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## Liquid Crystals

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# Ordering of a lateral crown ether and terminal short POE chains in some symmetrical nematogens by $^{13}\text{C}$ NMR

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A lateral crown ether fragment can be introduced on symmetrical mesogens containing only three aromatic rings. The replacement of the terminal alkoxy chains by chains containing oxyethylene units decreases the melting and clearing temperatures allowing one to obtain nematic compounds near room temperature. These compounds dissolve  $\text{LiBF}_4$  salt only to a small extent, but the nematic arrangement, is thereby destroyed. The carbon chemical shift anisotropy and the local C–H bond order parameters were obtained for the nematic phase for the crown ether fragment and the terminal chains. This study indicates that the crown ether average conformation changes insignificantly on decreasing the temperature. The lateral crown ether protrudes markedly from the core with the consequence that the molecular shape is far from rod-like in geometry.

## 1. Introduction

Liquid crystals containing the oxyethylene (OE) unit in polyoxyethylene (POE) chains or crown ether motifs are new materials which possess the unique feature of dissolving ionic salts and still presenting a mesophase [1–4]. They combine two interesting properties: the anisotropy of the liquid crystal phase and also the potential for ionic conductivity as POE chains have [5–8]. Therefore, adding POE chains to a nematogenic structure can lead to monodirectional conductivity properties.

In pure POE polymers containing lithium salts, the ionic conductivity is a maximum for a ratio  $\text{Li}/(\text{number of OE units})$  of 0.1 [5–7]. Thus, it is advisable to synthesize liquid crystals with the maximum number of OE units. Unfortunately, if the OE units are introduced as terminal chains, ordered phases are obtained for a relatively small number of OE units. A possible alternative is to introduce some of these units at a lateral position. In fact, when the core anisotropy is rather large, one or two nearby lateral flexible substituents can be introduced in a molecule without destroying the

mesogenic properties. These lateral substituents can be alkoxy chains, substituted benzyloxy fragments or even lateral alkane rings [8–10]. The choice of a lateral ring is of interest as this can increase the thermodynamic stability of the mesophase. This means in effect that for equivalent cores a lateral ring leads to a higher clearing temperature than do two lateral alkoxy chains containing the same number of carbons as the ring [8–10].

The possibility of introducing a lateral crown ether has been successfully explored and a nematic phase was obtained with compounds containing four rings in the main core [10, 11]. In fact, lateral flexible substituents were shown to adopt a peculiar conformation folded back along the core, preserving the favourable molecular anisotropy and packing needed for the thermodynamic stability of the mesophase. It is certainly more difficult for a lateral ring to adopt a favourable conformation in the liquid crystal phase. Two of the major questions concern knowing the conformation of the lateral ring in the liquid crystalline phase and whether this conformation stays constant or is affected by the nematic field on decreasing the temperature. These questions can be answered by the study of the ordering properties of

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these compounds by  $^{13}\text{C}$  NMR [12, 13]. For this type of study, it is preferable to have compounds which possess clearing temperatures below  $100^\circ\text{C}$  and are symmetrical, leading to fewer signals in the spectrum and making the analysis easier.

Therefore in this paper, we describe the synthesis and the mesomorphic properties of several compounds possessing the same core, containing only three aromatic rings, and laterally substituted by a lateral 15-crown-5 and having alkoxy or POE terminal chains which contain 1, 2 or 3 OE units. The compounds depicted in figure 1 are symmetrical and some of them have a clearing temperature below  $100^\circ\text{C}$ . The solvation of  $\text{LiBF}_4$  salt into the nematic phase of these compounds was also investigated.

The ordering behaviour of the carbons in the OE units has been determined by measurement of the C–H dipolar couplings using the  $^{13}\text{C}$  2D-SLF method [14] and by analysis of the chemical shift evolution [15] in the compound CINPOE1Bu. The correlation between the order parameter and the chemical shift evolution allows us to check change in the conformation of the lateral ring [11, 16].

## 2. Results and discussion

### 2.1. Synthesis

The general synthetic scheme for the compounds of series CINPOEm containing 1, 2 or 3 OE units in the terminal chains is summarized in figure 2. As an example, we describe the synthesis of compound CINPOE1. 3-Hydroxybenzo-15-crown-5 was prepared by selective etherification of 1,2,3-trihydroxybenzene in ethanol following the Pedersen procedure [17]. After chromatography in  $\text{CH}_2\text{Cl}_2$ /ethyl acetate (50/50), the phenol was coupled under basic conditions with the diazonium salt prepared from sulphanic acid. The mixture was acidified and  $\text{SnCl}_2$  added to reduce the azo bond. After heating this mixture for 1 h at  $80^\circ\text{C}$ , it was cooled and the insoluble materials were filtered off. Sulphuric acid was added and then a slow addition of sodium dichromate was carried out to oxidize the amino group. The mixture was then extracted several times with chloroform. After solvent evaporation, the crude quinone was purified by chromatography using  $\text{CH}_2\text{Cl}_2$ /MeOH (94/6) [18–20]. The purified quinone was dissolved in acetonitrile and reduced with sodium dithionite dissolved in water at room temperature. After solvent evaporation,

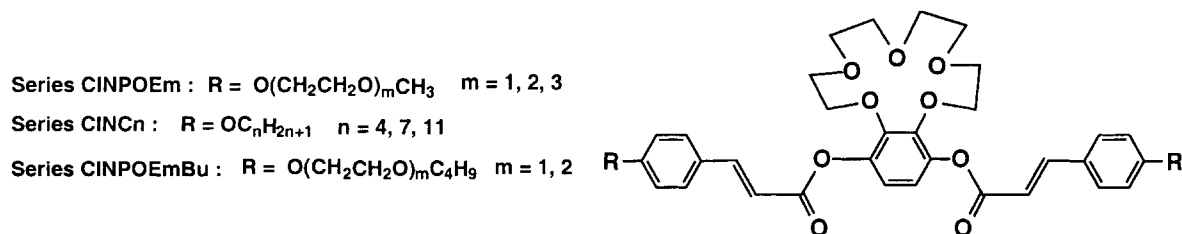


Figure 1. Different symmetrical series containing a lateral crown ether.

