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Ordering of some liquid crystals containing the 2-phenylindazole core

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Molecules containing the 2-phenylindazole core present liquid crystalline properties even if the two terminal chains do not point along the same axis. ^{13}C NMR in the liquid crystalline phase shows that the molecular long axis is nearly aligned with the *para*-axis of the phenyl moiety of the 2-phenylindazole core. This implies that the first fragments of the chain belonging to the indazole moiety do not lie along the molecular long axis. To promote liquid crystal properties, this chain needs to possess at least six carbon atoms.

1. Introduction

Mesogens having a lateral *N*,*N*-dialkylaminomethylene or *n*-alkoxybenzoyloxymethylene lateral fragment in the *ortho*-position to an azo link can undergo an internal cyclization in the isotropic or in the nematic phase [1, 2]. A new mesogenic core is obtained containing a 2-phenylindazole motif. This motif is rather rigid and slightly bent due to the presence of the five membered ring attached to the *para*-disubstituted aromatic ring (figure 1) [2, 3].

Bent mesogenic structures have recently been a pole of attraction for many scientists due to the unusual packing properties of the molecules into the smectic phase, which under certain conditions may give a chiral phase composed of an achiral material [4–6]. The occurrence of liquid crystal properties in such slightly bent structures is of interest for understanding how the conformation of terminal molecular chains may influence packing in the anisotropic medium. Moreover, the angle made by the terminal bonds in these bent structures can be monitored by changing the type of heterocyclic ring. Therefore, we present the synthesis and mesomorphic properties of four new series of compounds having the 2-phenylindazole core onto which two different terminal chains are grafted. As the 2-phenylindazole fragment is fairly rigid due to the presence of only one rotatable bond, the emergence of the liquid crystalline properties and the phase type will be due mainly to the length and type of the chains attached to the core. Knowledge of the ordering of the chains within the liquid crystalline phase will lead to an understanding of the appearance of the liquid crystalline properties. 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. The evolution of the chemical shifts on entering the liquid crystalline phase and the dipolar C–H coupling give some idea about the ordering of the different fragments by comparison with the behaviour of conventional structures [7–10].

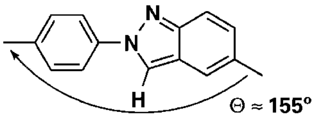

Figure 1. Bent structure of the 2-phenylindazole motif.

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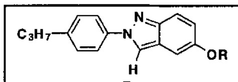	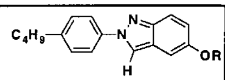	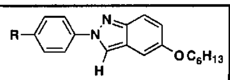	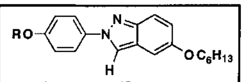
Series **I** : **3On**	Series **II** : **4On**	Series **III**: **nO6**	Series **IV**: **nOO6**
n=2,3,4,5,6,7,8,9,10	n=2,3,4,5,6,7,8,9,10	n=1,2,3,4,5,6,7,8	n=2,4,6,8,10,12,14,16

Figure 2. Structures of the different series.

2. Experimental

2.1. *Synthesis*

Four different series of compounds were synthesized (figure 2) in order to delineate the influence of the chain length and type on each side of the molecule on the mesomorphic behaviour. For example, series **I** contains a propyl chain on the *para*-substituted aromatic ring and an alkoxy chain of variable length on the indazole ring (labelled **3O*n***, where *n* is the number of carbons in the alkoxy chain).

The different series were prepared according to a similar scheme presented for series ***n*O6** in figure 3, and the synthesis is briefly described in the following text.

An alkylaniline was diazotized in water when the alkyl chain was short, or in a mixture of dioxan and water for longer chains. The diazonium salt was added dropwise to an aqueous solution of the phenate of 3-hydroxybenzylalcohol. Then, the crude product was alkylated under phase transfer catalysis conditions in water using Aliquat 336 as catalyst. The alkylated compound was extracted into ether and then chromatographed on silica gel (60–200 mesh) with CH_2Cl_2 as eluent. The cyclization was brought about by heating in PEG at 220°C during 15 min. After ether extraction, the final indazolic compound was chromatographed on silica gel (60–200 mesh) with CH_2Cl_2 as eluent. The final products were recrystallized from a mixture of chloroform/ethanol until constant transition points were obtained. These transition points were measured by DSC (Mettler FP 52) using a heating and cooling rate of 10°C min^{-1}.

