

Influence of large lateral substituents on the nematic liquid crystalline properties studied by ^{13}C NMR

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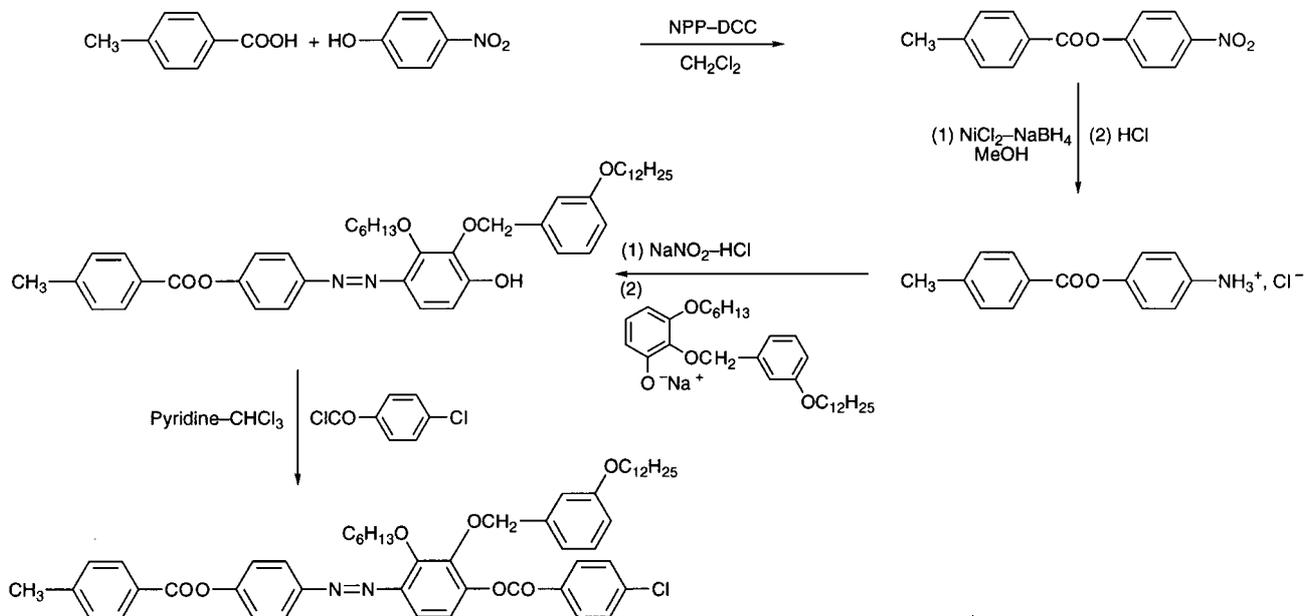
It has been shown that two nearby large lateral substituents can be introduced on the same side of a mesogenic core without destroying the nematic range, even if the pattern of substitution is not favourable. The newly synthesized compounds contain four rings in the main core, a lateral hexyloxy chain and a lateral aromatic branch. This aromatic ring itself is modified by different substituents at the *meta* or *para* position with respect to the core linkage. Two isomeric compounds containing a dodecyloxy chain in these positions have been studied by ^{13}C NMR spectroscopy in the liquid crystalline phase. On entering the nematic phase, the ^{13}C chemical shift showed a positive jump for the oxomethylenes attached to the core, but a negative jump for the oxomethylene on the aromatic lateral branch. It is found that the two lateral substituents are folded back along the core, implying a *gauche* conformation for the first fragment. However, in the dodecyloxy chain, the first and the subsequent methylene carbons have negative order parameters, showing a classical all-*trans* mean chain conformation. The values of the order parameters were derived from the transient oscillations observed during variable contact-time ^1H - ^{13}C cross-polarization experiments. The order parameter values are not very dependent on the substitution position of the dodecyloxy chain. As a consequence, the dodecyloxy chain aligned in the nematic field affects the average molecular shape and the mean orientation of the whole molecule.

Influence de substituents latéraux volumineux sur les propriétés cristal liquide étudiée par RMN ^{13}C . Nous avons synthétisé des nouveaux composés nématogènes contenant quatre cycles aromatiques dans le coeur central et possédant deux substituents latéraux adjacents. Le premier est une chaîne hexyloxy, le second contient un cycle aromatique lui-même substitué en *para* ou *méta* par des groupements rigides ou par une chaîne alkoxy. Les groupements rigides perturbent peu les propriétés mésogènes de ces composés, à l'inverse de ce qui est observé pour les chaînes alkoxy. Deux composés isomères ayant une chaîne dodécyloxy greffée sur le cycle latéral ont été étudiés par spectroscopie RMN ^{13}C . Lors du passage dans la phase nématique, les déplacements chimiques présentent un saut positif pour les oxométhylènes directement accrochés au coeur, tandis que l'oxométhylène de la chaîne dodécyloxy montre un saut négatif. Ceci implique que les deux substituents latéraux sont globalement alignés le long du coeur mésogène, impliquant une conformation *gauche* pour le premier fragment, tandis que la chaîne dodécyloxy présente une conformation moyenne *trans*, quelque soit le composé. Les paramètres d'ordre des carbones des chaînes ont été déterminés à partir des oscillations dipolaires C-H observées lors des montées de polarisation. Les valeurs des paramètres d'ordre sont peu dépendantes de la position des carbones dans la chaîne dodécyloxy. Ceci implique que cette chaîne est alignée dans le champ nématique, ce qui affecte la forme moléculaire ainsi que l'orientation moyenne de la molécule.