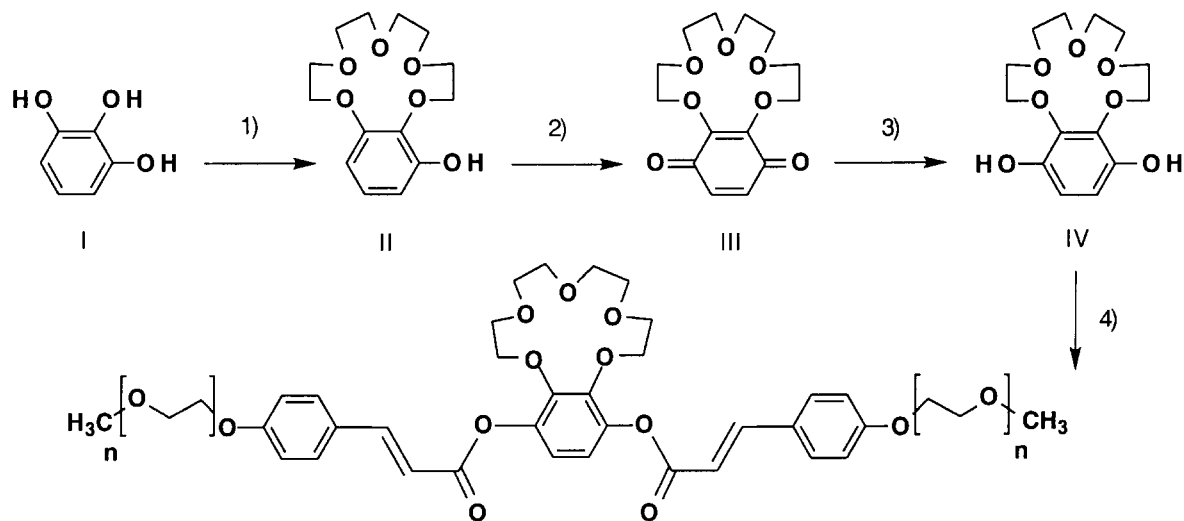


Figure 2. Synthetic scheme for the CINPOEm series. (1) i,  $\text{ClCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{Cl}$ , **I**, EtOH; ii, NaOH; iii, HCl (6M). (2) i, sulphanic acid, HCl conc,  $\text{NaNO}_2$ ,  $\text{H}_2\text{O}$ ; ii, **II**, NaOH,  $\text{H}_2\text{O}$ ; iii,  $\text{SnCl}_2$ , HCl,  $\text{H}_2\text{O}$ ; iv,  $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ . (3) **III**,  $\text{CH}_3\text{CN}$ ,  $\text{Na}_2\text{S}_2\text{O}_4$ ,  $\text{H}_2\text{O}$ . (4) **IV**, pyr,  $\text{RCOCl}$ ,  $\text{CHCl}_3$ .

the slurry was extracted with chloroform. The diphenol obtained was pure enough for the next step, but if necessary could be purified by chromatography, eluent  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (92/8). The 4-[methoxy(ethoxy)]cinnamic acid was obtained from the aldehyde using a conventional procedure [21] and recrystallized from acetonitrile. In the last step, the diphenol was esterified with the 4-substituted cinnamoyl chloride in  $\text{CHCl}_3/\text{pyridine}$  (50/50) as solvent. The final mesogen was chromatographed twice with  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (90/10) mixture on silica gel (60–220 mesh). Finally, the solid mesogens were recrystallized from  $\text{CHCl}_3/\text{ethanol}$  mixture until constant transition temperatures were obtained.

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

$\delta$  ( $^1\text{H}$ , 250 MHz,  $\text{CDCl}_3 + \text{pyridine-d}_5$ ) (ppm, (integration, multiplicity)). **II**: 3.74 (8H, broad), 3.88 (2H, AA'BB'), 3.99 (2H, t), 4.16 (2H, AA'BB'), 4.28 (2H, t), 6.44 (1H, dd), 6.57 (1H, dd), 6.88 (1H, t). **III**: 3.68 (8H, s), 3.82 (4H, t), 4.51 (4H, t), 6.48 (2H, s). **IV**: 3.71 (8H, s), 3.94 (4H, t), 4.27 (4H, t), 5.48 (2H, broad s), 6.61 (2H, s). CINPOE1: 3.48 (6H, t), 3.69 (8H, s), 3.81 (4H, AA'BB'), 3.83 (4H, t), 4.20 (4H, AA'BB'), 4.28 (4H, t), 6.53 (2H, d), 6.91 (2H, s), 6.93 (4H, AA'BB'), 7.54 (4H, AA'BB'), 7.84 (2H, d). Mass (high resolution):  $m/z$  731.26778 ( $\text{C}_{38}\text{H}_{44}\text{NaO}_{13}$ ,  $\Delta = 0.2$  ppm).