2.2. *NMR experiments*

The ^{13}C NMR spectra in $CDCl_3$ solution were recorded on 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 [11]. All B_0 gradients have a sinusoidal shape of 1.5 ms duration. The HMBC 2D ^1H–^{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 and with a static sample. The 1D spectra were obtained near the isotropic–nematic transition using a single pulse, and using a standard CP sequence with strong decoupling for lower temperatures. To avoid rf overheating, a 15 s recycle delay time was used. Temperature calibration was made by observing the nematic to isotropic transition of the compound under study. The pulse sequence used in the 2D separated local field (SLF) experiment is identical to the one already published [10]. The pulse sequence contains four times: an initial CP contact of 1 ms, a delay where the proton magnetization is destroyed, followed by the oscillatory transfer between H and C reservoirs under Lee–Goldburg conditions and finally the acquisition under proton decoupling. Using the Lee–Goldburg decoupling [12] permits a reduction of the homonuclear dipolar coupling during the cross-polarization step, thus 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 [10].

3. Results and discussion

3.1. *Transition temperatures*

The transition temperatures of the compounds synthesized in the four series are given in the table. In series **I** labelled **3O*n***, an enantiotropic phase is obtained for the C6, C8 and C10 members; in series **II** labelled **4O*n***, the enantiotropic phase is obtained only for the C6 member (see figure 4). The melting temperatures

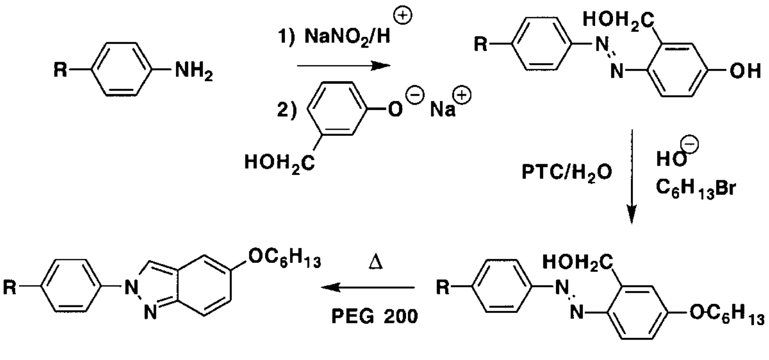

Figure 3. Synthetic scheme for series **III**.

Table. Transition temperatures (in °C) in the four series **3O*n***, **4O*n***, ***n*O6** and ***n*OO6**. These values were taken with increasing temperature for *T*melt (heating rate 10°C min^{-1}, and with decreasing temperature for *T*I–N, *T*N–Sm, *T*I–Sm and *T*solid (cooling rate 10°C min^{-1}).

n	*T*melt	*T*I–N	*T*N/I–Sm	*T*solid
*Series **I***				
2	130.0	88.0		78.0
4	85.5	80.5		52.5
5	89.0	73.0		66.0
6	71.0	80.5		58.0
7	83.0	77.0		70.0
8	73.0	80.5	70.0	52.0
10	80.5	81.5	77.5	67.0
*Series **II***				
2	111.0	72.0		63.0
4	84.0	70.0		66.0
5	79.5	64.5		59.0
6	65.0	70.0	55.0	50.0
7	78.0	71.0	66.0	62.0
8	75.0		69.0	66.0
10	81.5		74.0	70.0
*Series **III***				
1	75.0	65.0		49.0
2	57.5	57.0		45.0
3	71.0	80.5		62.0
4	65.0	70.0	53.0	50.0
5	68.0	87.0	86.0	51.0
6	64.0		85.5	53.0
7	66.0		94.5	51.0
8	64.0		98.0	52.0
*Series **IV***				
2	77.0		124.0	58.0
4	71.5		126.0	53.0
6	73.0		126.0	55.0
8	78.0		124.0	58.0
10	84.0		123.0	60.5
12	91.0		122.0	72.5
14	93.0		118.0	78.0
16	98.5		115.0	79.0

exhibit an odd–even behaviour which is more marked for series **3O*n*** where the terminal methyl group of the propyl chain is more or less aligned with the core axis. Within the molecule, the core is certainly quite rigid. The X-ray structure of the parent compound shows the coplanarity of the fused indazole ring and the phenyl ring resulting from the partial conjugation of the nitrogen lone pair with the two rings [2]. The two chain directions cannot be aligned due to the non-colinearity of the N–C and C–O bonds at each side of the indazole structure. The angle between these two bonds was found to be 157° which is very near to the 155° angle measured in a related compound [3]. This indicates that the molecular long axis of the molecule is certainly not far away from the *para*-axis of the phenyl ring. The chain attached to the phenyl ring lies along the molecular long axis of the indazole fragment, whereas the alkoxy chain lies off that axis. As the alkoxy chain length increases, there is a competition between the alignment effect of this flexible chain and the rest of the molecule. Lengthening the chain on the indazole ring has two opposite effects: (1) to help the alignment of the chain with the consequence of increasing the stability of the mesophase, and (2) to reduce the mesophase stability due to the increased disordering caused by the increase in the number of flexible CH_2 groups. In addition, the melting temperatures show a large decrease from that of the first member of both series as short chains pointing away from the molecular long axis will diminish the intramolecular interactions within the solid phase. For six or more carbons in the alkoxy chain the melting temperatures are more or less constant. Keeping this in mind we can try to analyse the transition temperature evolution for series **I** and **II**.

