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Felix Perez; Patrick Judeinstein; Jean-Pierre Bayle; Frederick Roussel; B. M. Fung

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The effect of a lateral aromatic branch on the orientational ordering of laterally alkoxy substituted nematics

by FELIX PEREZ, PATRICK JUDEINSTEIN, JEAN-PIERRE BAYLE*

Laboratoire de Chimie Structurale Organique, Université Paris XI, U.R.A. 1384, 91405 Orsay Cedex, France

FRÉDÉRICK ROUSSEL† and B. M. FUNG

Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019-0370, U.S.A.

Two new mesogenic series have been synthesized. They have the same main core which contains four aromatic rings, with two lateral substituents on the same side of one of the inner rings. One of the substituents is a 4-chlorobenzyloxy group and the second is an alkoxy chain. The positions of the lateral substituents are different in the two series. Despite the large aromatic branch, an enantiotropic nematic phase is obtained for most of the compounds. The orientational ordering behaviour of these new compounds has been investigated by C-13 NMR, and two isomeric compounds containing a lateral dodecyloxy chain were chosen for the study. The order parameters of the chain were obtained by a 2D C-13 NMR technique with variable angle spinning. The temperature dependence of the order parameters was determined using the C-13 chemical shifts with slow spinning of the sample parallel to the magnetic field. The first methylene fragment in each lateral substituent of each compound has a positive C–H bond order parameter, implying that this fragment adopts a *cis*-conformation in the nematic phase. The two lateral substituents are folded back along the mesogenic core in opposite directions. The lateral chain is found to be roughly aligned along the molecular long axis imposed by the core, whereas the *para*-axis of the phenyl ring in the lateral aromatic branch makes a considerable angle with the molecular long axis. It was also found that the different patterns of substitution do not affect the position of the molecular long axis to any large extent.

1. Introduction

Lateral substituents introduced into mesogen molecules depress the thermal stability of the mesophases. This effect is related to the overall anisotropic broadening of the molecule and its consequence on the cooperative packing needed in the mesophase [1]. This depression depends on several parameters such as the phase type, the substituent type, and the substituent position within the core.

The effect of a lateral substituent in depressing the mesophase stability is larger for more ordered phases like smectics than for less ordered phases like nematics [2]. For a rigid substituent, the change in the nematic range is related to its van der Waals radius [3]. For a flexible substituent, the depressive effect reaches a limit as the number of carbons in the chain increases, because the chain is supposed to be roughly aligned along the core [4–10]. For a given substituent, a larger nematic range is obtained when the substitution is, as far as possible, located in the most rigid part of the molecule [11].

When a second rigid or flexible substituent is introduced near to the first one, it usually fills the empty space created by the first substituent, giving only a small additional perturbation [12, 13]. Thus, we have shown recently that in a four-ring mesogenic core, it was possible to introduce two lateral alkoxy chains on the same side of an inner ring without depleting the liquid crystal properties [14]. The orientational orderings of the two lateral chains in the nematic phase were obtained by one and two dimensional C-13 NMR studies [15]. As already found in compounds containing a single lateral chain [14, 15], the two alkoxy chains are folded back along the mesogenic core. Along each chain the ordering is quite constant and does not exhibit any odd–even effect.

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*Author for correspondence.

†On leave from Laboratoire de Dynamique et Structure des Matériaux Moléculaires, Université du Littoral, U.R.A. 801, 59379 Dunkerque Cedex, France.

In this paper, the problem addressed is the replacement of one chain by a bulkier substituent containing an aromatic ring. We first present the synthesis of two isomeric series containing the same four-ring main core with a lateral chain and a lateral aromatic ring. Then, the effect of the lateral aromatic substitution on the mesomorphic properties is discussed. By comparing the order parameters of the lateral chains in two isomeric compounds, the effect of the lateral aromatic substitution on the molecular long axis is analysed.

2. Experimental
2.1. Synthesis

The two series: 2-(4-chlorobenzyloxy)-3-*n*-alkoxy-4-(4-chlorobenzoyloxy)-4′-(4-methylbenzoyloxy)azobenzenes (*n*RC) and 2-*n*-alkoxy-3-(4-chlorobenzyloxy)-4-(4-chlorobenzoyloxy)-4′-(4-methylbenzoyloxy)azobenzenes (*n*LC) were prepared according to the same procedures. As an example, the synthetic scheme for the *n*RC series is presented in scheme 1.

