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Online publication date: 06 August 2010

To cite this Article Rayssac, Vincent , Judeinstein, Patrick , Bayle, Jean-Pierre , Kuwahara, Daisuke , Ogata, Hironori and Miyajima, Seiichi(1998) 'NMR investigation of the oxyethylene unit ordering in some related dialkoxy laterally substituted nematogens', Liquid Crystals, 25: 3, 427 — 436

To link to this Article: DOI: 10.1080/026782998206245

URL: http://dx.doi.org/10.1080/026782998206245

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LIQUID CRYSTALS, 1998, VOL. 25, NO. 3, 427–436

NMR investigation of the oxyethylene unit ordering in some related dialkoxy laterally substituted nematogens

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(*Received 6 January 1998; accepted 18 April 1998*)

Laterally dialkylated nematogens containing a short terminal polyoxyethylene chain present a wide nematic range starting from room temperature. The ordering of the oxyethylene (OE) unit has been studied by ^{13}C NMR in the liquid crystalline phase. The values of the order parameters were derived from the transient oscillations observed during variable contact-time cross-polarization experiments. Along the oxyethylene chain, the order parameters decrease monotonically. These order parameter values do not present the usual odd–even effect and are noticeably smaller than those found for terminal alkoxy chains. Entering the nematic phase, the ^{13}C thermal evolution of the field-induced chemical shift in the OE unit is far smaller than the one usually observed for terminal alkyl or alkoxy chains, regardless of their non-negligible order parameters. In addition, no linear correlation between the order parameter and the field-induced chemical shift is observed for the carbons in the OE unit. This is an indication that the proportion between *gauche*- and *trans*-conformations in the OE unit is temperature dependent.

1. Introduction

Nematic liquid crystals are anisotropic fluids. To obtain liquid crystal nematic properties, two major molecular moieties are required: a more or less rigid rod-like core which induces the anisotropic packing in the liquid crystalline phase and at least one flexible fragment (alkyl or alkoxy chain), which decreases the melting point and thus increases the thermodynamic stability of the mesophase [1]. For many applications, room temperature liquid crystals are needed and the choice of the chain type, length and position within the core is of major importance in reducing the melting temperature. In conventional mesogens, alkyl or alkoxy chains are used as terminal fragments. The chain conformation in the solid phase of these compounds is usually *trans* and the crystal cohesion which contributes to the value of the melting temperature is mainly due to core–core interactions. Thus, in a series, the melting temperatures can be monitored by increasing the chain length, with the consequence also of strongly decreasing the mesophase stability due to the enhancement of the conformational disordering along the chain. A nice alternative for decreasing these core–core interactions in the solid phase is to introduce the flexible fragments at a lateral position. In the solid and the nematic phase, the lateral flexible substituents adopt a mean conformation more or less parallel to the mesogenic core in such a way that this peculiar arrangement does not greatly perturb the anisotropic packing needed for the mesophase stability [2–4]. The lateral chains are less disordered than the terminal ones, in accordance with their peculiar conformation along the core. As a consequence, in a homologous series, the melting temperatures can be adjusted by changing the number of carbons within the terminal and/or lateral chains [5–7]. In fact, with two large flexible lateral substituents introduced on a mesogenic core containing four rings, a wide nematic range can be obtained near room temperature.

Polyoxyethylene ether (POE) chains can be used as flexible substituents in liquid crystal structures [8–10]. These chains are interesting as head groups in non-ionic surfactants with the interesting feature of complexing alkali metal cations [11]. In addition, POE chains adopt different conformations when forming complexes with inorganic salts or when different solvents are used. In fact, in the solid phase, a POE chain adopts a *trans*-(COCC)-*gauche*-(OCCO)-*trans*-(CCOC) arrangement for the monomer unit [12]. As a consequence, a helical

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structure is obtained containing seven units and two turns. It is interesting to note that the monomer (ethylene glycol) stays in that conformation in solution [13] or when dissolved in a nematic lyotropic phase [14]. The problem of the mean conformation of a POE chain hooked onto a mesogen is of interest as it can influence the packing within the solid and the liquid crystal phase and thus can have some influence on the melting and the clearing temperature. We have shown recently that introducing a short POE chain as a terminal substituent in a dilaterally substituted compound can lead to a low melting nematic [15]. In this paper, we describe the synthesis, the mesomorphic properties and the ^{13}C NMR study of several compounds possessing four rings in the main core and substituted by two lateral hexyloxy chains and a terminal POE chain which contains 1, 2 or 3 OE units with a final methoxy or butoxy group. The ordering behaviour of the carbons inside the OE unit have been determined by the measurement of the dipolar oscillations during the cross-polarization (CP) process. Then, the correlation between the order parameter and the field-induced chemical shift has been compared to the one encountered in a normal terminal alkoxy chain.

