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## Liquid Crystals

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# Nematogens incorporating a lateral flexible ring

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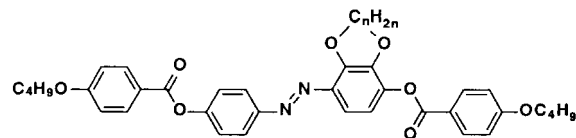
A lateral flexible ring can be introduced on a mesogenic core containing four rings. Lateral aliphatic rings containing up to 12 atoms have been synthesized. Despite this large lateral protruding substituent, a large nematic range is obtained. A compound with a benzo-15-crown-5 lateral ring has been successfully obtained and shows the possibility of designing nematic liquid crystals with a crown ether moiety at a lateral position.

## 1. Introduction

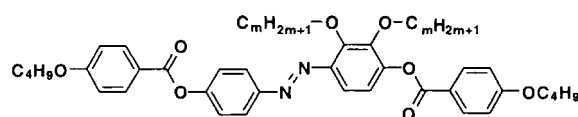
If the core of a mesogen molecule is large enough, it is possible to introduce flexible lateral substituents even if these compounds deviate from having the classical rod-like molecular shape [1]. In fact, if the core contains four rings (aromatic or alicyclic), two nearby neighbouring branches can be added on one of the inner rings without destroying the liquid crystal phase. In our systematic study, we have succeeded with several combinations of lateral fragments: two lateral alkoxy chains [2], one alkoxy chain and a benzyloxy fragment [3, 4] and two benzyloxy fragments [5]. In all these series, a large nematic range was obtained. The existence of the single enantiotropic nematic phase is due to the lateral fragments which space the molecules in the liquid crystal phase with the effect of decreasing the interactions between the cores which are usually considered as responsible for the appearance of more ordered phases. In the nematic phase, the lateral fragment has a peculiar mean conformation folded back along the core. This mean conformation preserves a non-negligible molecular anisotropy [6]. This lateral fragment does not therefore give a large conformational disordering as it is aligned along the rather rigid core. So, the possibility of introducing a more bulky flexible lateral fragment is of interest.

Therefore, in this paper, we will examine the possibility of introducing a new type of lateral fragment: a flexible ring. This flexible ring can incorporate mainly carbon atoms or ethyleneoxy fragments leading to the existence

of a crown ether lateral ring. Introducing crown ether fragments can lead to ionic liquid crystals by dissolving suitable salts in the mesophase. These mixtures may possess ionic conductivity properties in the liquid crystalline phase. Thus, we present the synthesis and the mesomorphic properties of some compounds with four rings in the main core and substituted by a lateral ring attached on one side of one of the inner rings (series **CCn** with  $n = 1, 2, 3, 4, 5, 6, 7$  and 8).



Series **CCn** ( $n = 1, 2, 3, 4, 5, 6, 7$  and 8)



Series **DiCm** ( $m = 1, 2, 3,$  and 4)

To compare the effect of the lateral ring, four related compounds with two lateral open chains having the same carbon numbers were synthesized (series **DiCm** with  $m = 1, 2, 3$  and 4). In addition, a compound **BC15** containing a benzo-15-crown-5 lateral ring was obtained to study the influence of the oxygen atoms contained in the lateral ring on the stability of the mesophase and the possibility of obtaining a liquid crystalline phase when a salt is dissolved in this compound.

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## 2. Experimental procedure

These new compounds were prepared according to the scheme shown below in figure 1:

The synthesis of the dialkylated phenols used in the coupling reaction involved the use of a mixture of polyethylene glycol ( $MW=200$ )/dioxan (30/70) as solvent and potassium bicarbonate as base in order to accomplish the etherification [7]. For the cyclized compound, the etherification was performed in two steps; the dibromide and pyrogallol (1:1) were mixed with 1.1 eq. of  $\text{KHCO}_3$  in a mixture of polyethylene glycol ( $MW=200$ )/dioxan (30/70) and kept under nitrogen at  $80^\circ\text{C}$  during 12 h. This leads mainly to monoalkylation on the 2-position of pyrogallol. Then, 1 eq of  $\text{K}_2\text{CO}_3$  was added to give the cyclization and the mixture was kept at the same temperature for a further 12 h. After evaporation of the dioxan, the mixture was acidified and shaken three times with ether. Then, the substituted phenol in the extract was purified by chromatography using a mixture of heptane/ $\text{CH}_2\text{Cl}_2$  (20/80) as eluent. As expected, the yield decreases with the chain length of the dibromide; for example in the case of dibromo-octane a yield of 12% was obtained after chromatography.