In series **I**, the chain attached to the phenyl ring is a propyl chain. The last C–C bond in the chain is aligned with the *para*-axis. This gives a nice odd–even effect on all the transition temperatures. The only enantiotropic compounds are those with a hexyloxy, an octyloxy or a decyloxy chain on the indazole moiety. In series **II**, the phenyl chain contains four carbons. The last C–C bond in the chain is no longer aligned with the *para*-axis. This induces a perturbation due to reorientation of the methyl group leading to a damping of the odd–even effect. In addition, the liquid crystalline phase seems less thermodynamically stable with an even number of carbons in the phenyl chain. Nevertheless, we still observe an enantiotropic nematic phase for the C6 member. Considering this fact, we chose to synthesize two other series containing a hexyloxy chain on the indazole part and a variable chain on the phenyl ring. In series ***n*O6** (**III**) and ***n*OO6** (**IV**), an alkyl chain and an alkoxy chain were introduced on the phenyl ring, respectively.

As expected, the mesomorphic range is larger for an even number of carbons in the alkyl chain on the phenyl part. The smectic A phase is thermodynamically stable starting with $n = 5$. Longer chains permit the segregation of the rigid core and the chains with the consequence of favouring the smectic phase. By introducing another lateral dipole (series **IV**) through the oxygen atom in the phenyl chain, the stability of the smectic phase is noticeably increased and this liquid crystalline phase is observed up to sixteen carbons in the chain. This is related to the change in the mean axis of the chain when the first CH_2 fragment is replaced by an oxygen.

3.2. *Isotropic chemical shifts*

The isotropic chemical shifts were assigned using the group contribution method, the *J* coupling pattern, and HMBC and HMQC 2D experiments. A typical HMBC

