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Chiral Nematogens Having an Asymmetric Carbon in the Lateral Aromatic Branch

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A chiral center can be introduced in the lateral substituent of mesogens containing four rings in the main core. The racemic compounds present a consequent nematic range. Comparison with compounds having a linear chain indicates that the bifurcated character of the chain does not affect drastically the nematic range. Bulky substituents like aromatic fragments can be also introduced on the chiral center. Preliminary results on the properties of one optically enriched compound are presented.

Keywords: chiral nematogens; laterally substituted nematogens

INTRODUCTION

Various flexible lateral substituents can be grafted on an elongated core without disturbing the liquid crystal properties [1-5]. On compounds containing linear lateral chains, we have shown that the appearance of the mesophase is due to the folding of the lateral chain along the core. This folding back preserves the molecular anisotropy needed for the packing in the mesophase. Thus, the mean conformation of the lateral chain involves a gauche conformation for the C_{ring}-O-C-C fragment as depicted in Figure 1.

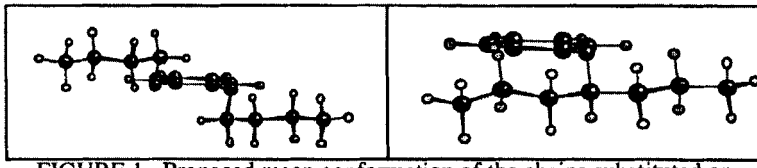


FIGURE 1 Proposed mean conformation of the chains substituted on the inner ring of the mesogen, two alkoxy chains or a bifurcated chain.

Assuming the folding back of the bifurcated chain, we can expect some mesogenic properties for compounds having a chiral center in the lateral fragment. This mean conformation is expected to give some shape anisotropy to the molecule.

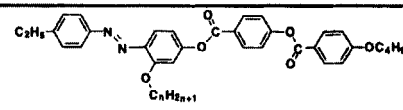
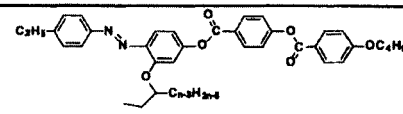
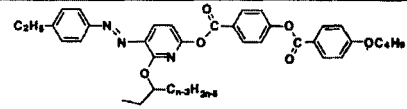
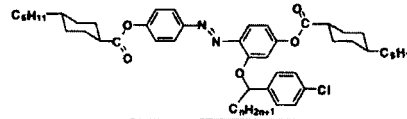
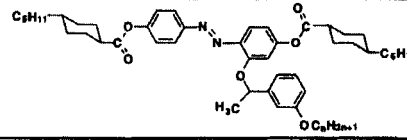
Series I n = 4, 7, 10	
Series II n = 4, 7, 10	
Series III n = 4, 7, 10	
Series IV n = 1, 2, 3, 4	
Series V n = 1, 4, 7, 10	

FIGURE 2 Structure of the five series of compounds. In series I, II and III, three compounds have been synthesized having 4, 7 or 10 carbons in the lateral chain. In series II and III, the bifurcated chain possesses an ethyl fragment. In series IV, the compound with n=4 was obtained with an enantiomeric excess.

Therefore, in this paper, we present the synthesis and the mesogenic properties of some racemic compounds containing four aromatic rings and having a bifurcated chain (series II and III). We also explore the possibility to replace one of the lateral bifurcated parts by a *para* or *meta* substituted benzylic fragment (series IV and V). In addition, the synthesis and the mesogenic properties of one optically enriched compound is presented. Series I has a linear lateral chain which contains the same number of carbon atoms than Series II and III in order to analyze the perturbation introduced by the bifurcated chain. Series II and III have a similar core than series I, the lateral chain has a chiral center with an ethyl fragment. In addition, series III has a pyridine ring instead of an aromatic ring. This pyridine ring was chosen to evaluate the steric effect of the hydrogen atom on the lateral chiral chain alignment. Three compounds have been synthesized in each series I, II and III containing 4, 7 and 10 carbons. Series IV and V have the same core length, but contain two aromatic rings terminated by two cyclohexyl substituents. They differ by the substitution of the lateral benzylic fragment and the length of the lateral chain.