2-(4-Chlorobenzyloxy)-3-*n*-alkoxyphenols and 2-*n*-alkoxy-3-(4-chlorobenzyloxy)phenols were prepared in two steps by selective etherification of 1,2,3-tri-hydroxybenzene (THB) using a standard procedure [16]. The first step is a mono-etherification of 1,2,3-trihydroxybenzene. The reaction was carried out in a solvent mixture containing PEG/dioxane (15/85 by volume), and stoichiometric ratios for THB, *R*Br and KHCO₃ were used. After 15 h reaction time at 80°C, the mixture contained 9% of dialkylated compound, 64%

of 2-alkylated compound, and 27% of the 1-alkylated compound. Using chromatography on silica gel (60–200 mesh, CHCl₂ eluent), dialkylated compound can be easily separated from the mono-alkylated isomers. However, it was impossible to separate the two mono-alkylated isomers by chromatography. Consequently, we used the property of 1,2-dihydroxybenzenes to form stoichiometric complexes with lead(II) (scheme 2). Thus, for the separation, the mixture containing both isomers was dissolved in methanol and heated for one hour with 1·1 eq of lead(II) acetate with respect to the molar equivalent of 1-alkoxy-2,3-dihydroxybenzene. After cooling, the complex was filtered and the methanol evaporated. The residue was dissolved in ether and washed several times with dilute acid. The ethereal phase was dried over sodium sulphate and evaporation of the ether gave pure 2-alkoxy-1,3-dihydroxybenzene. The second alkylation was performed in the same solvent mixture with 2-alkoxy-1,3-dihydroxybenzene, *R*Br and KHCO₃ in stoichiometric ratio. The mixture contained some trisubstituted compound (10%), the expected dialkylated compound (80%) and some starting material (10%). Therefore, the mixture was chromatographed on silica gel (60–200 mesh) using CH₂Cl₂/pentane (70/30 by volume) as eluent, and the dialkylated compound was collected as the second fraction.

p-Toluic acid was esterified with nitrophenol using the DCC method [17]. Selective reduction of the nitro group was obtained using the NiCl₂/NaBH₄ reducing system [18]. The free amine was not generated, and the
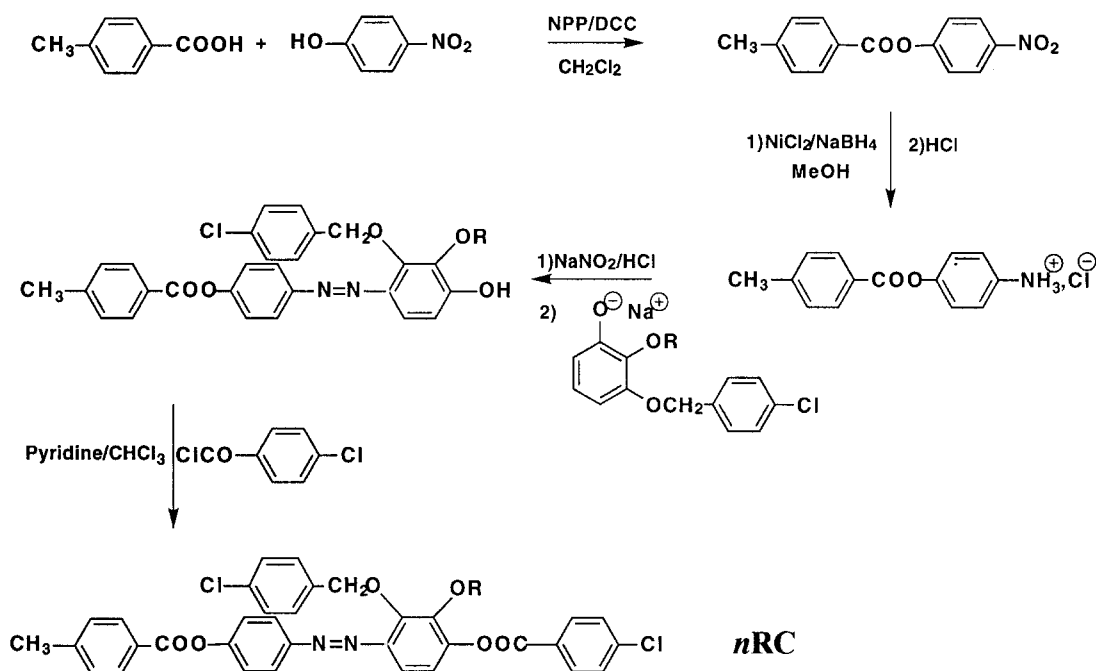
Scheme 1.
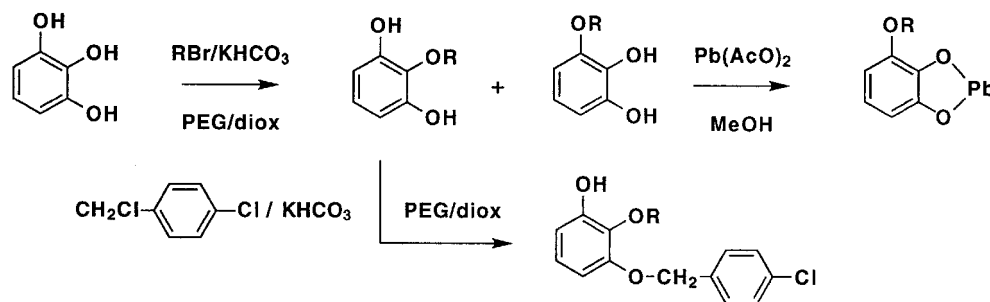
Scheme 2.