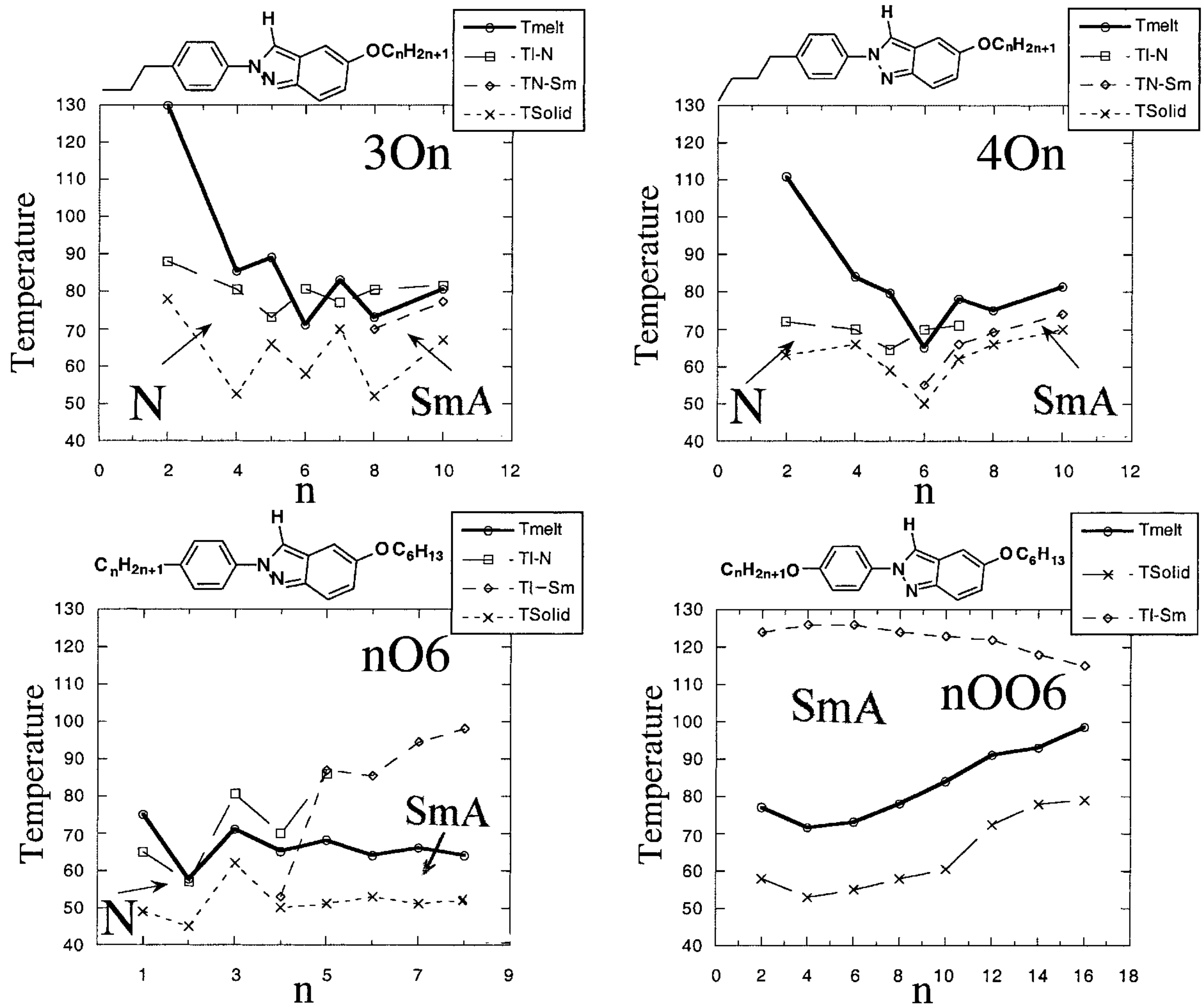

Figure 4. Mesomorphic behaviour of the four mesogenic series **3O*n***, **4O*n***, ***n*O6**, ***n*OO6**. The transition temperatures were measured by DSC (Mettler FP 52) using a heating rate of 10°C min^{-1}. *T*melt, *T*I–N, *T*N–Sm, and *T*solid are respectively associated with the melting of the sample with increasing temperature, and with the isotropic–nematic, nematic–smectic, isotropic–smectic and solidification temperatures with decreasing temperature.

2D spectrum is presented in figure 5. Let us consider the interesting case of H7 and H9, the two hydrogens *ortho*-to the alkoxy chain. These hydrogens are shielded as expected for this type of environment. Nevertheless, there is a huge difference of nearly 20 ppm in the associated ^{13}C chemical shifts of C7 and C9 which is quite unusual.

In the literature, the central heterocyclic core is considered as a delocalized aromatic system rather than as dienes with localized bonding [13]. However, we have found from the X-ray structure of the parent compound that the bond lengths in the six-membered ring of the indazole system reflect the bond order of the C–C bonds in the ring. Indeed, the C6–C7(1.423 Å), C8–C9(1.423 Å), C10–C11(1.417 Å) and C6–C11(1.421 Å) bonds are longer than the C7–C8(1.356 Å) and C9–C10(1.365 Å) bonds [1].

A very simple but informative way to analyse the electron density is to consider the oxygen lone pair delocalization on the ring system. As the double bonds seem to be localized, the increase in the electron density is larger on C7 than on C9. The 20 ppm difference in the chemical shift values of these two carbons reflects the difference in the enhancement of the electron density at these two sites. The extended conjugation of the oxygen lone pair also leads to C5 shielding.

3.3. *Anisotropic chemical shifts*

We chose to study two low melting compounds, **3O6** which is purely nematic and **6O6** which is purely smectic. Usually smectic compounds are quite difficult to orient in a magnetic field especially when no nematic phase is present between the smectic and the isotropic liquid.

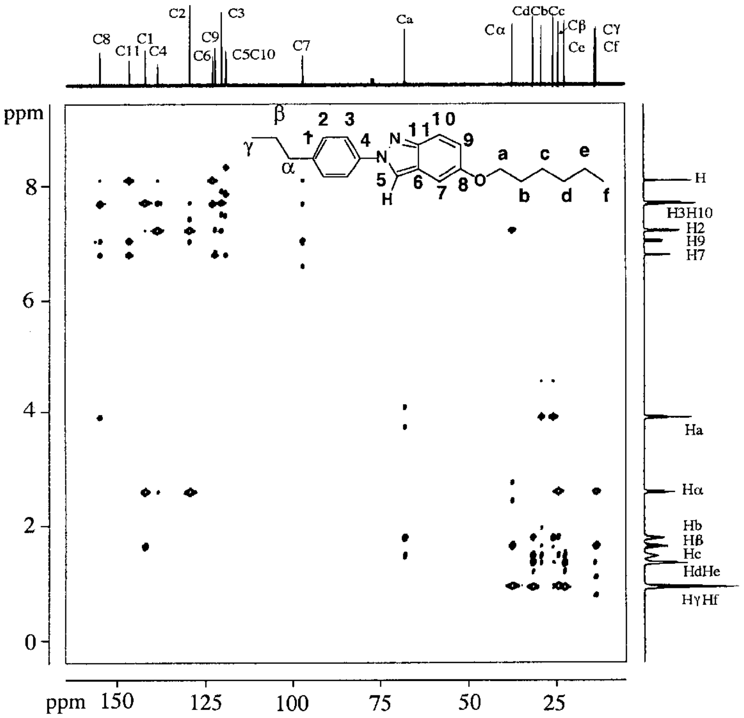

Figure 5. HMBC 2D spectrum of **3O6** dissolved in $CDCl_3$.

