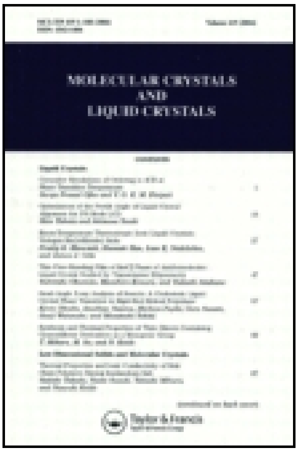

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Influence of the Spacer in a Series of Chiral Non-Symmetric Dimesogens

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INFLUENCE OF THE SPACER IN A SERIES OF CHIRAL NON-SYMMETRIC DIMESOGENS

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Abstract : We have synthesized and characterized a new series of chiral non-symmetric dimesogens, similar to a previous series but bearing a different chemical linkage between the spacer and the shorter mesogen. Unlike the previous one with an ester group in the spacer, the series described in this paper, which is constituted with an ether linkage, does not exhibit any alternance of the mesomorphic behaviour with the spacer parity. But an odd-even oscillation of the transitionnal and physical properties has been observed.

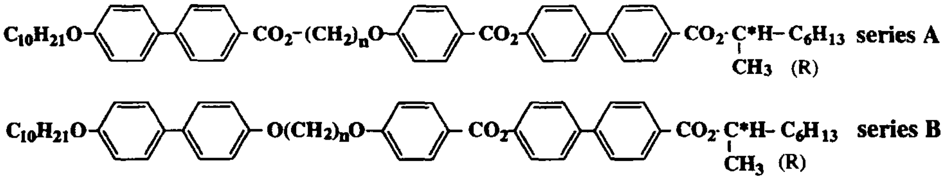
INTRODUCTION

During the last few years, dimeric liquid-crystals have been much investigated : they are constituted with two mesogenic units linked via a methylenic spacer. They pay much attention for their ability to act as model compounds for main-chain liquid-crystalline polymers[1], and also for their specific properties, quite different to the low molar mass compounds. In particular, their transition properties often depend on the spacer parity[2].

More recently, a new architecture consisting of two different mesogenic units linked via a flexible spacer[3] has been introduced and gives rise to frustration phenomena[4, 5].

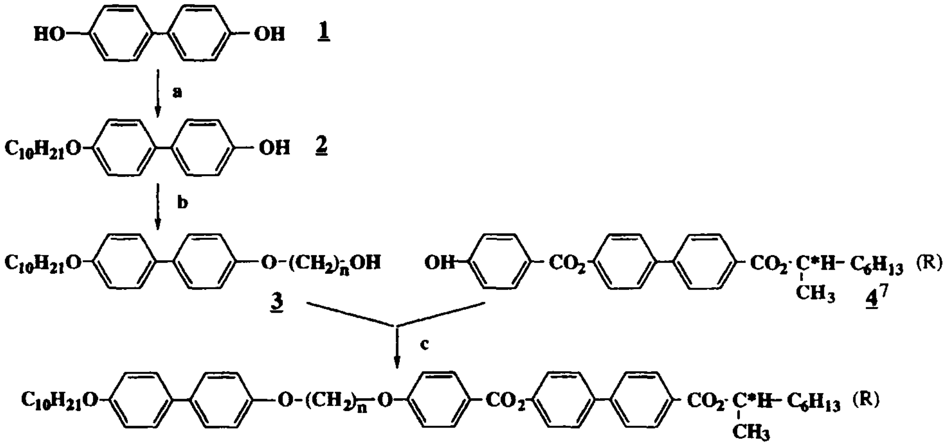
Within the framework of our synthesis of new antiferroelectric liquid crystals (AFLC), we have synthesized chiral non-symmetric dimesogens : one low molar mass AFLC compound[6] with a chiral three phenyl rings core is attached to a non-chiral mesogen having a different length. The series A, abbreviated 10BPnBBP8*, has already been reported[7] and it displays a very interesting liquid-crystalline behaviour. The mesomorphic sequence alternates with the spacer parity : antiferroelectric phases ($S_C{}^*{}_A$, $S_C{}^*{}_{FI}$, $S_C{}^*$, $S_C{}^*{}_\alpha$) exist for even spacers, whereas a bidimensionnal $S\tilde{C}^*$ phase is observed for odd ones.

In this paper, we report the synthesis and the characterization of an analogous series B of chiral non-symmetric dimesogens, where both rigid parts are linked to the spacer through ether groups (instead of an ester and an ether in the series A). The series B is abbreviated 10BPOnBBP8*.



