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Online publication date: 06 August 2010

To cite this Article Berdague, P.(1999) 'Nematogens with more flexible chains than aromatic rings in the core', Liquid Crystals, 26: 2, 211 — 218
To link to this Article: DOI: 10.1080/026782999205344
URL: http://dx.doi.org/10.1080/026782999205344

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LIQUID CRYSTALS, 1999, VOL. 26, NO. 2, 211–218

Nematogens with more flexible chains than aromatic rings in the core

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(*Received 6 May 1998; in final form 18 September 1998; accepted 25 September 1998*)

Mesogens containing four rings in the main core can accommodate one terminal and two nearby lateral chains on each outside aromatic ring. These compounds containing six chains present an enantiotropic nematic range which is influenced by the rigidity of the links. The conformational behaviour of the first methyleneoxy group within the chains was investigated by one and two dimensional ^{13}C NMR. The sign of the jump in chemical shifts when entering the nematic phase indicates the folding of each lateral branch. Dipolar oscillations during cross-polarization contact provide the values of the bond order parameter. The two first lateral fragments do not behave in the same way, demonstrating the influence of the fragment along which the chain is back folded.

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1. Introduction

Mesogens containing a large proportion of paraffinic chains can be expected to present some new and interesting properties. For example, when a small dissolved molecule interacts with chains of a mainly low ordered nature, it can be anticipated that this molecule will have a low order parameter. This low order parameter is a key-point in deciphering strongly coupled complex spectra [1]. Considering a linear rigid core with two terminal chains, an increase in the percentage of paraffinic chains can be achieved through the introduction of lateral chains. The lateral chains can be introduced on the inner rings as shown by Weissflog and Demus [2–4] or on the outer rings to lead to polycatenar compounds [5–7]. We have shown recently that a core containing four aromatic rings can accommodate one or two lateral flexible substituents and still support liquid crystal properties. Although these mesogens deviate from the classical rod-like shape, they may exhibit a large nematic range [8–11]. In our previous papers, the alkoxy chains were introduced on one of the inner rings, leading to a large enantiotropic nematic phase. We have pointed out for numerous structures that the nematic field enforces the folding back of the chains along the mesogenic core. This folding back preserves the molecular anisotropy which is a necessary condition for the thermodynamic existence of the mesophase. We have already explored different substitution patterns. Mesogenic compounds containing four rings in the core were synthesized with one lateral chain [8, 9], with two nearby lateral chains [10], with one lateral chain and a lateral aromatic fragment [11, 12] and with a bifurcated chain instead of two lateral chains [13]. We have shown that introducing two nearby chains enhances the nematic range, because the second chain fits in the empty space created by the first one [10]. It is of phenomenological interest to introduce these two lateral chains on the outer rings as their effects on the mesophase stability can differ. In fact, the mesophase type depends on the position of the second chain. Usually, when this second chain is introduced near the terminal one, a smectic phase is typically observed, while a nematic phase is obtained when the lateral chain is introduced in the *meta*-position with respect to the terminal one. Some symmetrical compounds containing six chains have been described in the literature where the two lateral chains are introduced in the *ortho*- and *meta*-positions with respect to the terminal one on each outer ring [14, 15]. Many of these compounds have a small nematic range or monotropic properties.

In this paper, we will re-examine the problem of four-ring mesogens containing six chains in order to delineate the influence of these lateral chains on the

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Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online ©1999 Taylor & Francis Ltd
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liquid crystalline range and on the ordering in the nematic phase. Therefore, we present the synthesis and the mesomorphic properties of three new series having four rings in the mesogenic core and six chains grafted on the two outer rings, but differing in the links between the aromatic rings. Series **I** and **II** shown in figure 1 can be considered as dimers, which facilitates the NMR study of these series. The shape of the whole molecule is mainly dependent on the first methyleneoxy fragment of the lateral chains. To study the conformational behaviour of these fragments, ^{13}C NMR in the liquid crystal phase can be used through the chemical shift anisotropy and the C–H bond order parameter. For a static sample, the sign of the chemical shift anisotropy observed on entering the nematic phase gives the sign of the order parameter [16], whereas its magnitude is evaluated from the C–H dipolar couplings. In the present work, these dipolar couplings have been determined by using transient dipolar oscillations during the cross-polarization process on a static sample [17–19].

