Racemic nematogens having a chiral center in the lateral chain

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L e t t e r

A chiral center can be introduced in the lateral alkoxy chains of mesogens containing four rings in the main core. The compounds present a large nematic range. Comparison with compounds having a linear chain indicates the bifurcate character of the chain does not drastically affect the nematic range. ^{13}C NMR spectra in the nematic phase give some indications about the folding of each branch of the chiral chain along the core.

Nématogènes racémiques possédant une chaîne latérale chirale. Nous avons synthétisé des composés nématogènes possédant une chaîne latérale alkoxy chirale. Ces composés possèdent un domaine nématique peu différent de celui observé pour les composés ayant une chaîne linéaire possédant le même nombre de carbones. La RMN C-13 donne des indications sur le repliement des deux fragments de la chaîne chirale le long du coeur mésogène dans la phase nématique.

Laterally alkoxy-substituted mesogens deviate from the classical rod-like shape. However, they may exhibit a large nematic range if the core anisotropy is large enough.[1–4] Although it has been shown that many flexible lateral substituents can lead to mesogenic properties, the substituent position is quite important for the phase behavior. If the lateral alkoxy chain belongs to one of the outer rings, an enantiotropic smectic phase is enforced by a *meta* substitution with respect to the link; meanwhile, a monotropic nematic phase is generally observed when the substitution is in the *ortho* position with respect to the link.[2] If the lateral alkoxy chain is introduced on the inner ring, an enantiotropic nematic phase is always obtained. We have shown that introducing a methyl group near the alkoxy chain in that position enforces the nematic range, because this methyl group fits the empty space.[5] This interesting phenomenon is also observed when two lateral alkoxy chains are displayed on the same inner ring of a main core containing four aromatic rings. In the solid phase and the nematic phase, the two chains are folded back in opposite directions along the core allowing the molecular anisotropy to be preserved.[6,7] To assure such a geometry, the first two fragments within the chains adopt opposite *gauche* conformations (Fig. 1a). Therefore, the idea to replace these two alkoxy chains pointing in opposite directions by a single bifurcate one is of interest as we may expect a similar effect (Fig. 1b). By molecular modelling, a minimized conformation
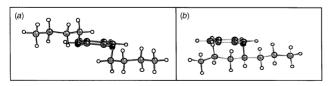
can be found with the two parts of the bifurcate chain folded back along the core if the first fragment is in a *gauche* conformation. Thus, this possible conformation will allow the anisotropic arrangement of the molecules inside the liquid crystalline phase. In addition, it is a very elegant way to introduce a chiral center in the vicinity of the core. The lateral chain will have fewer degrees of freedom due to the expected folding of the chain along the core. Thus, we can expect a stronger influence of the asymmetric center with comparison to the one introduced in a terminal chain.

In this note, we present the synthesis and the mesomorphic properties of the first racemic mesogens having a lateral chiral chain. Series I compounds (referred to as **Res*n**) contain four aromatic rings and the lateral chain is introduced on one of the inner rings (Fig. 2). This series is compared with two other series differing by the lateral substitution or the structure of the inner ring. Series II (**Pyr*n**) has a pyridine ring instead of the aromatic ring. This pyridine ring was chosen to quantify the steric effect of the hydrogen atom on the lateral chiral chain alignment. Series III (**Res n**) has a linear lateral chain, instead of the chiral chain, that contains the same carbon number in order to analyze the perturbation introduced by the bifurcate chain. Three compounds containing 4, 7 or 10 carbons have been synthesized in each series. The chiral chain always has an ethyl fragment. The different series were prepared according to the scheme shown for series II (Fig. 3).