2. Results and discussion

2.1. *Synthesis*

The general synthetic scheme for the compounds containing 0, 1, 2 or 3 OE units is summarized in figure 1. As an example, we describe the synthesis of 2,3-di-*n*-hexyloxy-4-{4-[2-(2-methoxyethoxy)ethoxy]-benzoyloxy}-4′-(4-methylbenzoyloxy)azobenzene. 2,3-Di-*n*-hexyloxyphenol was prepared by selective etherification of 1,2,3-trihydroxybenzene in a mixture of polyethyleneglycol (PEG) 200/dioxan (30/70) as solvent using a standard procedure [16]. *p*-Toluic acid was esterified with nitrophenol using the DCC method in dichloromethane [17]. The nitro group in this compound was selectively reduced using the $NiCl_2/NaBH_4$ reducing system [18]. After acidification, the crude solid aniline hydrochloride, which had precipitated, was used for the diazotization step which was performed at room temperature in PEG 200 as solvent. Coupling of the diazonium salt with the disubstituted phenol was effected under basic conditions. The crude phenol was chromatographed with CH_2Cl_2 as eluent and in the next step was esterified with the appropriate 4-substituted benzoyl chloride in $CHCl_3$/pyridine (50/50) as solvent. The required benzoic acid was obtained in one step by mixing 4-hydroxybenzoic acid with potassium hydroxide (1/2 ratio) in PEG 200 in order to obtain the dianion, and then adding one equivalent of 2-(2-methoxyethoxy)ethoxy tosylate. The final mesogen was chromatographed twice using ethyl acetate/hexane mixture on silica gel (60–220 mesh). The relative amount of ethyl acetate used was 15, 25 or 50% with respect to the number of OE units (1, 2 or 3). When the compounds were solid at room temperature, they were recrystallized from $CHCl_3$/methanol mixture until constant transition temperatures were obtained. The final compounds differ in the terminal chain containing ***n*** OE units ($n=0$, 1, 2 and 3) and the final alkyl group *R* of the OE chain containing ***m*** carbons ($m=1$ or 4); as a consequence the compounds are denoted hereafter as ***n*POEC*m***.

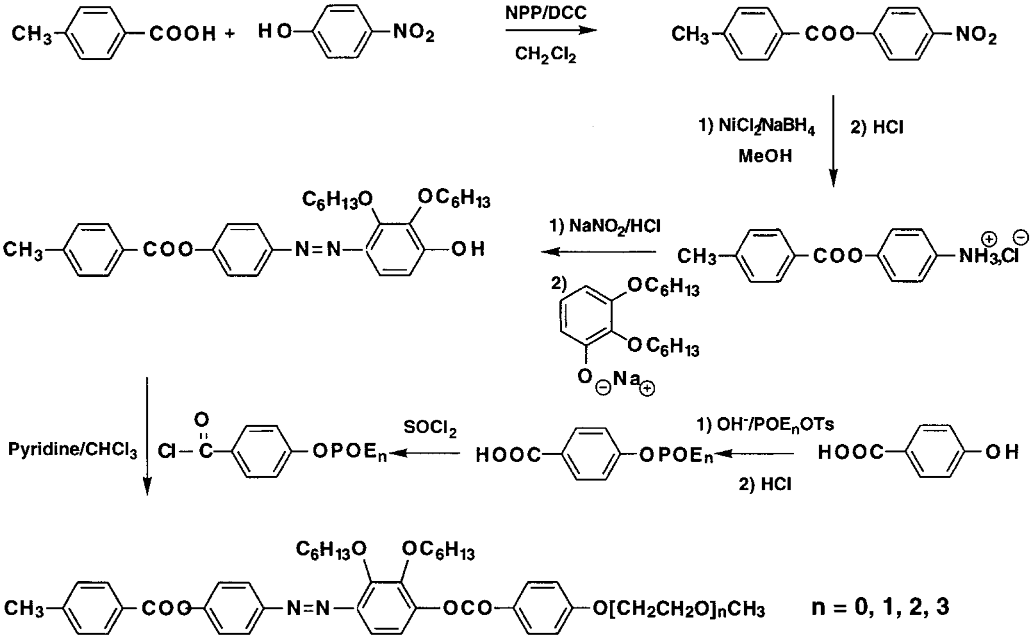


Figure 1. Synthetic scheme for the homologous compounds.

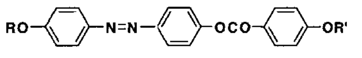
In addition, four rod-like compounds were synthesized (table 1) in order to examine the influence of the POE chain on conventional mesogenic structures. These compounds have the same rod-like core containing three aromatic rings, but differ in the types of terminal chain containing eight atoms, i.e. heptyloxy or 2-(2-methoxyethoxy)ethoxy (2-POE).

2.2. *Transition temperatures*

From the transition temperatures given in table 1, it is clear that, for conventional mesogens, the replacement of the C7 chain by a POE chain reduces the melting and the clearing temperatures. The effect on the melting temperatures is particularly marked when the POE chain is linked to the more conjugated fragment. However, if the POE chain is introduced on the less conjugated fragment, there is almost no effect on the melting temperatures, and only the clearing temperatures are decreased.