2. Experimental

2.1. *Synthesis*

The synthetic scheme for series **III** is presented in figure 2 and the synthesis is now briefly described.

2,3,4-Trihexyloxybenzaldehyde was prepared in one step by total etherification of 2,3,4-trihydroxybenzaldehyde (THB) using phase transfer catalysis. The reaction was carried out in aqueous conditions under nitrogen by mixing the aldehyde (1 eq. mol), hexyl bromide (3 eq. mol) and Aliquat 336 as phase transfer catalyst. The solution was brought to 80°C and a solution of NaOH (3 eq. mol) in water was added over a 4 h period. The reaction time was 12 h. After extraction into ether, the aldehyde was chromatographed on silica gel (60–200 mesh) with CH_2Cl_2 as eluent.

For series **I** and **II**, the Schiff base was obtained by reacting the 2,3,4-trialkoxybenzaldehyde with the corresponding diamine in boiling ethanol.

For series **III**, the 2,3,4-trialkyloxybenzaldehyde (1 eq. mol) and 4-nitrotoluene (1.5 eq. mol) were dissolved in PEG 200 at room temperature. A homogeneous solution of potassium *t*-butoxide (1.5 eq. mol) in PEG was then added to the above solution. The temperature was raised to 80°C and the reaction mixture was left at this temperature during 12 h. After cooling, the mixture was shaken three times with ether, and the ethereal solution was washed with dilute acid. Evaporation of the ether and recrystallization from ethanol led to the pure 2,3,4-alkyloxy-4′-nitrostilbene. Then, the reduction coupling of the nitro group was effected using zinc in ethanol under basic conditions [20]. Due to the precipitation of the azoxy compound, the azo compound is not obtained. The crude product was chromatographed on silica gel (60–200 mesh) with CH_2Cl_2 as eluent. The final product was recrystallized from a mixture of chloroform/ethanol

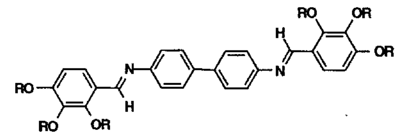
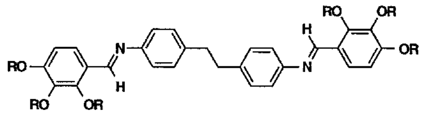
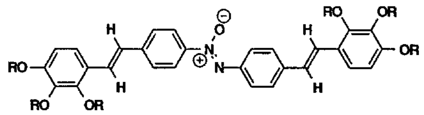
Series **I** **BSBn** n= 4, 6, 8, 10, 12	
Series **II** **PSBn** n= 4, 6, 8, 10, 12	
Series **III** **AZOn** n= 4, 6, 8, 10, 12	

Figure 1. Structure for the three series synthesized. Each series contains 6 chains with $n = 4$, 6, 8, 10 and 12 carbons in each chain.

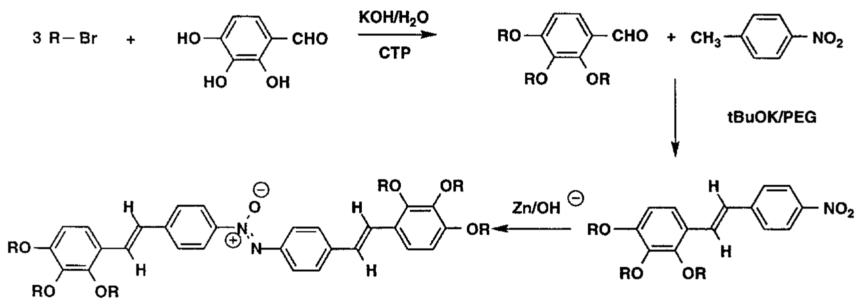


Figure 2. Synthetic scheme for series **III**.

until constant transition points were obtained. These transition points were measured by DSC (Mettler FP 52) using a heating rate of 10°C min^{-1}.