RESULTS AND DISCUSSION

The different series were prepared according to a similar already published scheme [3,5,7]. The synthetic scheme for the chiral compound is detailed on Figure 3 and in the experimental appendix.

The structure and the purity of the intermediates and final products were checked using ^1H NMR on an AM 250 Bruker spectrometer, with $CDCl_3$ as solvent. The enantiomeric purity of the compound **C*** (Series IV, n = 4) was measured using the PBLG method [12]. 30 mg of solute (alcohol or the final cholesteric molecule) were dissolved in a mixture of 100 mg PBLG (mol wt 150000-300000 from Sigma) and 400 µl of CH_2Cl_2. Deuterium spectra of the intermediate alcohol and the final cholesteric **C*** molecules are presented on Figure 4. In a mixture of enantiomers, each isomer gives a doublet because they are differently oriented in the PBLG lyotropic medium.

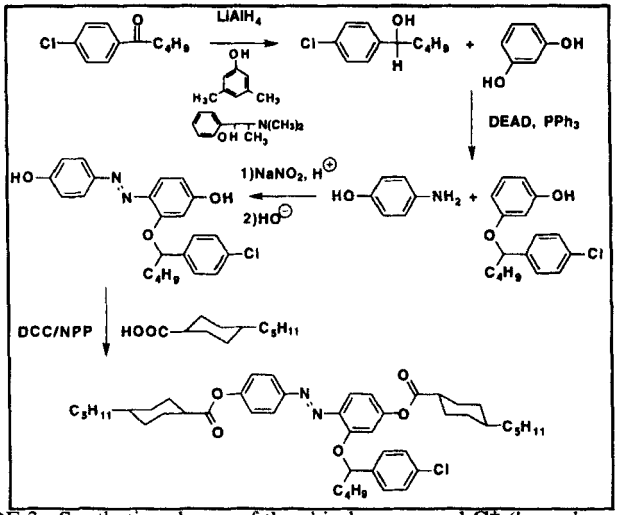


FIGURE 3 Synthetic scheme of the chiral compound **C*** (homologous to compound n=**4** in series IV). In the first step, a mixture of $LiAlH_4$ and $LiAlD_4$ was used to perform the asymmetric reduction in order to introduce some deuterium atoms on the chiral center. This deuterium atom was introduced to determine the enantomeric purity of the final compound.

We can note on Figure 4, that the final chiral molecule is more oriented than the starting benzylic alcohol molecule due to its elongated shape. But even if this large molecule dilutes the diastereoisomeric interaction with the PBLG lyotropic medium, enantiomers are still discriminated. Integration of the signals leads to the percentage of each enantiomer. For the final molecule, the lines of both enantiomers overlapp, thus, line shape fitting was used to give the enantiomeric excess. Following our synthetic procedure, the R enantiomer is preponderant for the benzylic alcohol (80% R, 20% S) [7] whereas the S enantiomer is preponderant for the cholesteric molecule and the ratio is inverted (80% S, 20% R). This proves the asymmetric efficiency in our synthesis of the Mitsunobu reaction [9].

The transition temperatures of the five series are given in Table 1. All compounds exhibit an enantiotropic nematic phase. Figure 5 compares the transition temperatures between the compounds belonging to series I, II and

III with respect to the total number of carbons in the lateral chain. In each series, the clearing temperatures decrease with the number of carbons in the chain; for the same carbon number in the chain, the clearing temperatures have the following order: series I > series II > series III.

