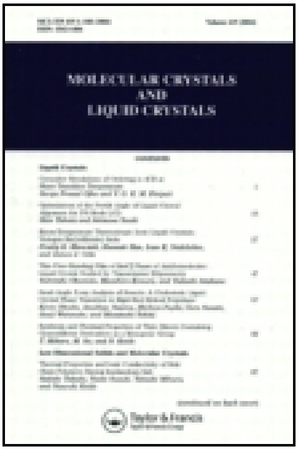

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Synthesis and Mesomorphysm of Some New Ferro-Electric Smectic Liquid Crystals

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SYNTHESIS AND MESOMORPHYSM OF SOME NEW FERRO-ELECTRIC SMECTIC LIQUID CRYSTALS

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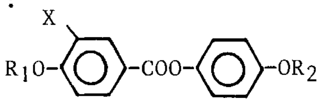
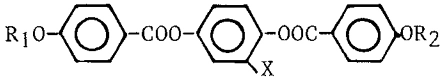
91401 ORSAY (France)

Abstract : In this work, compounds having the general formula :

(I) 

(II) 

with (X = H,Br,CN,Cl) and (R_1 (or/and) R_2 = 3-methyl-hexyl or 2-methyl-butyl, n-alkyl were prepared and their phase transition temperatures and mesomorphic properties determined.

INTRODUCTION

R. Meyer and al[1] have shown in 1975 that chiral compounds in the smectic C^* phase can exhibit a spontaneous polarisation P and that these phases are ferroelectric ; so it is possible to couple the polarisation with an external electric field and in 1980, a new ferroelectric smectic device structure, the Surface Stabilized Ferroelectric Liquid Crystal (SSFLC) structure was reported[2,3]. The experimental investigations have almost exclusively concerned DOBAMBC and HOBACPC[4,5,6,7]. These compounds melt around 70°C and are not very stable.

DOBAMBC (P-decyloxybenzylidene P'amino 2-methyl butyl cinnamate)

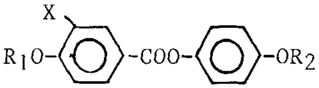
$$\begin{tikzcd}
K \arrow[r, "76°"] & SmC^* \arrow[r, "95°"] \arrow[dl, "63°"] & SmA \arrow[r] & I \\
SmH \arrow[u] & & &
\end{tikzcd}$$

HOBACPC (P-hexyloxybenzylidene P'amino 2-chloro α-propyl cinnamate)

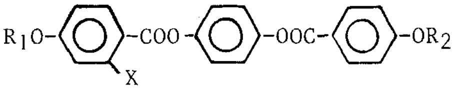
$$K \xrightarrow{60°} SmH^* \xrightarrow{64°} SmC^* \xrightarrow{78°} SmA \xrightarrow{135°} I$$

In this paper, we report a number of new compounds which exhibit smectic C^* phases. They have been used as pure samples and as mixtures. So, we describe here, the synthesis of materials of the following type :

(I)



(II)



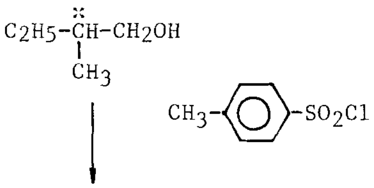
with (X = H,Br,CN,Cl) and (R (or/and) R_2 = 3-methyl hexyl 2-methyl butyl, n-alkyl).