2.2. *NMR experiments*

The ^{13}C NMR spectra in CDCl$_3$ solution were recorded with a Bruker DRX-400 NMR spectrometer at $B_0 = 9.39$ T. The heteronuclear correlation sequence was the gradient enhanced version of the HMBC sequence [21]. All B_0 gradients have a sinusoidal shape of 1.5 ms duration. The HMBC 2D ^{1}H-^{13}C was obtained with GARP decoupling.

The 1D and 2D ^{13}C NMR experiments in the nematic phase 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 using a standard CP (cross-polarization) sequence with strong decoupling for lower temperatures. To avoid rf overheating, a 15 s delay time was used. The temperature calibration was made by observing the nematic to isotropic transition. The pulse sequence used in the 2D separated local field (SLF) experiment was identical to the one already published [19]. The pulse sequence contained four times: an initial CP contact of 1 ms, a delay where the proton magnetization was destroyed, followed by the oscillatory transfer period between H and C reservoirs under Lee–Goldburg conditions and finally the acquisition time under proton decoupling. Using Lee–Goldburg decoupling [22] permits a reduction of the homonuclear dipolar coupling during the cross-polarization step, so giving a better resolution along the dipolar axis. Due to the high power used during the Lee–Goldburg decoupling, a 45 s recycle delay was used [19].

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3. Results and discussion

3.1. *Transition temperatures*

The transition temperatures of the compounds synthesized in the three series are given in table 1. An enantiotropic nematophase is observed for all the compounds with the exception of the first and the last members in series **I** and **II** (figure 3). The C12 compounds in series **I** and **II** are monotropic in behaviour. All the nematogens give a large supercooled mesophase range.

As expected, the nematic range is rather sensitive to the links between the rings. Less conjugative links depress the mesophase stability and the transition temperatures. In all series T_{NI} falls as the chains lengthen, but the nematic range increases with n up to the C8 member which presents the largest nematic range. We assume that folding back of the lateral chains occurs with overlapping (figure 4) of the *ortho*-lateral chains, but when $n > 8$, the width of the molecule is increased and this appears to influence the molecular packing in the crystal such that the m.p. falls less sharply or increases, curtailing the nematic range. Accordingly, the maximum phase range should appear for the C8 or C9 member depending on the absence or presence of a diatomic link in the central part of the molecule.

Table 1. Transition temperatures (in °C) in the three series **BSB*n***, **PSB*n*** and **AZO*n***. These values were measured with increasing temperature (DSC heating rate 10°C min^{-1}). Cr: solid, N: nematic, I: isotropic. Temperatures in parenthesis are monotropic temperatures and were obtained with decreasing temperature (DSC cooling rate 10°C min^{-1}).

Compound	Cr	→	N	→	I
BSB4	•	152			•
BSB6	•	94.5	•	105	•
BSB8	•	68	•	90	•
BSB10	•	61	•	75	•
BSB12	•	71		(67)	•
PSB4	•	80			•
PSB6	•	51.5	•	70	•
PSB8	•	35.4	•	64	•
PSB10	•	36.5	•	52.5	•
PSB12	•	47		(46)	•
AZO4	•	150.5	•	180.5	•
AZO6	•	82	•	147	•
AZO8	•	54	•	127	•
AZO10	•	61	•	107.5	•
AZO12	•	75	•	91	•

It should be noted that the C12 member of series **III** which still gives an enantiotropic mesophase has the chemical formula of $C_{100}H_{166}N_2O_7$, and that this nematic compound contains more than twice the number of carbon atoms in the chains than in the core.