The transition temperatures of the three series are given in Table 1. All compounds exhibit an enantiotropic nematic phase. Fig. 4 shows the comparison of the transition temperatures between the compounds with respect to the total number of carbons in the lateral chain. In each series, the clearing temperatures decrease with the number of carbons in the chain; for the same carbon number in the chain, the clearing temperatures have the following order: **Res n** > **Res*n** > **Pyr*n**. The melting temperatures follow roughly the same order, but are less regular. The chiral chain does not add too much perturbation to the molecular arrangement in comparison with the linear chain. This means that the two branches of the bifurcate chain certainly point towards opposite directions as shown in Fig. 1. The short branch fills

Fig. 1 Proposed mean conformation of the chains substituted on the inner ring of the mesogen: *a* two alkoxy chains, *b* a single chiral chain
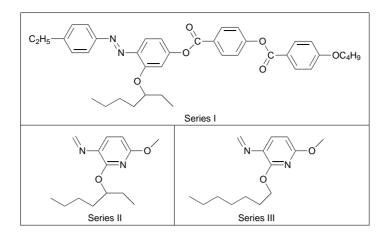
Fig. 2 Structure of three series of compounds. In each series three compounds have been synthesized having 4, 7 or 10 carbons in the lateral chain. In series I and II, the bifurcate chain always has an ethyl fragment

only the empty space created by the long branch without adding too much conformational disordering. Unfortunately, the introduction of the pyridine ring does not enlarge the nematic range as proposed. This indicates that there is no steric interaction between the *ortho* hydrogen and the chain. Amazingly, the pyridine ring lowers the melting temperatures, resulting in a nematic compound near room temperature for **Pyr*10**.

As proposed previously,[5,6] the appearance of the liquid crystal phase in these laterally substituted compounds is induced by the parallel conformation taken by the lateral chain with respect to the mesogenic core. In order to check the alignment of the bifurcate chain, we have obtained the evolution of the ^{13}C chemical shifts with temperature for compound **Res*10** (Fig. 5).
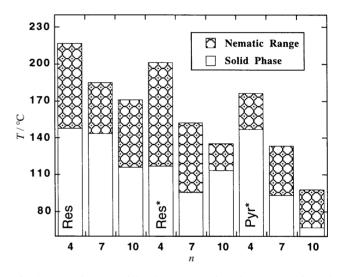

Fig. 4 Nematic range of the three mesogenic series **Res n**, **Res*n** and **Pyr*n**. The transition temperatures were measured by DSC (Mettler FP 52) using a heating rate of 10 °C min^{-1}

Table 1 Transition temperatures (in °C) in the three series **Res n**, **Res*n** and **Pyr*n**. These values are taken with increasing temperature (heating rate 10 °C min^{-1})

Compound	K → N	N → I
Res 4	148	217
Res 7	143.5	185
Res 10	116	171
Res*4	117	201.5
Res*7	95.5	152.5
Res*10	113.5	135.5
Pyr*4	147	176.5
Pyr*7	93	133.5
Pyr*10	67	98

Fig. 3 Synthetic scheme for series II. Three compounds have been synthesized with 4, 7 or 10 carbons in the chiral chain
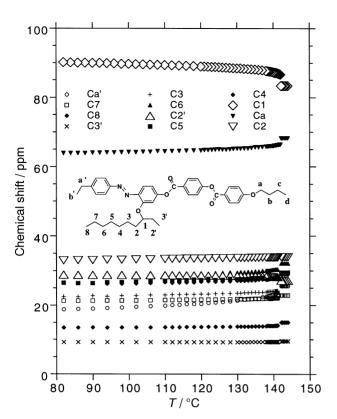
Fig. 5 The chemical shifts of the aliphatic signals of **Res*10** plotted against temperature as obtained with decreasing temperature from the isotropic melt

The jump at the isotropic–nematic transition T_{NI} in the ^{13}C chemical shifts gives some valuable information on the mean conformation of the fragment.[6] Usually, for a terminal chain each CH_2 fragment experiences a negative jump with decreasing temperature. In many cases, we have shown that the inverse behavior is observed for the first CH_2 in the lateral linear chain due to the particular mean conformation of this fragment within the nematic phase; the second CH_2 exhibits a tiny negative or no obvious jump and the subsequent CH_2 groups show the usual negative jump. Fig. 5 presents two interesting features: the expected positive jump for C1, which is proof of the folding of the chain in the nematic phase, and the unexpected positive jump for C2′ and negative jump for C2. This indicates that the two branches in the chiral chain in **Res*10** do not act in exactly the same way. This interesting behavior will be analyzed in a forthcoming paper.