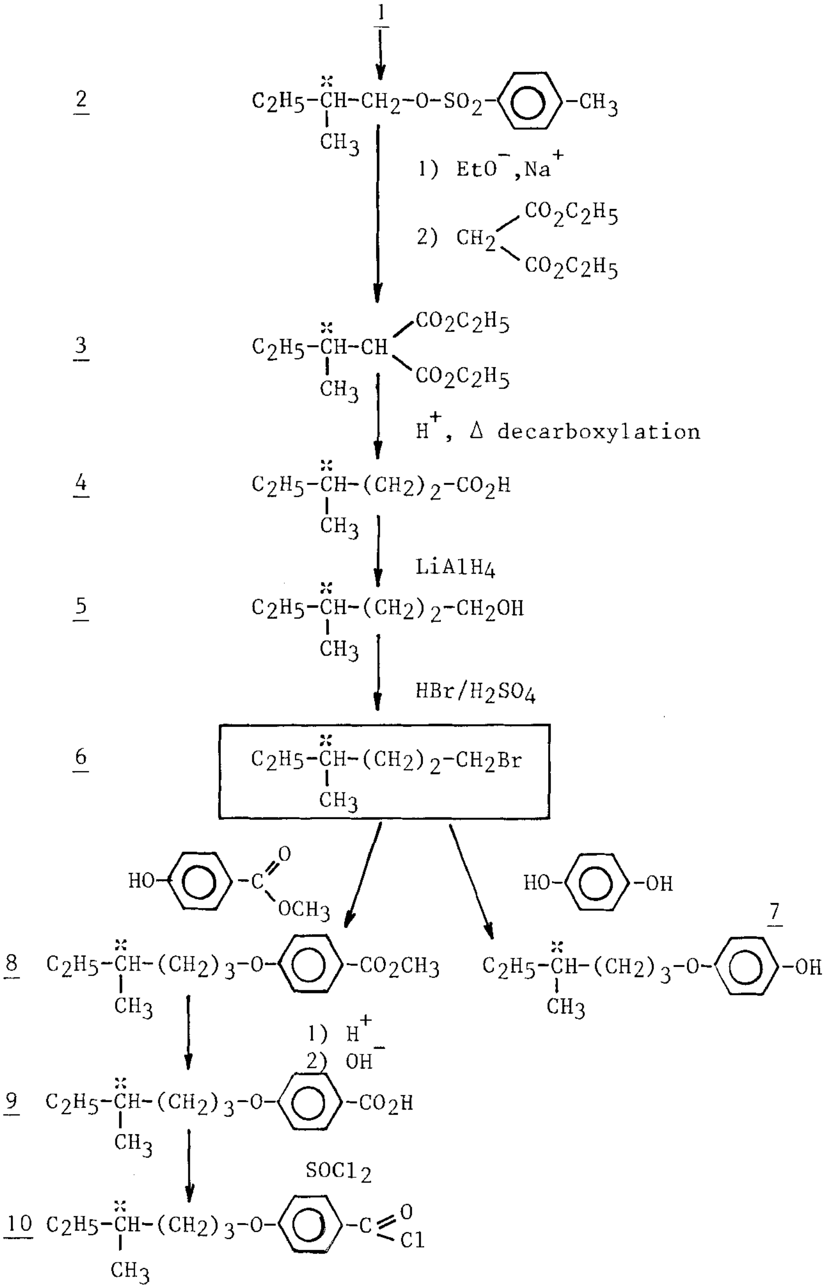
DISCUSSION AND RESULTS

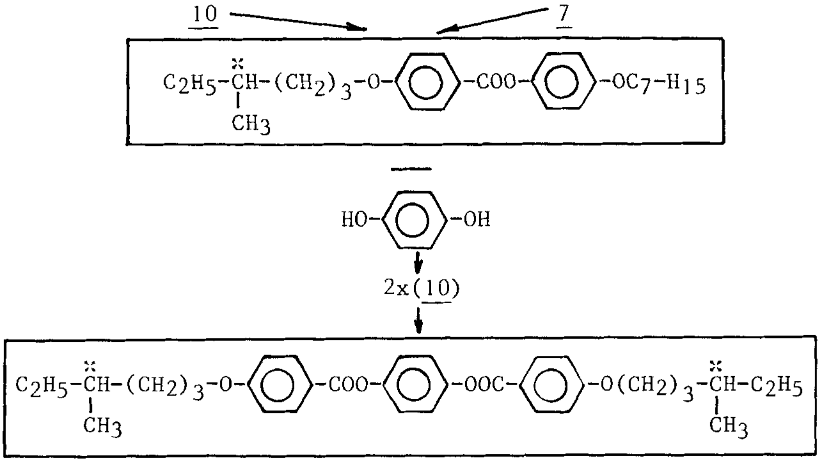
1) Synthesis

Compounds of formula (I) were prepared from (-)-2-methylbutan-1-ol, hydroquinone and 4-hydroxy benzoïc acid using the following scheme.