The mixtures with the salt  $\text{LiBF}_4$  were prepared by dissolving both materials in dry THF under an inert atmosphere (typically 100 mg of the mesogen with the appropriate mass of the salt). The solvent was then evaporated under inert atmosphere and with mechanical stirring at the boiling point of THF. Then, the mixtures were kept in an oven at  $100^\circ$  for several days.

## 2.2. Transition temperatures of the mesogens

The 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 are given in table 1. All the compounds exhibit an enantiotropic liquid crystal phase as shown in figure 3, with the exception of CINPOE0 and CINPOE3 which have monotropic phases. All the compounds give a supercooled nematic phase over a reasonable range of temperature which makes NMR measurements feasible.

It should be noted that the analogous compound to CINC4 obtained by replacing 4-butoxycinnamic acid by 4-butoxybenzoic acid presents no enantiotropic nematic phase. This is clear evidence for the need for an elongated core to support the packing perturbation introduced by the lateral crown ether.

Table 1. Transition temperatures (in  $^\circ\text{C}$ ) of some related compounds having one or two POE terminal chains and a lateral crown ether. These values are taken with increasing temperature (heating rate  $10^\circ\text{C min}^{-1}$ ).

Compound	Cr	→	N	→	I
CINPOE1	•	127	•	141	•
CINPOE2	•	73	•	85	•
CINPOE3	•			32	•
CINC1	•			185	•
CINC4	•	140	•	164	•
CINC7	•	122	•	147	•
CINC10	•	102	•	125	•
CINPOE1Bu	•	75	•	90	•
CINPOE2Bu	•			65	•

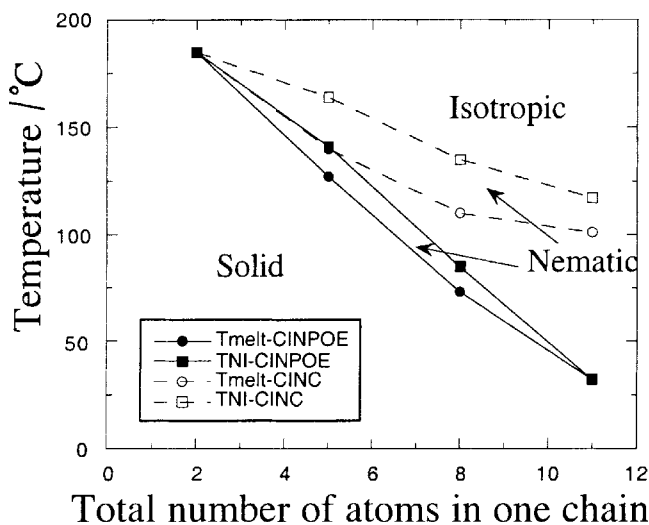


Figure 3. Plot for the transition temperatures in compounds containing a lateral crown ether fragment and terminal alkoxy chains (series CINC $n$ ) or terminal short POE chains (series CINPOE $m$ ).

We have shown recently in conventional mesogens that the replacement of carbons by one OE unit within the terminal chain decreases the melting and clearing temperatures, keeping the nematic range quite unaffected [15]. This behaviour is clearly seen on figure 3 and is enforced in the case of two terminal chains. This trend was interpreted as an effect of the *gauche*-conformation taken by OE units in the solid phase. This conformation of each unit leads to a helicoidal arrangement for the chains. The consequence is rather simple: these chains

occupy a larger volume than the usual alkyl or alkoxy chains which adopt in the solid phase an all-*trans*-conformation. In the solid phase, this helicoidal conformation and the presence of lateral substituents induce a slight decrease in the core–core interactions leading to a lowering of the melting temperatures. In the liquid crystal phase and especially in laterally substituted compounds, the preferred *gauche*-conformation does not perturb to a large extent the thermodynamic stability of the mesophase.

By comparing CINPOE3, CINPOE2Bu and CINC10, which have the same number of atoms within the terminal chains, we can note that the decrease in the melting temperatures is related to the number of OE units. This is contradictory to what has been observed for compounds having two lateral hexyloxy chains [16]. In these compounds, the major decrease in the melting temperature was induced by the first OE unit within the terminal chain. This different behaviour may be related to the larger volume of the crown ether lateral fragment.

### 2.3. Behaviour of the salt mixture

Adding LiBF<sub>4</sub> salt (in the range 0.05 to 0.5 molar equivalent) to all the compounds, with or without POE chains, destroys their enantiotropic liquid crystal phases. This behaviour is different from that observed for compounds having a lateral crown ether hooked onto a four ring core [10]. This is very surprising, as the only differences between the two series are the *para*-substituents on the aromatic ring bearing the lateral crown and the length of the rod.

DSC measurements indicate that the mixtures with LiBF<sub>4</sub> melt at a temperature very near the clearing temperature of the starting organic molecule. Cooling slowly, this mixture leads to a heterogeneous mixture which undergoes vitrification at a temperature depending on the amount of salt and on the temperature ramp used. This behaviour is reproducible on further heating/cooling cycles.

In mixtures containing large amounts of salt, it can be seen by optical microscopy that some insoluble ionic material is present in the liquid phase just after the isotropization temperature. On further heating, when the salt concentration is low enough, the ionic material dissolves. On cooling, the sample then looks like a glass after vitrification.

<sup>13</sup>C and <sup>7</sup>Li NMR have been used to explore the static mixture of CINPOE2/LiBF<sub>4</sub> (1/0.2). On decreasing the temperature from the melt, the <sup>13</sup>C NMR spectrum stays isotropic. Lines for the different carbons gradually broaden (this effect is faster in the aromatic region) with no anisotropic shift at all, indicating again that no liquid crystal phase is present in the sample. At lower temperatures, the signal disappears, indicating glass formation.

