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FERROELECTRIC LIQUID CRYSTALS WITH NEW CHIRAL BUILDING BLOCKS

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Abstract:Esterification of 4-nitrocinnamoyl chloride by new chiral alcohols((d) and (l) 2-butanol;(d) 2-heptanol),followed by reduction of the nitro group by a new reagent($SnCl_2$), gives new chiral 4-aminocinnamates.Condensation of these amines with 4-alkyloxybenzaldehydes or terephthaldehyde gives Schiff bases showing in some cases chiral smectic C phases. A comparative study of the mesomorphism of both these compounds and the compounds of the DOBAMBC family is made, in order to evaluate the effect of the chiral building block structure on the liquid crystalline properties.During this study,a new compound has been prepared,which exhibits the smectic O phase:((d) 1-methylhexyl)terephthalidene Bis 4-aminocinnamate.

INTRODUCTION

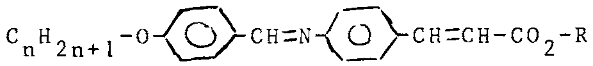
Ferroelectricity in chiral smectic C phases was discovered by R.Meyer et al. in 1975[1].However, even if the subject has attracted great fundamental[2-4] and practical[5,6] interest since that time, almost all the experimental work published has been made on two compounds, 4-decyloxybenzylidene-4'-amino((S)2-methylbutyl)cinnamate(DOBAMBC)[1,7] and 4-hexyloxybenzylidene-4'-amino((R)2-chloropropyl)cinnamate(HOBACPC)[8].

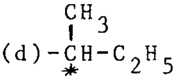
Recently, some efforts have been done in order to synthesize new ferroelectric liquid crystals[9-15], but all the new compounds prepared so far included in their structures the chiral group (2-methylbutyl) issued from (S)2-methylbutanol.

Clearly, new chiral building blocks are needed in order to diversify the families of ferroelectric liquid crystals available both for fundamental works and applications. In this paper, we report some results on the synthesis of chiral compounds containing chiral groups derived from (d) and (l) 2-butanol and (d) 2-heptanol.

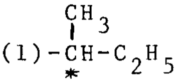
RESULTS AND DISCUSSION

We have prepared some chiral liquid crystals by incorporation of chiral alcohols((d)and(l)2-butanol;(d)2-heptanol)in the 4-alkyloxybenzylidene-4'-aminocinnamates and terephthalidene Bis 4-aminocinnamates series. This has provided us with a few series of materials with the general structures(1) to (7).

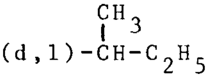


(1) 

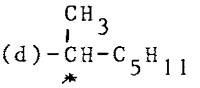
$\mathrm{R} = (\mathrm{d})\text{-}\overset{\mathrm{CH_3}}{\underset{*}{\mathrm{C}}}\mathrm{H\text{-}C_2H_5}$ (1a n=6; 1b n=8; 1c n=10)

(2) 

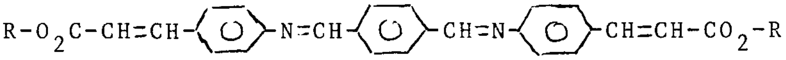
$\mathrm{R} = (\mathrm{l})\text{-}\overset{\mathrm{CH_3}}{\underset{*}{\mathrm{C}}}\mathrm{H\text{-}C_2H_5}$ (2a n=6; 2b n=8; 2c n=10)

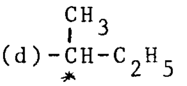
(3) 

$\mathrm{R} = (\mathrm{d,l})\text{-}\overset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{H\text{-}C_2H_5}$ (n=10)

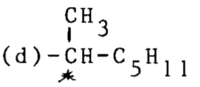
(4) 

$\mathrm{R} = (\mathrm{d})\text{-}\overset{\mathrm{CH_3}}{\underset{*}{\mathrm{C}}}\mathrm{H\text{-}C_5H_{11}}$ (4a n=6; 4b n=8; 4c n=10)

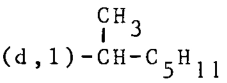


(5) 

$\mathrm{R} = (\mathrm{d})\text{-}\overset{\mathrm{CH_3}}{\underset{*}{\mathrm{C}}}\mathrm{H\text{-}C_2H_5}$

(6) 

$\mathrm{R} = (\mathrm{d})\text{-}\overset{\mathrm{CH_3}}{\underset{*}{\mathrm{C}}}\mathrm{H\text{-}C_5H_{11}}$

(7) 

$\mathrm{R} = (\mathrm{d,l})\text{-}\overset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{H\text{-}C_5H_{11}}$

These compounds have been chosen intentionally since they are structurally related with the most popular ferroelectric liquid crystal,DOBAMBC,with differences only at the level of the chiral groups. So,a comparison between the mesomorphism of compounds of DOBAMBC family[7] and the one of our new series will give us the opportunity to compare directly the effect of the chiral building blocks on the liquid crystalline properties.