The diazotation step was achieved in dioxan and the resulting phenol was purified by chromatography with  $\text{CH}_2\text{Cl}_2$  as eluant. The esterification step was carried out in chloroform with the acid chloride, using pyridine as base. The final compound was purified by chromatography using a mixture of heptane/ $\text{CH}_2\text{Cl}_2$  (20/80) as eluant. After this purification, the compounds were recrystallized from chloroform/ethanol (30/70) until constant transition temperatures were obtained.

For compound **BC15**, the cyclization was obtained using the Pedersen procedure [8]. The further steps

were conducted in a similar way to those described above, with the exception of the chromatographic eluant which was pure ethyl acetate for the azophenol and a mixture of ethyl acetate/ $\text{CH}_2\text{Cl}_2$  (50/50) for the azo ester.

The structure and the purity of the products were checked by  $^1\text{H}$  NMR using an AM 250 Bruker spectrometer and the molecular masses were confirmed by high resolution mass spectrometry.

The mixtures between **BC15** and  $\text{LiBF}_4$  salt were obtained by dissolving both components in boiling THF. The solvent was then evaporated and the resulting solids were dried under vacuum for several hours at  $80^\circ\text{C}$ .

## 3. Results and discussion

Phase transitions were observed and characterized by using an Olympus polarizing microscope fitted with an FP 82 Mettler heating stage and an FP 85 Mettler DSC.

The transition temperatures for the different compounds are given in the table. These measurements were made using the previously unmelted sample. The **CCn** compounds are rather unstable on reaching the isotropic phase, and the  $T_{N1}$  transition temperature decreases constantly on further heating cycles. The compound **CC1** exhibits a large exothermal peak (corresponding to an approximate enthalpy of  $-210\text{ kJ mol}^{-1}$ ) at the clearing temperature indicating that a chemical reaction occurs at this temperature.

All the compounds exhibit a surprisingly large range enantiotropic nematic phase. Introducing a lateral ring does not destroy the stability of the mesophase, even if this ring markedly protrudes from the long rod-like core. Figure 2 shows a comparison of the transition temperatures for **CCn**, **DiCm** and **BC15**.

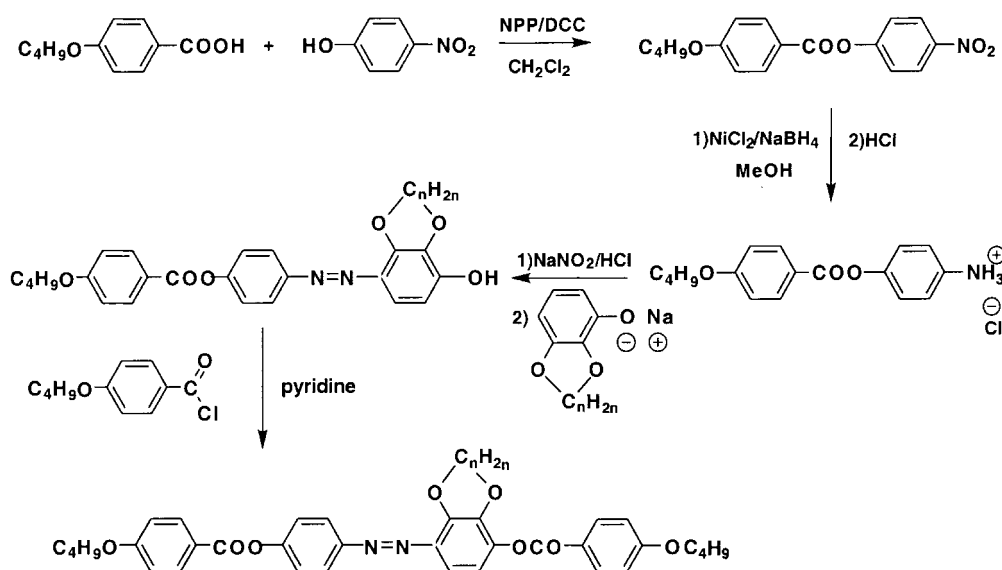


Figure 1. Synthetic scheme for the **CCn** series.