Laterally substituted mesogens substantially deviate in shape from the classical rod-like mesogens.¹⁻⁴ A terminal alkoxy chain in a classical mesogenic molecule can be switched to a lateral position with some interesting features such as decreases in the core-core interactions, conformational entropies and transition temperatures. It has been shown that two lateral substituents on the same side of one inner ring do not destroy the liquid crystal phase; namely, an enantiotropic nematic phase has been obtained with wide nematic range.⁵⁻⁷ Several combinations of two lateral substituents have been studied: an alkoxy chain and a methyl group,⁵ two alkoxy chains⁶ and an alkoxy chain and a *para*-chlorinated aromatic branch.⁷ We have shown that flexible substituents take a peculiar conformation to accommodate themselves to the anisotropic packing encountered in the nematic phase. On the other hand, a less flexible aromatic branch cannot act in the same way; the *para* axis of this lateral aromatic ring makes a non-negligible angle with the long molecular axis.⁷ Thus, the terminal substituent on this ring certainly hinders the molecular packing in the mesophase and consequently decreases the

nematic range. Changing the substituent position in the lateral aromatic ring is of interest as we can expect a different free spacing filling in the nematic phase. We can expect some further decrease in the core-core interactions, leading to a better thermodynamic stability of the nematic phase. In addition, to relate the anisotropy of the lateral substituent groups and the mesogenic properties may give conceptual ideas that may lead to further synthetic efforts.

Thus, in this paper, the addressed problem is rather simple: can rigid groups or alkoxy chains on the lateral aromatic branch help the mesogenic properties? To answer this question, we present the synthesis and mesomorphic properties of some new compounds having the same core as in previous series^{6,7} but differing by the lateral substituents. One of the inner rings bears a lateral hexyloxy chain and one aromatic branch. Additional substituents are introduced in the *meta* or *para* position of the branched aromatic ring. We thus obtain doubly-branched mesogenic molecules. The effect of the substituent type and position on the mesomorphic properties of the compounds are discussed. The liquid crystalline properties



Scheme 1 Synthetic scheme for 3-C12 compound

are highly related to the mean geometry adopted by the flexible fragments in the mesophase, which can be studied by ^{13}C NMR spectroscopy⁸ through the bond order parameter. We chose to obtain chain order parameters for two isomers having a dodecyloxy chain in the *meta* and *para* positions on the lateral aromatic branch. For a static sample, the alignment-induced shift observed on entering the nematic phase gives the sign of the order parameter.⁹ The magnitude of the order parameters can be evaluated from the C–H dipolar couplings of each molecular segment within the molecule. In the present work, these dipolar couplings have been determined by use of transient dipolar oscillations during the cross-polarization process on a static sample.^{10–12}

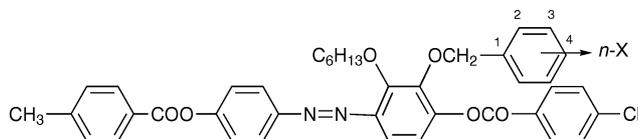
Experimental

Synthesis

The compounds were prepared according to a similar scheme. As an example, the synthesis of 3-(3-*n*-dodecyloxybenzoyloxy)-2-*n*-hexyloxy-4-(4-chlorobenzoyloxy)-4'-(4-methylbenzoyloxy)-azobenzene is presented in Scheme 1.

2-(3-*n*-Dodecyloxybenzoyloxy)-3-*n*-hexyloxyphenol was prepared in two steps by the selective etherification of 1,2,3-trihydroxybenzene using a standard procedure.^{7,13} *p*-Toluic acid was esterified with *p*-nitrophenol using the DCC method in dichloromethane.¹⁴ After imide filtration and solvent evapo-

Table 1 Transition temperatures (°C) and transition entropies (in parentheses) of laterally disubstituted compounds. K: crystal, N: nematic, I: isotropic, (mono): monotropic nematic. The compounds are referred to as *n*-X where *n* is the substitution position on the lateral branch and X the substituent



Compound	K ₁	→ ($\Delta S_{KK}/R$)	K ₂	→ ($\Delta S_{KK}/R$)	K ₃	→ ($\Delta S_{KN}/R$)	N	→ ($\Delta S_{NI}/R$)	I
3-Cl (1)	•					107.5 (24.8)	•	136.5 (0.15)	•
4-Cl (2)	•					126.5 (25.9)	•	161.5 (0.33)	•
3-Me (3)	•	83.5 (15.3)	•	91 (6.9)	•	98 (1.37)	•	144 (0.20)	•
4-Me (4)	•					114 (26.2)	•	161 (0.26)	•
3-C12 (5)	•							95 (mono) (28.9)	•
4-C12 (6)	•					94 (40.9)	•	107.5 (0.16)	•
3-C6 (7)	•	84.5 (13.5)	•			94 (12.6)	•	109.5 (0.19)	•