Therefore, it was quite surprising to obtain high resolution spectra in the smectic phase of **6O6**. Under microscopic observation, the compound in the smectic phase appears very fluid.

Figure 6 shows in (*a*) the spectrum in the isotropic melt of **3O6**. This spectrum is very similar to that obtained in solution (figure 5). The two spectra (*b*) and (*c*) were taken 5°C below the I–N transition and I–SmA transition of **3O6** and **6O6**, respectively. The larger jump in the chemical shifts of the smectic **6O6** compared with the nematic **3O6** is quite evident especially for the quaternary carbons. The assignment in the liquid crystalline phase is more tedious. For example, let us consider the case of the quaternary carbons C4, C1, C8 and C11. Among these four peaks, two peaks are broader. This broadening may arise from the dipolar coupling with the two nitrogens present in the molecule. Accordingly these broad peaks were assigned to C4 and C8. This broadening is still obvious on the peak corresponding to C5.

The ^{13}C chemical shift changes can be related to the macroscopic order parameter by the semi-empirical equation [14]:

$$\delta_{\mathrm{obs}} = \delta_{\mathrm{iso}} + aS_{zz} + b = \delta_{\mathrm{iso}} + b + aS_{\mathrm{o}}(1 - T/T^{\dagger})^{F} \tag{1}$$

where a and b are constants that depend on the components of the chemical shift tensors in the axis system chosen to define the order parameter. They are assumed to be independent of the temperature within experimental error. $T^{\dagger}$ is a temperature slightly higher than T_{NI} and S_{o} is the limit of the bond order parameter of the fragment relative to the director [15]. The quantity S_{o} gives an estimate of the mean angle between the fragment under investigation and the molecular long axis, since S_{o} is roughly a product of two limiting order parameters: the segmental one relative to the molecular long axis and the molecular one relative to the director.

Figures 7 (*a*) and 7 (*b*) give a comparison of the evolution of the aromatic chemical shifts for **3O6** and **6O6**. The evolution is rather flat in **6O6** compared with that observed in **3O6**, indicating that the ordering inside the smectic phase does not increase noticeably on decreasing the temperature. At $T/T_{\mathrm{NI}} = 0.9$ near the LC–solid transition, the aromatic part of the chemical shifts in the two compounds are nearly identical giving a clear indication that the chain length on the phenyl ring does not have significant influence on the ordering of the rigid 2-phenylindazolic core. As already noticed, this chain is globally in alignment with the mean molecular axis of the core.

Usually quaternary carbons present the largest chemical shift anisotropy, especially for quaternary carbons in *para*-disubstituted aromatic rings where one component of the chemical shift tensor is aligned with the *para*-axis and is not modulated by the rotation of the ring [14]. In figure 7 (*c*) the anisotropy of the chemical shifts in compound **6O6** is plotted. The quaternary carbons in the core present different chemical shift anisotropies.