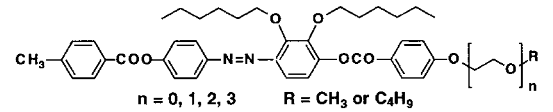
To compare this behaviour in non-conventional mesogens, a POE chain containing 1, 2 or 3 OE units was introduced into some related compounds containing two lateral hexyloxy chains. The transition temperatures are given in table 2. Only an enantiotropic nematic phase is observed for all the compounds. Clearly, the replacement of carbon by oxygen atoms within the terminal chain decreases the melting and clearing temperatures. By comparing **0POEC7**, **1POEC4** and **2POEC1** which have the same number of atoms within the terminal chain, it is obvious that the major decrease in temperature arises from the first OE unit introduced into the structure. Amazingly, the nematic range is quite unaffected when OE units are introduced. Therefore, a room temperature liquid crystal was obtained for the compound having 3 OE units in the terminal chain (figure 2). As already noticed for laterally substituted nematogens, it is worth remarking that all the compounds give strong supercooling of the nematic phase [4–7].

Table 1. Transition temperatures (in °C) for the 4-*n*-alkoxy-4′-(4-alkoxybenzoyloxy)azobenzene series. These values were measured by DSC with increasing temperature (heating rate 10°C min^{-1}).



R*-*R′	Cr	→	N	→	I
C7-C7	•	107·5	•	219	•
C7-2POEC1	•	106	•	196·5	•
2POEC1-C7	•	87	•	190	•
2POEC1-2POEC1	•	88·5	•	169·5	•

Table 2. Transition temperatures (in °C) of some related compounds having the core substituted with two hexyloxy chains and differing in the terminal chain. These values were obtained by DSC with increasing temperature (heating rate 10°C min^{-1}).



n*POEC*m	Cr	→	N	→	I
0POEC1	•	110	•	160·5	•
0POEC6	•	81	•	168	•
0POEC7	•	80·5	•	163	•
0POEC8	•	70	•	159·5	•
1POEC1	•	67	•	165·5	•
1POEC4	•	56·5	•	139	•
2POEC1	•	50	•	122	•
3POEC1	•	<20	•	106	•

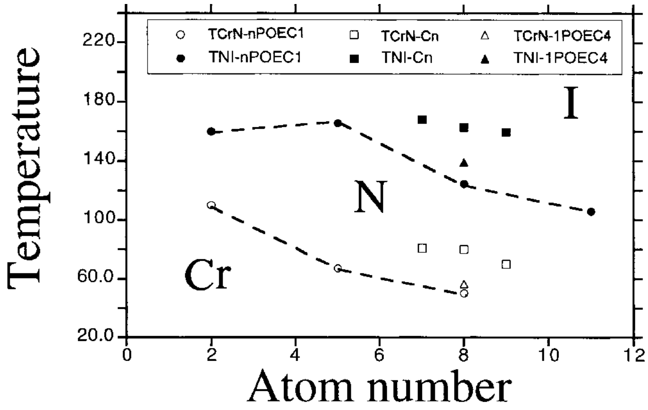


Figure 2. Phase behaviour of the related compounds versus the number of atoms in the terminal chain. The transition temperatures were recorded by DSC (heating rate 10°C min^{-1}).

2.3. ^{13}*C NMR measurements*

For the liquid crystal samples, the ^{13}C NMR experiments were performed using a Bruker DSX400 NMR spectrometer and a 100 mg sample sealed under vacuum in a standard 5 mm NMR tube after a freeze–pump–thaw cycle. The ^{13}C chemical shifts measurements were obtained on the static sample aligned parallel to the magnetic field, using a ^{13}C single pulse experiment with strong decoupling of the hydrogens. Dipolar oscillations were obtained by increasing the contact time in a classic cross-polarization experiment on the static sample. Flip-back of ^{1}H magnetization was used at the end of the decoupling period. To avoid r.f. overheating due to the strong decoupling, the recycle delay between each FID acquisition was 6 s. The temperature was calibrated by observing the nematic to isotropic transition. Thermal equilibration duration was 10 min prior to each measurement. A typical ^{13}C spectrum of **3POEC1** is shown in figure 3.

2.3.1. *Chemical shifts analysis*

The 50–90 ppm aliphatic region contains the OE carbon signals and the other CH_2O and CH_3O signals. In order to obtain the field-induced shift in the nematic phase, the first step was to assign the signals in the isotropic phase. In the analogous compound having a chlorine atom instead of a POE chain at the same terminal position, the two downfield peaks were attributed to the C1′ and C1 carbons belonging to the lateral chains [2]. The isotropic chemical shifts of these carbons should not be sensitive to the change of the terminal substituent. Thus, two downfield peaks at the average chemical shifts of 74·4 ± 0·1 and 76·6 ± 0·1 ppm were assigned to C1 and C1′ in all the compounds. In order to decipher the assignment of the POE chain carbons, the ^{13}C-^{1}H correlation and a long range ^{13}C-^{1}H correlation (COLOC), 2D experiments in $CDCl_3$ solution were performed on a related compound [15]. In addition, with the POE chain, there is a very weak influence of the substituents in the γ and δ positions on the isotropic chemical shifts [19]. Thus, in the isotropic melt spectra, the chemical shift of Ca within the first OE unit is not dependent on the terminal chain substitution. Thus, the Ca isotropic chemical shift is found to be 68·7 ± 0·2 ppm in all the compounds. Cb experiences the same substituents in the α and β positions (except for compound **1POEC1**), giving an average isotropic chemical shift of 69·8 ± 0·2 ppm. For the same reasons Cc, Cd in **2POEC1** have similar chemical shifts to Ce, Cf in **3POEC1**, respectively. These assumptions give the final assignments in the melt proposed in table 3.

