to the electric field. The measurement was done with a capacitance

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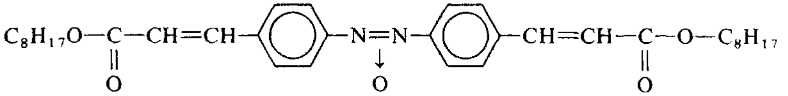
† This compound is



K 92,4 S_C 162,3 S_A 175,3 I

We thank Dr. Demus for giving us a sample of this product.

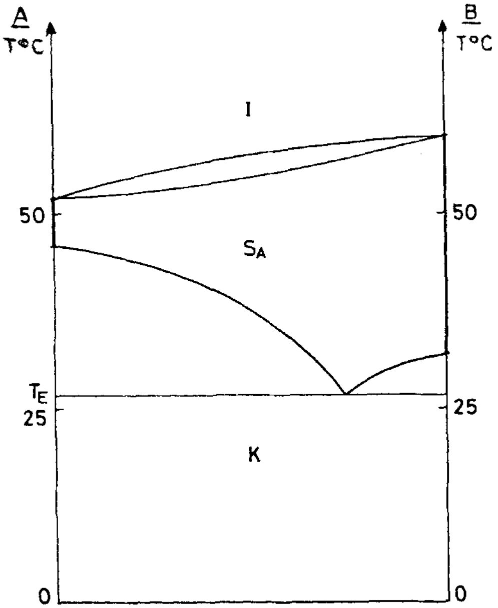
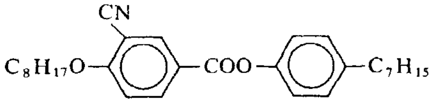
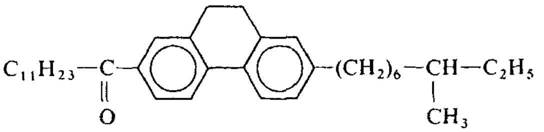


FIGURE 1a Miscibility diagram of

A:


B:


bridge supplied with a low frequency a.c. field (5 kHz), at room temperature (22°C).

Some of the synthesized compounds are not mesomorphic, some are smectic and others exhibit high melting points. In order to make measurements under the same conditions, each compound in Tables I, II and III was mixed with 4-pentylphenyl 4-methoxybenzoate (A); this compound is nematic at room temperature, its dielectric anisotropy is near zero ($\varepsilon_a = +0.1$), so the anisotropy of the mixture is essentially due to that of the compound under study (B). The ratio of the mixture was always 0.20 for B, 0.80 for A (molar fraction). Such mixtures are nematic at room temperature.

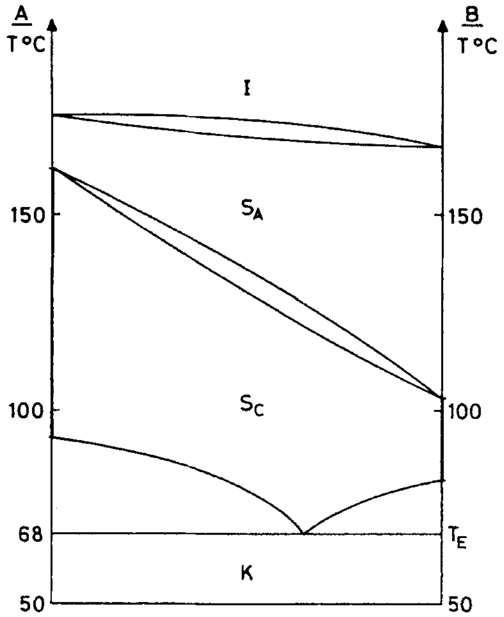
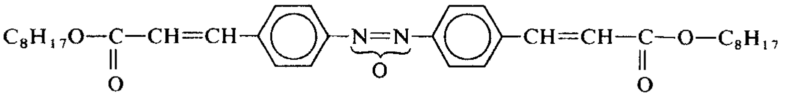
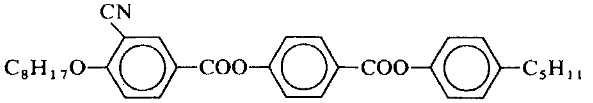


FIGURE 1b Miscibility diagram of

A:


B:


The measured dielectric anisotropies are listed in Tables I, II and III. When we exceptionally did the measurement of ε_a with the pure compound, the result is written in italics.