crude solid aniline hydrochloride was used for the diazotization step. The diazotization was performed, using PEG 200 solvent, by coupling the diazonium salt with the dialkoxyphenol under basic conditions. Diazotization occured mainly in the position *para* to the remaining hydroxyl group. The crude product was chromatographed on silica gel (60–200 mesh) with CH_2Cl_2/ethyl acetate (80/20 by volume) 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 products were recrystallized from a mixture of toluene/ethanol/4-methylpentan-2-one (10/80/10 by volume) until constant transition points were obtained. These transition points were measured by DSC (Mettler FP 52) using a heating rate of 10°C per minute. Table 1 gives the ^1H chemical shifts of the different compounds synthesized in scheme 1.

2.2. *NMR experiments*

The 2D C-13 NMR experiments using separated local field spectroscopy (SLF) with variable angle spinning (VAS) [19, 20] were performed using a Varian XL-300 NMR spectrometer at $B_o = 7·05$ T. The angle between the spinning axis and the magnetic field was set at *c.* 47°. The exact value of the angle was determined for each experiment by measuring the ratio of the $^{19}F–^{19}F$ dipolar coupling of 2,2-difluoro-1,1,1,2-tetrachloroethane dissolved in the nematic phase of ZLI-1291 with and without sample spinning. The data from the XL-300 NMR spectrometer were processed on a VXR-4000 data station [21].

C-13 NMR experiments with slow spinning were performed using a Varian VXR-500 NMR spectrometer ($B_o = 11·07$ T) equipped with an indirect detection probe manufactured by Narolac Cryogenic Corporation. The sample was put in a standard 5 mm tube and spun along the magnetic field so that the director aligned parallel to the magnetic field. To avoid rf overheating, a 0·8% decoupler duty cycle was used. The temperature calib-

ration was made by observing the nematic to isotropic transition. Due to the transition temperatures of the dodecyloxy derivatives being lowest in each series, we have studied the C-13 NMR of these two compounds and compared the results. The chain *ortho* to the carboxylate link is labelled **R** and the one *ortho* to the azo link is labelled **L**. For example, for $R = n\text{-}C_{12}H_{25}$, the last compound in scheme 1 is called **12RC**.

3. Results and discussion
3.1. *Transition temperatures*

The transition temperatures and the $\Delta S_{NI}/R$ values of the two homologous series studied are given in tables 2(*a*) and 2(*b*). An enantiotropic nematic mesophase is observed for eight compounds in the two series (figure 1). **16LC** is monotropic and **0RC** exhibits no liquid crystal-line properties at all. It should be noted that all compounds with the exception of **0RC** give an extensively supercooled nematic phase. This can be attributed to the two lateral substituents that prevent interaction between polar groups in the nematic phase.

As already noticed in compounds with one or two lateral chains, the existence of a lateral motif induces the nematic phase, preventing the more ordered in-plane molecular association needed for smectic arrangement [14, 21]. The presence of a dipolar group in the lateral aromatic branch does not affect this property. For both series, there is a strong decrease in the clearing temperature as the carbon number increases from 0 to 12. The nematic range is more or less constant for $n = 0$–8 for the *n*LC series and $n = 4$–12 for the *n*RC series, but decreases for longer chains. In the *n*LC series, but not the *n*RC series, the first member has a nematic range which is not negligible. This may be due to the influence of the nearby link within the core as the carboxylate link is more flexible than the azo link and can more easily undergo some conformational change to accommodate the lateral aromatic branch. For the same reason, the nematic ranges for the *n*LC series with shorter chains are larger than those for the *n*RC series.