In order to have a better view of the influence of the lateral chains on the mesophase stability, we synthesized some compounds with 2, 4 or 6 hexyloxy chains in different positions. Usually, when a rigid lateral substituent is introduced directly into the core, the anisotropic broadening of the molecule perturbs the cooperative packing needed to form the mesophase so that the change in the clearing temperature is related to the substituent's Van der Waals radius [23]. In the case of a single flexible substituent in a mesogenic series, it was observed that every additional carbon in the lateral chain causes only a slight additional perturbation of the liquid crystal properties, indicating that the lateral flexible substituent is oriented along the molecular long axis and presents less conformational disordering [24]. In addition, the mesogenic properties are related to the shape anisotropy of the molecule which is dependent on the different conformations of the lateral fragment itself, influenced by the near substituents or rigid fragment.

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Figure 3. Nematic ranges for the three mesogenic series **BSB*n***, **PSB*n*** and **AZO*n***. The transition temperatures were measured by DSC (Mettler FP 52) using a heating rate of 10°C min^{-1}. Compounds **BSB12** and **PSB12** are monotropic in behaviour.

For the monosubstituted compounds, the 4-substituted compound has a large liquid crystalline range starting at $T = 221°\mathrm{C}$ with a smectic phase. Changing the terminal position of the chain induces a drop in the melting temperatures. The clearing temperatures are however reduced to a larger extent leading to the disappearance of the mesogenic properties. This is a consequence of the replacement of a terminal chain by the lateral one, which, in the solid, reduces the core–core interactions and, in the mesophase, the molecular shape anisotropy.

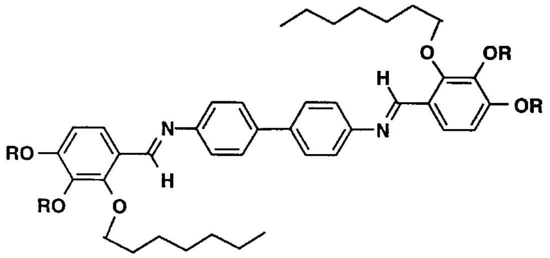


Figure 4. Proposed mean conformation for the overlapping of the *ortho*-chains.

For disubstituted compounds, only the 2,4-disubstituted compound gives a narrow mesophase. The two chains contribute to the shape anisotropy preventing the segregation of the aromatic and aliphatic parts. This leads to the observed nematic phase. The introduction of a chain in position 3 increases the mesophase stability. This additional chain does not change the molecular shape anisotropy and permits a lesser degree of conformational disordering due to the steric hindrance of the first chain fragments. Therefore, three lateral chains are better than two to enhance the nematic stability. In addition, rather low melting temperatures can be obtained even if the molecular weight is quite large.

3.2. *Isotropic chemical shifts*

We have studied only the symmetric compounds by ^{13}C NMR. The isotropic chemical shifts were assigned using the group contribution method, the J coupling pattern, and HMBC and HMQC 2D experiments. A typical HMBC 2D spectrum is presented in figure 5. As an example, the Ha hydrogen is connected to the C11

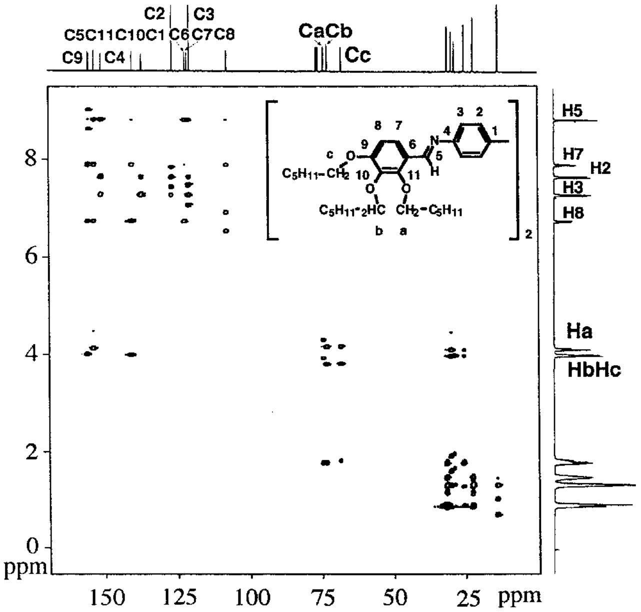


Figure 5. HMBC 2D spectrum of **BSB6** dissolved in $CDCl_3$.

carbon which is found to be also connected to the imine hydrogen H5.