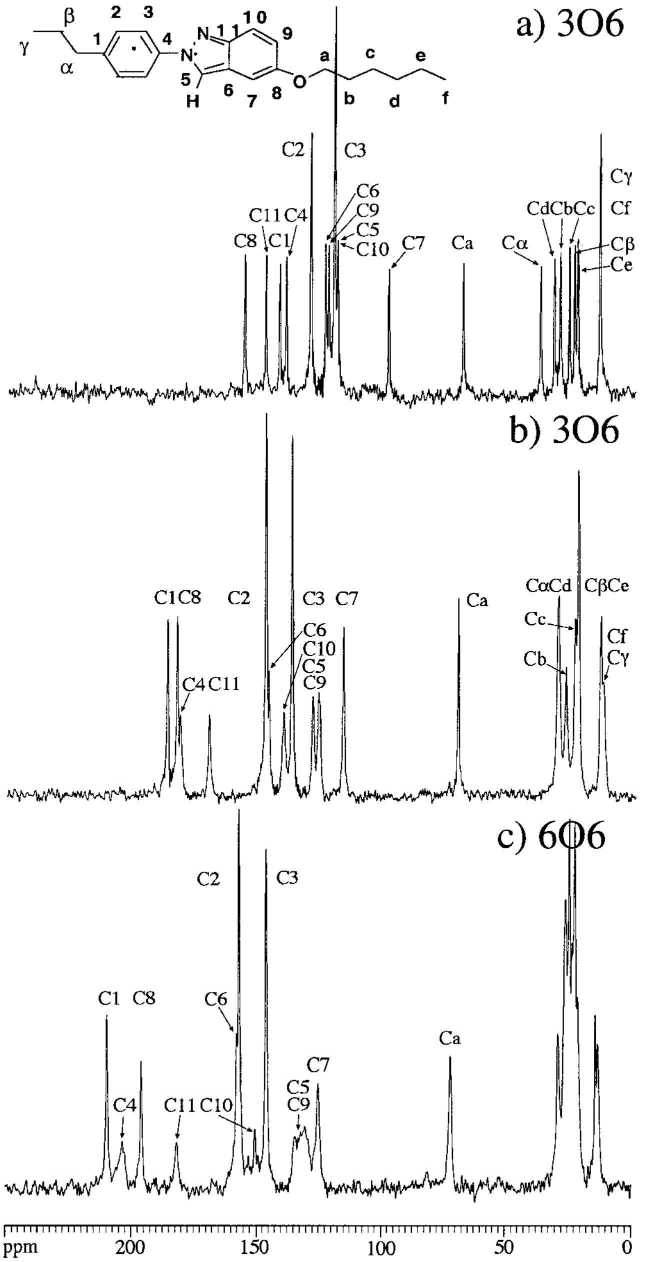

Figure 6. ^{13}C NMR spectra of **3O6** in the isotropic phase (*a*), in the nematic phase, 5°C below the I–N transition (*b*), and of **6O6** in the smectic phase, 5°C below the I–SmA transition (*c*). For each spectrum, the acquisition parameters were: number of scans = 32, acquisition time = 0.019 s, recycle delay = 15 s, decoupling power = 40 kHz.

Carbons C4 and C1 in the *para*-substituted ring have the largest anisotropies, whereas the anisotropies of carbons C8, C11 and C6 in the indazole moiety are far smaller. This is strong evidence that the *para*-axis of this phenyl ring is nearly aligned with the molecular long axis. This is in accordance with the rigidity of the indazole ring determined by X-ray.

C8 which bears the alkoxy chain presents a much lower anisotropy. When this type of carbon is aligned with the molecular long axis, the chemical shift anisotropy is larger by more than 40 ppm than that measured in the present work [16]. This indicates that C8 does not lie on the molecular long axis and that its chemical shift anisotropy tensor is modulated by the whole reorientation of the molecule along the molecular long axis. This trend is also observed for C11 which is expected to have a large anisotropy due to the linked nitrogen. The consequence is that the first bond belonging to the hexyloxy chain is far off the molecular long axis.

Figure 7(*d*) gives the aliphatic part of the chemical shifts. We observe two different behaviours. The peaks below 40 ppm (for example the Cα carbon) present a negative jump in the chemical shift at the isotropic–nematic transition. This behaviour is usually observed for carbons belonging to a terminal chain. The $-OCH_2-$ peak experiences a small positive shift. This positive shift has been observed already in the $-OCH_2-$ attached to a ring in a lateral position [7–16]. This means that, in equation (1) at least one quantity S_o or a is small. In the next section we will see that the order parameter of the C–H bond is not negligible, implying that a is very small. The change in the aliphatic chemical shift on entering the liquid crystalline phase is an average over different factors: the probability of finding a conformation, the ordering matrix of the C–H fragment involved in that conformation and the chemical shift tensor of the observed carbon in that conformation. Due to the peculiar averaging of the chemical shift tensor, a carbon can experience a negligible jump in chemical shift on entering the nematic phase with a non-negligible order parameter. We can understand that some conformations are hindered for the first $-OCH_2-$ group as the $C_{ring}-O$ bond makes a non-negligible angle with the molecular long axis. This bond rotation will give conformations which may strongly perturb the packing in the mesophase. When the most favourable conformations are populated for this carbon, the far part of the chain will be more free to move and will act like a normal terminal chain leading to the different behaviour observed for the first and subsequent carbons in that chain.

3.4. *Analysis of the dipolar couplings*

The dipolar splittings in the nematic phase were obtained using the 2D SLF method. In the 2D experiment presented in figure 8, the cross-peaks corresponding to the carbons in the hexyloxy and propyl chains have different separations, indicating different orderings. Experimentally, the following values for $\Delta\nu$ in kHz are found: Ca 6.3, Cb 9.4, Cc 5.1, Cd 5.8, Ce 3.0, for the methylene carbons in the alkoxy chain; and Cα 10.8,