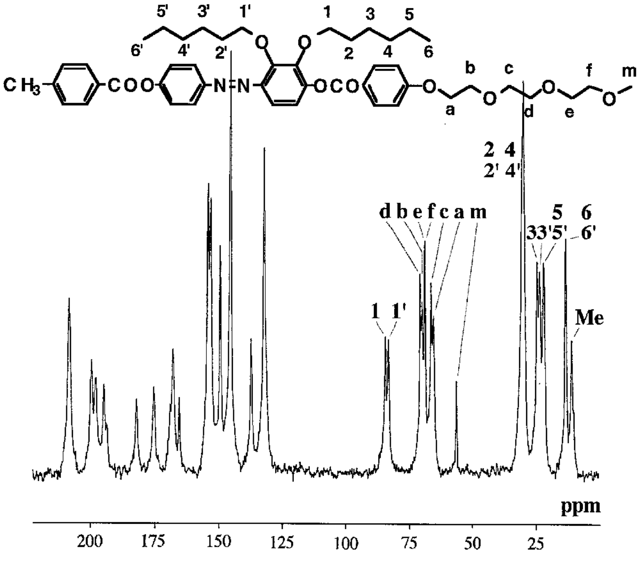


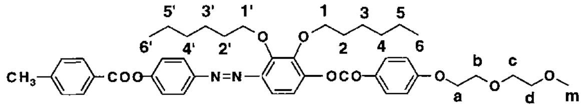
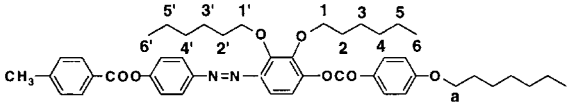
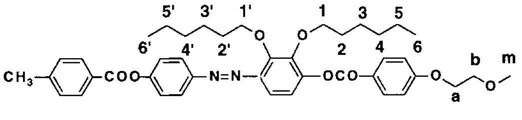
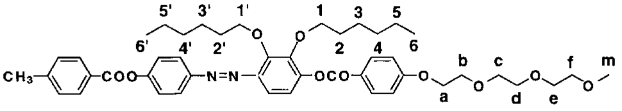
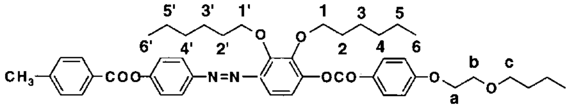
Figure 3. Proton decoupled ^{13}C spectrum for the nematic phase of **3POEC1** at 100·624 MHz and aliphatic carbon labelling. Acquisition parameters: CP with flip-back, contact time = 1 ms, recycle delay = 6 s, number of scans = 100, temperature = 87°C.

In the typical spectrum of **3POEC1** presented in figure 3, nine peaks are expected in the 50–90 ppm region, but only eight are displayed at this temperature. The chemical shift evolutions of the aliphatic downfield peaks as a function of temperature in **3POEC1** and **1POEC4** are shown in figure 4. For all the compounds, the chemical shift evolutions have similar shapes. Going from the isotropic melt to the nematic phase, the usual large positive jump in the chemical shift is observed for the two first carbons C1′ and C1 in the lateral chains. This positive jump has been associated with the folding back of the lateral chains that induces a positive order parameter for these carbons [2]. On the contrary, carbons belonging to a terminal chain or to the far part of the lateral chains experience a negative jump due to the peculiar mean orientation of their C–H bonds with respect to the molecular long axis. But, it is worth noting that some carbons have a very unusual flat behaviour of the alignment-induced shift. Specifically, Cb exhibits a very small alignment-induced shift. This unusual behaviour begins by a decrease of the chemical shift just after the transition, followed by a tiny increase of the chemical shift while decreasing the temperature. The change in the chemical shift on entering the nematic phase is an average involving different factors: the probability of finding a conformation, the ordering matrix of the C–H fragment involved in that conformation and the chemical shift tensor of the observed carbon in that conformation. To decipher these different factors is difficult, but an empirical relationship for the alignment-induced shift ($\delta_N - \delta_{iso}$) of the aliphatic carbons in the nematic phase has been expressed as [20]:

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

Here 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 of 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. The quantity S_o gives an estimate of the mean angle between the fragment under investigation and the molecular long axis since S_o is roughly a product of two limiting order parameters—the segmental one relative to the molecular long axis and the molecular one relative to the director. The F value gives an indication of the way in which a fragment is reaching its limiting value of ordering and is related to the fragment rigidity. Then, a small alignment-induced shift means that at least one

Table 3. ^{13}C isotropic chemical shifts of the OCH_2 carbons in ***n*POEC*m*** and in some related compounds.