1




1
2
C2H5-CH-CH2-O-SO2-C6H4-CH3
CH3
1) EtO⁻,Na⁺
2) CH2(CO2C2H5)2
3
C2H5-CH-CH(CO2C2H5)2
CH3
H⁺, Δ decarboxylation
4
C2H5-CH-(CH2)2-CO2H
CH3
LiAlH4
5
C2H5-CH-(CH2)2-CH2OH
CH3
HBr/H2SO4
6
C2H5-CH-(CH2)2-CH2Br
CH3
HO-C6H4-C(=O)OCH3
HO-C6H4-OH
7
8
C2H5-CH-(CH2)3-O-C6H4-CO2CH3
CH3
C2H5-CH-(CH2)3-O-C6H4-OH
CH3
1) H⁺
2) OH⁻
9
C2H5-CH-(CH2)3-O-C6H4-CO2H
CH3
SOCl2
10
C2H5-CH-(CH2)3-O-C6H4-C(=O)Cl
CH3



(+)2-methylbutyl-p-toluene sulfonate (2)and diethyl 2(S) methylbutyl malonate (3) were prepared according the method described in experimental part. Compounds 5 and 7 were obtained by the preparative procedures described in refs 8 and 9. 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 and II. The structures of the smectic phases were identified by their isomorphy with a known reference compound.

2) Experimental

2-methylbutyl-p-toluenesulfonate

44 g (0,5 mole) of 2-methylbutyl alcohol was dissolved in pyridine (400 ml), cooled in an ice bath, and 200 g of p-toluenesulfonyl chloride was added. The reaction was stirred for three hours and left overnight in the refrigerator. The mixture was diluted with an excess of water, stirred for two hours in an ice bath, and extracted with ether. The ether extract was washed with cold 6N HCl until all the pyridine had been removed, and then washed with water ; the organic

TABLE I - Compounds having the Formula (I)

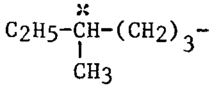
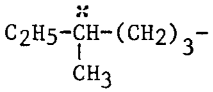
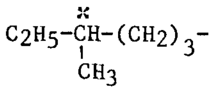
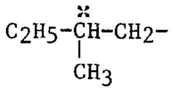
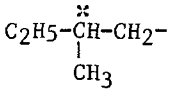
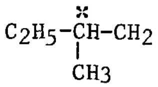
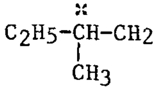
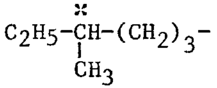
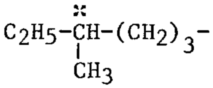
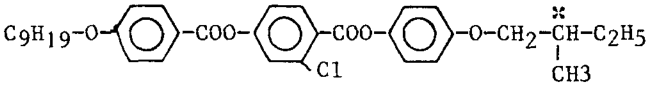
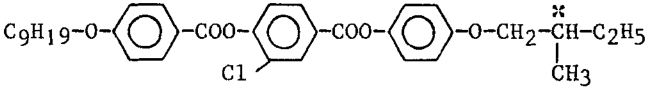
N°	X	R_1	R_2	Combustion Analysis		
				% C	% H	% O
1	H	 $C_2H_5-\underset{\displaystyle CH_3}{\overset{*}{C}H}-(CH_2)_3-$	$C_7H_{15}-$	75,4	9,2	15,4
2	H	 $C_2H_5-\underset{\displaystyle CH_3}{\overset{*}{C}H}-(CH_2)_3-$	 $C_2H_5-\underset{\displaystyle CH_3}{\overset{*}{C}H}-(CH_2)_3-$	75,4	9,2	15,4
3	H	$C_{10}H_{21}$	 $C_2H_5-\underset{\displaystyle CH_3}{\overset{*}{C}H}-CH_2-$	75,7	9,4	14,9
4	H	$C_7H_{15}-$	 $C_2H_5-\underset{\displaystyle CH_3}{\overset{*}{C}H}-CH_2-$	74,6	8,8	16,6
5	Br	$C_8H_{17}-$	 $C_2H_5-\underset{\displaystyle CH_3}{\overset{*}{C}H}-CH_2$	63,5	7,1	13
6	CN	$C_8H_{17}-$	 $C_2H_5-\underset{\displaystyle CH_3}{\overset{*}{C}H}-CH_2$	74	8	14,6

TABLE II - Compounds having the Formula (II)

N°	X	R_1	R_2	Combustion Analysis		
				% C	% H	% O
7	H	 $C_2H_5-\overset{*}{C}H(CH_3)-(CH_2)_3-$	 $C_2H_5-\overset{*}{C}H(CH_3)-(CH_2)_3-$	73,5	8	18,5
8				69,4	1,5	18
9				69,4	1,5	18

layer was dried over sodium sulfate.
The solution was filtered and ether evaporated to give 100 g (85 %) of tosylate.