The results obtained with <sup>7</sup>Li NMR are similar. The spectrum contains a single line at any temperature where the sample contains some fluid parts. At least, this indicates that some salt is dissolved in these parts. During the cooling process, this isotropic line broadens and fades away.

Finally, LiBF<sub>4</sub> salt can be introduced into the melt of the mesogens as an ionic solute when the concentration of this salt is rather small (the amount depending on the compound). After this limit, no more salt dissolves. In all cases, the liquid crystal properties are lost for the mixtures studied. This may be due to two factors. (1) The conformation of the crown ether cavity induced by the two surrounding carboxylate groups; this peculiar cavity may not be suitable for complexing the Li<sup>+</sup> cation. (2) The change in local geometry of the mesogen induced by the complexation; the short length of the rod may not be sufficient to counterbalance the deleterious effect of the dissolved salt on the molecular geometry.

### 2.4. <sup>13</sup>C NMR measurements on one pure nematogen

We chose to study by NMR the compound CINPOE1Bu which possesses only one OE unit in the terminal chain, in order to have fewer signals in the OCH<sub>2</sub> region. The <sup>13</sup>C experiments were performed using a Bruker DSX-300 NMR spectrometer at  $B_0 = 7.05$  T on the static sample. The 1D spectra were obtained near the isotropic–nematic transition using a single pulse, and for lower temperatures the cross-polarization sequence with strong decoupling was used. To avoid rf overheating, a 15 s delay time was used. The temperature calibration was made by observing the nematic to isotropic transition. The chemical shift calibration was made by assuming that the terminal methyl group has the same chemical shift in the melt and in the case of the isotropic spectrum obtained in CDCl<sub>3</sub> solution. Three spectra for CINPOE1Bu are displayed in figure 4: (a) in the solid phase (after preliminary melting and cooling of the sample), (b) in the isotropic melt and (c) in the nematic phase.

The spectrum of the solid phase obtained before (not presented) and after melting, figure 4(a) presents no large differences compared with that observed for the isotropic phase, indicating for instance that the conformation of the crown ether lateral fragment does not change greatly in the crystallized sample, in the sample solidified in the magnet and in the melt sample.

On the contrary, the effect of the orientation of the nematic sample ( $\Delta\chi > 0$ ) in the magnetic field is obvious. In the 100–200 ppm region, the usual positive chemical shift is observed for the core carbons belonging to the aromatic rings and the carboxyl groups. The 50–90 ppm aliphatic region containing the CH<sub>2</sub>O signals is more surprising, as we can see that many peaks in that region

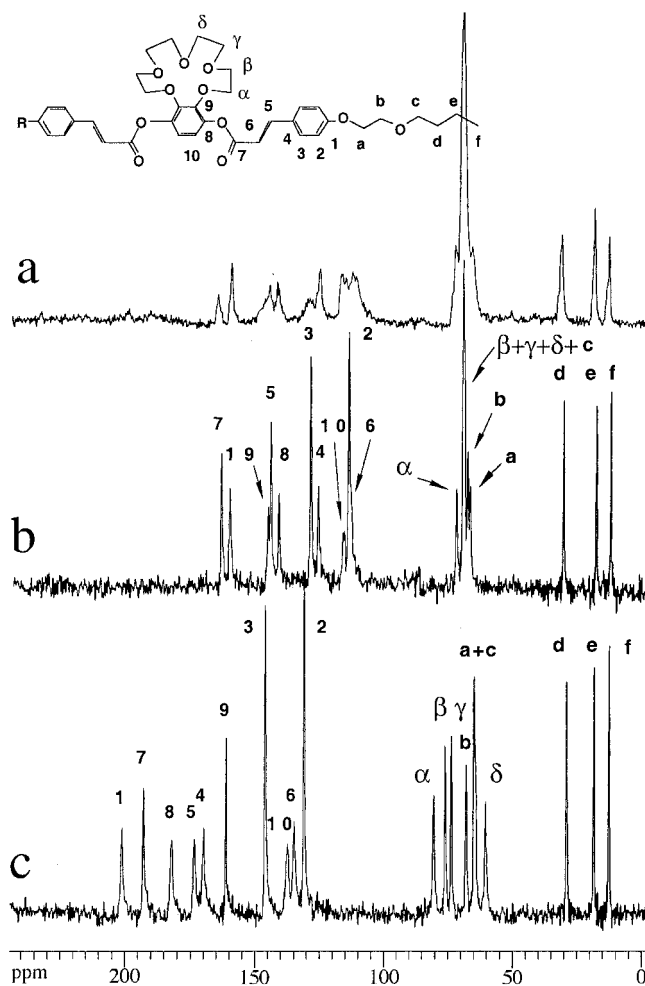


Figure 4. Proton decoupled  $^{13}\text{C}$  spectra of pure CINPOE1Bu at 75.475 MHz: (a) in the solid phase after melting of the sample (r.t.), (b) in the isotropic phase ( $T/T_{\text{NI}} = 1.02$ ), and (c) in the nematic phase ( $T/T_{\text{NI}} = 0.983$ ). Acquisition parameters: static sample, single pulse, pulse width =  $3\ \mu\text{s}$ , recycle delay = 15 s, number of scans = 128.

are overlapping in the isotropic spectrum, but are quite spread in the nematic phase (some peaks present a positive shift, some a negative shift), indicating the differential ordering of these carbons. We will return to this behaviour in the next paragraph.