Molecule	Chemical shift
	$\delta_1 = 74{\cdot}5$ $\delta_{1'} = 76{\cdot}6$ $\delta_a = 69{\cdot}3$
	$\delta_1 = 74{\cdot}5$ $\delta_{1'} = 76{\cdot}6$ $\delta_a = 68{\cdot}8$ $\delta_b = 71{\cdot}5$ $\delta_m = 59{\cdot}0$
	$\delta_1 = 74{\cdot}4$ $\delta_{1'} = 76{\cdot}6$ $\delta_a = 68{\cdot}6$ $\delta_b = 70{\cdot}0$ $\delta_c = 71{\cdot}2$ $\delta_d = 72{\cdot}5$ $\delta_m = 58{\cdot}7$
	$\delta_1 = 74{\cdot}3$ $\delta_{1'} = 76{\cdot}5$ $\delta_a = 68{\cdot}6$ $\delta_b = 69{\cdot}9$ $\delta_c = 71{\cdot}3$ $\delta_d = 71{\cdot}3$ $\delta_e = 71{\cdot}3$ $\delta_f = 72{\cdot}5$ $\delta_m = 58{\cdot}7$
	$\delta_1 = 74{\cdot}4$ $\delta_{1'} = 76{\cdot}6$ $\delta_a = 68{\cdot}9$ $\delta_b = 69{\cdot}6$ $\delta_c = 71{\cdot}6$

quantity, S_o or a, is small. But, the sign change in the chemical shift evolution can only be interpreted by a gradual change in the a value when decreasing the temperature, indicating that a and b are no longer constant for the carbons inside the OE unit. We will return to that interesting behaviour in the next paragraph.

In figure 4, we can note that the first carbon (Ca or Cc) in each OE unit has a larger alignment-induced shift than the second one in the same unit (Cb or Cd). This phenomenon is observed for all the compounds. This is quite reasonable, as the chemical shift tensors of the two linked carbons inside the same unit should have nearly the same orientation and components. Therefore, for these carbons, the magnitude of the alignment-induced shift is directly related to the bond order parameter which decreases along the chain. It is also observed that Cc has a more pronounced temperature dependence of alignment-induced shift than Ca.

2.3.2. *C–H bond order parameters*

In order to probe the magnitude of the local order parameter, we have studied the C–H dipolar couplings. Individual values of the C–H dipolar coupling can be obtained by analysing the dipolar oscillations obtained by increasing the contact time t_{cp} in a standard cross-polarization sequence. For a static sample aligned with the magnetic field, an oscillatory magnetization transfer between ^{1}H spin and ^{13}C spin networks occurs, damped out by the spin diffusion among hydrogens. Thus, the individual normalized intensity of any methylene carbon can be expressed as a function of the contact time t_{cp} [21–23]:

$$M/M_o = 1 - 0{\cdot}5\exp(-t_{cp}/T_{II}) - 0{\cdot}5\exp(-3t_{cp}/2T_{II})\cos(2^{-1/2}D_{C\text{–}H}t_{cp}) \qquad (2)$$

where T_{II} is the spin diffusion time among hydrogens and $D_{C\text{–}H}$ is the C–H dipole–dipole coupling constant of the directly bonded hydrogens. This equation assumes that the cross-polarization occurs due to the energy exchange with the directly bonded hydrogens, and that the other dipolar effects of farther hydrogens are negligible. In the case of overlappings peaks, deconvolution of the spectra was used to obtain the individual magnetization intensities. Then, the C–H coupling constants were determined from equation (2) using the data points in the range [0, 500] μs. 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 the amplitude of the fluctuations about these orientations. This motional averaging is measured by the bond order parameter $S_{C\text{–}H}$. Assuming a cylindrical symmetry for the C–H bond and a C–H distance of 0·110 nm, the bond order parameter $S_{C\text{–}H}$ is then related to the dipolar