In conclusion, a chiral chain containing two alkyl branches can be introduced in a lateral position on the inner ring of a main core containing four aromatic rings without a deleterious effect on the liquid crystalline properties. Moreover, the liquid crystal range is similar for the compounds with linear or chiral chains. ^{13}C NMR spectroscopy indicates that each branch within the chiral chain is folded along the core. Further investigations dealing with the chiral chain conformations in the solid and liquid crystal phase are under way and will be reported elsewhere.

Experimental

2,6-Dihydroxypyridinium chloride is mixed with two equivalents of potassium hydroxide in polyethylene glycol (MW = 200) and the solution is stirred at 100 °C for one hour.[8] The bromide is then added to the cooled mixture and the temperature is set again to 100 °C for two hours. The mixture is extracted with three volumes of dichloromethane. The monoalkylated compound is obtained through chromatography using dichloromethane as eluent. The diazotization was performed in water with one equivalent of diazonium salt and two equivalents of pyridine, in order to obtain the monodiazotized compound as the major component. The monoalkylated compound was then purified by chromatography with $CHCl_3$ as eluent. The esterification step was performed in dichloromethane using the dicyclocarbodiimide (DCC) method.[9] Alkoxybenzoic acid was added in slight excess, in order to consume the phenol totally. After filtration of the amide and evaporation of the solvent, the crude mixture was chromatographed with CH_2Cl_2 as eluent and then recrystallized several times in chloroform–ethanol until constant transition temperatures were obtained.

The structures and the purity of the intermediates and final products were checked using ^1H NMR on an AM 250 Bruker spectrometer, with $CDCl_3$–$[^2H_5]$pyridine as solvent. The data are expressed in the form of chemical shifts in ppm (integration, multiplicity).

2-Hydroxy-6-[(1-methyl)propoxy]pyridine (**A4**): 0.94 (3H, t), 1.31 (3H, d), 1.7 (2H, m), 4.40 (1H, h), 5.64 (1H, dd), 6.29 (1H, dd), 7.48 (1H, dd).

2-Hydroxy-3-[(4′-ethyl)-azobenzene]-6-[(1-methyl)propoxy]-pyridine (**B4**): 1.03 (3H, t), 1.27 (3H, t), 1.45 (3H, d), 1.83 (2H, m), 2.71 (2H, q), 5.33 (1H, h), 6.32 (1H, d), 7.30 (2H, d), 7.70 (2H, d), 8.21 (1H, d).

Pyr*4: 1.03 (6H, 2t), 1.29 (3H, t), 1.46 (3H, d), 1.54 (2H, m), 1.76 (2H, m), 2.73 (2H, q), 4.06 (2H, t), 5.28 (1H, h), 6.78 (1H, d), 7.00 (2H, d), 7.33 (2H, d), 7.39 (2H, d), 7.86 (2H, d), 8.06 (1H, d), 8.16 (2H, d), 8.33 (2H, d).

The phase transitions were observed and characterized by using an Olympus polarizing microscope fitted with a FP 82 Mettler heating stage and a FP 85 Mettler DSC. The NMR experiments on **Res*10** in its isotropic and nematic phases were conducted using a Varian VXR-500 NMR spectrometer ($B_0 = 11.07$ T) equipped with an indirect detection probe manufactured by Narolac Cryogenic Corporation. The sample was put in a standard 5 mm tube and spun slowly along the magnetic field so that the director aligned parallel to the magnetic field. To avoid radio frequency overheating, a 0.8% decoupler duty cycle was used. The temperature calibration was made by observing the nematic to isotropic transition.

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