Table. Transition temperatures of the synthesized compounds measured with increasing temperature ( $10^{\circ}\text{ min}^{-1}$ ).

| Compound | Cr | →     | N | →          | I |
|----------|----|-------|---|------------|---|
| CC1      | •  | 138   | • | 331* (dec) | • |
| CC2      | •  | 164   | • | 319        | • |
| CC3      | •  | 143   | • | 308        | • |
| CC4      | •  | 143   | • | 296        | • |
| CC5      | •  | 141.5 | • | 272        | • |
| CC6      | •  | 151   | • | 276        | • |
| CC7      | •  | 140   | • | 258        | • |
| CC8      | •  | 149.5 | • | 242        | • |
| DiC1     | •  | 137.5 | • | 318        | • |
| DiC2     | •  | 78.5  | • | 260        | • |
| DiC3     | •  | 103   | • | 227        | • |
| DiC4     | •  | 94    | • | 217        | • |
| BC15     | •  | 133   | • | 229        | • |

\* The  $T_{N1}$  temperature was obtained by microscopic measurement: (dec)= decomposition.

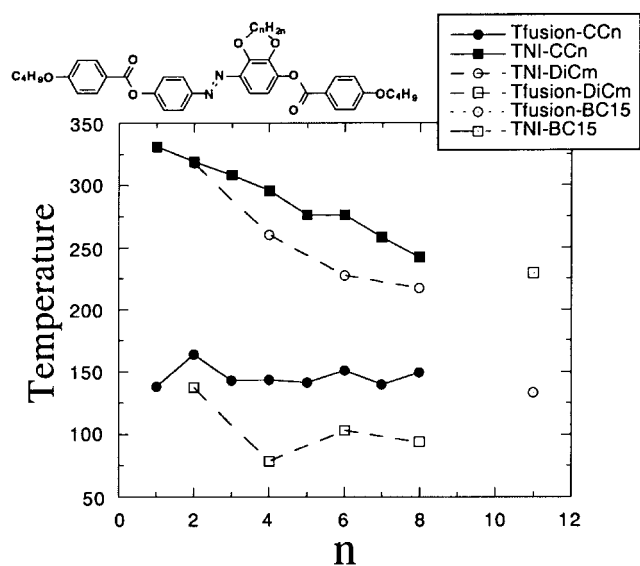


Figure 2. Plot of the transition temperatures of the **CCn**, **DiCm** series and compound **BC15**.

Using a cycle instead of two lateral chains leads to a more stable nematic phase. This behaviour can be explained by the lower mobility of the lateral ring. The melting temperatures are also lower for series **DiCm** compared to series **CCn**, and this may be interpreted in terms of conformational effects and the size of the lateral substituents. In the solid phase, we have found for some related compounds that for short lateral chains, these chains are folded back along the core partially masking the core–core interactions in the solid phase. The two chains overlap a larger fraction of the core and dilute the interactions between molecules in the solid phase better than the lateral ring.

The melting temperatures of the **CCn** series are fairly constant when the number of carbons is increased in the lateral ring. It appears that a small odd–even effect is observed and this may reflect the different arrangements in the solid phase when the lateral ring has an odd or even carbon number. It appears that there are two regimes in the clearing temperature decrease for the **CCn** in figure 2. Going from **CC1** to **CC4**, the size of the lateral ring does not perturb the stability of the meso-phase to a large extent. After compound **CC5**, this decrease is more important, reflecting the impact of ring flexibility on the phase stability. In fact, compound **CC6** possesses a higher clearing temperature than **CC5** despite the larger ring, indicating that for large ring sizes an odd–even effect on the clearing temperature occurs. This effect levels off with higher members.