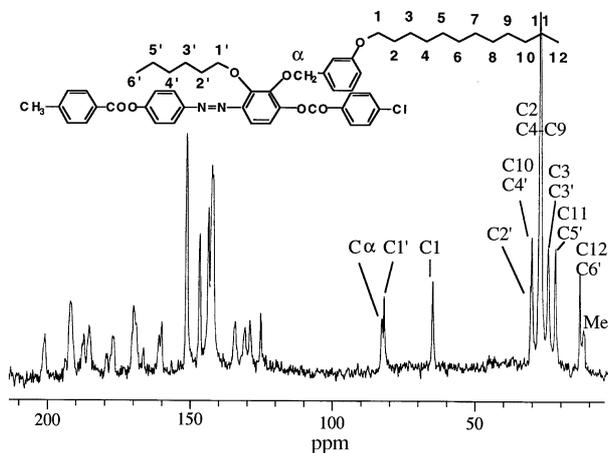


Fig. 1 Proton-decoupled ^{13}C spectrum of **3-C12** in the nematic phase at 67.942 MHz with aliphatic carbon labelling. Acquisition parameters: cross-polarization (CP) with flip-back, contact time = 1 ms, recycle delay = 6 s, number of scans = 300, temperature = 84 °C

ration, the crude ester was chromatographed on silica gel (60–200 mesh) with CH_2Cl_2 as eluent. The purified ester was collected as the first fraction. The nitro group in this compound was selectively reduced using the $\text{NiCl}_2\text{-NaBH}_4$ reducing system.¹⁵ The amine was not regenerated, but the crude solid aniline hydrochloride was filtered and used without further purification for the diazotization step. Then, the diazotization was performed at room temperature in PEG 200 solvent, by coupling the diazonium salt with the disubstituted phenol under basic conditions. Diazotization occurred mainly in the *para* position to the remaining hydroxyl group. The crude product was chromatographed on silica gel (60–200 mesh), with CH_2Cl_2 –ethyl acetate (80 : 20) as eluent, and the compound was collected as the last fraction. Finally, the phenol was esterified with 4-chlorobenzoyl chloride in CHCl_3 –pyridine solvent. After chromatography (silica gel, 60–200 mesh, eluent CHCl_3 , first fraction), the final product was recrystallized in a mixture of toluene–ethanol–4-methylpentan-2-one (10 : 80 : 10) until constant transition temperatures were obtained. The transition points were measured by DSC (Mettler FP 52) using a heating rate of $10^\circ\text{C min}^{-1}$. All compounds contain the same core and the same lateral hexyloxy chain. Therefore, they are labelled *n*-X according to the position (*n*) and the type of substituent on the lateral aromatic branch (X) (Table 1). As an example, the compound in Scheme 1 is referred to as **3-C12**.

^{13}C NMR measurements

The ^{13}C NMR experiments were performed using a JEOL GSX-270 NMR spectrometer operating at the Larmor frequency of 67.942 MHz. A 150 mg mass of each sample was introduced in a 6 mm Pyrex tube and sealed in vacuum after a freeze-pump-thaw cycle. ^{13}C chemical shifts were measured on a static sample aligned parallel to the magnetic field using a ^{13}C single pulse and strong decoupling of the hydrogens. Transient dipolar oscillations were obtained by increasing the contact time in a classical cross-polarization (CP) experiment. Flip back of ^1H magnetization was used at the end of the decoupling period. The rf power was 38 kHz on both nuclei. To avoid rf overheating due to the strong decoupling, a 6 s recycle delay was used between acquisitions. The temperature calibration was made by observing the nematic-to-isotropic transition. A thermal equilibration time of 20 min was provided prior to each measurement. We chose to study by NMR the **3-C12** and **4-C12** isomers in order to examine the influ-

ence of this long chain position on the ordering of different fragments of the mesogens. A typical ^{13}C spectrum of **3-C12** is presented in Fig. 1. The aromatic region is quite crowded due to the presence of the five aromatic rings. In the nematic phase, the assignment for the aromatic carbons is always tricky due to line crossings of the quaternary carbons, which have larger chemical shift anisotropies. Here, this assignment is particularly difficult due to strong peak overlapping and will not be presented. Fortunately, the line crossings are rare in the aliphatic region, due to the smallness and similarity in chemical shift anisotropies of these carbons. The assignment within the aliphatic region is given in Fig. 1.

Results and Discussion

DSC measurements

The phase transitions were observed with a Mettler DSC 30 and characterized by using an Olympus polarizing microscope fitted with a Mettler FP 82 heating stage. The transition temperatures of the compounds are given in Table 1. All compounds exhibit an enantiotropic nematic phase except for **3-C12**, which exhibits a monotropic nematic phase. We synthesized the **3-C6** analog, which possesses an enantiotropic nematic phase. Thus, the monotropic property of **3-C12** arises from the chain length of this compound. The introduction of a chain on the lateral aromatic branch does not change the melting points too much, but markedly depletes the nematic range. It is interesting to note that all compounds have a wide temperature range for the supercooled nematic phase. This is a consequence of the lateral substituents, which reduce the polar intermolecular interactions. The width of the supercooled liquid crystalline phase is found to be larger in compounds having *para*-substituted aromatic branches.

Fig. 2 shows a comparison of the transition temperatures. The magnitudes of the substitution effect are similar in all compounds and seem to be relatively independent of the substituent types. In fact, when the substituent position changes from *para* to *meta*, a 12–25 °C decrease in T_{NI} is observed for the three analogs.