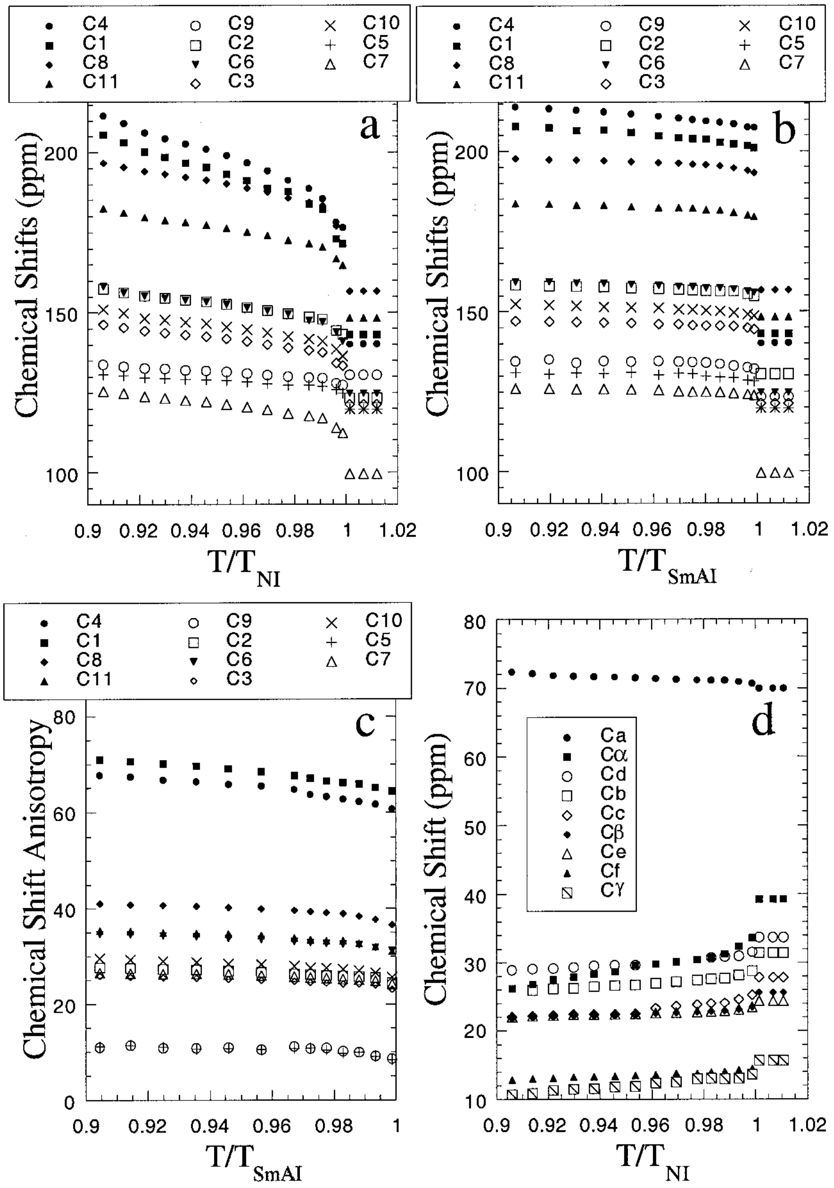

Figure 7. The chemical shifts of the aromatic parts of **3O6** (*a*), and **6O6** (*b*), the anisotropy of the chemical shifts in **6O6** (*c*) and the aliphatic part of the chemical shifts in **3O6** (*d*) plotted against the reduced temperature. These plots were obtained by decreasing the temperature from the isotropic liquid.

Cβ 5.3 for the methylene carbons in the propyl chain. Usually, the dipolar splittings decrease along the chain with some odd–even effect [10]. The rather small value of the dipolar splitting of carbon Ca indicates that the hexyloxy chain does not behave like a terminal chain.

The dipolar coupling constants can be extracted from the observed carbon–proton splitting ($\Delta\nu$) in the 2D experiment using equation (2) [10]:

$$\Delta\nu = f(2)^{1/2}[2D_{\text{C-H}} + J] \tag{2}$$

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 $-\text{OCH}_2-$ carbons). Then, the C–H bond order parameter can be obtained from the corresponding dipolar coupling constants by:

$$S_{\text{C-H}} = -4.407\times 10^{-5}\, D_{\text{C-H}}. \tag{3}$$

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 [19–21]. Thus, it can be positive or negative depending on the mean orientation of the C–H bond vector with respect to the molecular long axis.