SYNTHESIS

The synthetic route is briefly summarized below :



a : (1) $C_{10}H_{21}Br$, KOH, EtOH, (2) HCl ; b: (1) Br-$(CH_2)_n$-OH, KOH, EtOH, (2) HCl ; c : DEAD, TPP, CH_2Cl_2.

The final compounds have been purified by chromatography on silica gel using CH_2Cl_2 as eluent and recrystallized from absolute ethanol.

MESOMORPHIC BEHAVIOUR

The thermal behaviour was investigated by differential scanning calorimetry (Perkin-Elmer DSC7) and the phase identification was carried out by thermal optical microscopy, using a Zeiss Ortholux polarizing microscope equipped with a Mettler FP5 hotstage.

The thermodynamic DSC data are summarized in table 1. Almost all members exhibit smectic phases. For n=6 to 10, their mesomorphic sequence includes S_C* and S_A

phases. For n=11, only the S_A phase is observed and the N* phase appears. For longer compounds (from n=12), smectic tendancies are cancelled and only the N* phase is observed.

Other smectic phases are also detected at low temperature, which probably possess a long range ordering within the layers. The enthalpies corresponding to their transition in a fluid phase are very high (more than 5 $kJ.mol^{-1}$).

The clarification and melting temperatures oscillate with the spacer parity. In each case of odd or even n value, the clarification temperatures decrease while the spacer length increases and the gap between two successive n is gradually attenuated. The S_A-I entropies follow the same alternation : it is much higher when n is even ($\Delta S/R$ is close to 4) than when n is odd ($\Delta S/R$ closer to 2). Such an oscillation is well-known for the N-I transition[1] : the orientational order of the nematic phase is strongly affected by the spacer parity, which governs the molecular conformation[8]. Therefore, the bent shape of the odd dimesogens leads to a weaker orientational order than for the rod-like even members. In the case of a fluid lamellar phase, the orientational order within the layer can also vary with the molecular conformation and the S_A-I entropies follow a zig-zag evolution with the spacer length.

TABLE 1 Transition temperatures (°C) and their corresponding enthalpies ($kJ.mol^{-1}$) for the 10BPOnBBP8* series [$\Delta S/R$ for S_A-I or N*-I transition].

n	K	S_{ord}	S_C*	S_A	N*	I
6	• 128	• (124.7)	• 179.2	• 191.3	-	•
	33	*4.82*	*0.67*	*15.9 [4.11]*		
7	• 113	-	• 127.7	• 148.5	-	•
	43		*0.95*	*8.5 [2.44]*		
8	• 115	• 124.3	• 157.2	• 168.1	-	•
	46	*5.82*	*1.87*	*15.2 [4.13]*		
9	• 111	• (108.9)	• 116.7	• 135.2	-	•
	39	*8.88*	*2.66*	*6.62 [1.95]*		
10	• 119	• 130.7	• 143.7	• 150.0	-	•
	42	*8.98*	*4.35*	*13.2 [3.74]*		
11	• 106	• 115.5	-	• 122.8	• 126.2	•
	25	*22.1*		*1.47*	*0.43 [0.13]*	
12	• 122	• 131.8	-	-	• 137.2	•
	45.5	*16.7*			*3.61 [1.0]*	

Unlike the 10BPnBBP8* series[7], the mesomorphic sequence remains the same whatever the spacer parity and no S_C*_A nor $S\tilde{C}*$ phase are observed.

Since the transitionnal properties depend on the spacer parity, we suggest to investigate the liquid-crystalline physical properties in each case of even and odd spacer. (n=9 and 10).

HELICAL PITCH MEASUREMENTS

The helical pitch of the S_C* phase has been measured at various temperatures.We have used a well-known method as previously described[9] : the sample consists of a prismatic cell made of rubbed glass plates, in which the liquid crystal presents a complanar texture and presents a lattice of regular Grandjean-Cano steps. The selectively reflected light is analyzed too : it corresponds to the first order ($\lambda = 2np$) if the pitch p is higher than 0.27 µm, and to the second order ($\lambda = np$) if it is lower.

For n=10, on heating, the pitch increases over the whole S_C* range (from 0.27 µm at 129°C to 0.33 µm at 142°C), and suddenly drops at the S_C*-S_A transition. The first order of the selective reflected light is observed. For n=9, the pitch is much smaller and only the second order of the selective reflected light is visible. The pitch smoothly decreases over the range (from 0.2 µm at 112°C to 0.103 µm at 118.8°C). As for n=10, the usual decrease of the pitch at the S_C*-S_A transition is not observed due to the first-order character of the present transition.