The chiral Schiff bases(1) to (7) were synthesized by reaction between appropriate aldehydes (4-alkyloxybenzaldehydes or terephthaldehyde)and chiral 4-aminocinnamates(prepared from chiral 4-nitrocinnamates by a new reduction reaction^{16}-see experimental).

The melting and transition points for the prepared compounds are shown in TABLE 1 and 2.Identifications of the mesophases have been done by examination of the textures$^{7,17-19}$exhibited by thin samples sandwiched between two glass slides and by miscibility studies.

TABLE1 Mesomorphic properties of series (1), (2),(3) and (4). (T in °C).(()=monotropic transition)

Compound	K	SC	SA	I
1a	● 91,5	(● 88)	● 114	●
1b	● 93	(● 85)	● 107	●
1c	● 67,5	● 85	● 103	●
ΔH (Kcal.M^{-1})	(9,1)	(0,008)	(1,51)	
2a	● 92	(● 87,5)	● 114,5	●
2b	● 93,5	(● 88,5)	● 107	●
2c	● 67,5	● 83	● 103	●
3	● 65	● 83	● 107	●
4a	● 96		(● 90)	●
4b	● 102			●
4c	● 99			●

From the data given in TABLES 1 and 2,it can be seen that the mesomorphism is strongly a function of the chiral alcohol used.

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3	● 65	● 83	● 107	●
4a	● 96		(● 90)	●
4b	● 102			●
4c	● 99			●

From the data given in TABLES 1 and 2,it can be seen that the mesomorphism is strongly a function of the chiral alcohol used.

TABLE2 Mesomorphic properties of compounds (5), (6) and (7). (T in °C).

Compound							
5	K	154	SC	222	SA	238	I
6	K_1	82	K_2	98	SO	157	I
$\Delta H(Kcal.M^{-1})$		(2,04)		(4,82)		(0,59)	
7	K	97,5	SO	156	I		
$\Delta H(Kcal.M^{-1})$		(7,24)		(0,83)			

All the compounds prepared with (d),(l)and(d,l) 2-butanol(series 1 to 3 and 5),give a chiral smectic C phase (either monotropic or enantiotropic) associated with a smectic A phase.The behaviour of these series is very similar with the one of the 4-alkyloxybenzylidene-4'-amino((S)2-methylbutyl)cinnamates(DOBAMBC family).Clearly,the replacement of (S)2-methylbutanol by a bulky chiral alcohol has little effect on the mesomorphism,as shown by the following comparison:

DOBAMBC	K 76 (SI 63) SC 92 SA 118 I
1c	K 67,5 SC 85 SA 103 I

We can just notice the disappearance of the ordered smectic phases commonly found in the DOBAMBC family[7,8,20,21].

On the other hand,incorporation of (d)2-heptanol has a dramatic effect,destroying almost completely the mesomorphism in compounds (4) and generating a new smectic phase for ((d)1-methylhexyl)terephthalidene-Bis-4-aminocinnamate(6).

This new smectic phase is isomorphous(see figure1) with the M_1 mesophase(or smectic O)of the chiral (1-methylheptyl)terephthalidene-Bis-4-aminocinnamate, recentlydescribed by us[19].

