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Mesomorphic Properties of Bromo and Cyano Substituted Diarylethanes

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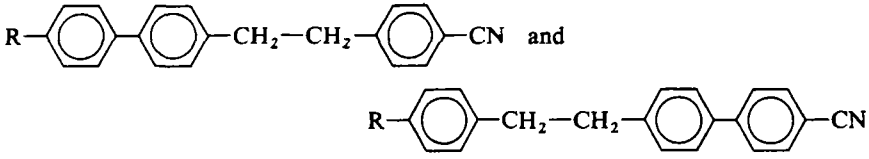
Two homologous series of diarylethanes: 1-(4-alkoxy or alkyl-benzoyloxyphenyl)-2-(4'-bromo or cyanophenyl) ethanes (series I) and 1-(4-alkoxy 3-bromo or cyanobenzoyloxyphenyl)-2-(4'-pentylphenyl) ethanes (series II) have been synthesized. The influence of the bromo or cyano group, in the meta or para position, on the mesomorphic range and the clearing point, is studied. In the series I, the bromo group induces a smectic polymorphism, whereas the cyano group induces nematic mesophases. In the series II, the larger the meta substituant, the lower the clearing point.

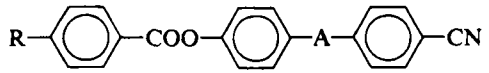
INTRODUCTION

Gray *et al.*[1] previously published the following two series of biphenyls:



these compounds are chemically and photochemically stable.

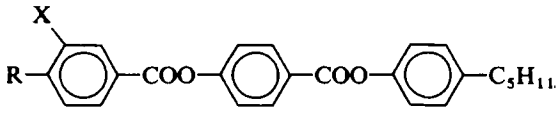
In order to complete the series of compounds with the general formula:



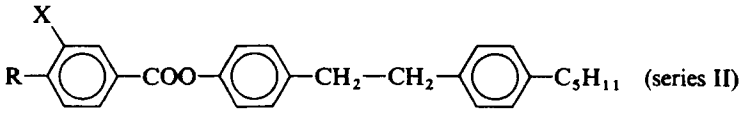
where A is: —COO—,[2] —CH=N—,[3] —N=N—,[4] —CH=CH—,[5] —CH=C(CN)—,[6] nothing,[7] we synthesized the compounds with A = —CH_2—CH_2— (Series I).

Moreover, in order to obtain mesomorphic products with a negative dielectric anisotropy and to compare them to the previously prepared

diesters,[8] with the general formula:



with X = Br or CN and R = *n*-alkyl or *n*-alkoxy, we synthesized the following series:



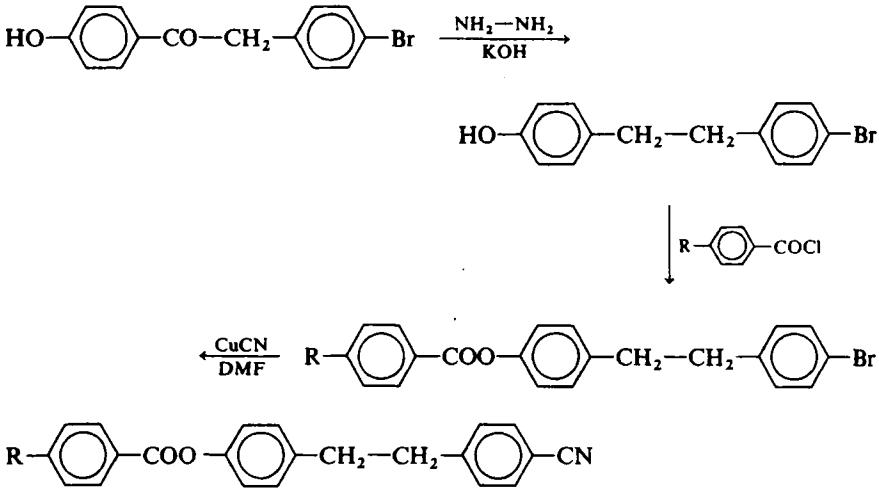
where X = −Br or CN and R = $C_nH_{2n+1}O$.

