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New Achiral Non Symmetric Banana-Shaped Mesogens: Mesomorphic and Electro-Optical Properties

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The first series of achiral non symmetric banana-shaped mesogens has been synthesized. The mesophases observed for these compounds depend on the whole number of carbons in the alkyl chains (N). They were investigated by optical microscopy, calorimetry, X-ray diffraction experiments and electro-optical measurements. For intermediate and long chains ($N \geq 20$) the liquid crystal phase is smectic (Sm?) and for shorter chains ($N < 20$) the mesophase appears to be columnar ordered (Col?). Yet the structure of neither one is fully resolved. Both phases exhibit a ferroelectric behaviour.

Keywords: Non symmetric banana-shaped molecules; mesophases; binary mixtures; X-ray; electro-optical properties

INTRODUCTION:

In 1996 Niori et al.[1] reported a novel ferroelectric smectic phase formed by achiral banana-shaped molecules. Up to now only two series of this type of molecules are reported: one based on resorcinol bis[4-(4-alkoxy or alkylphenylimino)benzoate][2-5] and more recently one based on bis[4-(4-alkoxybenzoylthio)phenyl] isophtalate[6]. These homologous series of banana-shaped materials exhibit different mesophases, mainly smectics.

In order to understand the influence of parameters such as local dipoles, position of different charges and conjugation on the mesophase existence, and its properties such as transition temperatures and ferro or

antiferroelectric character, it is necessary to vary the chemical constitution of the molecules. For this purpose we synthesized the first series of non symmetric banana-shaped molecules according to the molecular architectural model with alternated charges on the five phenyl rings[6] as shown in figure 1. The compounds (**Cmn**) studied have the following general formula:

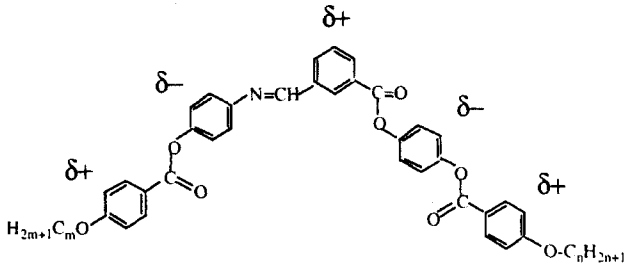
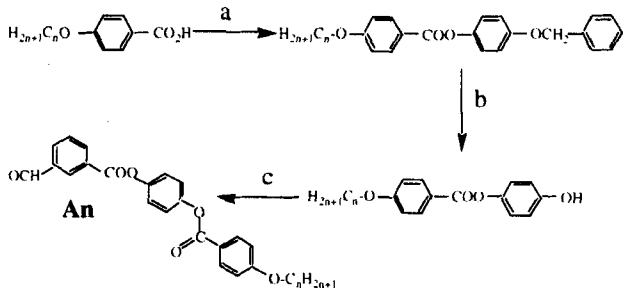


FIGURE 1: **Cmn** molecular structure showing the alternated charges on the phenyl rings.

In this paper we present the synthesis, the mesomorphic properties and the electro-optical behaviour of this series.

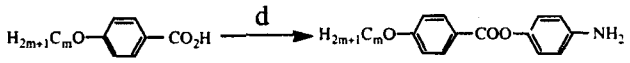
Materials:

For the synthesis of **Cmn** two intermediate compounds **An** and **Bm** were prepared according to the following schemes:



a) 4-(benzyloxy)phenol, DCC, DMAP, CH_2Cl_2 b) H_2, Pd/C, EtAcO

c) 3-carboxybenzaldehyde, DCC, DMAP, CH_2Cl_2



Bm

d) 4-aminophenol, DCC, DMAP, CH_2Cl_2

Finally **Cmn** was prepared:

An + **Bm** $\xrightarrow{e}$ **Cmn**

e) EtOH(abs), AcOH (a few drops), Δ

The 4-alkoxybenzoic acid reacts with the 4-(benzyloxy)phenol in dichloromethane with DCC and DMAP as catalysts. The 4-benzyloxyphenyl 4-alkoxybenzoate obtained, is hydrogenated with palladium 10% on activated carbon in ethyl acetate. The 4-(4-alkoxybenzoyloxy)phenol stemmed from the hydrogenation is mixed with the 3-carboxybenzaldehyde in dichloromethane with DCC and DMAP to give **An**. **An** was purified by chromatography on silica gel with dichloromethane as eluent.

Bm is obtained by the esterification of the appropriate 4-alkoxybenzoic acid with the 4-aminophenol in dichloromethane with DCC and DMAP.

Finally the condensation between **An** and **Bm** in absolute ethanol in presence of a few drops of acetic acid, under reflux yields the compound **Cmn**. It was purified by three successive recrystallisations from ethanol-toluene.

The banana-shaped molecules obtained are mesomorphic and display different mesophases.

MESOMORPHIC PROPERTIES:

The phase transitions were determined both by optical microscopy and calorimetric measurements (DSC7 Perkin Elmer). The transition temperatures (°C) and the transition enthalpies ($kJ.mol^{-1}$) of compounds **Cmn** are given in table 1.