5 RESULTS AND DISCUSSION

5.1 Phenylbenzoates

Looking at Tables I and IV, we can see that the presence of a 3-polar substituent on 4-4′-disubstituted phenylbenzoates leads to a decrease of the mesophase stability. Each compound of the 4-alkoxy-4′-pentyl series exhibits a nematic phase and for a long alkoxy chain, a smectic A phase appears.

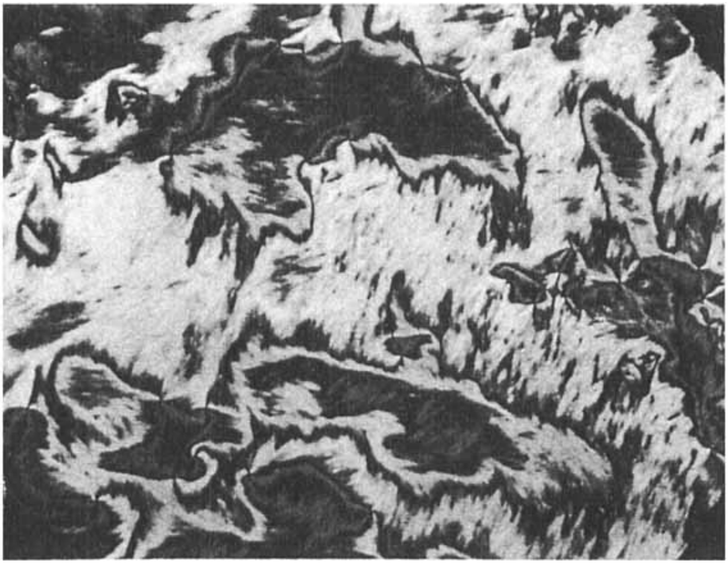


FIGURE 2a Schlieren texture of the S_C phase of 4-*n*-pentylphenyl 4-(3-cyano 4-octyloxybenzoyloxy) benzoate.

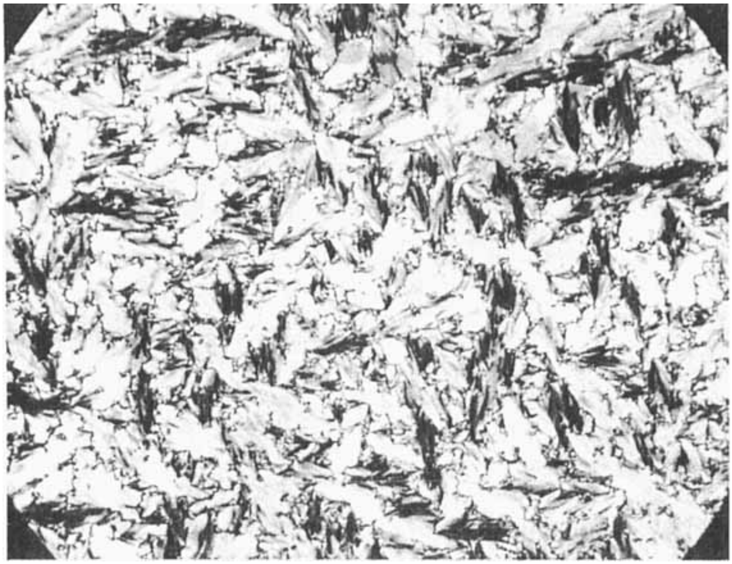
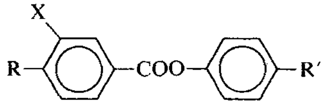


FIGURE 2b Focal conic texture of the same S_C phase, on cooling from a S_A phase.