RESULTS AND DISCUSSION

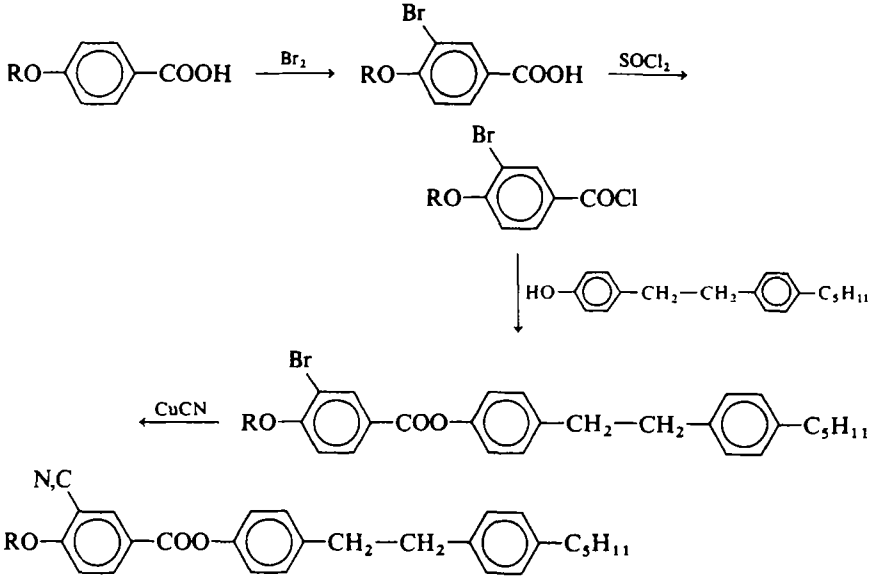
1 Synthesis

Compounds of these two series are prepared according to Schemes 1 and 2, as shown below.

Scheme 1 (Series I)



Scheme 2 (Series II)



The 4-bromo-4′-hydroxydeoxybenzoin, used in Scheme 1, was prepared according to Ref. (5).

The 4-alkoxy-3-bromobenzoic acid and the 4-hydroxy-4′-pentyldeoxybenzoin, used in Scheme 2, were prepared following Refs. (9) and (5) respectively.

The transition temperatures of the obtained compounds, observed by means of a polarizing microscope and determined by differential scanning calorimetry, are listed in Tables I, II and V.

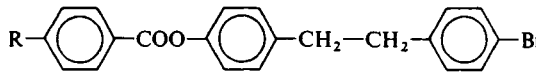
The structures of the smectic phases were identified by their isomorphy with a known reference compound.[10]

2 1-(4-alkoxy or alkylbenzoyloxyphenyl) 2-(4′-bromo or cyanophenyl) ethanes (series I)

p-bromo substituted compounds When R = $C_nH_{2n+1}O$— (Table I), the first two compounds are only nematic. The third and the fourth have, in addition, two monotropic smectic phases, S and S_B. From the pentoxy, the compounds exhibit three smectic phases, S_A and S_B phases are enantiotropic, S remains monotropic. The nematic phase disappears for long chains (from $n = 8$). The nematic existence range becomes smaller while the smectic A range becomes larger (Figure 1). The odd-even effect on the

TABLE I

Transition temperatures of compounds with formula:



R		K	S	S_B	S_A	N	I
$C_nH_{2n+1}O$—:	*n*						
	1	147	—	—	—	—	162
	2	163	—	—	—	—	171
	3[a]	148	(129)	(135)	—	—	159
	4	132	(113)	(129)	—	—	164
	5	112	(105)	135	139		157
	6	102	(98)	130	144		153
	7	96	(94)	137	154		155
	8	94	(92)	136	156	—	—
	9	90	(89)	134	158	—	—
	10	86.5	(81)	127	152	—	—
	11	86	(80.5)	127	152	—	—
	12[b]	90	(76.5)	126	152.5	—	—
C_nH_{2n+1}—:	*n*						
	3	126	132	144	—	—	—
	5	128	131	151	—	—	—
	6	98	110	143	—	—	—
	7	100	110	144	—	—	—
	8	84	104	143	—	—	—

[a] Second melting: K_2 136 S (129) S_B (135) N 159 I.
[b] First melting: K_1 79.5 K_2 88 K_3 90 S (76.5) S_B 126 S_A 152.5 I.