Generally, for compounds containing terminal chains,

Table 1. NMR data (^{1}H, 250 MHz, CDCl$_3$) for the different compounds synthesized in scheme 1 [H type: ppm (integration, multiplicity)].
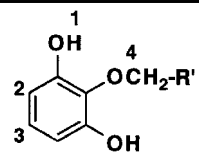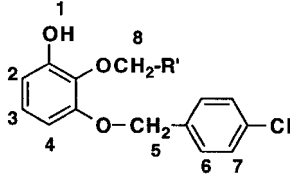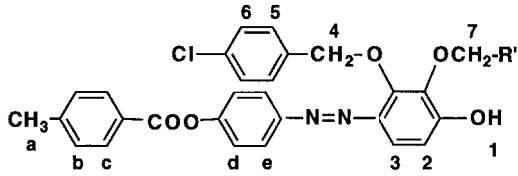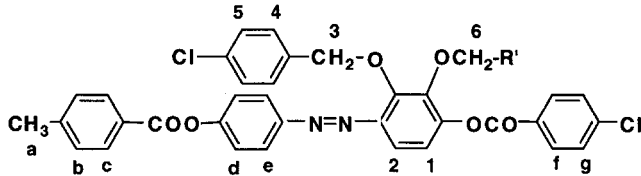
Molecule	^{1}H chemical shifts	
	H1: 5·4 (2H, s) H2: 6·5 (2H, d) H3: 6·9 (1H, t) H4: 4·0 (2H, t)	
	H1: 5·8 (1H, s) H2: 6·5 (1H, dd) H3: 6·9 (1H, t) H4: 6·6 (1H, dd)	H5: 5·1 (2H, s) H6: 7·4 (2H, s) H7: 7·4 (2H, s) H8: 4·1 (2H, t)
	H1: 6·1 (1H, s) H2: 6·8 (1H, d) H3: 7·5 (1H, d) H4: 5·3 (2H, s) H5: 7·3 (2H, d) H6: 7·4 (2H, d)	H7: 4·2 (2H, t) Ha: 2·5 (3H, s) Hb: 7·4 (2H, d) Hc: 7·9 (2H, d) Hd: 7·3 (2H, d) He: 8·1 (2H, d)
	H1: 7·0 (1H, d) H2: 7·5 (1H, d) H3: 4·1 (2H, t) H4: 7·3 (2H, d) H5: 7·4 (2H, d) H6: 4·1 (2H, t)	Ha: 2·5 (3H, s) Hb: 7·3 (2H, d) Hc: 7·9 (2H, d) Hd: 7·4 (2H, d) He: 8·1 (2H, d) Hf: 8·2 (2H, d) Hg: 7·5 (2H, d)

Table 2. (a). Transition temperatures (in °C) and related entropies for compounds in the 2-*n*-alkoxy-3-(4-chlorobenzyloxy)-4-(4-chlorobenzoyloxy)-4′-(4-methyl-benzoyloxy)azobenzene series (*n*LC). These values are taken with increasing temperature (heating rate 10°C min^{-1}).

n	Cr	$\overset{\rightarrow}{(\Delta S_{KN}/R)}$	N	$\overset{\rightarrow}{(\Delta S_{NI}/R)}$	I
0	●	191 (83·9)	●	231 (1·2)	●
4	●	141·5 (58·8)	●	187·5 (1·0)	●
8	●	106 (57·9)	●	142·5 (0·5)	●
12	●	105 (53·6)	●	118 (0·3)	●
16	●	117 (72·5)			●

Figure 1. Nematic ranges for members of the two mesogenic series *n*LC and *n*RC. The transition temperatures were measured by DSC (Mettler FP 52) using a heating rate of 10°C per minute.

$\Delta S_{NI}/R$ increases with the number of carbons due to the increase in conformational entropy. In the case of lateral chains, the opposite behaviour is observed, the entropy decreasing slightly or remaining constant with increasing chain length [8]. This is observed in our series (table 2) with a striking feature that these entropy values are slightly smaller than the corresponding values obtained for compounds containing a single lateral chain ($\Delta S_{NI}/R$ typically in the range of 0·5 to 0·8) [8, 14] and larger than the values obtained for compounds containing two

alkoxy chains ($\Delta S_{NI}/R$ typically in the range of 0·15 to 0·2) [15]. Furthermore, these entropy values decrease with the length of the chain. This indicates that, in comparison with an alkoxy chain, the lateral aromatic branch adds some conformational entropy which is reduced by increasing the length of the second chain.

3.2. *Ordering of the lateral chains*

The VAS C-13 spectra of **12LC** and **12RC** in the nematic phase were recorded by using the 2D SLF technique. Only the first three methylene peaks on both sides of the chain are resolved in the aliphatic region. The carbon assignment below $\delta = 35$ was made according to previous studies [21, 22]. In the OCH$_2$ region, we used the assignment obtained for the dialkoxy compounds **diCn** [15]. In the isotropic melt of the **diCn** compounds, the downfield resonance ($\delta = 76.59$) was assigned to the first chain carbon in the *ortho*-position with respect to the ester linkage, and the upfield peak ($\delta = 74.16$) to the chain carbon in the *ortho*-position with respect to the diazo linkage. Thus, in the isotropic melt of **12LC**, the peaks at $\delta = 74.88$ and $\delta = 76.56$ were attributed, respectively, to the OCH$_2$ in the chain and in the aromatic branch. In the isotropic melt of **12RC**, the peaks at $\delta = 74.09$ and $\delta = 76.59$ were assigned to the OCH$_2$ group in the aromatic branch and in the chain, respectively. Therefore, in our 2-D experiment, the two OCH$_2$ in the chain appear as triplets, whereas the OCH$_2$ in the lateral aromatic branch appear as singlets. All the other upfield aliphatic methylene carbons show the expected triplets in the ω_1 dimension with the exception of the last methyl group.

