Molecular Crystals and Liquid Crystals

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To cite this article: Nguyen Huu Tinh, A. Zann & J. C. Dubois (1979): Synthesis of 1 - (4-Alkoxy or Alkyl- Benzoyloxy-Phenyl) - 2- (4′- Pentylphenyl) - Ethanes. Influence of the Central Group on the Mesomorphic Properties, Molecular Crystals and Liquid Crystals, 53:1-2, 43-54

To link to this article: http://dx.doi.org/10.1080/00268947908083982

Mol. Cryst. Liq. Cryst., 1979, Vol. 53, pp. 43–54

Printed in Holland

Synthesis of 1-(4-Alkoxy or Alkyl-Benzoyloxy-Phenyl)-2-(4′-Pentylphenyl)-Ethanes. Influence of the Central Group on the Mesomorphic Properties

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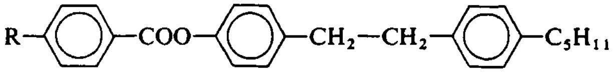
(Received October 25, 1978; in final form December 21, 1978)

An homologous series of mesomorphic compounds, the 1-(4-alkoxy or alkyl-benzoyloxy-phényl)-2-(4′-pentylphenyl)-ethanes, has been synthesized. The compounds with R = alkyl have low-melting points and wide mesomorphic ranges, for example from 33.5°C to 106.5C. The compounds with R = alkoxy exhibit a smectic polymorphism; for example a compound of this series is successively smectic B, F and C. The influence of the central linkage when the ethane group is replaced by an ester, single bond, ethylene, azomethine, azo, methylene-cetone or cetone groups, is discussed.

INTRODUCTION

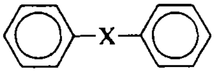
Recently, we synthesized some liquid crystalline benzoyloxystilbenes.[1,2] These compounds exhibit successively the three smectic phases B, F and C and they allowed us to confirm the succession of these three smectic phases. Looking at these results, we synthesized new compounds which have a chemical structure very closed from the benzoyloxy-stilbenes: the 1-(4-substituted benzoyloxy-phenyl)-2-(4′-pentylphenyl)-ethanes, with the following formula:



(1)

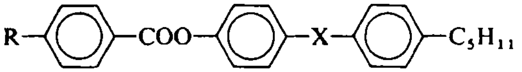
where R is *n*-alkyl or *n*-alkoxy. These later compounds will be, in addition, more chemically and photochemically stable than the former.

Comparative studies on the ability of different central linkages to induce mesomorphic phases have already been done on a series of compounds:[3,4]



(2)

with X = $-COO-$, $-CH{=}CH-$, $-CH{=}N-$ investigations by means of Depolarized Rayleigh Diffusion (D.R.D.) were also given.[5,6] A similar discussion will be given here on the following series:

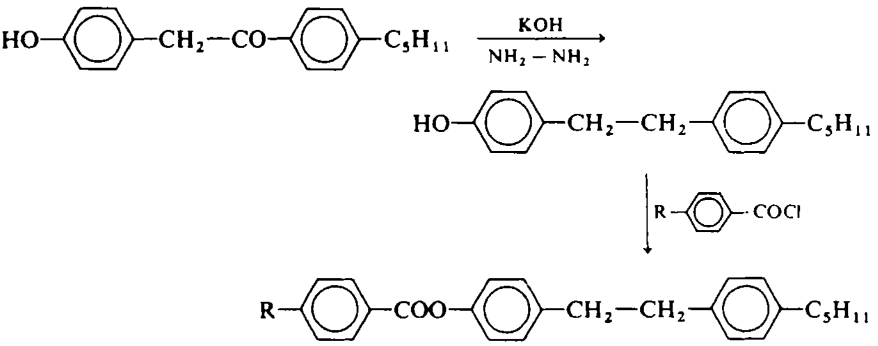


(3)

with X = $-COO-$, single bond, $-CH_2-CH_2-$, $-CH{=}CH-$, $-CH{=}N-$, $-N{=}N-$, $-CH_2-CO-$ or $-CO-$.