Usually, when a rigid lateral substituent is introduced on a rod-like molecule, the decrease of T_{NI} within a series is directly related to the van der Waals volume of the substituent.¹⁶ This decrease is relatively independent of the length of the mesogenic core. For example, a lateral methyl group introduced on a core containing two or more rings induces a 40 °C decrease in T_{NI} .^{17,18} This has to be compared to the 12–25 °C observed in our compounds when the substituent on the lateral aromatic branch is changed from the *para* to *meta* position. In addition, the mesogenic range is in general strongly reduced, which is not observed here. Therefore, the change in T_{NI} ,

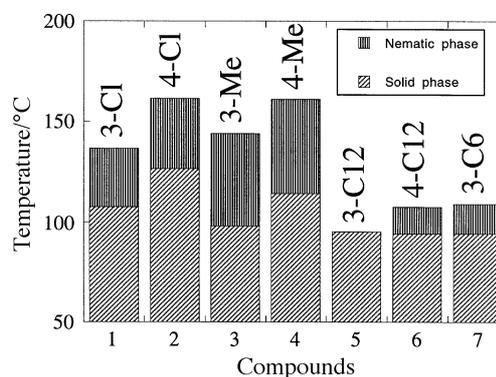


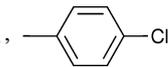
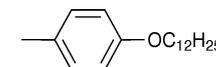
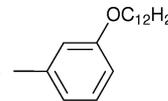
Fig. 2 Comparison of the nematic range (°C) for the different compounds

which is rather independent of the substituent, is not fully related to the steric influence of the substituent itself. On the contrary, the introduction of a dodecyloxy chain on the lateral branch reduces to a large extent the nematic range without affecting too much the melting temperatures. The liquid crystal phase appearance in the laterally substituted compounds is induced by the parallel conformation taken by the flexible substituent with respect to the mesogenic core.^{19–21} Thus, the strong decrease in the nematic range may be attributed to the length of the chain, which is too long to only overlap the core. It can be noted that the *para*-dodecyloxy chain perturbs less the mesophase stability. The entropy changes at the nematic-isotropic temperature ($\Delta S_{NI}/R$) are slightly higher than the ones obtained for compounds having the same core but containing two lateral alkoxy chains ($\Delta S_{NI}/R$ typically in the range of 0.15 to 0.2).⁶ Furthermore, these entropy values do not increase by adding the chain on the lateral aromatic branch. This indicates that the lateral aromatic branch, compared to a lateral alkoxy chain, adds some conformational entropy. But it is not increased by the length of the chain on this fragment.

¹³C chemical shift analysis

The temperature dependence of the chemical shift was studied and the results are presented in Fig. 3(a) (down-field peaks) and 3(b) (up-field peaks) for the **4-C12** compound. The assignment for the up-field peaks is quite straightforward as we clearly have evidenced that the first methylene carbon in the *ortho* position with respect to the diazo link, numbered as 1', has a chemical shift of 76.59 ppm in the isotropic melt.²¹ This chemical shift stays constant in the isotropic melts of all the compounds under investigation (Table 2). Thus, the chemical shift of the OCH₂ of the dodecyloxy chain is located at 68.54 and 68.15 ppm for **4-C12** and **3-C12**, respectively. Referring to the well-known data on 4-*n*-alkoxy-4'-cyanobiphenyls,²² the isotropic chemical shifts of the C1' and C α carbons are unusual. This may be understood because these two OCH₂

Table 2 ¹³C chemical shifts of the —OCH₂— fragment in the isotropic melt of some related compounds having the same core. R, A and acronym are given for each compound

Compound or series R, A	$\delta_{1'}$ /ppm	δ_{α} /ppm
diCn —C _{n-1} H _{2n-1} , —C _{n-1} H _{2n-1}	76.59	74.16
12LC —C ₁₁ H ₂₃ , 	76.56	74.88
4-C12 —C ₅ H ₁₁ , 	76.60	75.92
3-C12 —C ₅ H ₁₁ , 	76.60	75.73

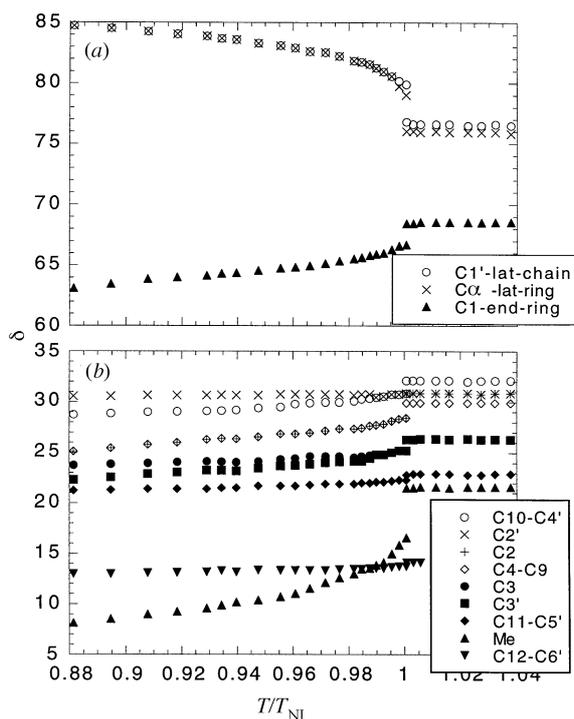


Fig. 3 Temperature dependence of the ¹³C chemical shifts of **4-C12** in a static sample: (a) the three —OCH₂— carbons, (b) the remaining methylene and methyl carbons

groups experience strong steric hindrance. The nearby substituents deplete some conformations (*γ-gauche* conformations, for instance) and as a consequence increase drastically the chemical shift. The assignment for the up-field peaks is given according to previous studies.⁷ In that region, we expect 14 methylene resonances, but only 6 and 7 peaks are resolved for **4-C12** and **3-C12**, respectively. It is interesting to note that two carbons having similar positions within each of the two chains have the same chemical shifts and similar evolutions, except for the C2 and C2' carbons [Fig. 3(b)]. This is a good indication that the carbons after the first two methylenes in each of the chains have similar environments and conformations.

