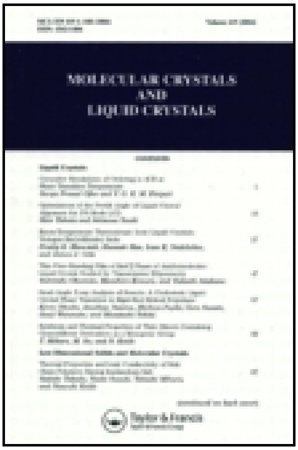

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Mesomorphic and Electro-Optical Properties of New Achiral Banana-Shaped Molecules

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Two new series of achiral banana-shaped molecules have been prepared. Their mesomorphic, electrooptical and structural properties have been investigated. The first series of hydrogenated molecules shows the nematic phase with short chains (n=8–10), N and SmC phases with intermediate chain lengths (n = 11–13) and SmC plus an unknown smectic phase with long chains. The second series of fluorinated molecules is more peculiar, exhibiting four disordered smectic phases. Two of these have broken fan-shaped or schlieren optical textures like the S_C phase, whereas the two others show slightly different textures with more or less mosaic domains. These phases display various switching characteristics, including but not limited to the "antiferroelectric" one reported for the Niori series. The relation between molecular structure and mesomorphic properties is discussed.

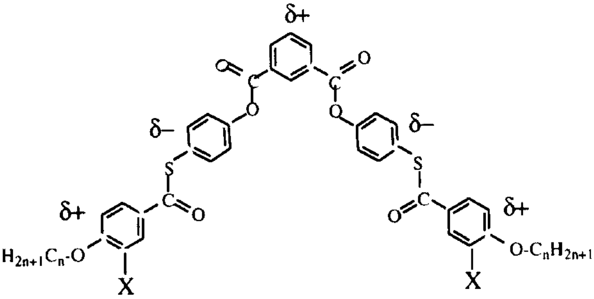
Keywords: banana-shaped mesogens; smectic mesophases; electro-optical properties; X-ray

INTRODUCTION

Since the discovery of new "ferroelectric" smectic phases formed by achiral banana-shaped molecules in 1996 by Niori et al[1], the search for new interesting materials has accelerated. Nevertheless, only one series with some slight modifications on the core or on the chains has been reported[2-5] to date. This difficulty to find new compounds suggests that the existence of banana mesophases depends not only on the shape of the molecules but also on different parameters such as local dipolar moments, position of different charges and extent of conjugation.

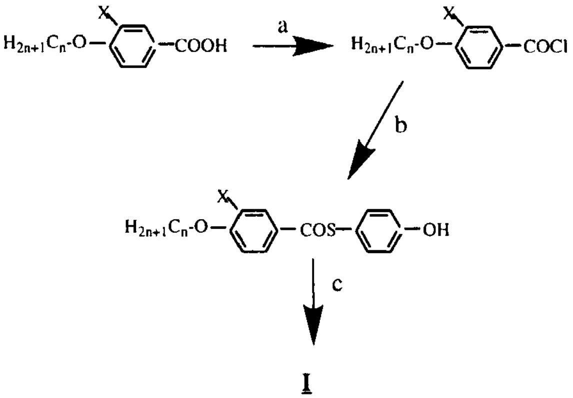
The ferro- or antiferroelectric character of the phase exhibited by this known series has not yet been fully clarified.

In this paper, we report two new series with the banana-shaped general structure **I** where X= H (series **IA**) or F (series **IB**):



I

Materials: The compounds of series **I** have been prepared following the scheme:



a) $(COCl)_2$, toluene b) 4-HS-Ph-OH, CH_2Cl_2, 0°C

c) isophthalic acid, DCC, DMAP, CH_2Cl_2

The 4-alkoxy or 4-alkoxy-3-fluorobenzoic acid[6] is first transformed into the acid chloride with oxalyl chloride in toluene. Then the acid chloride is condensed with 4-hydroxythiophenol in dichloromethane at 0°C to afford the thiobenzoate[7], which reacts with isophthalic acid in dichloromethane with DCC and DMAP as catalysts to give the desired material. The final compounds were purified by chromatography on silica gel with toluene-ethyl acetate (9:1) as eluent and recrystallized from ethanol-toluene.

MESOMORPHIC PROPERTIES

The phase transitions were determined both by optical microscopy and calorimetric measurements (Perkin-Elmer DSC7).