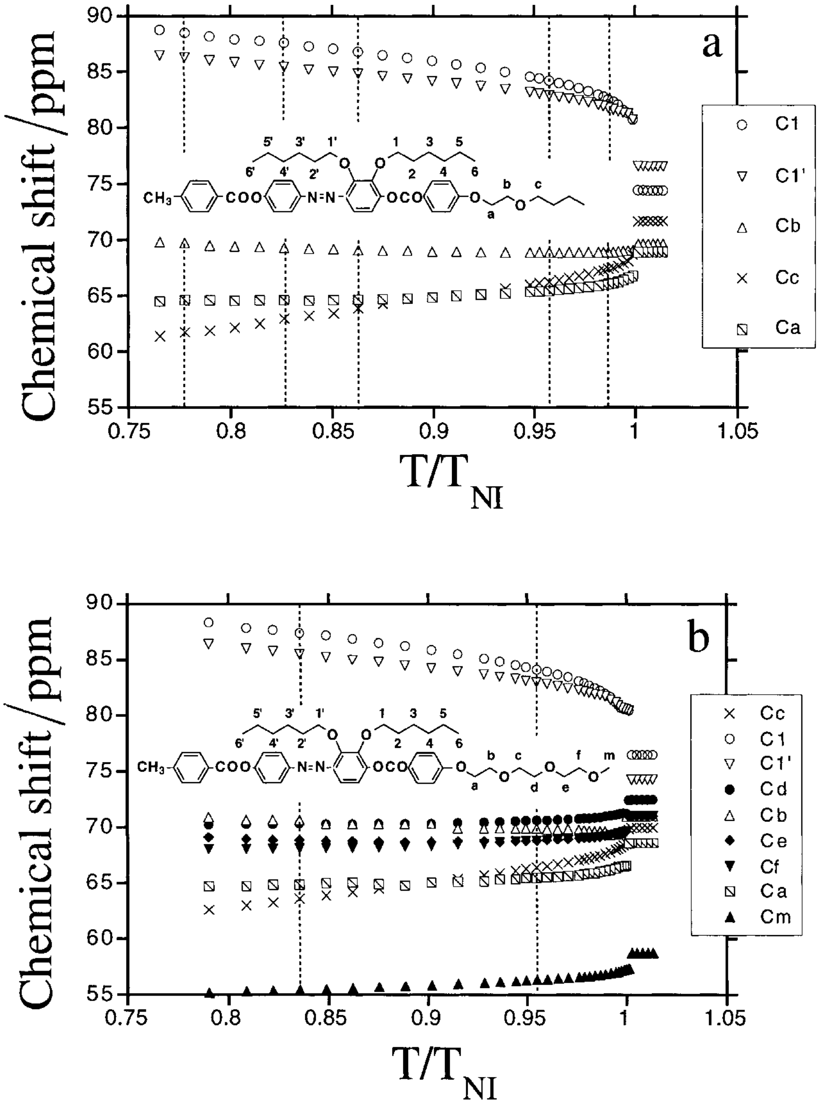


Figure 4. Temperature dependence of the ^{13}C chemical shifts in the static sample of **1POEC4** (*a*) and **3POEC1** (*b*) for the OCH_2 and OCH_3 carbons. The dashed lines indicate the reduced temperatures where dipolar oscillations were measured.

coupling constants ($D_{C\text{-}H}$) of the individual methylene by the equation:

$$S_{C\text{-}H} = -4{\cdot}407 \times 10^{-5} D_{C\text{-}H}. \qquad (3)$$

Table 4 gives the values calculated using equations (2) and (3) for the five compounds at different values of T/T_{NI}.

Within the POE chain the order parameters decrease monotonically with increasing distance from the core. This behaviour constrasts with the odd–even effect usually observed in a terminal alkoxy of alkyl chain ordering [24–26]. The lack of odd–even effect has been interpreted by the change in the probabilities for the different conformations along the POE chain [15]. The first carbon Ca in the POE chain possesses a lower $|S_{C\text{-}H}|$ value compared with that found for **7OCB** ($S_{C\text{-}H} = 0{\cdot}221$ at $T/T_{NI} = 0{\cdot}972$) [27]. However, this order parameter is similar to that measured in **0POEC7** which possess the same core. Therefore, this smaller value is not related to the chain type, but the mesogenic core difference. The position of the molecular long axis is rather dependent on the alkoxy chain in **7OCB** as the core contains only two aromatic rings, and is tilted with respect to the aromatic ring *para*-axis. In ***n*POEC*m*** or **0POEC7**, the core contains four aromatic rings and the influence of the terminal chain on the position of the molecular long axis has to be less important. Then the molecular long axis makes a smaller angle with the individual *para*-axes of the rings. The second carbon Cb has the smallest field-induced shift (figure 3), but its C–H bond order parameter is quite significant (table 2). Due to the peculiar average of the chemical shift tensor, a carbon can experience a negligible field-induced shift with a non-negligible order parameter. Thus, the C–H bond order parameter analysis from the field-induced shift may lead to criticism.

Table 4. Order parameters obtained by the fitting of the dipolar oscillations with equation (2) in the range [0, 500] μs at different reduced temperatures. The absolute error in the order parameter is estimated at 5%. Two peaks (-) have the same NMR frequency; therefore it was not possible to obtain accurate values of their dipolar couplings.

Compound	Carbon							
T/T_{NI}	C1	C1′	Ca	Cb	Cc	Cd	Ce	Cf
1POEC1								
0·962	0·0605	0·0629	−0·152	−0·114				
0·916	0·0670	0·0707	−0·182	−0·133				
0·860	0·0820	0·0903	−0·227	−0·177				
0·803	0·0923	0·110	−0·262	−0·200				
0·713	0·102	0·132	−0·308	−0·243				
1POEC4								
0·984	0·0517	0·0546	−0·140	−0·105	−0·0576			
0·957	0·0638	0·0711	−0·167	−0·139	−0·0701			
0·863	0·0823	0·0997	−0·228	−0·189	−0·0966			
0·826	0·0924	0·117	−0·249	−0·206	−0·107			
0·778	0·0978	0·128	−0·273	−0·226	−0·120			
0POEC7								
0·960	0·0678	0·0782	−0·180					
0·896	0·0820	0·100	−0·229					
0·827	0·0870	0·111	−0·275					
0·769	0·0912	0·121	−0·308					
2POEC1								
0·960	0·063	0·066	−0·167	−0·121	−0·066	−0·043		
3POEC1								
0·956	0·0646	0·0725	−0·177	−0·141	−0·0698	−0·0508	(-)	(-)
0·836	0·0873	0·106	−0·252	(-)	−0·0996	(-)	−0·0635	−0·0317