TABLE IV

Influence of 3-polar substituents on mesomorphism of phenylbenzoates



R	R′	X	Transition temperatures	Sign of ε_a
$C_8H_{17}O—$	$—C_5H_{11}$	H	K 56 S_A 56.5 N 66 I	#0
$C_8H_{17}O—$	$—C_5H_{11}$	F	K 71 I	—
$C_6H_{13}O—$	$—OC_6H_{13}$	F^2	K 66.5 N 70 I	
$C_6H_{13}O—$	$—OC_6H_{13}$	Cl^2	K 74 I	—
$C_8H_{17}O—$	$—C_5H_{11}$	CN	K 46 S_A 52 I	—
$C_8H_{17}O—$	$—C_5H_{11}$	Br	K 69 I	

None of the 3-fluoro analog compounds exhibit mesophases. One example of a nematic 3-fluoro compound[2] is known, the 4-4′-dihexyloxy derivative (Table IV). The mesophase is probably stabilized when the *n*-alkyl chain is replaced by an *n*-alkoxy chain. We can see also in Table IV that neither a 3-chloro, nor a 3-bromo compound is mesomorphic. With the 3-cyano substituent, a smectic A mesomorphism appears over a short range of temperature for compounds with long alkoxy chains (e.g. octyloxy).

All these compounds exhibit negative dielectric anisotropy (Table I). The 3-cyano compounds are much more negative than the 3-fluoro compounds. This fact is in good agreement with the dipole moment values[13]: $\mu(\varphi\text{-CN}) = -4.05\ D$, $\mu(\varphi\text{-F}) = -1.47$ D. The most negative is the 4-*n*-pentylphenyl 4-octyloxy-3-cyanobenzoate: $\varepsilon_a\,(0.20) = -1.12$.

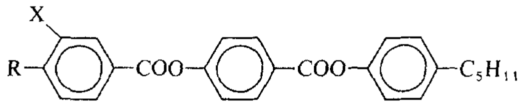
Knowing that *p*-*p*′-alkyl- or alkoxy-phenylbenzoyloxybenzoates[3] exhibit a wide range of mesomorphism, we prepared the 3-bromo- or 3-cyano-substituted analogs, in order to enhance mesomorphism and negativity.

5.2 Phenylbenzoyloxybenzoates

Looking at Table V, we can see that the behaviour of 3-substituted compounds is quite different depending whether the substituent is Br- or -CN. With the 4-*n*-pentylphenyl 4-(3-bromo-4-*n*-alkyl or 4-*n*-alkoxybenzoyloxy)-benzoates, the temperature range of liquid crystallinity decreases with regard to the non-3-substituted analog: forty degrees for the former, hundred degrees for the latter. The melting points of the 4-alkyl-3-bromo- and 4-alkoxy-3-bromo compounds are very different; the 4-octyl derivative melts at 53.5°C, the 4-octyloxy at 125°C. Their mesomorphic state is essentially nematic. A monotropic smectic C phase only appears with long alkyl chains.

TABLE V

Influence of 3-polar substituents on mesomorphism of phenylbenzoyloxybenzoates



1. R = C_nH_{2n+1}

X	$\overline{\Delta T_m}$	$n = 1$	$n = 3$	$n = 6$	$n = 8$
H[3]	98		K 78 N 188 I	K 74 S_A 78 N 169 I	K 79 S_A 117 N 161 I
Br	40	K 113 N 121 I	K 76 N 118 I	K 57 N 117 I $\uparrow\downarrow$[48] S_C	K 53.5 N 104 I $\uparrow\downarrow$[48] S_C
CN	19	K 113 N 123 I	K_1 80 N 110 I $\uparrow\downarrow$[76] K_2 70 S_A	K 117 N 120.5 I $\uparrow\downarrow$[115] S_A	K 87 S_A 120.5 I

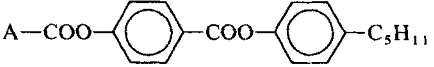
2. R = $C_nH_{2n+1}O$

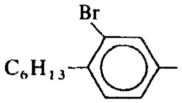
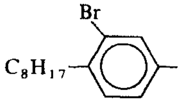
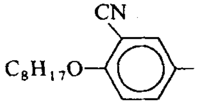
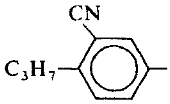
X	$\overline{\Delta T_m}$	$n = 1$	$n = 2$	$n = 4$	$n = 8$
H[3]	119	K 88.5 N 224 I		K 89 N 209.5 I	K 86 S_C 96 S_A 152 N 186 I
Br	41	K 125 N 163 I	K 117 N 176 I	K 124 N 167 I	K 125 N 150 I
CN	62	K 123 N 158 I	K 112 S_A 124 N 171 I	K 102 S_A 160 N 170 I	K 82.5 S_C 100 S_A 167 I