On going from the isotropic melt to the nematic phase, the change in the chemical shift depends on many factors: the anisotropy of the chemical tensor, the components of the ordering matrix for each conformation and the probability to find these conformations in the nematic phase. Therefore, some drastic approximations are needed to extract some information from the change in the chemical shift. In particular, we will focus the analysis on the first carbons in the chains. These carbons exhibit fewer conformations than the subsequent carbons, especially the lateral methoxy carbons are fairly hindered. Thus, we will discuss a mean conformation for these carbons, indicating that the experimental data may be analyzed using the most populated conformation. Let us consider the experimental data: a large positive jump in the chemical shifts is observed for the lateral carbons C1' and C α , whereas C1, belonging to the chain hooked on the aromatic lateral fragment [Fig. 3(a)] and the subsequent methylene and methyl carbons present the usual negative jump [Fig. 3(b)]. This peculiar behaviour is also observed in **3-C12**. The case of C2' in **4-C12** is interesting since its jump and temperature dependence in the nematic phase are negligible. It is also interesting to note that no dipolar oscillation was found for this C—H bond (see next section). These facts mean that the symmetry axis for the local chain motion at the C2' position points close to the magnetic axis and that the intramolecular

motion about this axis averages out both the chemical shielding and the C—H dipole-dipole interactions, although the principal axes system for these two interactions are different. It has been shown that the temperature dependence of the chemical shift (δ_N) in the nematic phase obeys the following semi-empirical equation:²³

$$\delta_N = A + B(1 - T/T^\dagger)F = \delta_{iso} + b + aS_0(1 - T/T^\dagger)F \quad (1)$$

where a and b are independent of temperature and involve the chemical shift tensor components, T^\dagger is a temperature slightly higher than T_{NI} and S_0 is the limit of the C—H bond order parameter relative to the director. The quantity S_0 is roughly a product of two limiting order parameters: the segmental one relative to the long molecular axis and the molecular one relative to the director. Recently, we have shown in some related nematogens that the long molecular axis is close to the nematic director;²⁴ thus, S_0 gives an estimate of the angle between the C—H bond and the long molecular axis. The F value gives an indication of the way that a segment reaches its limiting value of ordering and is related to the segment rigidity.²⁵ The quantity a is usually positive because the C—H axis is perpendicular to the most shielded axis in the local principal axis frame of the ¹³C chemical shielding. Therefore, the negative jump of the chemical shift usually observed for the alkyl chain carbons means that S_0 is negative. This is evidence that a *trans* chain conformation is preferred and that the chain axis points more or less along the director in the nematic phase. Our experimental finding in Fig. 3(a) shows that this is also the case for the C1 carbon belonging to the dodecyloxy chain in the *meta* or *para* positions of the lateral aromatic branch.

In contrast, the lateral C1' and C α carbons exhibit positive jumps at T_{NI} , showing that aS_0 is positive. Thus, if a and S_0 are both positive, the shielding tensor will remain more or less usual and the C—H bond prefers to align in a mean direction with an angle less than the magic angle. On the contrary, if a and S_0 are both negative, the shielding tensor is strongly affected because of the unusual bond angles around this unit and the C—H axis prefers to align as usual perpendicular to the molecular long axis. This second solution was overruled by the experimental finding that the splitting observed in the 2D VASS/SLF (two-dimensional variable-angle sample spinning/separated local field) NMR spectroscopy experiment for this lateral carbon in a homologous compound was found to be negligible.⁵ This non-detectable splitting shows that D_{C-H} and J_{iso} have opposite signs with the consequence that D_{C-H} was found to be negative and S_0 positive [see eqn. (3)]. Fig. 4(a) shows a comparison of the OCH₂ alignment-induced shift in three compounds: **3-C12**, **4-C12** and **4-Cl**. The three sets of data points (open square, circle and diamond) corresponding to the lateral C1' carbons show an amazing overlap. This overlap indicates a similar ordering and thus that the rigid azo aromatic fragment should have, in the three compounds, a similar orientation with respect to the long molecular axis. In contrast, the Cl (two compounds) and C α (three compounds) carbons in the aromatic branch have different behaviours, showing that the ordering of the aromatic branch is certainly influenced by the type and position of the substituent. We will return to this point in the next paragraph. In order to probe the effect of the lateral disubstitution on the ordering of the far part of the core, we use the temperature dependence of the terminal methyl resonances. This methyl group is directly attached to the terminal benzoate ring and it presents a noticeable alignment-induced shift, as shown in Fig. 4(b). The behaviour of the terminal methyl group resonance is similar in the three compounds **4-Cl**, **diC7**⁶ (details about acronyms are given in Table 2) and **4-C12**, but the alignment-induced shift is slightly larger for **4-C12**, indicating a larger limit for the order parameter of the terminal ring. Therefore, the position of the *para* axis of this fragment with respect to