To control the assignment of the methyleneoxy carbons within the lateral chains, let us consider the influence of the –OCH_2– isotropic ^{13}C chemical shift of the alkoxy chains in some homologous compounds dissolved in $CDCl_3$ (table 2). For monosubstituted compounds, we can check that the position of the chain on the aromatic ring slightly modifies the –OCH_2– chemical shift through the change of the oxygen electron density. For the 2,4-dihexyloxy compound, each –OCH_2– chemical shift does not depend on the other chain. This is not the case for the two other compounds having two nearby chains. For the 3,4-dihexyloxy compound, a downfield shift of roughly 1 ppm is observed for both signals, whereas for the 2,3-dihexyloxy compound downfield shifts of 0.6 and 6 ppm are measured. This different behaviour is due to the fact that the chemical shift is averaged over all the conformations. If the chain is locked in between two rigid substituents, the first carbons in the chain are free of any γ-*gauche*-effect. This means that the conformations where the methyleneoxy carbon is in a *gauche*-position with respect to the fourth carbon within the chain cannot exist. The disappearance of these γ-*gauche*-conformations induces a downfield shift [25, 26]. Therefore, in the 2,3-dihexyloxy compound, the 74.37 ppm chemical shift is attributed to the Ca carbon. The 68.84 ppm chemical is assigned to the Cb carbon which is less sterically hindered (the observed downfield shift is equivalent to that in 3,4-dihexyloxy compound). In the 2,3,4-trihexyloxy compound the Cc carbon presents a chemical shift of 68.64 ppm (downfield of 0.6 ppm by comparison with the monosubstituted compounds). The Ca carbon has a chemical shift of 74.78 ppm, slightly downfielded when compared with the 2,3-dihexyloxy compound. The Cb carbon is now in between two chains and presents a large downfield shift and has a chemical shift of 73.58 ppm. This assignment is consistent with the one indicated by the 2D experiment correlations.

3.3. *Anisotropic chemical shifts (figure 6)*

The ^{13}C chemical shift changes can be related to the macroscopic order parameter by the semi-empirical equation [27]:

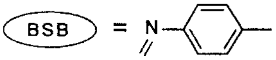
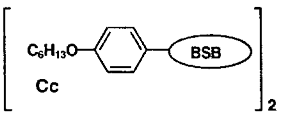
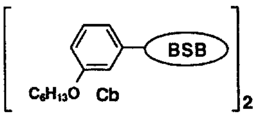
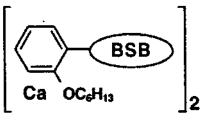
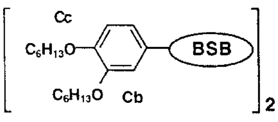
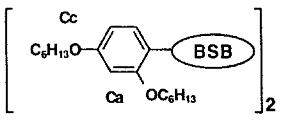
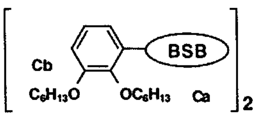
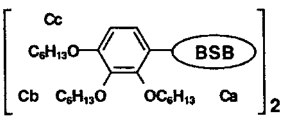
$$\delta_{obs} = \delta_{iso} + aS_{zz} + b \qquad (1)$$

where a and b are constants which are assumed to be independent of the temperature, within experimental error. If we assume a Haller [28] type dependence of the order parameter versus temperature, equation (1) can be rewritten as:

$$\delta_{obs} = A + B \times (1 - T/T\dagger)^{F} \qquad (2)$$

where $A = \delta_{iso} + b$ and $B = S_0 \times a$. The carbons belonging to the same *para*-disubstituted ring must have the same S_0 and F values. This has been used to help the assignment of different peaks in the spectrum. Thus, all the lines were fitted with equation (2) using the four parameters A, B, $T\dagger$ and F. The value of $T\dagger$ was found to be slightly higher than T_{NI} by ~1 K. Then, $T\dagger$ was fixed to its average value and the lines refitted with only three parameters. The higher F value indicates a more rigid fragment [29]. It is found that ring 1 is slightly more rigid than ring 2, as their F values are 0.19 ± 0.01 and 0.16 ± 0.01, respectively. Surprisingly, the individual F values of the tetrasubstituted ring are larger and less scattered compared with those obtained for other laterally substituted compounds [10–12]. The grafted lateral chains do not significantly affect the rigidity of ring 2, indicating that the lateral chains do not perturb the ordering process of this ring.