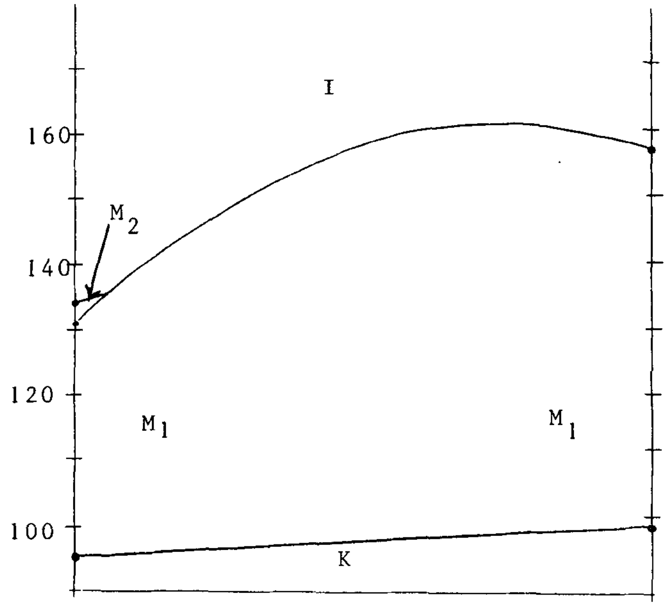
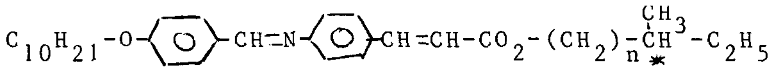


figure 1 Binary diagram of((1)1-methylheptyl)terephthalidene-Bis-4-aminocinnamate(on the left) with compound (6)(on the right).

This strong effect,produced by a small increase of the chiral chain length,is not found in the series of compounds[22,20,9]:



n=1	K76(SI63)SC92SA118I
n=2	K75SI83SC108SA121I
n=3	K72SI80SC107SA118I
n=4	K78SI91SC117,5SA120I
n=5	K72SI88SC115,5SA120I

Clearly, the lengthening of the chiral chain has no effect on the mesomorphism in this series.So, much work has to be done in order to understand the specificeffect of the (1-methylhexyl) group.

In conclusion,the limited exploration made in this work in order to find new chiral building blocks usable for the synthesis of ferroelectric liquid crystals has permitted(i)to demonstrate the potentialities of (d) and (l)2-butanol,(ii)to synthetize for the first time the two enantiomers and the racemate of a ferroelectric liquid crystal, (iii)to find a second compound which exhibits the recently discovered[19] smectic O phase.Many physical experiments have to be made on these compounds which appeared as very promising[23].

EXPERIMENTAL

Transition temperatures were measured by optical microscopy using a polarizing microscope(Leitz) fitted with a Mettler FP 82 hot stage and FP 80 control unit;they were checked by differential thermal analysis(Mettler 2000-DTA).

Satisfactory elemental analysis were obtained for all the materials.Structural checks were carried out using a Shimatzu IR-408 instrument for infrared spectra.Rotatory powers were determined with a Perkin Elmer 241 polarimeter.

Preparation of materials

The optically active alcohols,(d)2-butanol, (1)2-butanol,(d)2-heptanol,were purchased commercially(Alfred Bader Chemicals-Aldrich Co)and used without further purification.The rotatory powers for the actual compounds used during this work were: for (d)2-butanol $\{\alpha\}_D^{20} = +9,26$(neat)

for (1)2-butanol $\{\alpha\}_D^{20} = -10,35$(neat)

for (d)2-heptanol $\{\alpha\}_D^{20} = +6,93$(neat)

Chiral 4-alkyloxybenzylidene-4'-aminocinnamates and chiral terephthalidene-Bis-4-aminocinnamates were obtained by reacting chiral 4-aminocinnamates with,respectively,4-alkoxybenzaldehydes[24]and terephthaldehyde in ethanol at room temperature. The products were purified by recrystallization from ethanol solution several times.

Chiral 4-aminocinnamates were obtained from chiral 4-nitrocinnamates(prepared by classical schemes[25,26])by a new very simple reduction reaction[16] described below.

Preparation of (1-methylhexyl)4-aminocinnamate(as an example)

A mixture of (1-methylhexyl)4-nitrocinnamate (1,45g;0,005mole) and Stannous chloride dihydrate (5,6g;0,025mole) in 20ml of ethanol is refluxed for 30mn.After cooling down,the resulting yellow solution is poured onto ice and water.The pH of the solution is made slightly basic(pH7-8)by addition of solid sodium bicarbonate before being extracted with ether(2x100ml).The etheral solution is washed with water(3x150ml)and dried over sodium sulfate. Evaporation of the solvent leaves 1,16g(89%)of (1-methylhexyl)4-aminocinnamate which give one spot on tlc and give satisfactory IR spectrum.This compound is used without further purification in the subsequent condensation reaction with aldehydes.

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