SYNTHESIS OF 1-(4-SUBSTITUTED BENZOYLOXY-PHENYL)-2-(4′-PENTYL-PHENYL)-ETHANES

These compounds were obtained by the esterification of the appropriate 4-substituted benzoic acid chloride with the 1-(4-hydroxy-phenyl)-2-(4′-pentyl-phenyl)-ethane; this last product was prepared from the 4-hydroxy-4′-pentyl-deoxybenzoin,[1] following the scheme shown below:

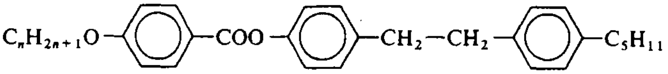


MESOMORPHIC PROPERTIES OF THE SYNTHESIZED COMPOUNDS

The mesophases were observed by means of a polarizing microscope equipped with a heating and cooling stage (Mettler FP 5). The transition temperatures were determined by means of a differential scanning calorimeter (DSC-1B Perkin Elmer). The results are listed in the Tables I and II. The

TABLE I

Transition temperatures of compounds with formula:



n	K		S		S_B		S_F		S_C		S_A		N		I
1	.	95	—	—	—	—	—	—	—	—	—	—	.	135	.
2	.	88	—	—	—	—	—	—	—	—	—	—	.	142	.
3	.	90	—	—	—	—	—	—	—	—	—	—	.	123.5	.
4	.	86	—	—	—	—	—	—	—	—	—	—	.	138	.
5	.	75	—	—	—	—	—	—	—	—	—	—	.	127.5	.
6	.	66	—	—	.	(59)	—	—	—	—	—	—	.	122.5	.
7	.	69	—	—	.	(69)	—	—	.	81	—	—	.	128	.
8	.	63	—	—	.	70.5	—	—	.	95	—	—	.	130	.
9	.	74	.	(48)	.	(70.5)	.	(74)	.	102	—	—	.	124.5	.
10	.	75	.	(56.5)	.	83.5	—	—	.	111	—	—	.	125	.
11	.	74	.	(65)	.	94	—	—	.	118	.	120	.	123	.
12	.	78	—	—	.	90	—	—	.	115	—	—	.	124	.

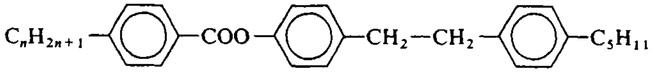
The meanings of the signs used in this table and in the following are:

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:

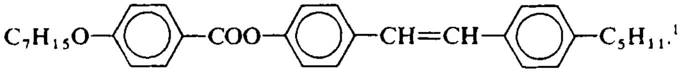


n	K		S		S_B		N		I
3	.	73	—	—	—	—	.	113	.
5	.	55	—	—	.	75	.	110	.
6	.	67	.	73.5	.	84	.	103	.
7	.	33.5	.	65	.	88	.	106.5	.
8	.	31	.	52	.	92	.	102.5	.

The notations are that of Table I.

structures of the smectic mesophases were identified, using the contact method, by their isomorphy with a known reference compound.[7]

For *alkoxy-compounds* (Table I), the smectic B and C phases appear respectively from $n = 6$ and $n = 7$. The smectic B and C phases of the heptyloxy-compound were identified by isomorphy with the following compound (Figure 1):