Table 2. Transition temperatures (in °C) and isotropic ^{13}C chemical shifts of the methyleneoxy carbons in some related compounds containing 2, 4 and 6 hexyloxy chains. Cr: solid, Sm: smectic, N: nematic, I: isotropic.

			
δ/ppm (OCH_2) Transition temp.	$\delta_c = 68.06$ $T_{CrS} = 221$ $T_{SmN} = 252$ $T_{NI} > 300$	$\delta_b = 68.02$ $T_{CrI} = 112$	$\delta_a = 68.36$ $T_{CrI} = 93$
			
$\delta_b = 69.09$ $\delta_c = 69.02$ $T_{CrI} = 171$	$\delta_a = 68.35$ $\delta_c = 68.1$ $T_{CrN} = 97$ $T_{NI} = 102$	$\delta_a = 74.37$ $\delta_b = 68.84$ $T_{CrI} = 133$	$\delta_c = 68.64$ $\delta_b = 73.58$ $\delta_a = 74.78$ $T_{CrN} = 94.5$ $T_{NI} = 105$

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Two behaviours are observed in plot (*b*) of figure 6, a positive jump for the chemical shifts of the lateral methyleneoxy carbons, and a negative one for the methyleneoxy carbon in the terminal chain. This positive jump has been associated with the folding back of the chains along the core, giving rise to a positive C–H bond order parameter. The assignment of the lines for the lateral methyleneoxy is more difficult as it is possible to have a crossing of the lines in the early stage of the transition. For this reason these two lines which possess a sufficient anisotropy were fitted with equation (2). The most deshielded line has a value for constant A, in equation (2), of 82.5 ppm and the less deshielded a value of 77.7 ppm. Assuming that the main contribution for constant A comes from $\delta_{\rm iso}$ and that b is usually small [29], this is a good indication that no crossing arises for these two lines. The two lines have nearly the same F value of 0.44 ± 0.02. This large value indicates the hindrance of the motions for these carbons [10].

3.4. *Analysis of the CP efficiency*

Figure 7 shows the 2D SLF spectrum of **BSB6** in the nematic phase. At the top, the 1D ^{13}C spectrum is presented as obtained with a contact time of 1 ms. In the aromatic region, the assignment is the one presented in figure 6 (*a*). In the aliphatic region, the signals from the chains overlap and no assignment is possible. The most striking feature of this spectrum is the difference in the efficiency of the polarization for C10 and C11; this difference is related to the geometry of the imine bond in the nematic phase. For a simple imine bond found in an unsubstituted benzylideneaniline, some *ab initio* calculations have been carried out to obtain the preferred conformation [30]. They indicate that the minimum energy conformation is obtained with 0° and 45° torsion angles for the C–phenyl and the N–phenyl parts, respectively [30]. Two factors are generally taken into account to explain such a large torsion angle around