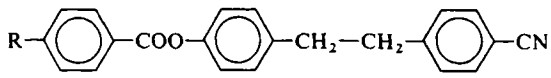
The meanings of the signs used in this table and in the following are:

K: crystalline phase
S: smectic phase(s) S_A, S_B, S_C . . . smectic phases A, B, C.
N: nematic phase.
I: isotropic liquid phase.
. : the phase exists.
— : the phase does not exist.

The temperatures are given in Celsius degrees. Metastable transitions are indicated between brackets.

TABLE II

Transition temperatures of compounds with formula:

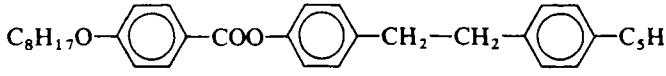


R		K		S		N		I
$C_nH_{2n+1}O$	n							
	1	168	—		—	199		
	2	144	—		—	199		
	4	108	—		—	185		
	7	83	—		—	169		
	8	85	—		—	166		
C_nH_{2n+1}	n							
	3	115	—		—	166		
	5	121	—		—	158		
	6	100.5	—		—	150		
	7	89	—		—	150		
	8	92		96		144		

The notations are that of Table I.

clearing point is rather well followed, except for the compound with $n = 6$.

The textures of the S_A phase are either with focal conics (Figure 2a) or homeotropic; the textures of the S_B phase exhibit large mosaics, or focal conics (Figure 2b), or they are homeotropic; the S phase may be either striated mosaics or striated focal conics (Figure 2c). The S_B structure of this series was identified by isomorphy with that of the compound:



(11);

the mesomorphic range of this later compound being: K 63 S_B 70.5 S_C 95 N 130 I (Figure 3). The S phase is not yet identified, but its texture looks like a S_E phase.

When R = C_nH_{2n+1}— (Table I), there are no nematic phases; the compounds have two smectic phases, S and S_B. Their textures are large striated mosaics and large mosaics respectively (Figures 4a and 4b). These two phases are miscible with the corresponding one of the alkoxy series described above. When the alkoxy chain lengthens, the clearing point is almost constant. We can point out too that these compounds exhibit a direct $S_B \rightarrow I$ transition, with no evidence of S_A phase.

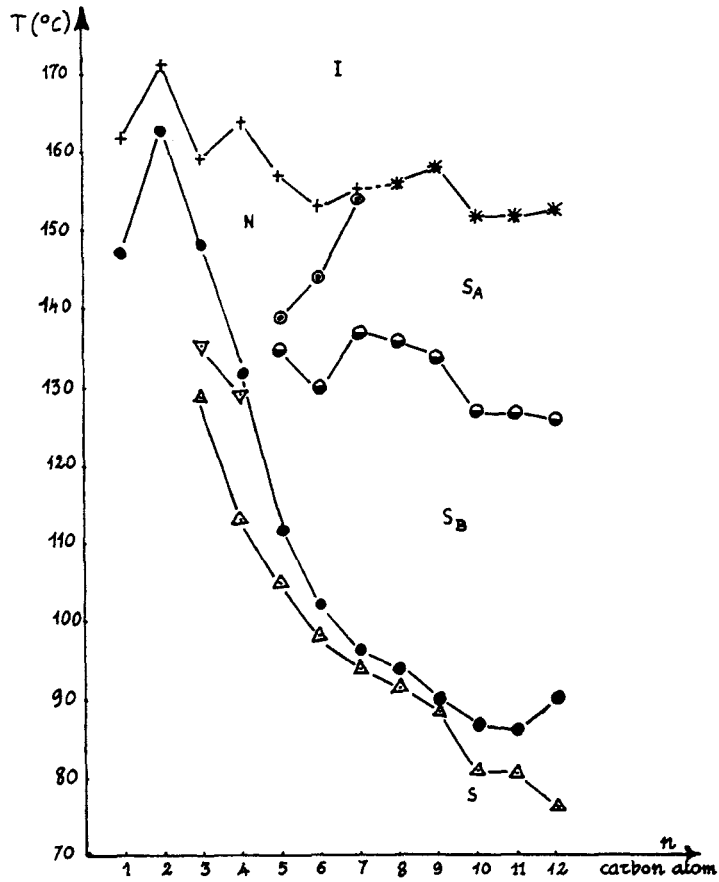
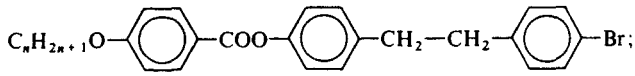