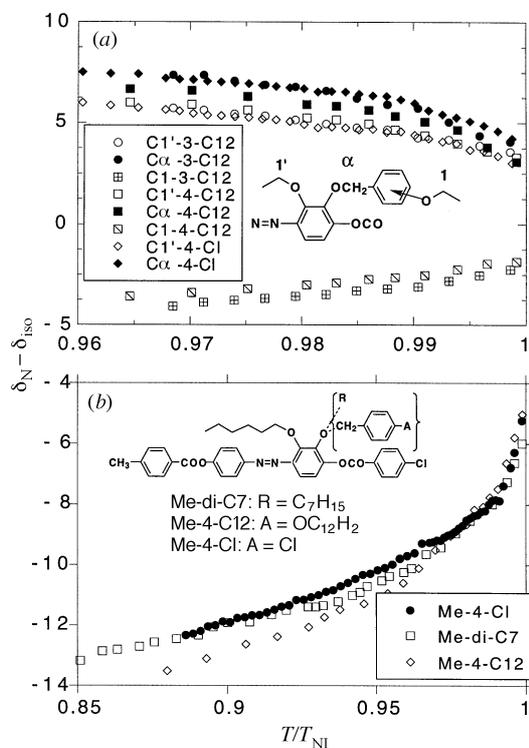


Fig. 4 Temperature dependence of the ¹³C alignment-induced shifts in three related compounds: (a) the —OCH₂— carbons, (b) the terminal methyl carbons

the long molecular axis is affected by the alkoxy chain on the aromatic branch. As it has been shown in previous studies,²⁶ a change in the molecular structure can influence the ordering of far parts of the molecule.

Order parameter analysis using C—H dipolar oscillation

To differentiate the contribution from the order parameter and the chemical shift tensor, use of the C—H dipolar interaction is advantageous. This interaction is less sensitive to the change in local electronic structure than the chemical shielding and therefore it reflects the local order parameter more directly. The order parameters probed by the C—H dipole-dipole interaction can be obtained in the liquid crystal phase by the use of off-magic-angle spinning combined with the separated local field spectroscopy method (VASS/SLF)^{8,27,28} or by the use of transient oscillations in NMR cross-polarization experiments.¹² In this work, the second technique is used and we will compare the order parameters obtained from the **4-C12** and **3-C12** compounds with the one obtained using the first technique on the homologous compound **12LC**.⁷ **12LC** is homologous to **4-Cl** and has a lateral dodecyloxy chain instead of a lateral hexyloxy chain, as shown in Table 2.

Dipolar oscillations have been obtained in magic angle spinning solids^{27–31}, in single crystals¹⁰ or in liquid crystals.^{11,12} In a liquid crystal sample aligned in the magnetic field, there is a preferential macroscopic orientation of the C—H bonds; thus, an oscillatory magnetization transfer between the ¹H and ¹³C spin networks can be detected by the standard CP sequence. The frequency of the magnetization oscillation is mainly related to the local dipolar field involving the directly bonded hydrogens. This oscillatory transfer is damped out by the spin diffusion among hydrogens. This leads to the following expression for the individual normalized

Table 3 Temperature dependence of the parameters obtained by the fitting of the experimental data points to eqn. (2) for compound **4-C12**

Line	D_{C-H}/kHz			$T_{II}/\mu\text{s}$			S_{C-H}		
	0.906	0.933	0.959	0.906	0.933	0.959	0.906	0.933	0.959
T/T_{NI}	0.906	0.933	0.959	0.906	0.933	0.959	0.906	0.933	0.959
$C\alpha + C1'$	2.00	1.86	1.58	683	701	723	0.088	0.082	0.069
C1	3.40	3.04	2.76	432	469	522	-0.149	-0.134	-0.122
C4-C9	2.95	2.57	2.14	396	603	534	-0.130	-0.113	-0.094