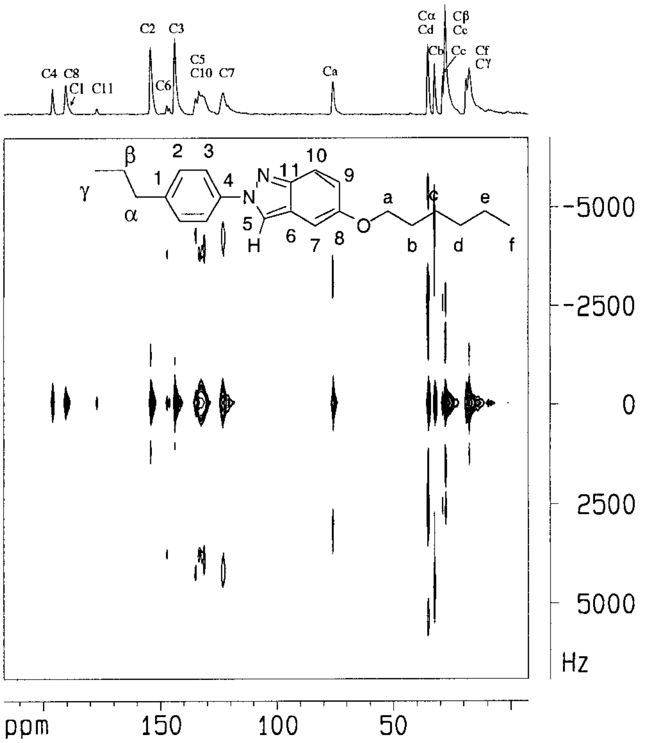

Figure 8. 2D SLF spectrum of **3O6** in the nematic phase at 349 K.

If the C–H mean angle is greater than the magic angle, the bond order parameter is negative; it is positive if this angle is less than the magic angle. From the experimental value obtained, we can calculate two opposite values of the order parameter equal to ± 0.12. This value is smaller than the one expected for a terminal chain [17]. However, it is very similar to that obtained in a biforked compound **R6R4** previously studied [18]. In this compound, due to the presence of the two nearby chains, the molecular long axis is tilted in comparison with the *para*-axis (figure 9). At the transition, the jumps in the chemical shifts were found to be positive for Cα′ and slightly negative for Cα. In the same range of reduced temperature, the bond order parameter was found to be positive and small for Cα′ and equal to − 0.12 for Cα. This indicates that the bond order parameter in **3O6** is certainly negative and the difference in the chemical shift evolution is related to the position of the molecular long axis with respect to the C–O direction. The subsequent carbons in the hexyloxy chain have the following bond order parameters: Cb, $S_b = -0.18$; Cc, $S_c = -0.10$; Cd, $S_d = -0.11$; Ce, $S_e = -0.06$; Cf, $S_f = -0.03$.

Figure 10 gives the comparison of $|S_{C\text{-}H}|$ values in **CIN6-2** (4-ethylphenyl 1-4-*n*-hexyloxycinnamate) [22] where the hexyloxy chain is at a typical terminal position; in compound **R6R4** where the chain is in the *para*-position, but where the molecular long axis is tilted with respect to the *para*-axis of the terminal aromatic ring; and in **3O6** where the chain is more or less at a lateral position. From this plot, we can conclude that the first CH_2 in the hexyloxy chain of **3O6** experiences a different mean conformation due to its peculiar position away from the molecular long axis, whilst the subsequent CH_2 behaves more or less like a typical CH_2 group in a terminal chain. The difference between the $|S_{C\text{-}H}|$ values arises from the angle between the mean position of the chain and the molecular long axis.

4. Conclusion

We have synthesized four new series of compounds containing the 2-phenylindazole core. Due to the presence of the five-membered ring, the first bonds of the two terminal chains do not point along the same axis. These two chains do not behave in the same way in promoting liquid crystalline properties due to their particular orientations. By applying 1D and 2D C-13 NMR techniques, the orientational orderings of some fragments have been estimated. They show that the molecular long axis is nearly aligned with the *para*-axis of the phenyl ring attached at position 2 with respect to the indazole

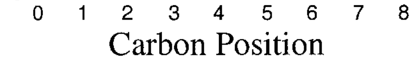

Figure 10. Comparison between the order parameters in **CIN6-2**, **R6R4** and **3O6** in the same range of reduced temperature.

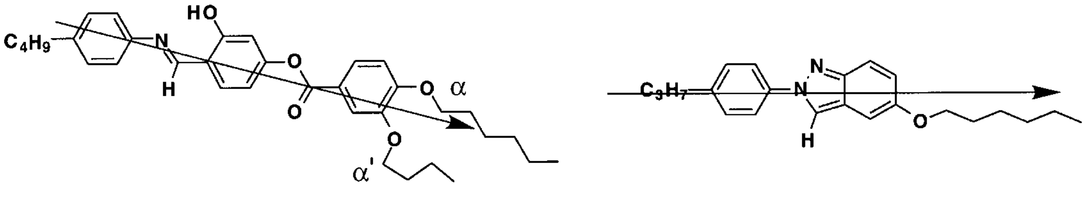

Figure 9. Comparison of the position of the molecular long axis in **R6R4** and **3O6**, respectively.

ring. The chain belonging to the phenyl ring behaves like a normal terminal chain, whereas the chain attached to the indazole part of the molecule presents a different behaviour indicating that the first fragments of this chain are not aligned with the molecular long axis. Further work is in progress to study the influence of the nature of a five-membered heterocyclic ring on the nature and the stability of the mesophase obtained.

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