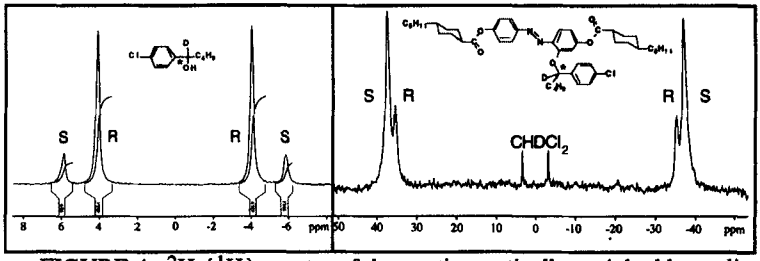


FIGURE 4 ^2H-{^1H} spectra of the starting optically enriched benzylic alcohol and the final cholesteric molecule C* obtained in the lyotropic mixture PBLG/CH_2Cl_2. Note in the second spectrum, the presence of two peaks assigned to $CHDCl_2$ arising from deuterium natural abundance.

TABLE 1 Transition temperatures (in °C) in the five series I, II, III, IV and V. These values were taken with increasing temperature (heating rate 10 °C/min).

Series/n	K	→	N	→	I	Series/n	K	→	N (or N*)	→	I
I/4	•	148	•	217	•	**IV/1**	•	75	•	195	•
I/7	•	143.5	•	185	•	**IV/2**	•	81	•	179	•
I/10	•	116	•	171	•	**IV/3**	•	95	•	175	•
						IV/4	•	91	•	149	•
II/4	•	117	•	201.5	•						
II/7	•	95.5	•	152.5	•	**C* IV/4**	•	90	•	176	•
II/10	•	113.5	•	135.5	•						
						V/1	•	63	•	188	•
III/4	•	147	•	176.5	•	**V/4**	•	82	•	174	•
III/7	•	93	•	133.5	•	**V/7**	•	89	•	149	•
III/10	•	67	•	98	•	**V/10**	•	88	•	115	•

The melting temperatures follow roughly the same evolution, but are less regular. The chiral chain does not induce a strong perturbation to the molecular arrangement in comparison with the linear chain. This means that certainly the two branches of the bifurcated chain certainly point towards

opposite directions as proposed in Figure 1. The short branch fills only the empty space created by the long branch without adding too much conformational disordering.

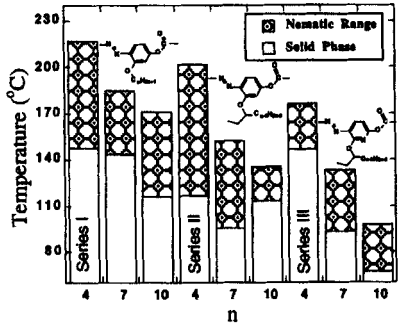


FIGURE 5 Comparision of the nematic ranges of the three mesogenic series I, II and III containing a linear or a bifurcated chain. The transition temperatures were measured by DSC (Mettler FP 52) using a heating rate of 10°C per minute.

Unfortunately, the introduction of the pyridine ring does not enlarge the nematic range as expected. This indicates that there is no steric interaction between the *ortho* hydrogen and the chain. It is interesting to note that the pyridine rings lower the melting temperatures resulting in a nematic mesophase near room temperature for the n=10 member of this series.

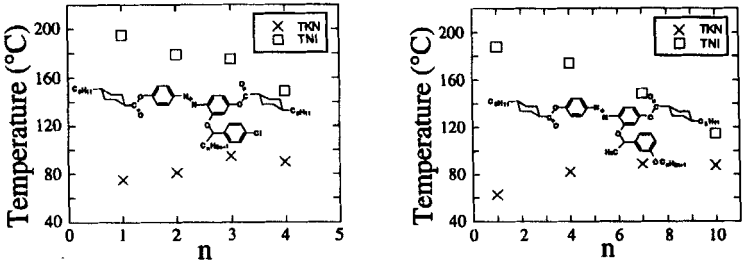


FIGURE 6 Nematic range of the two mesogenic series IV and V containing a lateral aromatic fragment. The transition temperatures were measured by DSC (Mettler FP 52) using a heating rate of 10°C per minute.