Series **IA** (X=H): The three compounds with n=8,9,10 exhibit only the nematic phase with threaded or marbled textures (table 1). The n=11 to n=13 derivatives, in addition to the nematic phase, display the schlieren texture of the smectic C phase. The optical textures of the N and SmC phases and also the N-SmC transition are identical to those of the classical N and SmC phases. The nematic phase disappears for the compound with n = 14, which displays SmC and an unknown smectic phase. The optical texture of SmC of this last compound changes with electric field, but we did not succeed to measure the polarization - maybe due to a very high threshold field.

The N-I transition enthalpies of these banana-shaped molecules are similar to those of the classical calamitic ones. The SmC-I transition enthalpy is higher (Table 1, for the compound with n=14), about the double of the classical SmC-I one. This indicates that the SmC phase in banana-shaped mesogens is more rigid than the classical smectic C phase.

TABLE 1: Transition temperatures (°C) and enthalpies in italics ($kJ.mol^{-1}$) of compounds **IA**

n	K		Sm?		SmC		N		I
8	•	157	–		–		•	179	•
		46						*1.6*	
9	•	154	–		–		•	174	•
		59						*1.6*	
10	•	157	–		–		•	173	•
		54						*1.9*	
11	•	156	–		•	(152)	•	168	•
		60				*2.8*		*2*	
12	•	157	–		•	162	•	167	•
		58				*4.2*		*2.3*	
13	•	149	–		•	152	•	163	•
		50				*2.8*		*2.9*	
14	•	156	•	160	•	169	–		•
		61		*0.03*		*14*			

Series **IB** (X=F):

The introduction of the fluorine atom on the first phenyl ring electronically impoverishes this ring and we obtain with this banana core alternating charges on the five phenyl rings. This favours the stacking of the molecules in the layer. Thus it is not surprising to observe that the nematic phase disappears completely in this series. With four mesophases, we obtained the richest mesomorphism shown by banana-shaped molecules (table 2). On cooling down from the isotropic phase, the X_4 phase appears with a SmC-like schlieren texture. On further cooling, we observed paramorphic textures with some mosaic or geometric domains for the X_2 and X_3 phases, whereas the X_1 phase has the same texture as X_4.

TABLE 2: Transition temperatures (°C) and enthalpies in italics (kJ.mol^{-1}) of compounds **IB** .

n	K		X_1		X_2		X_3		X_4		I
10	•	160	•	167	•	167.7	•	169.8	•	169.9	•
		61		*0.5*		*0.2*				*13.5**	
11	•	156	•	161.4	•	162.9	•	165.7	•	171	•
		59		*0.2*		*0.03*		*0.07*		*13.5*	
13	•	153.3	•	(152.4)	•	155.4	•	159.8	•	174.5	•
		53.5		*0.2*		*≈ 0*		*0.08*		*16*	
14	•	151	•	(147)	•	156	•	158.8	•	173	•
		53		*0.2*		*0.08*		*0.05*		*16*	

* *sum of transition enthalpies of* X_3-X_4 *and* X_4-I.

The I-X_4 transition enthalpies are high and comparable to the SmC-I enthalpy in the IA series . In contrast, the other mesomorphic transition enthalpies are very small and different from those of the Niori series [1]. Contact preparations between a member of the IA series and one of the IB series (both with n = 14) shows that the X_3 and X_4 smectic phases of the second series are miscible with those of the first series, where the X_4 phase is SmC and X_3 is an unknown Sm? phase.

X-ray investigations:

The X-ray diffraction with of a non-orientated sample was performed as follows: The CuKα radiation from a 18kW rotating anode X-ray generator (Rigaku-200) was passed through a flat germanium (111) monochromator, delivering a 1 mm^2 beam onto the sample. The scattered radiation was collected on a two-dimensional detector. The instrumental resolution was about 7 x 10^{-3} Å^{-1} (FWHM). Lindemann tubes (Φ = 1 mm) were filled by capillary action from the isotropic phase without any alignment procedure. X-ray diffraction experiments were performed over the whole temperature range of smectic phases. Figure 1 shows the smectic layer spacing plotted versus temperature for the n=11 derivative of the IB series. The layers have an approximately constant thickness over the X4 smectic or SmC phase of about 42.9 Å and we obtain a small jump to 43.1 Å for the other smectic phases. This distance is shorter than the length of the elongated molecule.