FIGURE 1 Plot of the transition temperatures against n, the number of carbon atoms in the alkoxy chain of

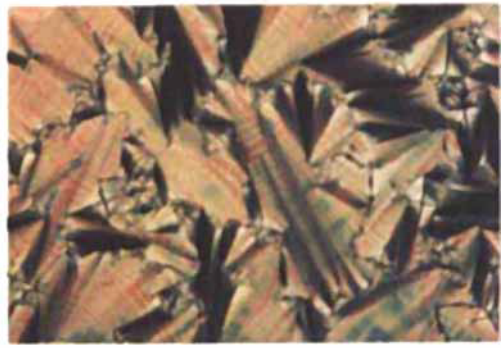


● C → Nor S_B; ⊙ S_A → N; ◒ S_B → S_A; △ S_B → S; ▽ N → S_B; + N → I; *SA → I

p-cyano substituted compounds The obtained alkoxy and alkyl compounds (Table II) are all nematic, except the compound with $R = C_8H_{17}$. This one exhibits, in addition, a smectic S phase which texturally looks like smooth focal conics. The nematic range is about 80°C for the alkoxy and 50°C for the alkyl. For the alkoxy the melting point shows a considerable decrease when n increase from 1 to 8.

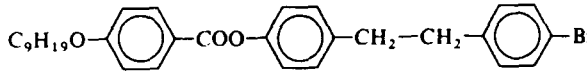
(a) S_A phase at T = 154°C.

(b) S_B phase at T = 120°C.



(c) S phase at T = 88°C.

FIGURE 2 Textures of the compound:



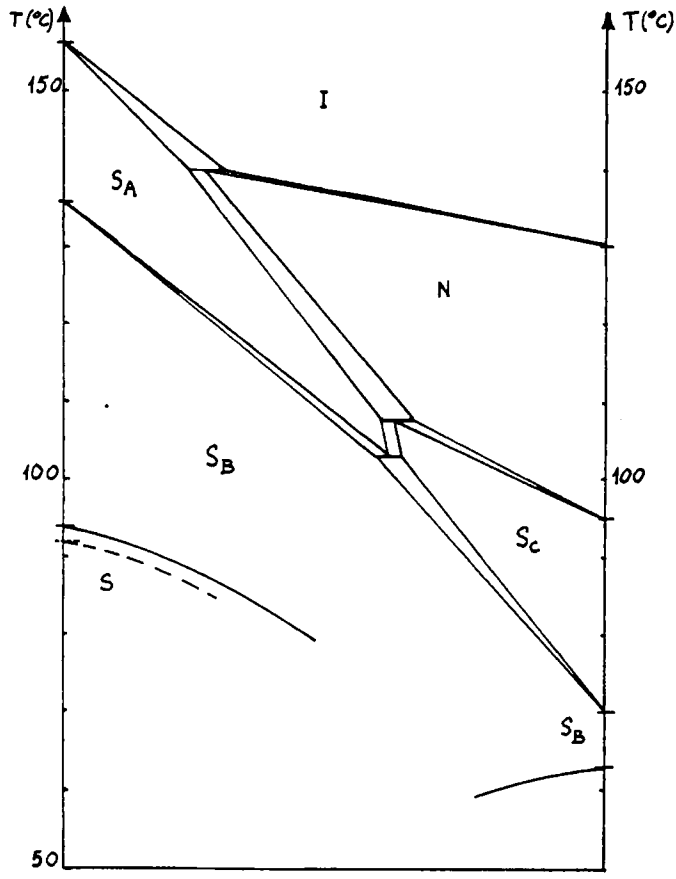


FIGURE 3 Diagram of isobaric state for the mixtures of:

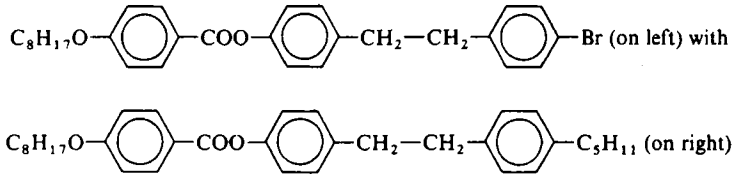
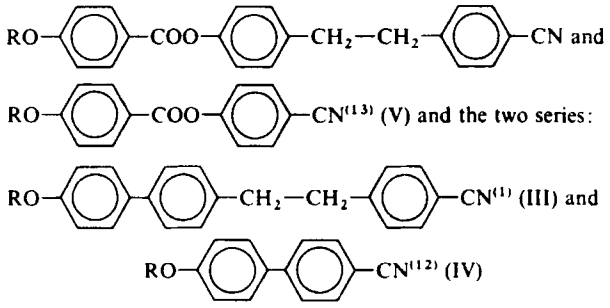


TABLE III

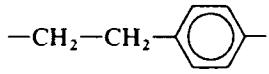
Transition temperatures of compounds of the two series:



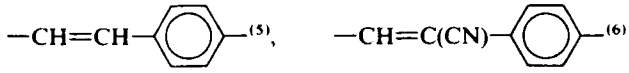
Series	R	K		S_A		N		I
III	C_7H_{15}—	.	83.5	.	85.1	.	157.4	.
IV	C_7H_{15}—	.	53.5	—	—	.	75	.
III	C_8H_{17}—	.	91.8	.	($\leq$80)	.	155.9	
IV	C_8H_{17}—	.	54.5	.	67	.	80	.
I	C_7H_{15}—	.	83	—	—	.	169	.
V	C_7H_{15}—	.	71.6	—	—	.	82	.
I	C_8H_{17}—	.	85	—	—	.	166	.
V	C_8H_{17}—	.	75.6	—	—	.	88	.

The notations are that of Table I.

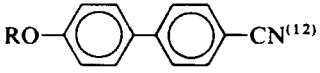
Now we can consider the influence of the introduction in a mesogenic molecule of the flexible group

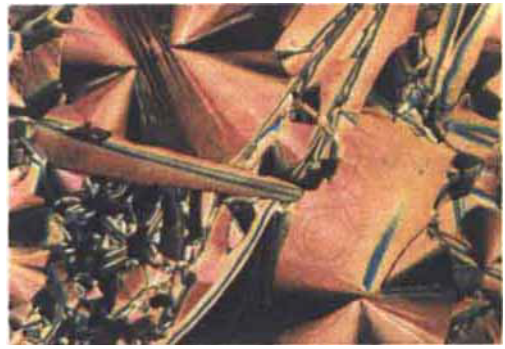


on the mesomorphic properties. It is known that the introduction of a rigid group, as for examples:

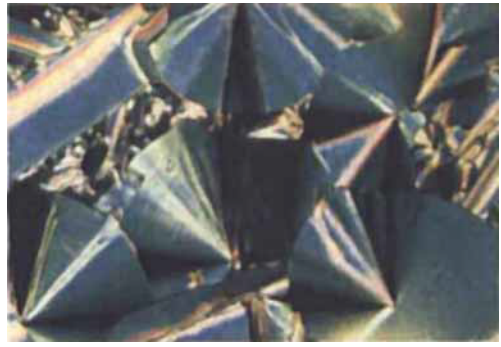


(Table IV) extends considerably the range of mesomorphism but simultaneously gives high melting points. Therefore such compounds are not very interesting for device applications. A flexible group, on the other hand, might be much more interesting; Gray *et al.* have obtained the first results on the biphenyl series: they introduce the flexible group on the series (IV) shown below:





(a) S_B phase at T = 135°C.



(b) S phase at T = 105°C.