The splittings for the OCH$_2$ group belonging to the chains are smaller than those for the other methylene carbons. This amazing behaviour is similar to that observed for the dialkoxy compounds previously studied [15]. In these compounds, the lateral flexible substituents are folded back along the mesogenic core. The mean angle between the C–H vector for these two carbons and the molecular long axis is less than the magic angle. Thus, the two OCH$_2$ fragments in the nematic phase have positive bond order parameters. Assuming a cylindrical symmetry for the C–H bond, the bond order parameter S_{C-H} is related to the dipolar coupling constants (D_{C-H}) by the equation:

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

If the bond order parameter is positive, the dipolar coupling constant (D_{C-H}) is negative. Then, the scalar coupling constant and the dipolar coupling constant have opposite signs and the observed carbon–proton splitting (Δv) in the 2-D experiment (equation (2)) is

small or negligible:

$$\Delta v = f[(3\cos^2\beta - 1)D_{C-H} + J] \qquad (2)$$

where f is the scaling factor, which is equal to 0·420 for BLEW-48, J is the scalar coupling constant determined from the coupled isotropic spectrum (J is positive), and β is the angle between the spinning axis and the magnetic field.

From the measured splittings, the C–H bond order parameters can be calculated from equations (1) and (2) for all resolved peaks within the lateral chain. Figures 2(a) and 2(b) show the smooth decrease in the absolute values of these order parameters with reduced temperature T/T_{NI} for **12RC** and **12LC**, respectively. Carbons 4 to 9 in the chains of both compounds give a superimposed peak which exhibits a nice, well resolved triplet
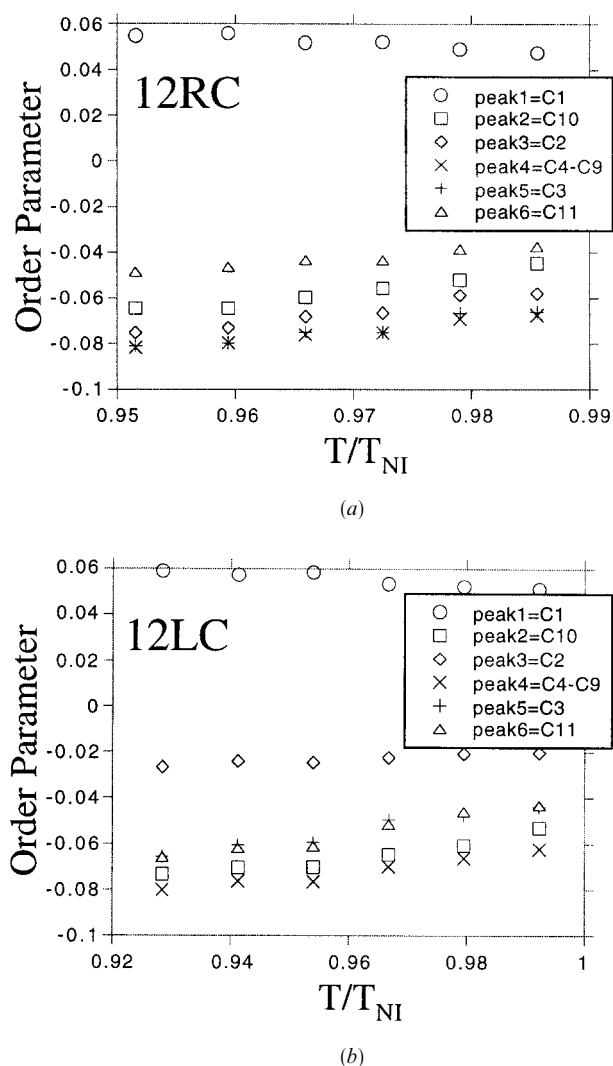

(a)

(b)

Figure 2. C–H bond order parameters for the lateral chain as a function of T/T_{NI} for compounds (a) **12RC**; (b) **12LC**.

in the 2-D experiment. Thus, we assume that these carbons have a similar bond order parameter.

On the average, the dodecyloxy chain behaves in the same way in both compounds. In order to compare the C–H bond order parameters systematically, the evolution of their values at $T/T_{NI} = 0.952$ as a function of the carbon position in three compounds **12RC**, **12LC** and **diC7** is given in figure 3. The data show that the variation of the order parameter within the chain is relatively small, and the well-known odd–even effect of the order parameter values is not observed. The chains in the two isomers behave in the same way as the chains in the compound **diC7**—see caption to figure 3. In **12RC**, the alkoxy chain points in the direction of the carboxylate link and exhibits larger negative order parameters than the chain in **12LC** which points in the direction of the azo link. As the two substituents are interacting only through their $-OCH_2$ fragments, the large lateral aromatic branch does not modify to a large extent the ordering of the lateral alkoxy chain.