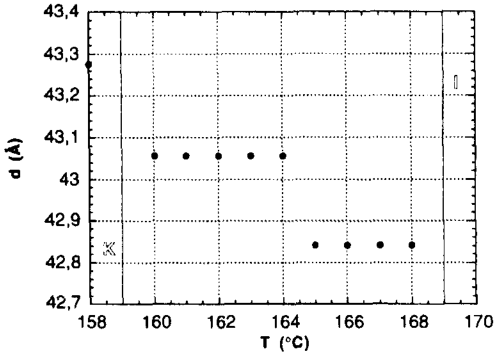


FIGURE 1: IB(n=11) layer spacings of smectic phases

Electro-optical studies:

A systematic electro-optical characterization has been performed on several compounds of the **IB** series. The samples were put into 3 or 6 μm thick commercial test cells (E.H.C. Corp). In order to avoid a fast decay of the sample purity, all preparation and measurement processes were done in a dry nitrogen atmosphere. When the inner ITO surfaces of the cell were covered with an insulating layer, it was possible to apply voltages up to 100 V. Without the insulating layer, short-circuits form at much lower applied voltages. The surfaces were finally covered with rubbed polyimide in order to promote planar alignment in SSFLC geometry. There was a clear trend to planar alignment, especially after having applied the field, but no uniform alignment could be obtained in any sample.

Square and triangular waveforms were applied to the sampes. The square wave reveals the thresholds when there is a ferroelectric phase induced by the electric field. For a compound like C13F (series IB), this threshold varies from 25 V at 150 °C to about 60 V at 158 °C. Fig. 2 shows that close to the threshold, in that case 30 V at 155 °C in C10F (IB), there is a double peak showing that there is a two-step mechanism for the polarization reversal.

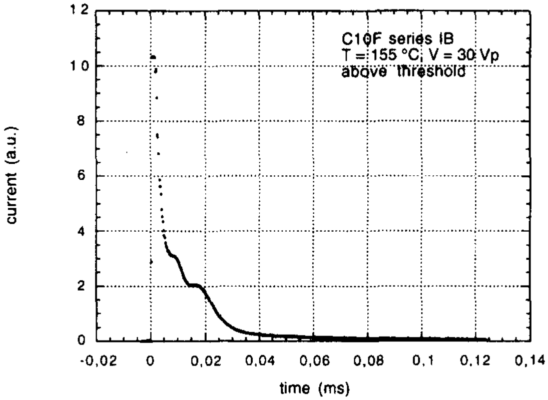


FIGURE 2: IB(n=10) Polarization current versus time (for square applied voltage).

When applying a triangular voltage, one may see the current peaks due to the polarization reversal of already ferroelectric phases and to the phase transition under field between a paraelectric and a ferroelectric phase or between different ferroelectric phases. In our preliminary investigations, we obtained many different multi-peak shapes of the current curves as illustrated in Fig. 3 for C10F (IB), indicating the presence of antiferro-, ferri- and ferroelectric structures. We did not find a discontinuous change of the electro-optical properties at several mesomorphic transitions.

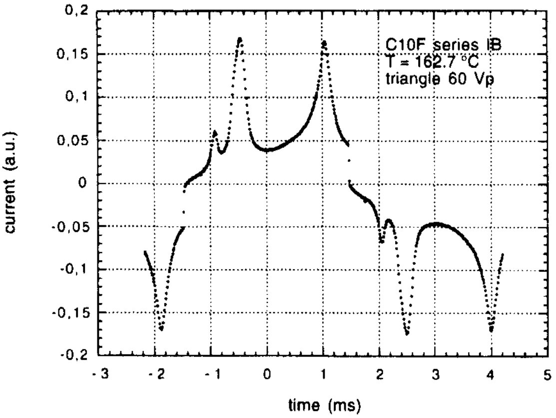


FIGURE 3: IB(n=10) typical polarization current (for a triangular applied voltage).

CONCLUSION

Following the molecular architecture model with alternating charges on the five phenyl rings, we have synthesized two new series of achiral banana-shaped molecules, IA and IB, which display up to four tilted smectic phases. Three of the four phases of the IB series exhibit antiferro- or ferrielectric behaviour.

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