FIGURE 4 Textures of the compound:

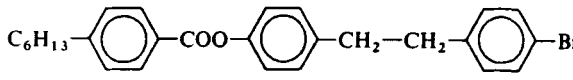
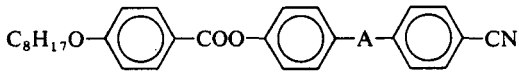


TABLE IV

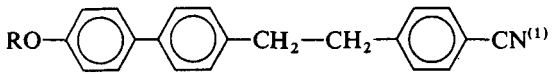
Transition temperatures of compounds with formula:



A	K	S	S_C	S_A	N	I
—CH=CH—[5]	95.5	—	—	140	247	283
—CH=C(CN)—[6]	133	—	—	—	—	237
—N=N—[14]	95	—	—	—	—	252
Nothing[7]	96.5	140	—	—	200	237
$—CH_2—CH_2—$	85	—	—	—	—	165

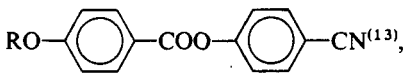
The notations are that of Table I.

and therefore produced the following series (III):



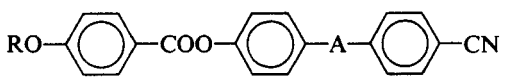
The later compounds have a mesomorphic range 45°C wider than the former and a melting point 30°C higher (Table III).

The same results are obtained on our series (I). Comparing our compounds (series I) to the same series without the flexible group, that means the series (V):



the mesomorphic range of I is 70°C wider than that of V and the melting point only 10°C higher (Table III). We can compare the mesomorphic properties of the two series with the flexible group (I) and (III). We observe (Table III) that their melting and clearing points are quite similar.

We can also compare compounds having the same general formula:



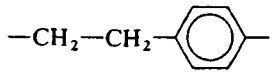
with various linkage A: A = —CH=CH—, —CH=C(CN)—, —N=N—, nothing, $—CH_2—CH_2—$. We can see immediately, in Table VII, that the compound with the ethane linkage exhibits the lowest melting point.

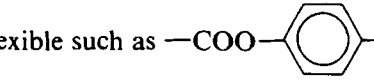
Another interesting flexible group is the cyclohexane ring. New mesomorphic compounds including this group are now known.[15,16] Lower melting points or stabilized mesophases are observed when replacing the phenyl by the cyclohexane ring.

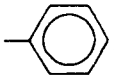
3 1-(4-alkoxy-3-bromo or cyanobenzoyloxyphenyl) 2-(4'pentylphenyl) ethanes (series II)

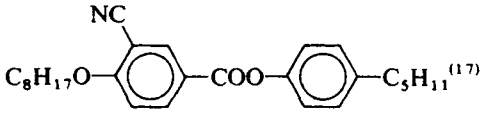
In that series, the bromo group in the meta position (Table V) induces a nematic phase and a smectic C phase; the cyano group (Table V) induces a smectic A phase. Their mesomorphic range is of less practical importance than those of the compounds of Series I.

As for compounds of series I, we can compare the influence of the introduction of a flexible group such as

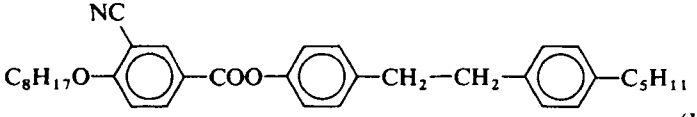


with a semi flexible such as  or with a rigid one such as

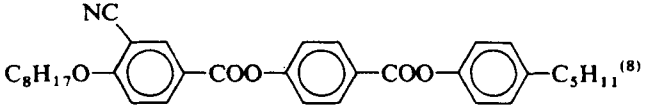
 . If we look at the transition temperatures of the following compounds:



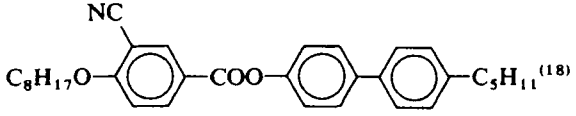
(VI) K 46 S_A 52 I



(II) K 65 S_A 108 I



(VII) K 82 S_C 100 S_A 167 I

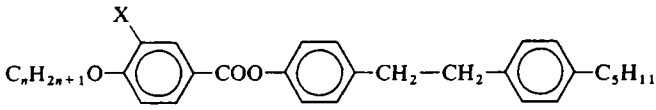


(VIII) K 99 S_C 158 S_A 159 I

we can see very well the gradation on the melting point and on the mesomorphic range: series (II) compounds are situated in between compounds IV and compounds VII and VIII.