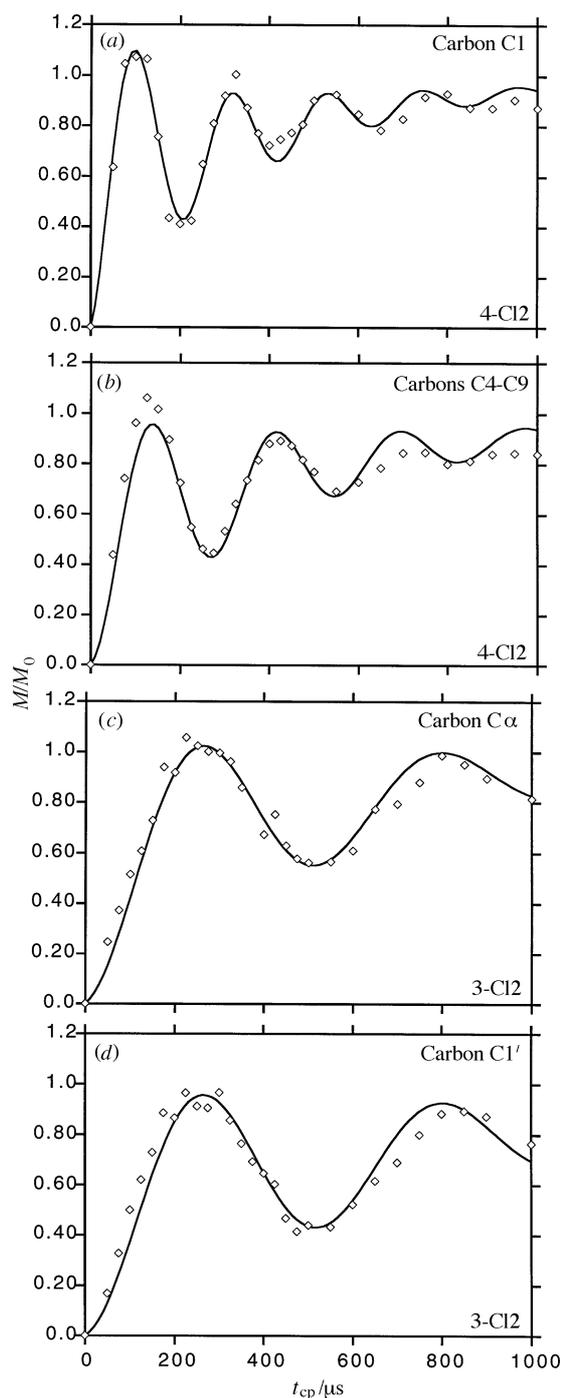
intensity of methylene carbons as a function of the contact time t_{cp} .^{10,12}

$$M/M_0 = 1 - 0.5 \exp(-t_{cp}/T_{II}) - 0.5 \exp(-3t_{cp}/2T_{II}) \times \cos[2^{1/2}(D_{C-H} + J_{C-H}/2)t_{cp}] \quad (2)$$

where T_{II} is the spin diffusion time among hydrogens, D_{C-H} is the effective dipole-dipole coupling constant of the directly bonded hydrogens and J_{C-H} the scalar coupling constant. This equation does not take into explicit account the possible dipolar interaction between the carbon under investigation and more remote hydrogens. We have obtained these dipolar oscillations at three temperatures for **4-C12** and at only one temperature for **3-C12**, owing to its monotropic behaviour. The oscillatory behaviour of some resonances as a function of the contact time is presented in Fig. 5. In the two compounds, all resolved lines, with the exception of $C2'$ and methyl chain carbons, show a pronounced oscillatory behaviour with a slow damping of the oscillation that indicates a small inter-hydrogen spin diffusion rate. The experimental data were fitted with eqn (2), leading to the D_{C-H} and T_{II} values summarized in Tables 3 and 4. The continuous lines in Fig. 5 give the best fit for the whole range of t_{cp} . In addition to the OCH_2 resonances, other lines resulting from the overlapping of several carbon lines were fitted [Fig. 6(b)], in order to have some indications on the similarity of their dipolar couplings. Unfortunately, the $C1'$ and $C\alpha$ peaks overlap in **4-C12** whereas they are well-separated in **3-C12**. Thus, the overlapped $C1'$, $C\alpha$ single line in **4-C12** was fitted with only one D_{C-H} value. It can be noted that the oscillating behaviours of $C1'$ and $C\alpha$ in **3-C12** are almost identical [Fig. 6(c) and 6(d)]. Owing to the deviations from experiment at longer times, D_{C-H} values were obtained by using only the data points before 500 μs . These D_{C-H} values were found to be higher than the ones obtained from the whole set of data points up to 1 ms. The relative error lies between 1 and 4%, and accordingly the error in the calculated dipolar coupling is estimated at 5%. The dipole-dipole coupling constant 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. This motional averaging is measured by the bond order parameter S_{C-H} . Assuming a cylindrical symmetry for the C-H dipole-dipole interaction, the bond order parameter

Table 4 Parameters obtained by the fitting of the experimental data points to eqn. (2) for compound **3-C12** at $T/T_{NI} = 0.979$

Line	D_{C-H}/kHz	$T_{II}/\mu\text{s}$	S_{C-H}
$C\alpha$	1.37	833	0.060
$C1'$	1.39	1092	0.061
C1	2.33	808	-0.103
C4-C9	1.92	781	-0.084

**Fig. 5** Intensity variation of some resonances as a function of the contact time during the cross-polarization experiment. For **4-C12** at 80.1 °C: (a) carbon C1, (b) aliphatic center peak containing 6 carbons. For **3-C12** at 84.1 °C: (c) carbon $C\alpha$, (d) carbon $C1'$

S_{C-H} is related to the motionally averaged dipolar coupling constant (D_{C-H}) by the equation:

$$S_{C-H} = -4.407 \times 10^{-5} D_{C-H} \quad (3)$$

where D_{C-H} is expressed in Hz. Tables 3 and 4 give the values calculated with eqns (2) and (3). The spin diffusion time constant is quite large compared with the ones found in MBBA.¹² In addition, these time constants diminish with decreasing temperature. In accordance with the chemical shift evolution in the nematic phase, order parameters were taken as positive for $C\alpha-H$ and $C1'-H$ bonds and negative for the other bonds. The calculated values of $|S_{C-H}|$ are relatively small for the lateral OCH_2 compared with other methylenes, but are in the same range as those found by the VASS/SLF technique.^{6,7}

Fig. 6 gives a comparison of these order parameters. The order parameters found for the OCH_2 in the lateral chain are similar. The slightly larger value obtained for **4-C12** is certainly a consequence of the single dipolar coupling used for the fit of the line containing the $C1'$ and $C\alpha$ carbons. This means that the ordering of the lateral chain is not too much affected by the change in the other lateral substituent. The mean order parameters obtained from the C4–C9 line for the dodecyloxy chain belonging to the lateral aromatic branch of **4-C12** are larger than those of the lateral dodecyloxy chain in **12LC**. In addition, they have a larger temperature dependence. This supports the idea that the chain in the lateral branch has a more or less terminal chain behaviour.