The temperature dependence of the chemical shift was studied, and the results are presented in figures 4 and 5 for the compounds **12RC** and **12LC**. As expected, in figure 4 (*a*), a large positive jump in the chemical shifts is observed for the OCH_2 on going from the isotropic melt to the nematic phase, while the subsequent methylene carbons present the usual negative jump (figure 4 (*b*)). It has been shown that the change in the chemical shift obeys the semi-empirical equation [22]:

$$\delta_{obs} = A + B(1 - T/T\dagger)^F = \delta_{iso} + b + aS_o(1 - T/T\dagger)^F \tag{3}$$
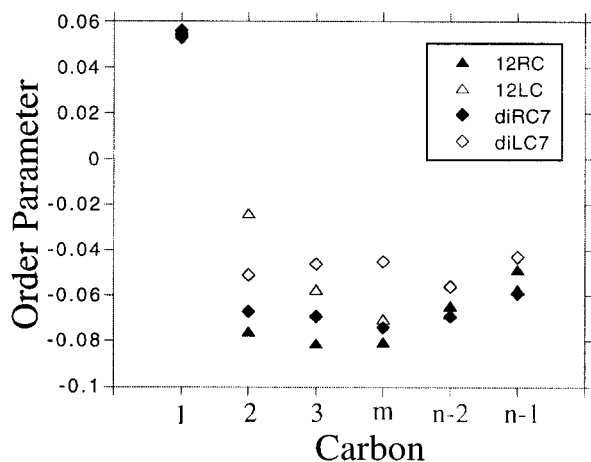

Figure 3. Comparison of the C–H bond order parameters for the lateral chains in the three compounds **12LC**, **12RC** and **diC7**. *n* is the number of carbon atoms (12 or 7) in the chain and m refers to the middle of the chain. The structure of **diC7** is that of the four ring mesogen *n*RC in scheme 1, but having 2 lateral OC_7H_{15} chains instead of a lateral 4-chlorobenzyloxy substituent and a lateral O*R* group.

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_o is the limit of the bond order parameter of the fragment. The *F* value gives an indication on the rigidity of the observed fragment [23]. For the aliphatic chains, *a* is positive and gives the main contribution to the chemical shift change. Furthermore, the sign of the jump is fixed by the sign of the order parameter. The jump in the C-13 chemical shifts is positive for the OCH_2 carbons and negative for the subsequent carbons within the chain. The sign change in the dipolar couplings for the two first methylene groups in the lateral alkoxy chains clearly indicates that the first fragment of the chain has to be in the *cis*-conformation [15, 22]. As determined from the 2-D experiments, since the C–H bond order parameters for the two OCH_2 groups in the alkoxy chains are similar in **12RC** and **12LC** (figures 2 (*a*) and 2 (*b*)), whereas the chemical shift jump is quite different (figure 4 (*a*)), the chemical shift tensor component must be noticably different. Then, all the lines having a noticeable chemical shift anisotropy were fitted with equation (4) using the four parameters *A*, *B*, $T\dagger$ and *F*.

In the second part of the calculation, $T\dagger$ was fixed at the average value of 118.7°C for **12LC** and 109°C for **12RC**. Then, each line was refitted with only three parameters. In order to compare the sets of *F* values for the three compounds, we give in table 3 the *F* values for the first three carbons. These values are larger than those found for terminal chains, but are comparable with those obtained previously for **diC7**, which has a similar core structure, but with two lateral chains [15]. The major difference in the relatively small *F* value found for C1 in **12RC** has to be related to the interaction between the two lateral substituents. Usually, a larger *F* value is correlated with a more rigid fragment. The rigidity of a fragment depends on its structure and on its interaction with nearby fragments. Because of the strong interaction between two rigid units (the azo link and the aromatic branch), the lateral chain near the less rigid link will have a smaller *F* value because it is going to take a larger temperature range for this fragment to reach its limiting value.