#### 2.4.1. Chemical shifts assignment

The isotropic chemical shifts for the different compounds in  $\text{CDCl}_3$  solution were assigned using the group contribution method, the  $J$  coupling pattern, HMBC and HMQC 2D experiments. The assignment of the OE unit carbons in  $\text{CDCl}_3$  solution is given for some compounds in table 2. In the crown ether fragment,  $\text{C}\alpha$  has a rather constant chemical shift of  $72.9 \pm 0.2$  ppm and the other three carbons have similar chemical shifts of  $70.6 \pm 0.3$  ppm. It has been noticed that in *p*-POE-

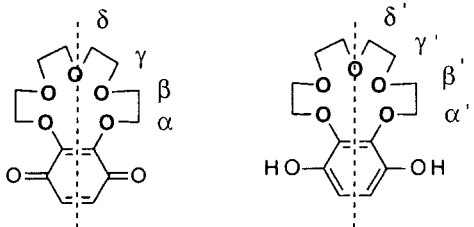
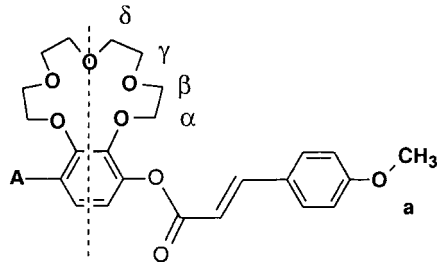
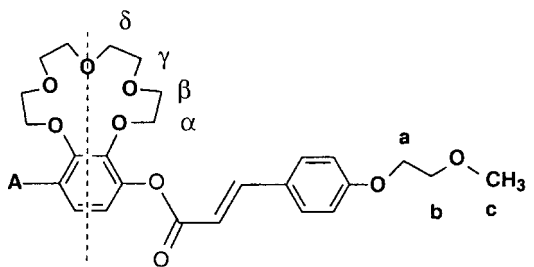
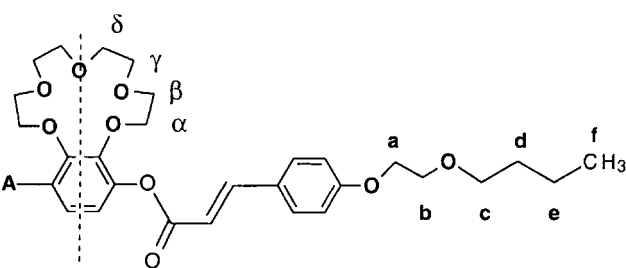
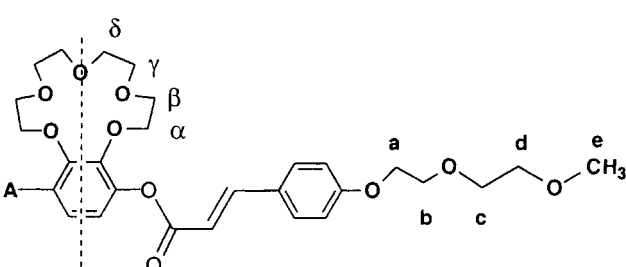
substituted benzoic acids or benzoate esters, there is in the first unit a very weak influence of the substituents in the  $\gamma$  and  $\delta$  positions on the isotropic chemical shifts [22]. Thus,  $\text{C}\alpha$  and  $\text{C}\beta$  isotropic chemical shifts were found in numerous compounds (containing the benzoate fragment) to be equal to  $68.7 \pm 0.2$  ppm and  $69.8 \pm 0.2$  ppm, respectively. Here, the first unit experiences the influence of the double bond linked to the carboxylate group and the ring; this influence modifies noticeably the  $\text{C}\alpha$  chemical shift average value ( $67.5 \pm 0.2$  ppm), but has less effect on the  $\text{C}\beta$  average value ( $69.8 \pm 0.2$  ppm).

In the spectrum of the melt, figure 4(b), only four peaks are seen ( $\delta = 72.7, 70.3, 68.5, 67.6$  ppm).  $\text{C}\alpha$  can be assigned to the most deshielded signal, and the three other carbons in the crown ether have the same chemical shift and are overlapped in the next peak with  $\text{C}\gamma$ . The two last shielded signals can be attributed to  $\text{C}\beta$  and  $\text{C}\delta$ , respectively.

In the aliphatic part of the nematic spectrum presented in figure 4(c), on going from the isotropic melt to the nematic phase, three lines experience a large positive jump in the chemical shifts. This positive jump has been associated in laterally substituted compounds with the peculiar conformation of the first  $\text{OCH}_2$  fragment. The folding back of the lateral chains induces a positive order parameter for the first carbon in the lateral alkoxy chain [23]. In contrast, carbons belonging to a terminal chain or to the far parts of the lateral chains experience a negative jump due to the peculiar mean orientation of their  $\text{C-H}$  bonds with respect to the molecular long axis. It seems reasonable to assign these three positive jumps to  $\text{C}\alpha$ ,  $\text{C}\beta$ ,  $\text{C}\gamma$ . Therefore  $\text{C}\delta$  should present a negative jump. We have shown recently that the carbons in the OE unit have a very unusual flat behaviour alignment-induced shift [16]: specifically,  $\text{C}\beta$  exhibits a very small jump. This unusual behaviour begins with a decrease of the chemical shift just after the transition followed by a tiny increase on decreasing the temperature. We have also noted in the case of several OE units, for example when two units are present, that the first carbon ( $\text{C}\alpha$  or  $\text{C}\gamma$ ) in each OE unit has a larger jump than the second one in the same unit ( $\text{C}\beta$  or  $\text{C}\delta$ ). Accordingly, we have assigned the larger negative jump to  $\text{C}\delta$  inside the crown ether fragment.