In that series, two compounds have special mesomorphic properties: the

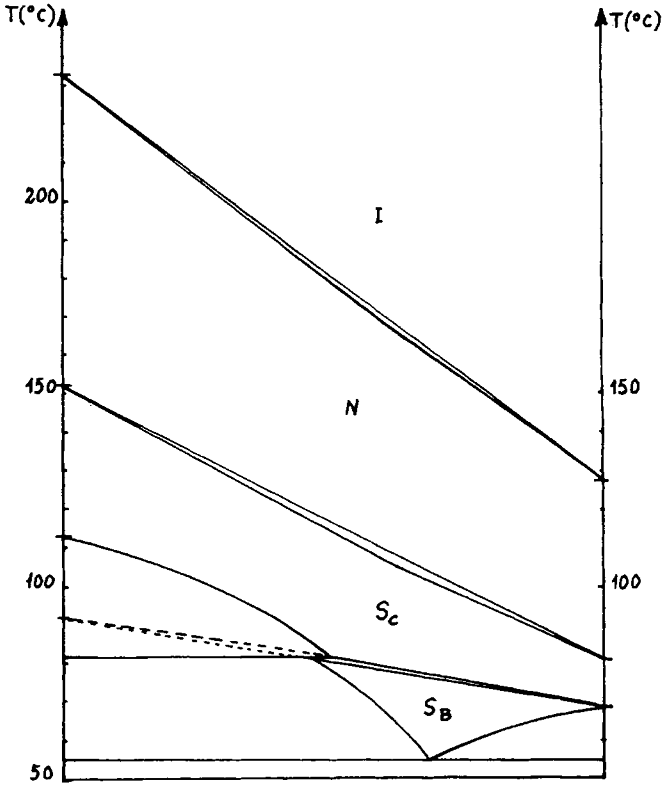
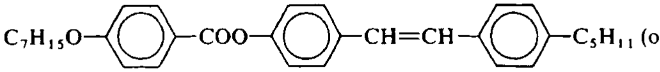
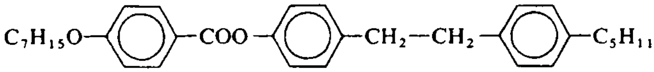


FIGURE 1 Diagram of isobaric state for the mixtures of:



(on left) with



(on right)

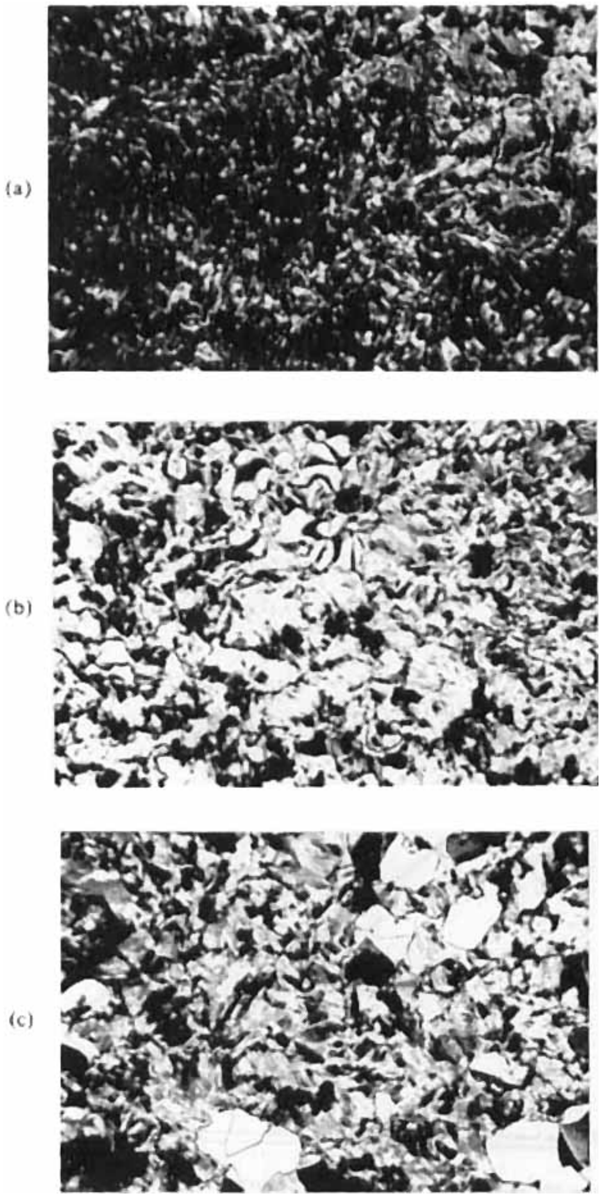
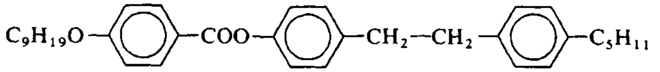
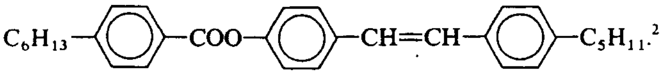


FIGURE 2 Textures of the compound:



(a) S_C phase at T = 101°C. (b) S_F phase at T = 72.5°C. (c) S_B phase at T = 69.5°C.

nonyloxy and the undecyloxy (Table I). The nonyloxy exhibits a smectic F phase between the B and C ones, and before the B phase, a smectic "S" phase not yet identified. The textures of the B, F and C phases are shown on Figure 2. The three smectic phases were identified by isomorphy with the phases of the following compound (Figure 3):



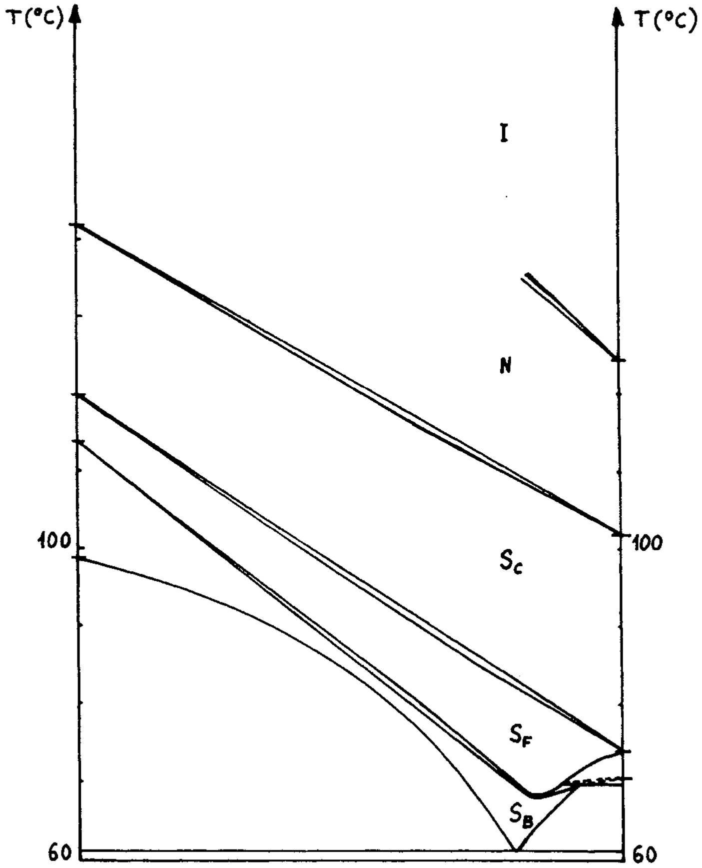
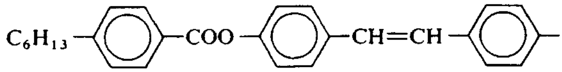
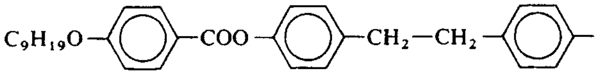


FIGURE 3 Diagram of isobaric state for the mixtures of:

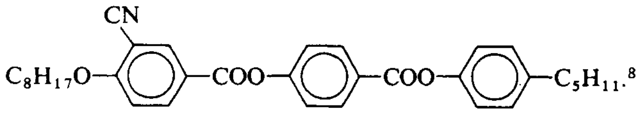


(on left) with



(on right)

The undecyloxy exhibits, in addition of the B and C phases, a smectic A phase and a "S" phase not yet identified. The C and A phases were identified with the following compound (Figure 4):