Some molecular modeling calculations were performed using the Nemesis program (Oxford Ltd.) on two isomers having a butoxy chain on the lateral aromatic branch. In these calculations, performed on a single molecule, the two lateral substituents were kept roughly in the mean plane of the mesogenic core and their folding back was assumed. In the starting conformation, the two OCH_2 linked to the core were placed above and below the mean aromatic plane to avoid steric interactions between these two fragments. The butoxy chain was supported to be in an all-*trans* conformation. Two energy-minimized conformations are presented in Scheme 2. The part of the rigid core containing the azo link and the two neighbouring aromatic rings is roughly planar. Conversely, the terminal aromatic rings linked by the less conjugative ester groups lie in a tilted plane. The two lateral substituents are roughly aligned along the mesogenic core. The butoxy chain in the lateral branch does not point out from the core. Therefore, irrespective of its position, the substituent does not play a predominant role in the intermolecular interactions. The 25 °C reduction in T_{NI} upon going from **4-X** to **3-X** compounds is certainly related to the lateral aromatic ring itself, which seems to present more steric interactions in the 3-X

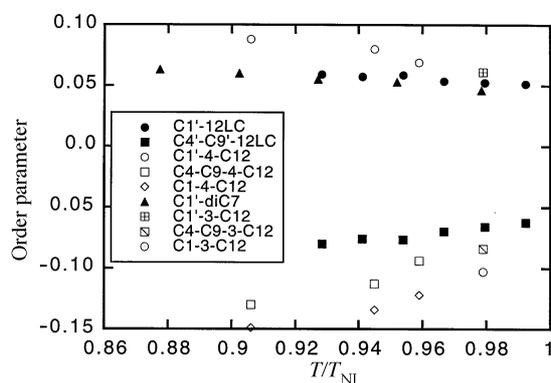
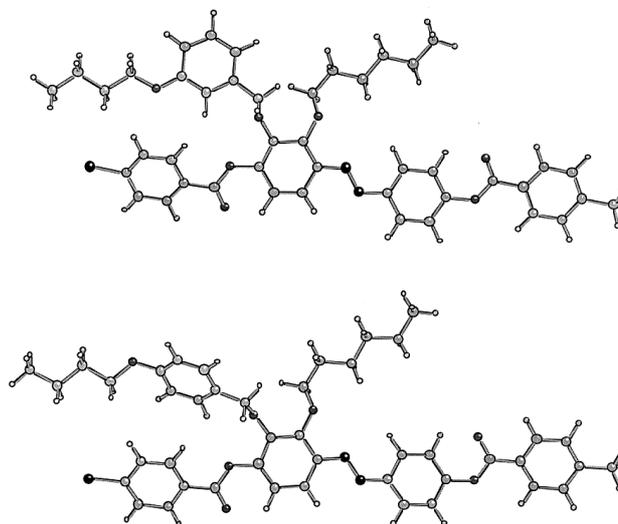


Fig. 6 Comparison of the order parameters obtained for **4-C12** and **3-C12** by the use of dipolar oscillations and in **diC7**⁶ and **12LC**⁷ by the use of the VASS/SLF technique



Scheme 2 Comparison of the minimized conformations in **4-C4** (bottom) and **3-C4** (top) obtained by molecular modeling using the Nemesis program (Oxford Ltd.)

compounds. The chain on the lateral branch is in an all-*trans* mean conformation, irrespective of the substitution position, and certainly can act like a typical terminal chain. These results are in agreement with the NMR data.

Conclusions

It has been shown that a rigid or flexible group can be introduced in the *meta* or *para* positions of a lateral aromatic branch without destroying the liquid crystalline properties of some disubstituted mesogens containing four rings in the main core. The nematic range and T_{NI} are slightly dependent on the relative positions of the rigid substituent attached on the lateral aromatic branch. However, the nematic range markedly decreases for a flexible substituent in these positions. The chain behaviour have been studied by ¹³C NMR spectroscopy in two isomeric compounds having a dodecyloxy chain introduced onto the lateral aromatic branch. The chemical shift evolution upon entering the nematic phase from the isotropic phase exhibited a positive jump for the lateral OCH_2 and a negative one for the OCH_2 belonging to the dodecyloxy chain. As a consequence, the two lateral substituents are folded back along the core, but the dodecyloxy chain exhibits a mean all-*trans* conformation, regardless of its *meta* or *para* position on the lateral branch. The order parameters of the aliphatic carbons have been obtained by the use of dipolar oscillations during the cross-polarization process. These values were compared with those obtained from related compounds by the VASS/SLF technique. The long molecular axis is slightly influenced by the long dodecyloxy chain. This chain is aligned in the nematic field and enforces the bent shape of the lateral aromatic branch.

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