The assignment of the lines in the aromatic region is somehow easier. In conventional mesogens, the quaternary carbons which are lying along the molecular long axis have the largest anisotropy due to the particular position of the *para*-axis with respect to the frame of the chemical shift tensor. The quaternary carbon in the *ortho*-position with respect to the molecular long axis has much less chemical shift anisotropy. Among the five deshielded signals we find the three quaternary carbons lying on the molecular long axis  $\text{C}1$ ,  $\text{C}4$  and  $\text{C}8$ , the carboxylate

Table 2.  $^{13}\text{C}$  isotropic chemical shifts of the  $\text{OCH}_2$  carbons in some related compounds containing the crown ether fragment.

Molecule	Chemical shift/ppm
	$\delta_\alpha = 73.02$ $\delta_\beta = 70.86$ $\delta_\gamma = 70.71$ $\delta_\delta = 70.30$ $\delta_{\alpha'} = 73.79$ $\delta_{\beta'} = 71.18$ $\delta_{\gamma'} = 71.50$ $\delta_{\delta'} = 71.88$
	$\delta_\alpha = 72.92$ $\delta_\beta = 870.72$ $\delta_\gamma = 70.38$ $\delta_\delta = 70.28$ $\delta_a = 55.24$
	$\delta_\alpha = 72.89$ $\delta_\beta = 70.68$ $\delta_\gamma = 70.35$ $\delta_\delta = 70.25$ $\delta_a = 67.20$ $\delta_b = 69.01$ $\delta_c = 59.00$
	$\delta_\alpha = 72.97$ $\delta_\beta = 70.78$ $\delta_\gamma = 70.46$ $\delta_\delta = 70.34$ $\delta_a = 67.47$ $\delta_b = 69.84$ $\delta_c = 71.29$ $\delta_d = 31.54$ $\delta_e = 19.13$ $\delta_f = 13.82$
	$\delta_\alpha = 72.99$ $\delta_\beta = 70.81$ $\delta_\gamma = 70.48$ $\delta_\delta = 70.37$ $\delta_a = 67.43$ $\delta_b = 69.49$ $\delta_c = 71.41$ $\delta_d = 70.81$ $\delta_e = 59.00$

carbon C7 and the protonated carbon C5; these last two carbons have large isotropic chemical shifts. The quaternary carbon C9 is assigned to the next peak, and this attribution is validated by the lack of cross-polarization of this carbon which is far from any hydrogen

atom (upper spectrum in figure 6). Peaks of carbons C2 and C3 can be easily found in the spectrum due to their larger intensity. The assignment between C10 and C6 signals is more difficult. Each carbon bears a hydrogen atom, but one of these carbons does not present a large

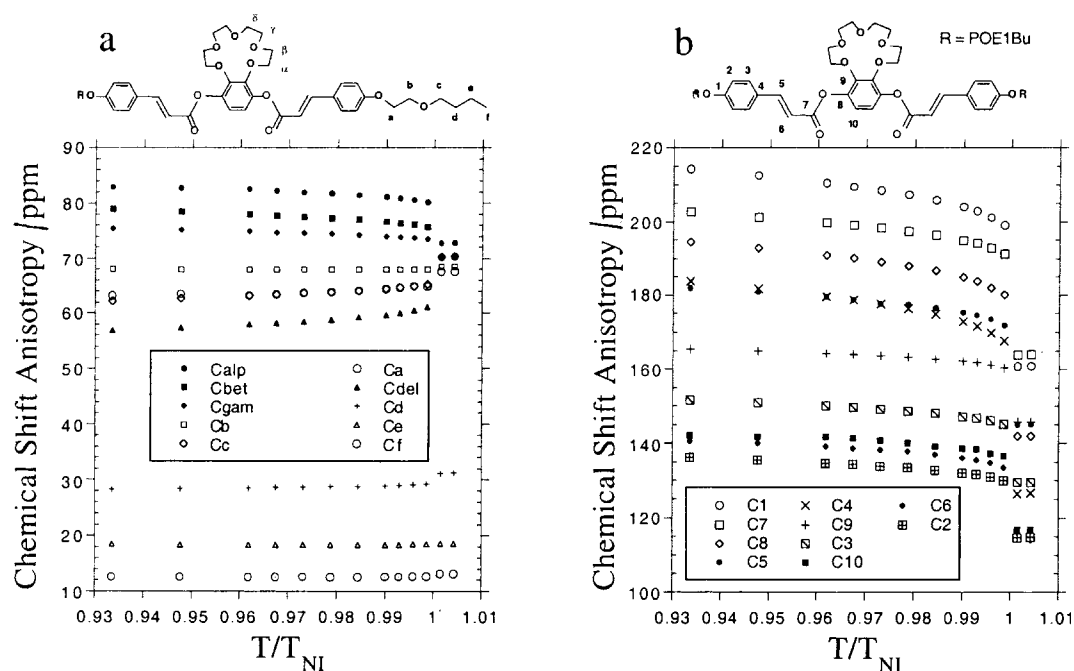


Figure 5. Chemical shift evolution of pure CINPOE1Bu at 75.475 MHz: (a) aliphatic part, (b) aromatic part.