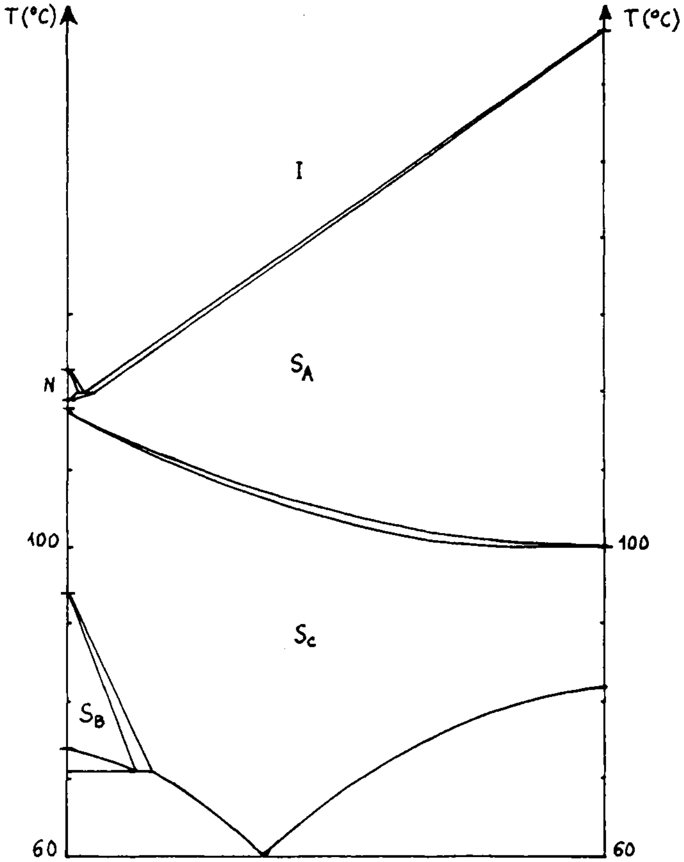
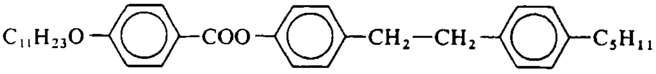
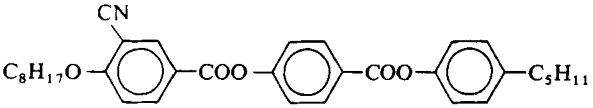


FIGURE 4 Diagram of isobaric state for the mixtures of:


(on left) with


(on right)

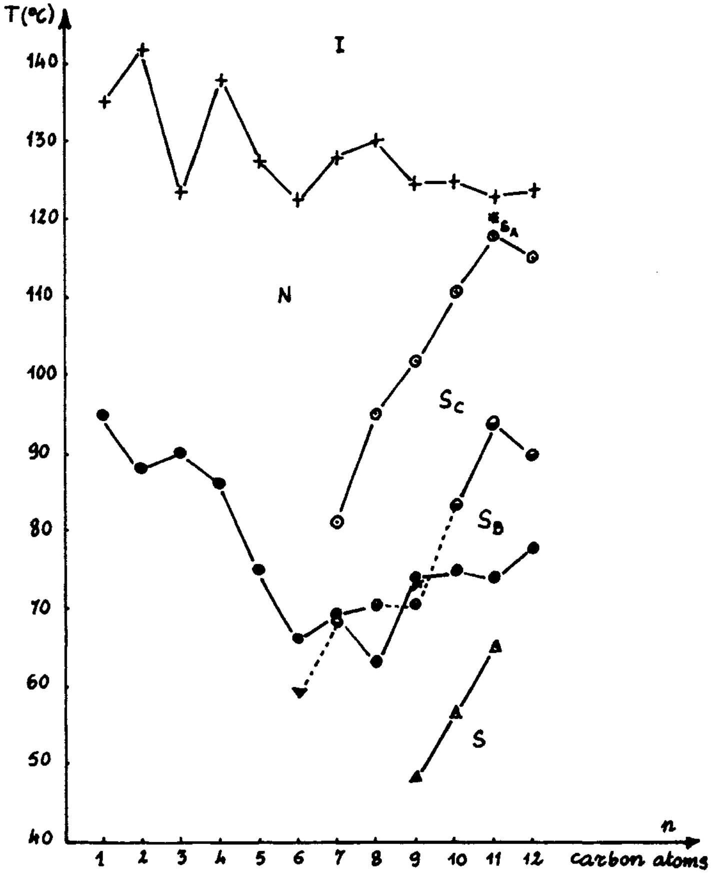
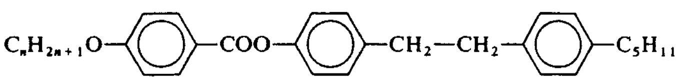


FIGURE 5 Plot of the transition temperatures against *n*, the number of carbon in the alkoxy chain, of:



The curve of the transition temperatures against *n*, number of carbon in the alkoxy chain, is plotted on Figure 5; we can see that there is little change on the melting and clearing points. The odd-even effect is very well observed except for the compound with $n = 6$.