TABLE VI

Two examples of eutectic mixtures

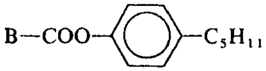
1. A negative nematic mixture

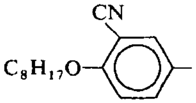
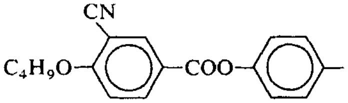
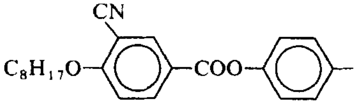
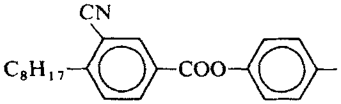


A:	Molar fraction:
	0.28
	0.31
	0.19
	0.22

Range K 15 N 120 I

2. A smectic A negative mixture



B:	Molar fraction:
	0.62
	0.08
	0.21
	0.09

Range K 19 S_A 90 I

The 3-bromo-4-alkyl compounds are very slightly positive. When the 4-alkyl chain is replaced by a 4-alkoxy chain, the compounds become negative. That is due to the perpendicular component of the alkoxy benzene dipole: $\mu(CH_3O - \phi) = 1.28\ D$ with $\theta = 72°$.[13]

Looking at the 4-*n*-pentylphenyl 4-(3-cyano-4-substituted benzoyloxy) benzoates (Table V), we can see that the mesophase of alkoxy-compounds is much more stable than that of the alkyl-compounds; medium temperature range of 62°C for the former and of 19°C for the latter. The nature of the mesophases is similar and quite the same as compared with the non-3-substituted-compounds, that is nematic for short chains and smectic A when the chain lengthens. Smectic C appears only with long alkoxy chains. All the 3-cyano compounds exhibit negative dielectric anisotropy; the 4-alkoxy-compounds are more negative than the 4-alkyl-compounds (Tables II and III). For example ε_a of a 0.20:0.80 mixture of B:A (see 4) is equal to -1.1 with the 4-octyl-compound and to -1.7 with the 4-octyloxy-compound. This last value is very high. If the linear law holds for binary mixtures then ε_a for the pure compound may be equal to about -8.5. Moreover the 3-cyano-derivatives are normally more negative than the 3-bromo analogs, according to their dipole moment value: $\mu(\varphi\text{-CN}) = -4.05$ D and $\mu(\varphi\text{-Br}) = -1.57$ D.[13]

6 APPLICATIONS

Appropriate mixtures† of these compounds must be very interesting. Nematic mixtures with high negativity and chemical stability can be used for dynamic scattering mode displays: a typical eutectic mixture is given in Table VI, with a nematic range from 15 to 120°C. Negative smectic A mixtures may be used in thermooptic storage displays.[16] The mixture given in Table VI is smectic A from 19 to 90°C.

7 CONCLUSION

More than thirty esters or diesters were synthesized. All were substituted in the 3-position by a polar group: F, Br, CN. When we compare 3-substituted and non 3-substituted benzoate derivatives, we can conclude that for phenylbenzoates, the mesophase disappears with the 3-fluoro substituent, and that for phenylbenzoyloxybenzoates the mesophase is essentially nematic with the 3-bromo substituent and smectic A with the 3-cyano substituent.

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† Eutectic mixtures can be calculated from the Schröder–Van Laar solubility laws.[14]

Appropriate mixtures of 3-cyano and/or 3-bromo compounds lead to products with a wide range of liquid cristallinity, including ambient temperature, and with a high negative dielectric anisotropy. Nematic materials may be used in dynamic scattering mode displays and smectic A materials in thermooptic storage displays.

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