2.3.3. *C–H bond order parameters and field-induced shift correlation*

It has been shown that a linear correlation between the order parameter and the field-induced shift can be obtained for the carbons in terminal alkyl or alkoxy chains, equation (2) [20]. Figure 5 shows this correlation for **1POEC4**; the linear correlation is observed for the methyleneoxy carbons in the lateral chains and terminal groups, but not for the methyleneoxy carbons within the OE unit. This amazing behaviour is encountered for all the compounds (figure 6). The conformational disordering is certainly weak for the first OCH_2 in the

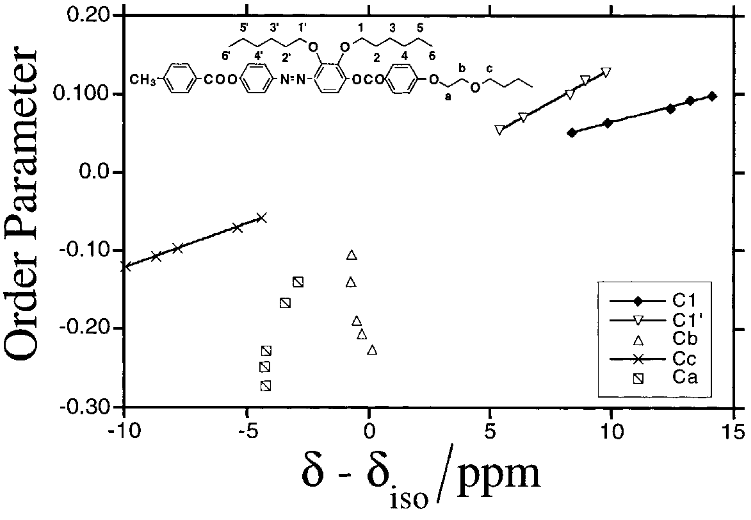


Figure 5. Correlation between the order parameters obtained from the dipolar couplings and the induced anisotropic chemical shifts for **1POEC4**.

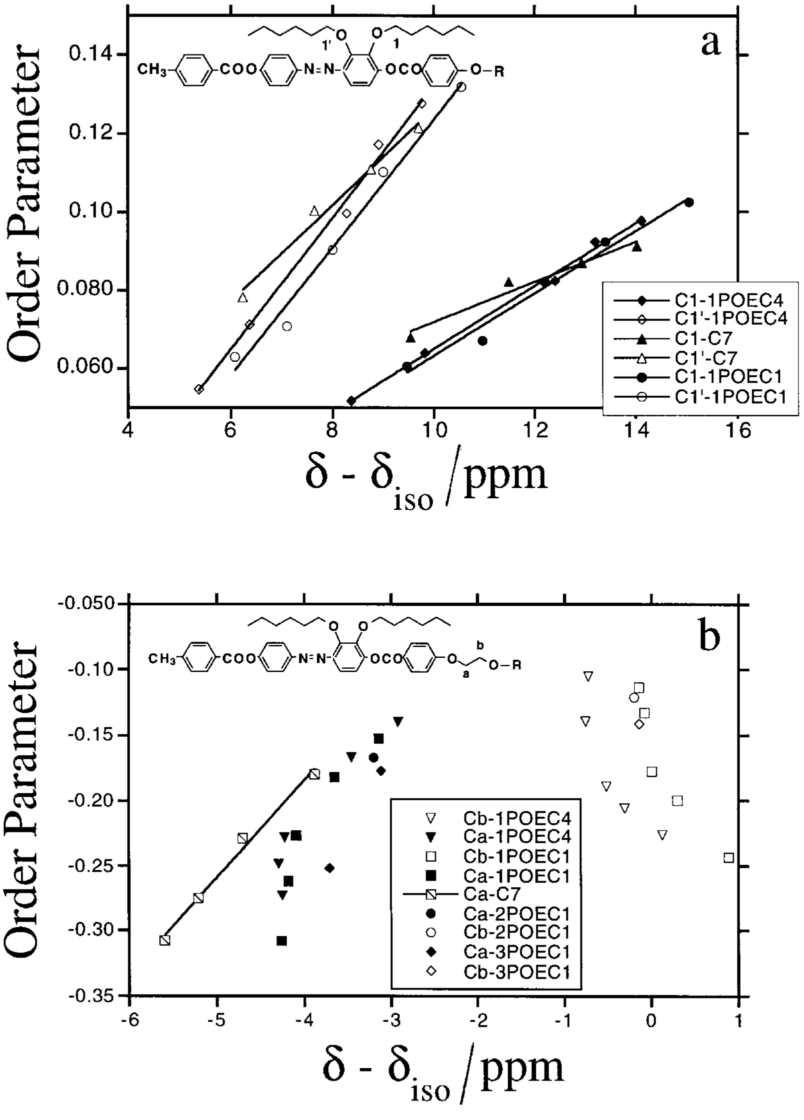


Figure 6. Correlation between the order parameters and the induced anisotropic chemical shifts: (*a*) C1 and C1′ carbons; (*b*) Ca and Cb.