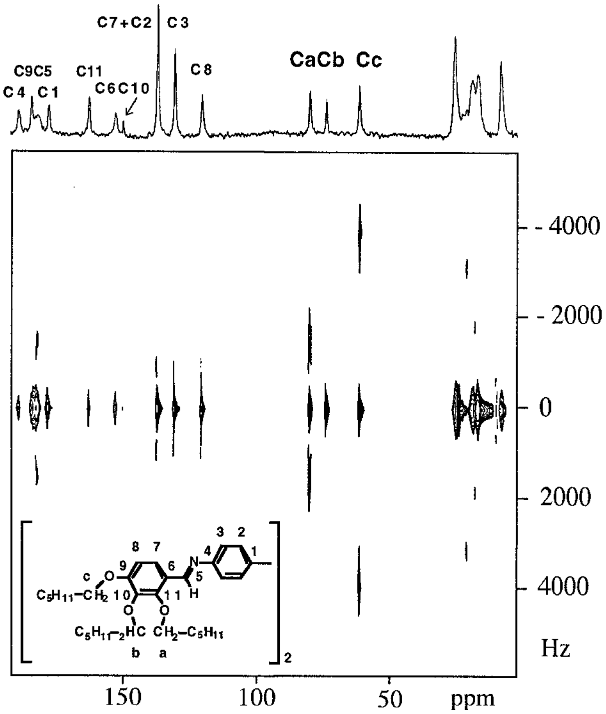

Figure 7. 2D SLF spectrum of **BSB6** in the nematic phase at 373.5 K.

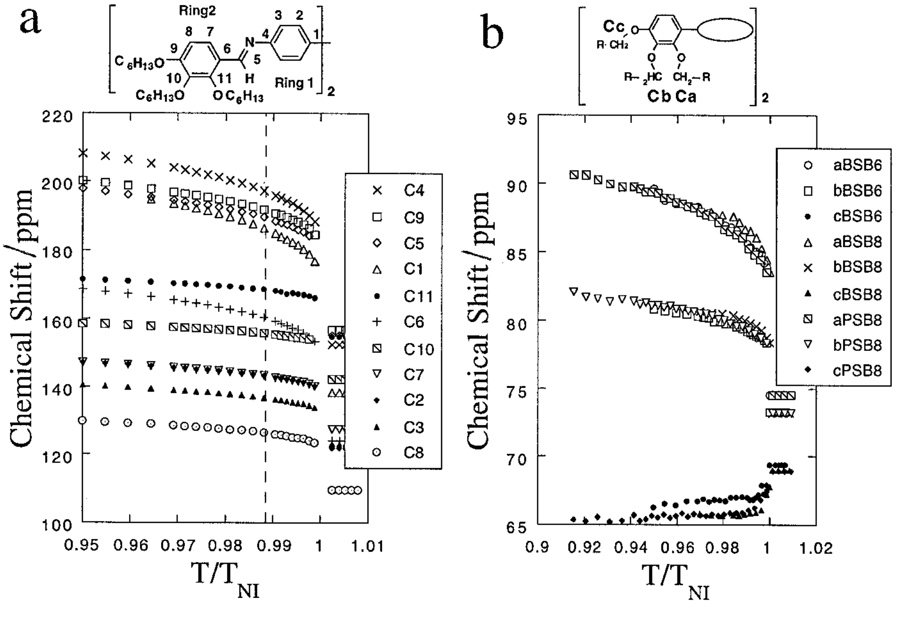

Figure 6. The chemical shifts of the aromatic part of **BSB6** (*a*) and the methyleneoxy region of **BSB6**, **BSB8** and **PSB8** (*b*) plotted against the reduced temperature. The chemical shifts were obtained with decreasing temperature from the isotropic melt. The dashed line in the (*a*)-plot indicates the reduced temperature where the 2D experiment was performed.

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the N–phenyl bond: first, the possibility of getting partial conjugation of the nitrogen lone pair with the π-system of the aniline ring; second, the non-bonding interaction between the hydrogen of the imine and the hydrogen in the *ortho*-position of the aniline ring. These two factors are competitive with the conjugation of the double bond with the π-system of the aniline ring that enforces the coplanarity motif. By molecular modelling on one *ortho*-alkoxy substituted compound, we have found that the N atom cannot lie on the same side as the lateral substituent due to steric interactions between the nitrogen and oxygen lone pairs. In accordance with this calculation, the hydrogen of the imine has to be located on the same side as C11. C11 and C10 are quaternary carbons, and they experience a similar H environment from the hydrogens belonging to the aromatic ring. It is straightforward to see from the trace above the 2D spectrum in figure 7 that during the cross-polarization step, they behave in different ways. C11 polarizes due to the coupling with the imine hydrogen. The most stable conformations, then, are the ones where the hydrogen of the imine points towards the oxygen. This explains why C11, which is spatially near the hydrogen of the imine, gives rise to a more intense line than C10.