The magnitude difference between the pitches of these two samples might be related to the difference of the molecular shape between odd and even dimesogens. Indeed, the alternation of the pitch has already been mentionned for cholesteric dimesogens[10] and for induced chiral S_C phases[11].

ELECTROOPTIC MEASUREMENTS

The ferroelectric properties of those dimesogens have been investigated using commercial cells (from E.H.C. Company) coated with ITO (indium-tin oxide) over a 0.16 cm^2 acitve area. Their inner surfaces were covered with an unidirectionnally rubbed polyimide film. A good planar alignment was obtained using a 3 µm-thick cell.

In the saturation conditions (2.5 $V.\mu m^{-1}$, 50 Hz), the spontaneous polarizations of both compounds (n=9 and 10) follow a similar thermal behaviour : they decrease while the temperature increases and have the same magnitude range (52 nC.cm^{-2} for n=9 and 55 nC.cm^{-2} for n=10 at $T_{S_C{*}\text{-}S_A}$-T= 6°C).

X-RAY SCATTERING

X-Ray diffraction experiments have been carried out to determine the layer thickness of the smectic phases.

The CuKα radiation of a 18 kW rotating anode X-Ray generator (Rigaku-200) was selected by a flat (111) Germanium monochromator, which delivered a 1 mm^2 beam onto the sample. The scattered radiation was collected on a two dimensional detector Imaging Plate system (sample-detector distance : 830 mm) through helium in order to lower absorption and diffusion. Then, the resolution was about 7.10^{-3} Å^{-1}. A Lindemann tube (Φ=1 mm) was filled by capillarity in the isotropic phase and introduced in an oven whose temperature stability was ±10 mK. The tube axis was vertical and perpendicular to the beam. Exposure times were 30 minutes.

FIGURE 1 : Temperature dependence of the layer spacing d (Å) for the 10BPO9BBP8*.

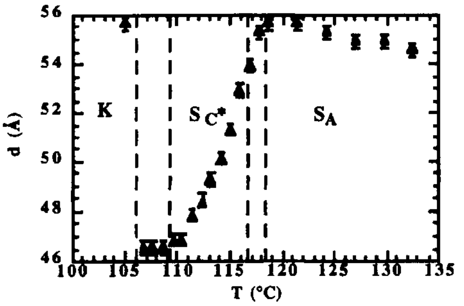
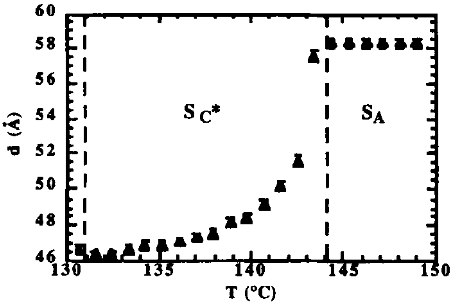


FIGURE 2 : Temperature dependence of the layer spacing d (Å) for the 10BPO10BBP8*.



On cooling from the S$_A$ phase, the layer distance remains quasi constant with the temperature and starts decreasing at the S$_C$*-S$_A$ transition, indicating a progressive tilt of the director from the layer normal. In the S$_A$ phase, the layer distance is close to the molecular length (L) of a dimesogen (calculated assuming that the spacer is in all-trans conformation and that the chiral chain lies perpendicular to the long axis of the three-phenyl rings mesogens[12]) : 56 Å for n=9 (L=59 Å), 58 Å for n=10 (L=65 Å). The large difference between two succesive n arise from the conformation alternance. Therefore, the smectic phases are monolayered : as for the 10BPnBBP8* series[7], a microsegregation phenomenon occurs, and the different moieties are confined into separated spaces. The different mesogenic behaviour of these two analogous series can not be explained by the type of lamellar ordering, but only by the chemical nature of the linkage between the spacer and the mesogen.

CONCLUSION

In this paper, we report the synthesis of a new series of chiral non-symmetric dimesogens : 10BPOnBBP8*. Most of these compounds exhibit S_C* and S_A phases. Their physical properties (transition temperatures, clarification entropies, and also the helical pitch of the S_C* phase) strongly depend on the spacer parity. But, unlike the previous series 10BPnBBP8*, the mesomorphic sequence does not alternate with the spacer length. The $S_C{}^*{}_A$ and $S\tilde{C}$* phases are no longer observed. The simple replacement of the ester linkage between the spacer and the short aromatic moiety by an ether group leads to their disappearance.

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