In the aromatic region, 32 peaks are expected, but only 20 are observed. Thus, the assignment is difficult due to strong overlapping. In order to probe the effect of the lateral disubstitution on the ordering of the core, we use the chemical shift of the terminal methyl group. This methyl group is directly attached to the core and presents a noticeable chemical shift anisotropy, as shown in figure 5. The methyl group attached to the phenyl ring behaves the same way in the three compounds (**12RC**, **12LC**, **diC7**), indicating that the position of
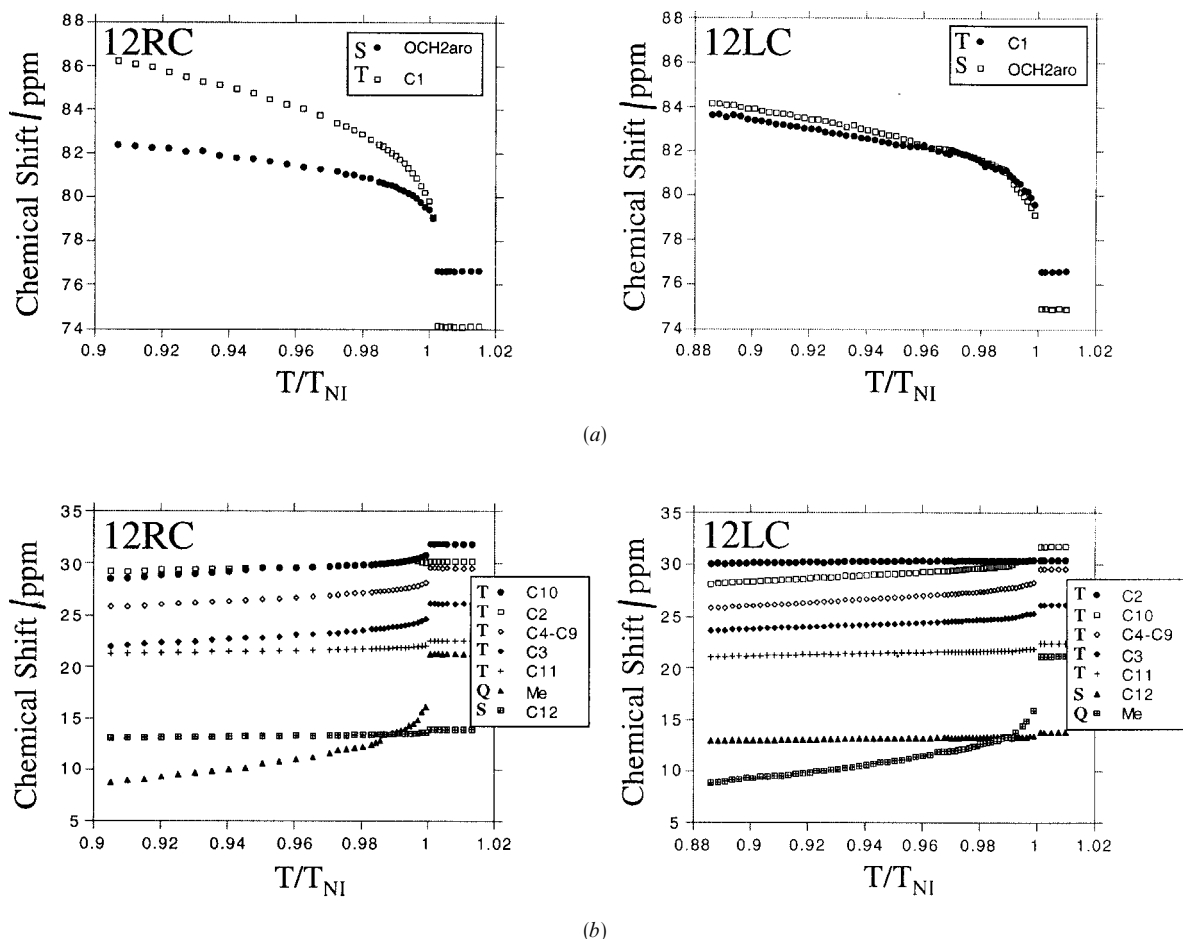
(a)

(b)

Figure 4. The chemical shifts of the aliphatic parts of (a) **12LC** and (b) **12RC** plotted against the reduced temperature, ranging from the nematic phase to the isotropic melt.
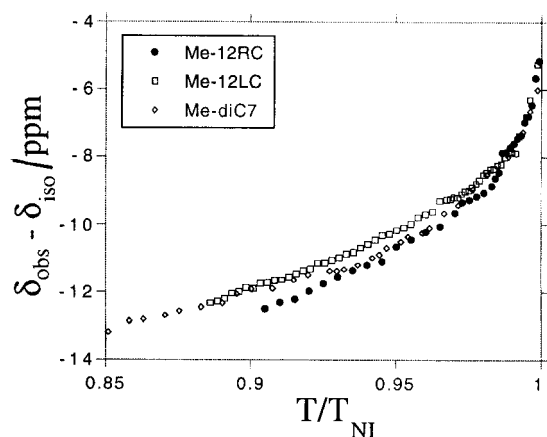

Figure 5. Comparison of the anisotropic chemical shift for the methyl group belonging to the main core in the three compounds **12LC**, **12RC** and **diC7**.