For *alkyl-compounds* (Table II), the melting points are quite low and decrease strongly when *n* increases. The propyl has only a nematic phase; the smectic B phase appears from $n = 5$; from $n = 6$ to $n = 8$ two smectic phases, S and S_B, exist. The texture of the S_B phase of the hexyl compound is shown on Figure 6.

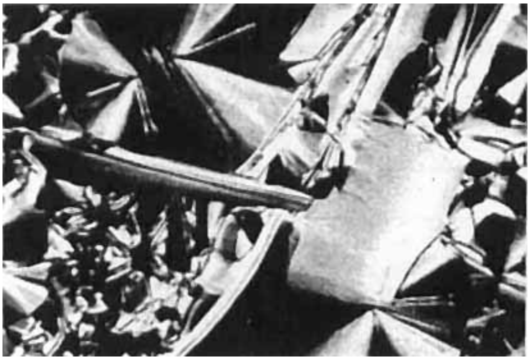
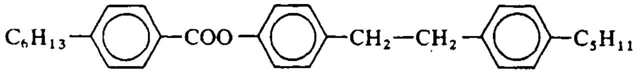


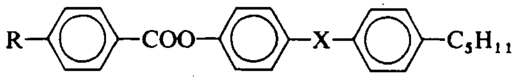
FIGURE 6 Texture of the S_B phase of the compound:



at T = 83°C.

INFLUENCE OF THE CENTRAL GROUP

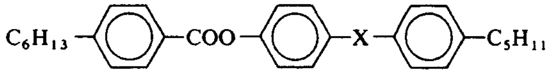
Now let us study the influence of the central group X on the mesomorphic properties of the following series:



In this paper we have just presented compounds with X = $—CH_2—CH_2—$. In previous papers, we presented compounds with X = —CH=CH—.[1,2] Mesomorphic properties of compounds with X = single bond[10] or X = COO[11] were already published. In order to have a better understanding about the influence of X, we synthesized some compounds with X = —CH=N—, —N=N—, $—CH_2—CO—$ and —CO—.[9] The influence of the central linkage X is studied here for compounds with R = C_6H_{13} or R = $C_7H_{15}O—$. Their transition temperatures and mesomorphic ranges are listed in Tables III and IV. We can point out that, for compounds with X equal to $—CH_2—CH_2—$, $—CH_2—CO—$ or —CO—, the ranges of mesomorphism are less large and the clearing points lower than for other central linkages. The three above cited groups are known as non mesogenic groups, the mesophases being destabilized either by the higher flexibility of the molecules (X = $—CH_2—CH_2—$, $—CH_2CO—$), or by their angular shape (X = —CO—). Among the other groups, the compounds with X equal to —CH=CH— exhibit the higher clearing points: for R = $C_6H_{13}—$,

TABLE III

Transition temperatures and mesomorphic range of compounds with formula:



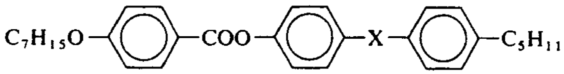
X	K	S	S_B	S_F	S_C	S_A	N	I	ΔT_M
single bond[10]	. 99	— —	— —	— —	— —	— —	. 164	.	65
—COO—[11]	. 74	— —	— —	— —	— —	. 78	. 169	.	95
—CH=N—[9]	. 96	— —	. (93)	— —	. 117.4	— —	. 191.4	.	95.4
—N=N—[9]	. 82	— —	— —	— —	— —	— —	. 187	.	105
—CH=CH—[1]	. 99	— —	. 114	. 120	. 142	— —	. 289	.	120
$—CH_2—CH_2—$	. 67	. 73.5	. 84	— —	— —	— —	. 103	.	36
$—CH_2—CO—$[9]	. 137	— —	— —	— —	— —	— —	— —	.	

ΔT_M: mesomorphic range—gap between the clearing and the melting points. The other notations are that of Table I.