The influence of the carbon number in the lateral ring is also shown by the different thermal behaviour on heating cycles for compounds containing an odd or even number of carbon atoms in the lateral ring. As an example, the two DSC curves for compounds **CC5** and **CC6** are given in figure 3. In compounds containing an even number of carbons (with the exception of **CC1**) in the lateral ring, a small exothermal peak is observed just before the solid–nematic transition which could reflect an exothermal change in the conformation of the lateral ring. This behaviour is also observed on the second run. In compounds containing an odd number, the first and second runs are completely different, showing after crystallization and reheating, a melting temperature lower than the one observed for the unmelted sample and indicating the formation of another solid form. If the sample is left at room temperature for a longer period, the initial DSC curve is again observed (with the exception of a continuous slight decrease of the clearing temperature which indicates a tendency to decomposition at high temperatures).

We have shown recently the possibility of obtaining fluid nematic phases with a terminal crown ether moiety through the use of lateral alkoxy chains [9]. These lateral chains were introduced to obtain reasonable melting temperatures and to diminish the interactions between the core responsible for the more ordered phases usually encountered in the case of crown ether-containing liquid crystals [10]. Therefore, we have tried to combine the two effects by introducing the crown ether moiety at a lateral position with no other lateral substituent. This compound (**BC15**), which contains 15 atoms in the lateral ring, still has a very large nematic range (figure 4). In figure 2, the transition temperatures nearly fit the trends observed in the **CCn** series.

Crown ether-containing liquid crystals are interesting due to their ability to complex suitable cations, leading

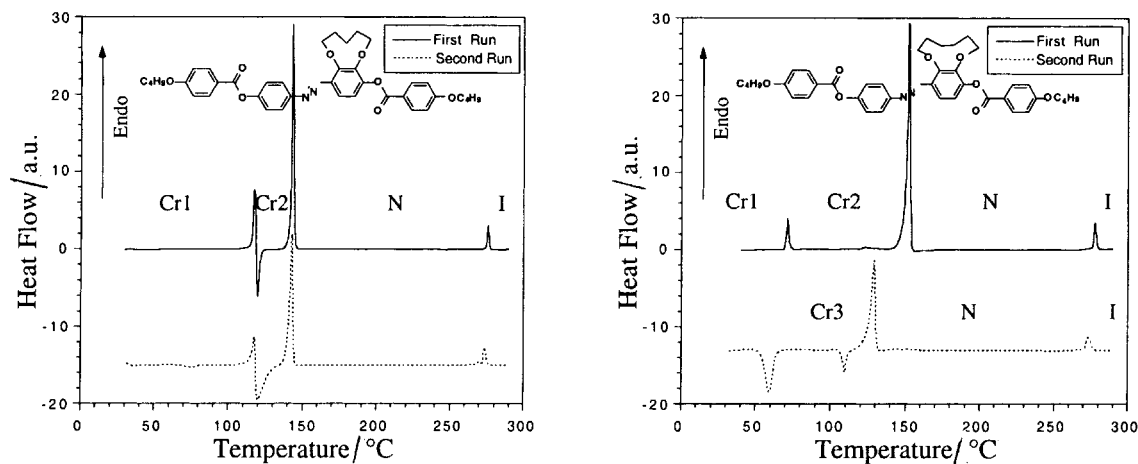


Figure 3. DSC curves of **CC5** and **CC6**. The first runs were obtained from the unmelted samples with a heating rate of  $15^{\circ}\text{C min}^{-1}$ . The second runs were recorded with the same heating rate after cooling ( $-15^{\circ}\text{C min}^{-1}$ ) and waiting for 5 min at room temperature.