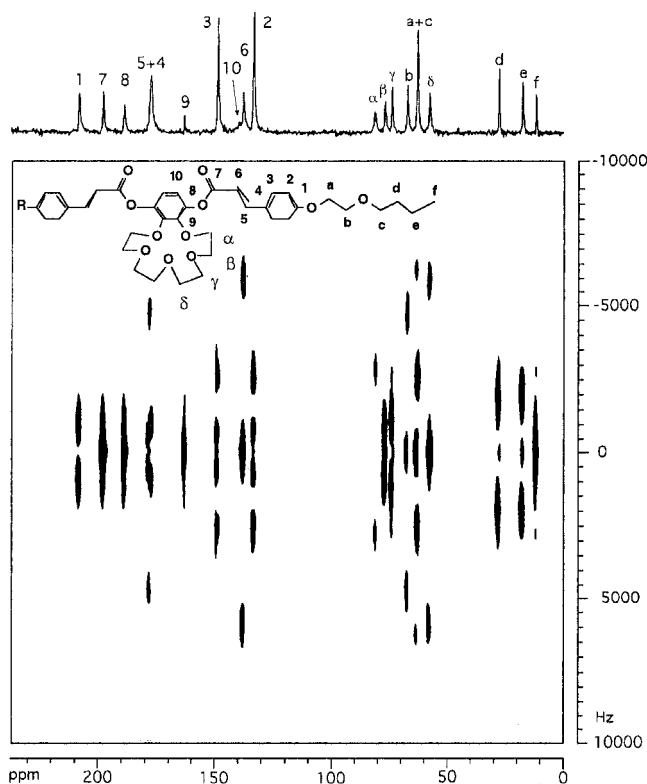


Figure 6. 2D SLF spectrum of CINPOE1Bu in the nematic phase at 349 K. Due to the sequence used, full splittings are measured.

cross-polarization (see the peak indicated by an arrow in the upper spectrum of figure 6). Accordingly, one of these C–H bonds should be near the magic angle and not in the vicinity of other hydrogen atoms. It is reasonable to choose C10 as we have shown that the two ethylenic carbons in some nematogens containing the cinnamic moiety give a large dipolar coupling [24]. Thus, due to the substitution, the central aromatic ring is no longer hexagonal. If we assume that the molecular long axis is aligned with the *para*-axis of this inner ring, the angle between the C–H bond belonging to the central ring and the *para*-axis is near to the magic angle.

#### 2.4.2. C–H bond order parameters

In order to probe the magnitude of the local order parameter in the OE units, we have studied the C–H dipolar splittings. The dipolar splittings in the nematic phase were obtained using the 2D SLF method as previously described [14]. From the peaks along the second dimension, the strength of the dipolar interaction between the carbons and the surrounding hydrogen atoms can be obtained. For example, even if Ca and Cc have the same chemical shift, they present two different dipolar splittings in the second dimension, the larger one being attributed to Ca, the first carbon within the chain. From this splitting, we can obtain the dipolar coupling between the carbon and the linked hydrogen



atoms if we neglect the dipolar contribution of the remote hydrogen atoms. This assumption is reasonably valid for carbons in the chains and in the crown ether and we will concentrate on these carbons. These C–H coupling constants depend on the different orientations of the C–H bond vector with respect to the magnetic field as well as on the amplitude of the fluctuations about these orientations. This motional averaging is measured by the bond order parameter  $S_{C-H}$ . Assuming a cylindrical symmetry for the C–H bond and a C–H distance of 0.110 nm, the bond order parameter  $S_{C-H}$  is then related to the dipolar coupling constant ( $D_{C-H}$ ) of the individual methylene by the equation:

$$S_{C-H} = -4.407 \times 10^5 D_{C-H}. \quad (1)$$

In the 2D spectrum shown in figure 6, we can note that the dipolar splitting decreases from  $C\alpha$  to  $C\gamma$  and increases for  $C\delta$ ; this is a strong indication that the average angle between the C–H bond direction and the molecular long axis is below the magic angle for carbons  $C\alpha$  to  $C\gamma$  and above the magic angle for  $C\delta$ . Then, the associated dipolar couplings are negative for carbons  $C\alpha$  to  $C\gamma$ , and positive for  $C\delta$ .

Molecular modelling on the central part of the single molecule shows clearly that the angle between the  $C\delta$ –H bond and the *para*-axis of the aromatic ring is above the magic angle (figure 7). We have an indication that the crown ether ring has, on average, a conformation in the nematic phase which should not be so far from that depicted in figure 7.

Within a short terminal POE chain it has been shown that the absolute values of the order parameter decrease monotonically with increasing distance from the core. This behaviour, which contrasts with the odd–even effect usually observed for terminal alkoxy or alkyl chain ordering, has been interpreted in terms of the change in the probabilities for the different conformations along the POE chain [16, 25–27].

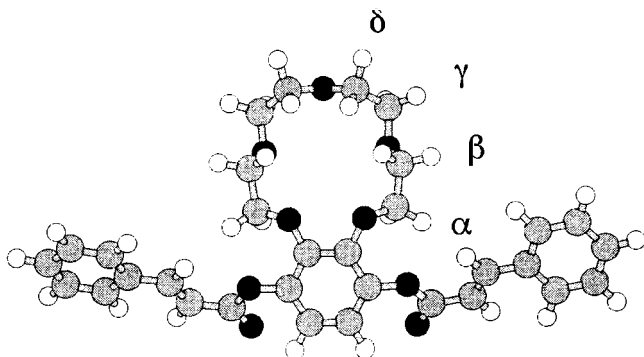


Figure 7. Molecular modelling of the central part of the molecule.