3.5. *Analysis of the dipolar couplings*

In the 2D experiment, the cross-peaks corresponding to the $-OCH_2-$ group of the terminal chain (Cc carbon) have a large separation ($\Delta\nu = 7900$ Hz). A smaller separation is observed for the Ca carbon ($\Delta\nu = 3250$ Hz), whereas no cross-peaks are observed for the Cb carbon. The linewidths of the axial peaks are respectively 850, 950 and 900 Hz. It is evident from these observations that the two first fragments in the lateral chains do not behave in the same way. The dipolar coupling constants can be extracted from the observed carbon–proton splitting ($\Delta\upsilon$) in the 2D experiment using equation (2):

$$\Delta\upsilon = f(2)^{1/2}[2D_{C\text{–}H} + J] \qquad (3)$$

where f is the scaling factor, which is equal to 0.82 for Lee–Goldburg decoupling, and J is the scalar coupling constant determined from the coupled isotropic spectrum (144 Hz for the $-OCH_2-$ carbons, 162 Hz for the imine carbon).

Then, the C–H bond order parameter can be extracted from the corresponding dipolar coupling constants by:

$$S_{C\text{–}H} = -4.407 \times 10^{-5}\, D_{C\text{–}H}. \qquad (4)$$

The bond order parameter depends on the mean orientation of the C–H vector with respect to the magnetic field as well as the amplitude of fluctuation about the mean orientation. Therefore, several drastic approximations are needed to extract some information from the value of the bond order parameter. In particular, we will focus the analysis on the first carbons in the chains. These carbons exhibit less conformational disordering than the subsequent carbons, due to their strong steric hindrance. For the terminal $-OCH_2-$ carbon, D is negative due to the particular C–H bond angle with the molecular long axis, if we assume the extended conformation of the chain and J positive. For the lateral Ca carbon, D is positive due to the folding back of the chain. This gives a bond order parameter of -0.16 for the terminal CcH bond and $+0.059$ for the CaH bond. Assuming a positive bond order parameter for the CbH bond, from the linewidth of the singlet peak in the 2D, its value has to be less than $+0.01$. For the CaH bond, the order parameter value agrees with the one observed for other laterally substituted compounds [11, 29], as it is folded back along the rigid core. For the CbH bond, the order parameter is very small. The C–H vector has to lie nearly parallel to the magic angle with respect to the molecular long axis. This behaviour is certainly consequent upon the folding of the chain along a more flexible fragment: the terminal chain. Some calculations were performed on a single molecule and indicate that the two C–O–C–C fragments in the lateral alkoxy chains may present a *gauche*-conformation to prevent strong steric interactions between the two $-OCH_2-$ groups.

In the case of the imine carbon the cross-peak separation, after scaling, is 3.88 kHz, a value nearly half of that (7.74 kHz) found in MBBA [18], which shows that the molecular long axis and the local geometry of the imine bond may depend on the lateral chain substitution.

4. Conclusion

We have synthesized new nematic compounds containing four aromatic rings and six alkoxy chains. These chains are introduced on each outer ring in 2,3,4-positions with respect to the links. These compounds deviate markedly from the classical rod-like shape, but they exhibit a nematic range which increases with the link rigidity. Thus, it was possible to obtain mesogens with a high content of paraffinic chains. By applying 1D and 2D ^{13}C NMR techniques, the orientational ordering of the first carbons in the aliphatic chains has been studied. This shows that the two lateral alkoxy substituents are folded back along the mesogenic core, involving a *gauche*-conformation for the first C–O–C–C fragment. The lateral chain along the core is more ordered than the one folded back along the terminal chain. The orientation of the molecular long axis is not much influenced by the presence of the lateral chains. Further work is under way to show the anisotropic solvent properties of these mesogens containing a large amount of alkoxy chains.

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