Table 2. (b). Transition temperatures (in °C) and related entropies for compounds in the 2-(4-chlorobenzyloxy)-3-*n*-alkoxy-4-(4-chlorobenzoyloxy)-4′-(4-methylbenzoyloxy)azobenzene series (*n*RC). These values are taken with increasing temperature (heating rate 10°C min⁻¹).

n	Cr	$(\overrightarrow{\Delta S_{KN}}/R)$	N	$(\overrightarrow{\Delta S_{NI}}/R)$	I
0	●		224·5 (125·3)		●
4	●	135 (52·1)	●	158·5 (0·7)	●
8	●	103·5 (46·8)	●	126 (0·6)	●
12	●	83·5 (44·7)	●	108 (0·4)	●
16	●	90 (49·7)	●	105 (0·2)	●

molecular long axis does not change too much when a lateral alkoxy chain is replaced by an aromatic branch.

To support these statements, some molecular model-ling calculations were performed using the Nemesis program (Oxford Ltd). In these calculations, the two lateral substituents were kept roughly in the mean plane
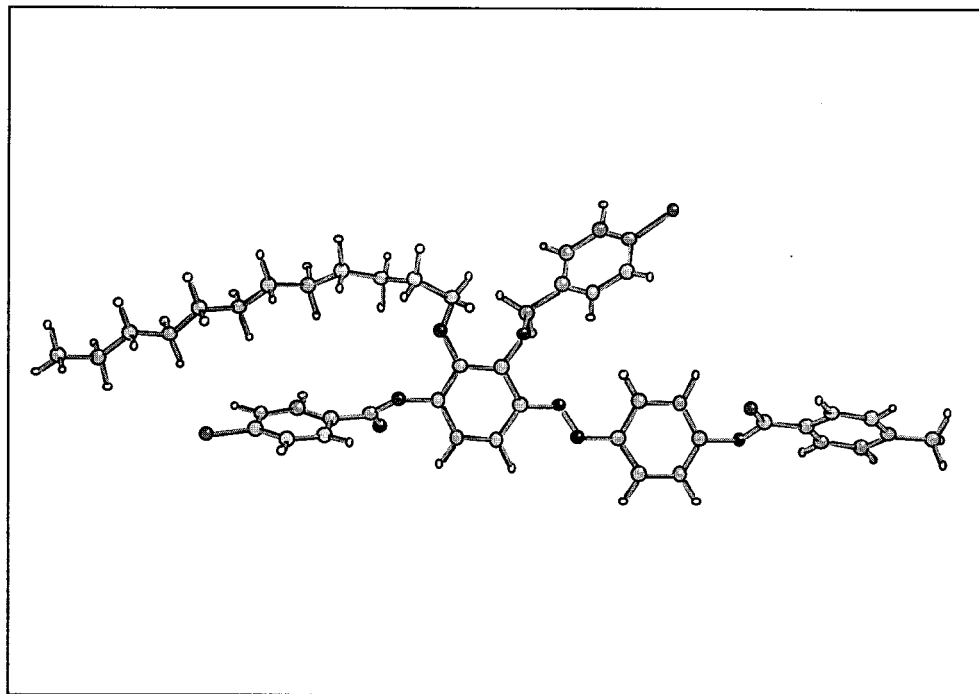
Figure 6.   Proposed mean molecular conformation for **12RC** obtained by molecular modelling.

Table 3.   Values of the exponent F for the chains in isomeric compounds determined by fitting the chemical shifts using equation (3). The standard deviation in the F values is ± 0.05.

Position:	1	2	3
12RC	0·09	0·55	0·39
arom. branch	0·19		
RCdiC7	0·25	0·43	0·45
12LC	0·16	0·53	0·32
arom. branch	0·19		
LCdiC7	0·24	0·49	0·42

of the mesogenic core and their folding back was assumed. The minimized conformation is presented in figure 6. 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 nearly perpendicular plane and are in the respective *cis* conformation with respect to the central rigid part. The lateral chain is aligned along the mesogenic core, whereas the *para*-axis of the lateral aromatic branch makes a large angle with the molecular long axis. The –CH₂– groups of these two lateral substituents lie outside the average plane of the azo linkage in order to minimize the steric interactions, while the other methylenes of the chain are in *trans* conformations. These results confirm the analysis of the NMR data.

4.   Conclusion

In an homologous series containing four aromatic rings in the main core and two nearby lateral alkoxy chains, one of these alkoxy chains can be replaced with a 4-chlorobenzyloxy branch without depleting the liquid crystal properties. The nematic range obtained is slightly dependent on the relative position of the lateral aromatic branch. By applying the 2D-SLF technique, the orientational ordering of the aliphatic parts of two isomeric compounds has been obtained. The two first carbons in the lateral substituents have a positive order parameter. These positive order parameters demonstrate that the two lateral substituents are folded back along the mesogenic core, involving a *cis* conformation for the first fragment. No odd–even effect is found along the chain for the bond order parameters. The *para*-axis of the aromatic ring in the lateral branch makes a non-negligible angle with the core. On the contrary, the molecular long axis is not influenced by the pattern of disubstitution. Further investigations on the order parameters of the *para*-disubstituted rings of some related mesogens are under way.

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