Diethyl 2(S)-methylbutyl malonate

To a solution prepared from 5 g of sodium and 100 ml ethanol was added 40 g of diethyl malonate. Then 50 g of 2-methylbutyl-p-toluenesulfonate was added during one hour and a dark precipitate later appeared. After one day long reflux, ethanol was evaporated and the residue shaken with water. The mixture was extracted with ether. The organic layer was dried over magnesium sulfate. Distillation gave 40 g of colorless liquid (200°C/18 mmHg).

4-methylhexane-1-ol

This was prepared from the 4-methylhexanoïc acid by reduction with Lithium Aluminium hydride (108° at 20 mmHg).

4-methyl-hexyl-bromide

This was prepared by a standard litterature method [8] by treating the alcohol with HBr.

4-methyl-3-hexyloxy 4'hydroxy-phenyl

This was obtained from 4-methylhexylbromide and hydroquinone by a standard litterature method [9].

Preparation of esters

These were obtained by interacting the 4-alkyloxy 4'hydroxyphenyl and the relevant acid in pyridine solution.
Compounds were purified by using chromatography on a silica gel column which was eluted with chloroform or toluene.
The esters were crystallised to constant melting point from methanol.

Their elementary analyses are summarized in Tables (I) and (II) and the phase transition temperatures in Table (III).

3) Mesomorphic properties

All the compounds of formula (I) and (II) are mesomorphic and were shown to exhibit chiral smectic C phases, except for X = Br,CN,Cl.

If the core is composed of two phenyls (one of them having a bromo or cyano group), linked by an ester function (5,6, 8,9), the C^* phase is affected and only S_A and N^* phases are observed.

Reversal of the position of the chloro group has interesting effects (8,9). The smectic A phase is eliminated and a direct cholesteric - crystal transition is observed.

The action of including two methyl branches in the ether terminal alkyl chain has the property of decreasing the stability of the Sm C^* phase (1,2).

4) Textures

Optical microscopy (using a Zeiss polarising microscope in conjuction with a Mettler hot stage) of the textures exhibited by the materials of formula (I) and (II) show typical focal conic for the smectic A phase, focal conic (homeotropic texture) and a texture with a bundle of oily streaks the with GRANDJEAN steps at the border of the preparation for the cholesteric phase (N^*), and a striped focal-conic for the chiral smectic C phase. The arcs in the fan texture are representative of either the pitch or half the pitch of the C^* phase [4]. The arcs in the fan textures for compounds (2 and 7) are wider than those exhibited for compounds (1,3,4). It seems that compounds with two chiral groups have greater pitches than those with only one chiral group).

TABLE III - Phase transition temperatures

Compounds N°	Phase trans temp (°C)
1	K 30 S_C^{*} 46 N^{*} 62,5 I
2	K 33 [S_C^{*}] 40 [S_A] 41,9 I m.p 47,7°C
3	K 43,5 S_C^{*} 61,5 S_A 64,5 I
4	K 37 [S_C^{*}] 38,2 [S_A] 49,3 N^{*} 55,4 I
5	K 75 I
6	K 62 S_A 63 I
7	K_1 97 K_2 99 S_C^{*} 110 N^{*} 165 I
8	K 56 S_A 103 N^{*} 121,5 I
9	K 55 N^{*} 135 I

The meanings of the symbols used in this table are :

K : crystalline phase
S : smectic phase(s) S_A , S_C^{*}
N^{*} : cholesteric phase
I : isotropic liquid phase
[] : monotropic phase

The temperatures are given in Celsuis degrees, metastable transitions are indicated between brackets.

CONCLUSION

Some molecules exhibiting chiral smectic C phases have been synthetized. They have been used as pure samples and as mixtures. The mixing of two compounds (1 and 3) provide an eutectic mixture which exhibits C^* phase at room temperature. The viscosity of these materials is too high and the polarisation too low. At 22°C for a 5 micrometers thick cell we get response times about 200 ms with an applied DC voltage of 5 V(10). This large response time results of the low macroscopic dipole moment P and the high viscosity of the material at ambient temperature. It is a first step towards new ferroelectric phases for memory displays.

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