In CINPOE1Bu, the terminal chains contain one OE unit, then a butyl fragment. Figure 8 is evidence that in mixed chains there is no odd–even effect of the order parameter values in the OE unit, whereas this effect is present in the far alkyl part proving that the odd–even effect originates from the electronic environment of each individual carbon and depends only on the atoms involved in the unit and the conformation of the unit.

#### 2.4.3. C–H bond order parameters and field-induced shift correlation

An empirical relationship for the alignment-induced shift ( $\delta_N - \delta_{iso}$ ) of the aliphatic carbons in the nematic phase has been expressed as [28]:

$$\delta_N - \delta_{iso} = b + aS_{C-H} = b + aS_o(1 - T/T^\dagger)^F \quad (2)$$

where  $a$  and  $b$  involve the chemical shift tensor components in the axis system chosen to define the order parameter;  $a$  and  $b$  were found to be constant indicating the slight change in the tensor components in the different populated conformations.  $T^\dagger$  is a temperature slightly higher than  $T_{NI}$  and  $S_o$  is the limit of the bond order parameter of the fragment relative to the director.

In the OE unit, it was shown that a change in the conformation probability with temperature will mean that  $a$  and  $b$  are no longer constants with temperature. This behaviour arises from the change of the chemical shift tensor components for the two carbons in the unit. These carbons experience a quite different electronic environment when the OE unit is in a *gauche*- or *trans*-conformation due to the in-space interactions with the lone pairs of the oxygen atoms. Thus, a change in the

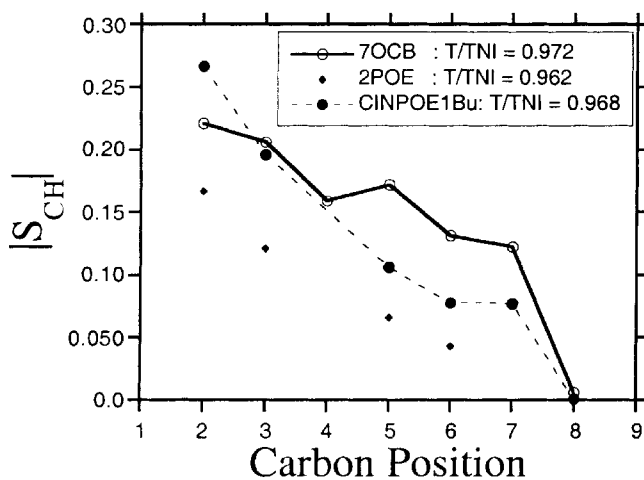


Figure 8. Comparison of the order parameters in terminal chains containing the same number of atoms: heptyloxy chain [27], a terminal  $-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_2-\text{CH}_3$  chain [15] and in CINPOE1Bu at the same reduced temperature (position 1 is devoted to the oxygen atom linked to the aromatic ring).

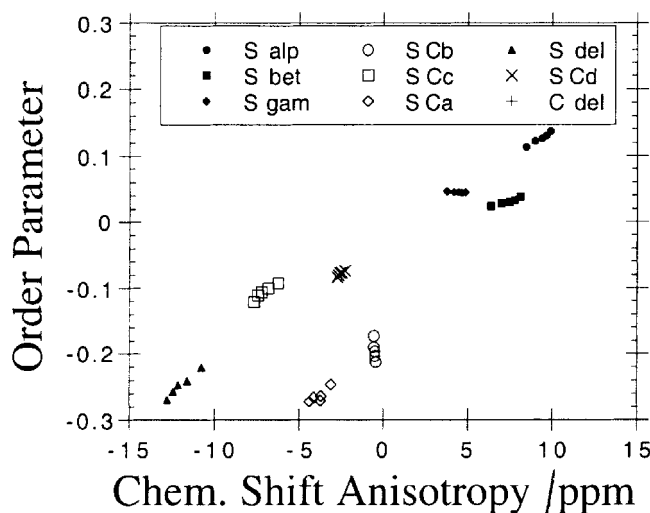


Figure 9. Correlation between the order parameter and chemical shift anisotropy for CINPOE1Bu.

conformation probabilities in the OE unit will give a non-linear correlation between the order parameter and the chemical shift anisotropy.

Even if the range of temperature explored is quite short (20°C), it seems that the carbons inside the lateral crown ether present a linear correlation between the order parameter and the chemical shift anisotropy (figure 9). This gives some indication that in the temperature range studied the conformation of the lateral crown ether does not change greatly.

### 3. Conclusion

Symmetrical compounds containing three rings in the main core and a lateral 15-crown-5-ether can present an enantiotropic nematic phase. The introduction of short terminal POE chains on the laterally substituted compound decreases the melting and clearing temperatures without destroying the nematic arrangement. These compounds which contain OE units do not dissolve a large amount of  $\text{LiBF}_4$  salt. The mixtures obtained present no liquid crystal properties.

$^{13}\text{C}$  NMR was undertaken for one compound containing two terminal  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}_4\text{H}_9$  chains. The isotropic chemical shifts in the solid phase and in the isotropic melt indicate that there is almost no change in the conformation of the lateral crown ether fragment between these two states. In the nematic phase, the chemical shift anisotropy is correlated with the order parameter which indicates that this rather flexible fragment stays in the same average conformation when the temperature is decreased. For the terminal chain, there

is no odd-even effect in the order parameter values in the OE units, whereas this effect is seen for the butyl end of the chain.

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