TABLE V

Transition temperatures of compounds with formula:



X	n	K		S_C		S_A		N		I
Br	1	.	113	—	—	—	—	.	(80)	.
	2	.	102	—	—	—	—	.	(96)	.
	4	.	84	—	—	—	—	.	93	.
	7	.	75	.	(55)	—	—	.	90	.
	8	.	61	.	(59)	—	—	.	91.5	.
CN	1	.	111.5	—	—	—	—	—	—	.
	2	.	78	—	—	.	(72)	.	90.5	.
	4	.	91.5	—	—	.	(97.5)	—	—	.
	7	.	71	—	—	.	105	—	—	.
	8	.	65	—	—	.	108	—	—	.

The notations are that of Table I.

4 Dielectric properties

The dielectric anisotropy ε_a was determined from the capacity measurement of a 50 μ liquid crystal cell. The molecules were orientated by a 10000 Oe magnetic field, parallel ($\varepsilon_{\parallel}$) or perpendicular ($\varepsilon_{\perp}$) to the electric field. For high melting products, ε_a was measured on a 10% mixture of the compound with the *p*-methoxybenzoate of *p*-pentylphenol ($\varepsilon_a = 0.1$).

The results are listed in Table VI.

TABLE VI

Dielectric anisotropy of compounds of the two series I and II

Series	R	X	Type of measure	ε_a or $\varepsilon_a^{0.1}$
I	C_6H_{13}	Br	$\varepsilon_a^{0.1}$ (26°C)	+0.67
I	C_6H_{13}	CN	$\varepsilon_a^{0.1}$ (26°C)	+2.1
II	$C_8H_{17}O$	Br	ε_a (70°C)	−1.17
II	$C_8H_{17}O$	CN	$\varepsilon_a^{0.1}$ (25°C)	−0.7

ε_a: dielectric anisotropy of a pure compound.
$\varepsilon_a^{0.1}$: dielectric anisotropy of a 10% mixture of the compound with the *p*-methoxybenzoate of *p*-pentylphenol.

CONCLUSION

The synthesis of compounds of the series I and II has been described. The introduction of a flexible group, $-CH_2-CH_2-\langle\bigcirc\rangle-$, between the central core and the chain, leads to compounds with relatively low melting points and large mesomorphic ranges.

In series I, the *p*-bromo group gives compounds with a smectic polymorphism, S, S_B and S_A, while the *p*-cyano group induces nematic phase. All these products have positive dielectric anisotropy.

On the other hand, compounds from series II exhibit negative anisotropy.

In both series, the compounds with a cyano group have a mesomorphic range and a clearing point higher than those of the compounds with a bromo group.

EXPERIMENTAL

p-alkoxybenzoic acids They were prepared from the *p*-hydroxybenzoic acid and the selected alkyl bromide following the method of Gray *et al.*[19]

p-alkylbenzoic acids They were prepared by the acetylation reaction of alkylbenzenes, followed by hypobromite oxidation of 4-alkylacetophenones.[20]

4-alkoxy-3-bromobenzoic acids They were obtained by reaction of bromine on the *p*-alkoxybenzoic acid dispersed in water.[9]

Acid chlorides They were obtained from reflux of the corresponding acid with an excess of $SOCl_2$. The latter was eliminated after by means of a vacuum evaporator.

1-(4-hydroxyphenyl)-2-(4'-pentylphenyl) ethane Its synthesis is described in Ref. 11.

1-(4-hydroxyphenyl)-2-(4'-bromophenyl) ethane It was prepared from the bromo-4-hydroxy-4' deoxybenzoin according to the Wolff-Kishner reaction.[11]

Esters The final compounds were obtained by esterification between the corresponding chloride acid and the corresponding phenol, from pyridine at room temperature during 24 hours. Esters of series I were recrystallized

from ethanol and those of series II from hexane, until their transition temperatures remain constant.

Cyano-esters They were all obtained from bromo-esters by heating them at 160°C with CuCN in dimethylformamide during 6 hours. They were purified by chromatography on silica gel column with a benzene: hexane mixture eluent. Then they were recrystallized from ethanol.

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