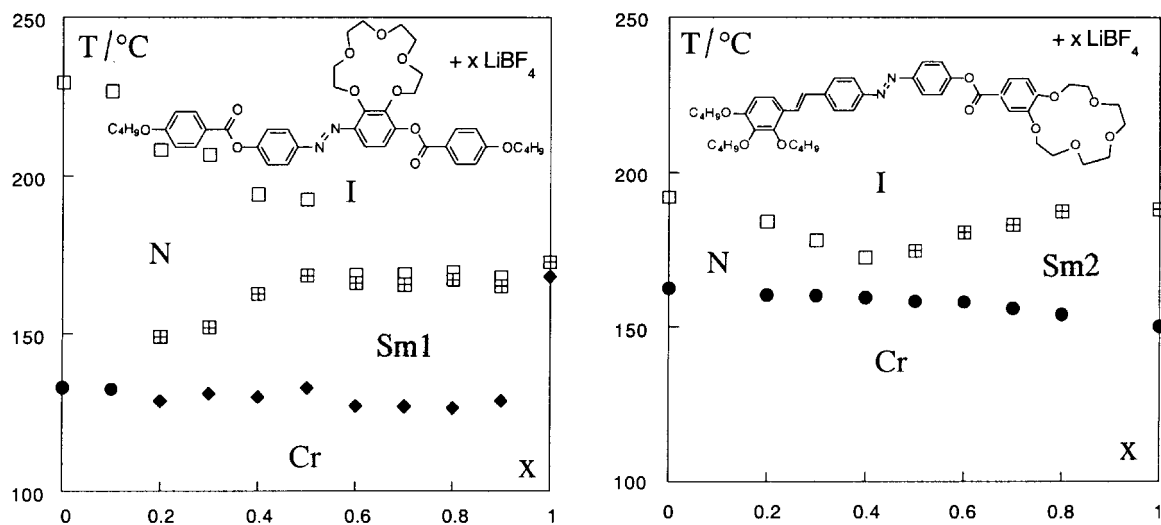


Figure 4. Phase diagrams for **BC15** and **CH4A** mixed with  $x$  molar equivalents of  $\text{LiBF}_4$ .

to the dissolution of inorganic salts in the organic anisotropic medium. These mixtures will certainly possess some ionic conductivity and the position of the complexation site within the core is evidently of prime importance. In fact, introducing the crown ether ring at the end of the rod or at a lateral position may lead to different properties of the liquid crystal phase, such as variation in the ionic conductivity. In addition, a terminal ring increases the anisotropy of the core, and lateral substituents are needed to obtain reasonable melting temperatures [9]. In the case of the lateral ring, this problem is not encountered; as the ring protrudes from the core, it plays itself the role of lateral substituent, decreasing the melting temperature and helping to generate the nematic phase. We can also expect a better interaction of the complexed crown ether rings in the

nematic phase due to some partial alignment of the ionic channels. Figure 4 gives the phase diagrams between  $\text{LiBF}_4$  and **BC15** ( $x$  is the molar equivalent of  $\text{LiBF}_4$ ) and a similar compound **CHA4** having a terminal crown ether moiety. The two phase diagrams are quite different. In the **BC15** diagram, for  $x \leq 0.5$ , the nematic range diminishes continuously, while conversely the smectic range increases. For  $x > 0.5$ , the smectic phase is predominant. In the **CHA4** diagram, the nematic phase exists for  $x < 0.5$  and the smectic phase for  $x > 0.5$ . The range of the smectic phase then increases with the percentage of salt, whereas it stays rather constant in the **BC15** diagram for  $x > 0.5$ . The disappearance of the nematic phase for  $x > 0.5$  may indicate that the stoichiometry of the complex is 2 crown ethers for one Li cation. For  $x > 0.5$ , the salt still dissolves in the mixture and

the stoichiometry of the complex may change. In addition, the two smectic phases Sm1 and Sm2, which were not identified, are non-miscible and seem to be different in their structures.

#### 4. Conclusion

We have shown that when a lateral flexible ring is introduced on the inner ring of a main core containing four aromatic rings the liquid crystalline properties are preserved and a large nematic range is obtained. This mesophase is more stable than for the analogous compounds having two identical alkoxy chains. Also, a wide range nematic phase is obtained for a compound having a lateral crown ether moiety. This compound dissolves a large proportion of  $\text{LiBF}_4$ . A nematic phase is obtained up to a 0.5 equimolar amount of  $\text{LiBF}_4$ , after which a more ordered phase appears. Compounds having more than one crown ether moiety within the structure have been obtained and results on their properties will be reported elsewhere.

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