lateral chain as this experiences strong steric hindrance, and we can assume that this carbon exhibits a preferential *gauche*-conformation, which is a necessary condition to the folding back of the lateral chain along the core. Thus, the observed linear correlation between the order parameter and the field-induced shift indicates that this mean conformation does not change too much when decreasing the temperature, leaving *a* and *b* constant in equation (2); see figure 6 (*a*). The terminal chain is far more free to move. If we take the crude approximation that the most populated conformations are the *trans*- and the two *gauche*-conformations, the non-linear correlation observed in the OE unit is due to some change in the probabilities amongst the three conformations which modulates the average of the chemical shift tensors. In fact, the chemical shielding tensor is rather sensitive to the change in local electronic structure. The two carbons in the OE unit experience a quite different electronic environment when the OE unit is *gauche* or *trans*, due to the in-space interactions with the lone pairs of the oxygen atom. When decreasing the temperature, the relative proportion of *gauche*- and *trans*-conformations is changing. This leads to some changes in the average chemical shielding tensor and consequently to some temperature dependence of the *a* and *b* values, equation (2). These thermal changes in the conformations of the OE unit have been demonstrated in POE melts by molecular dynamics simulations [28]. The more pronounced non-linearity for the Cb carbon behaviour may be due to the influence of the *gauche*-conformation of the oxygen atom directly attached to the aromatic ring, as this oxygen has a larger electronegativity in accordance with the partial conjugation with the aromatic ring.

From the linear correlations shown in figure 6 (*a*) for the two oxymethylene carbons in the lateral chain, constants *a* and *b* can be obtained by fitting. From these values obtained for the C1 and C1′ carbons, the values of $S_{C\text{–}H}$ can be calculated from the chemical shift using equation (1). This allows a large amount of data to be obtained, which tends to moderate the uncertainties of the $S_{C\text{–}H}$ measurements from the dipolar oscillations. As C1 and C1′ carbons are more or less stuck in their mean conformations, we can expect that the comparison of their order parameters will give some information on the change with temperature of the central core ordering. Figure 7 shows the ratio $S_{C1'\text{–}H}/S_{C1\text{–}H}$ obtained from the chemical shift using *a* and *b* values. For the three compounds, this ratio increases with decreasing temperature, showing that the angle between the molecular long axis and the *para*-axis of the aromatic ring bearing the lateral chains is changing in a coherent way. The ratio $S_{C1'\text{–}H}/S_{C1\text{–}H}$ is also chain length dependent. The values are similar for the terminal chains containing eight atoms, but different for the terminal chain having only five carbons.

3. Conclusion

The introduction of a short terminal POE chain to a dilaterally substituted compound leads to low melting nematogens. A wide nematic range is obtained starting from room temperature for a POE chain containing three units. The chain behaviour has been studied by ^{13}C NMR for several compounds having two lateral hexyloxy chains and a pure alkoxy chain, pure POE chains and mixed OE/alkyl chains. The chemical shift evolution of the first OE unit is similar in related compounds. On entering into the nematic phase from the isotropic phase, the first OCH_2 exhibits a negative jump and the second one a small negative jump followed by a slight increase of the chemical shift. The order parameters of the oxomethylene carbons were obtained by the use of dipolar oscillations during the cross-polarization process. They decrease smoothly along the chain. These order parameters do not show the odd–even effect usually observed with the terminal alkoxy chain. They decrease monotically along the POE chain with increasing distance from the core. In the OE unit, no linear correlation is observed between the order parameter and the field-induced chemical shift, indicating that chain conformational probabilities are changing during the ordering process.

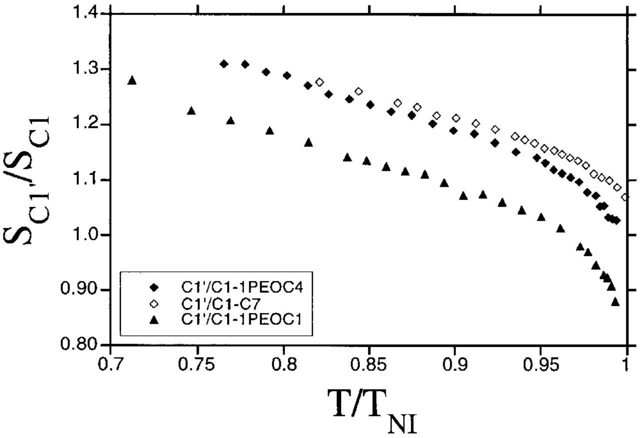


Figure 7. Comparison of the ratio of the order parameter of the oxymethylene carbons in the lateral chains.

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