T_{NI} is equal to 289°C and for R = $C_7H_{15}O—$, to 233°C. The three following central groups, —CH=CH—, —CH=N— and —N=N— exhibit the largest ranges of mesomorphism, between 95° to 130°C. This fact is probably in relation with the rigidity of the molecules given by the double bond. Another interesting point is the smectic polymorphism induced by the following groups: —CH=CH—, $—CH_2—CH_2—$, —CH=N—. In these three series, the smectic B phase exists for each compound and the smectic C for almost all the compounds (Tables III and IV). We have to point out that the smectic B phase was identified by isomorphy with the B phase of the terephtalbisbutylaniline or TBBA; the structure of this phase is now known as B tilted.[12]

TABLE IV

Transition temperatures and mesomorphic range of compounds with formula:

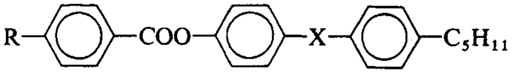


X	K	S_B	S_C	N	I	ΔT_M
—CH=N—[9]	. 71.5	. (66.5)	. 127	. 201	.	129.5
—N=N—[9]	. 91	— —	— —	. 205	.	114
—CH=CH—[1]	. 113.5	. (92)	. 152	. 233	.	119.5
$—CH_2—CH_2—$	. 69	. (69)	. 81	. 128	.	59
$—CH_2—CO—$[9]	. 130	. (111)	— —	. (113.5)	.	−16.5
—CO—[9]	. 73	— —	— —	— —	.	

The notations are that of Tables I and III.

CONCLUSION

The new mesogenic compounds described here are chemically and photochemically stable; they exhibit an interesting smectic polymorphism and some compounds are successively smectic B, F and C. This is the fourth series to exhibit these three successive phases; the three previous series were published by Gray *et al.*[13,14] and by us.[2] New compounds belonging to the following series:



with various central linkages X, were synthesized too. The non-mesogenic behaviour of X groups such as $—CH_2—CH_2—$, $—CH_2—CO—$, $—CO—$, is confirmed. Compounds with mesogenic X groups such as $—CH{=}CH—$, $—CH{=}N—$, $—N{=}N—$ exhibit very large mesomorphic range, until 130°C. The three central linkages, $—CH{=}CH—$, $—CH_2—CH_2—$, and $—CH{=}N—$, always induce smectic B mesophases.

EXPERIMENTAL

The transition temperatures and the textures of the various mesophases have been observed by means of a polarizing microscope (Nachet) equipped with a heating and cooling stage (FP 5 Mettler). The transition temperatures were measured with a differential scanning calorimeter (DSC-1B Perkin Elmer).

The microanalysis have been done by the Laboratory "Autonome de Travaux."

SYNTHESIS

p-alkoxybenzoic acids they were prepared from the *p*-hydroxybenzoic acid and the selected alkylbromide following the method of Gray *et al.*[15]

p-alkylbenzoic acids they were prepared by the reaction of acetylation of alkylbenzenes and then by the hypobromite oxidation of the 4-alkylacetophenones.[16]

acid chlorides they were prepared by reflux heating of the corresponding acid in an $SOCl_2$ excess.

1-(4-hydroxyphenyl)-2-(4'-pentylphenyl)-ethane 4.5 g (0.016 mole) of 4-hydroxy-4'-pentyldeoxybenzoine were added to a solution of 3 g of hydrazin, 10 ml of diethylene glycol and 4 g of KOH. The mixture was heated to reflux during one hour. The temperature reached 180°C; 3 ml of solvent were distilled. Then the temperature was maintained at 230°C during 3 hours. The mixture was then cooled and neutralized with a 5 ml concentrated HCl solution and 50 g of ice. The organic fraction was extracted with 150 ml of benzene. The product was purified by chromatography on silica with benzene as eluant. It was then recrystallized from benzene. 2.7 g of the product were obtained. The melting point was 102°C.

Esters they were prepared by the esterification reaction between the selected acid chloride and the 1-(4-hydroxyphenyl)-2-(4'-pentylphenyl)-ethane, in pyridine at room temperature during 24 hours. The obtained ester was recrystallized from ethanol until its transition temperatures were constant.

Acknowledgements

We wish to thank here Professor J. Billard for his help in the identification of the smectic mesophases.

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