Series IV and V were synthesized in order to investigate the influence of the group's bulkiness in the vicinity of the chiral center on the transition temperatures. The introduction of the lateral aromatic ring does not perturb the nematic range in comparision with series II. If we compare the two first members of these two series, the position and the type of the ring substituent does not change the nematic range. As already proposed, for such complex structures, only large modifications can affect the type and the range of the mesophase with the interesting feature that the molecule can accomodate dipolar groups leading to a negligible effect on the mesophase stability. If we compare the chain position, the mesophase stability is increased when the chain belongs to the lateral ring. When the chain length increases on the chiral center, there is a competition between the orientation of the chain and the one of the aromatic ring. Due to the fact that both fragments are hooked on the same carbon, this competition has a deletorious effect on the mesophase. Anyway, the optically enriched fourth member of series IV, **C***, was obtained (20% R, 80% S). This compound presents a single cholesteric phase. The range of the cholesteric phase is enlarged by nearly 30°C compared to the nematic one of the racemic compound. This indicates the best packing obtained in the cholesteric phase.

CONCLUSION

As a conclusion, a chiral carbon can be introduced in a lateral position of a mesogenic core. A large nematic range is obtained for racemic compounds whatever is the substitution of the chiral carbon. For the optically enriched compound, a single cholesteric phase is obtained with a larger range of the mesophase than the racemic compound. Further investigations dealing with a chiral carbon in the lateral chain and one chiral center in the terminal chain are under way and will be reported elsewhere.

EXPERIMENTAL PROCEDURE

The asymmetric reduction of 4-chloroacetophenone was performed using the procedure described by Vigneron et al [8]. The reductive reagent was a mixture of $LiAlH_4$ and $LiAlD_4$ (80/20) in order to introduce a deuterium atom on the chiral center. A solution of (1R,2S) N-methylephedrine (0.06 mol) in anhydrous ether (300 mL) was added dropwise to a stirred solution of the reductive reagent ($LiAlH_4$/$LiAlD_4$ (80/20)) (0.06 mol) in anhydrous ether (69 mL) under nitrogen at room temperature, followed by the addition of a solution of 3,5-dimethylphenol (0.06 mol) dissolved in anhydrous ether (100 mL). The solution was stirred at room temperature during 2 hours, and was cooled to -15°C. A solution of 4-chlorovalerophenone (0.05 mol) in anhydrous ether (30 mL) was added dropwise in one hour to the reaction mixture. The solution was stirred at -15°C during one hour. After hydolysis with a solution of hydrochloric acid (6M), the mixture was extracted with three volumes of ether. Then, the ether was evaporated under reduced pressure to give the crude product which was purified by chromatography on silica with dichloromethane as eluent. The benzylic alcohol was obtained with a yield of 90% and a good enantiomeric purity (80% R, 20% S). Diethyl azodicarboxylate (0.045 mol) was added dropwise to a stirred solution of triphenylphosphine (0.045 mol) in THF (100 mL) under nitrogen at 0°C [9]. After 5 mn., the reaction mixture turned yellow-orange and, after being allowed to warm to room temperature, resorcinol (0.09 mol) was added, followed by addition of the chiral alcohol (0.045 mol). The resulting solution was stirred at room temperature during 19 hours and then the solvent was evaporated under reduced pressure [10]. Efficient stirring in Et_2O (50 mL) gave a fine precipitate which was removed by filtration. Then, the filtrate was evaporated under reduced pressure to give the crude product which was purified by chromatography on silica with dichloromethane as eluent. The product was obtained with a yield of 32%. In the course of the Mitsunobu reaction, the configuration of the asymmetric center is reversed (20% R, 80% S).

The diazotation was obtained in dioxane with one equivalent of diazonium salt (0.01 mol) and one equivalent of phenol (0.01 mol), in order to obtain the monodiazotated compound as the major component [3]. Then, the monodiazoted compound was purified by chromatography with a mixture of CH_2Cl_2/CH_3COOEt (80/20) as eluent. The esterification step was performed in dichloromethane using the dicyclocarbodiimide (DCC) method [11]. The *trans*-pentylcyclohexancarboxylic acid was added slighty in excess, in order to totally consume the phenol. After filtration of the amide and evaporation of the solvent, the crude mixture was chromatographed with CH_2Cl_2 as eluent and then recrystallized several times in chloroform/ethanol until constant transition temperatures were obtained.

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