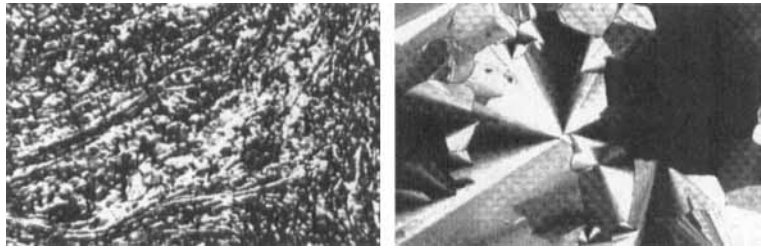
All compounds **Cmn** exhibit only one liquid crystal phase.

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

n	m	K		Col?		Sm?		I
8	**12**	•	**113.8**	-		•	**128.4**	•
			33				*16.9*	
9	**12**	•	**111.7**	-		•	**133**	•
			32.6				*17.1*	
10	**12**	•	**112**	-		•	**138.5**	•
			53.6				*18.9*	
11	**12**	•	**118.6**	-		•	**139**	•
			61.4				*19.1*	
12	**12**	•	**110**	-		•	**141**	•
			46.1				*19.6*	
13	**12**	•	**110**	-		•	**141.5**	•
			47.4				*19.8*	
14	**12**	•	**105**	-		•	**142**	•
			46.4				*20.4*	
8	**10**	•	**113**	•	**134**	-		•
			33.4		*18.6*			
9	**10**	•	**111**	•	**134**	-		•
			35.8		*18.6*			
10	**10**	•	**113.7**	-		•	**132**	•
			38.2				*18.7*	

The nature of this mesophase depends on the whole number of carbons in the alkyl chains. According to the observed textures, when the carbon number is greater or equal to 20 the compounds display a smectic phase (Sm?) as shown in figure 2(a). The optical texture of this mesophase (Sm?) is modified by an electric field. For a carbon number inferior or equal to 19 these molecules display a mesophase (Col?) which has a columnar texture as shown in figure 2(b). This texture is not affected by an electric field.

On the other hand it is remarkable that the non symmetric character of these compounds lowers the melting point and the clearing point of the banana-shaped molecules compared with the series previously studied[1-7].



a b

FIGURE 2: Optical microscopic texture of the pure C1010 at T=129°C (a) and optical microscopic texture of the pure C0910 at T=129°C (b).

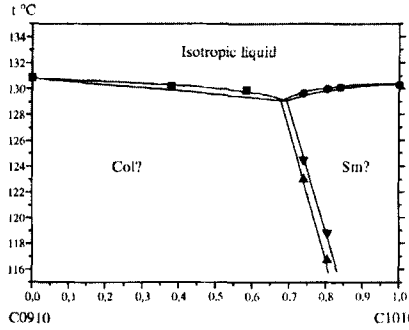
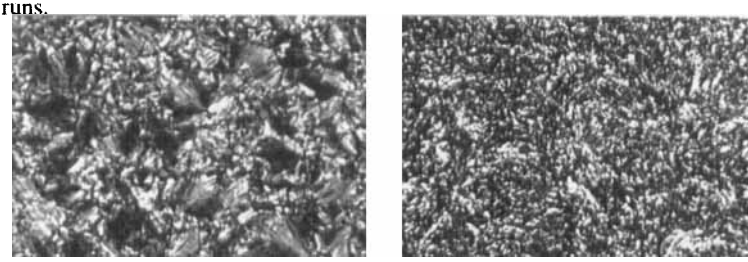


FIGURE 3: Phase diagram between C0910 and C1010 from DSC heating runs.



a b

FIGURE 4: Optical microscopic textures of C0910 mixed with 73.92 wt% C1010. a : T = 124°C; b : T = 129°C.

The clearification enthalpies are high like those of the series previously studied and firstly synthesized by T. Akutagawa *et al.*[7]. Therefore these

mesophases are rigid. This effect is probably due to a close packing of the bent molecules in the liquid crystal phases with strong interactions.

A phase diagram between C0910 and C1010 is depicted in figure 3. It shows that binary mixtures with about 75 wt% of C1010 exhibit the two phases. Optical microscopic textures of this kind of mixtures are shown in figure 4.

X-ray investigations:

The X-ray diffraction with non oriented samples was performed as follows. The CuK_α radiation from a 18kW rotating anode X-ray generator (Rigaku-200) was selected by 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 7.10^{-3} $Å^{-1}$ (FWHM). Lindeman tubes (Ø = 1mm) were filled by capillary action from the isotropic phase without any alignment procedure.

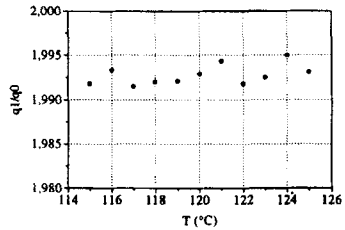


FIGURE 5: C1010 temperature dependence of q_1/q_0

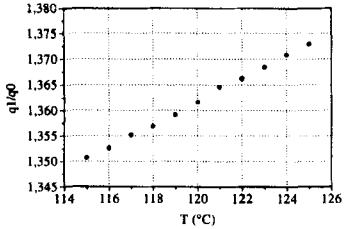


FIGURE 6: C0910 temperature dependence of q_1/q_0

X-ray diffraction experiments were carried out in the range 115°C to 125°C for both C0910, which exhibits the Col? phase, and C1010, which exhibits the Sm? phase. The X-ray results confirm that Sm? is a smectic phase. In this mesophase, the ratio of the first order wavevector (q_1) to the fundamental wavevector (q_0) is temperature independent and equals 2, as shown in figure 5 for the C1010. It is shown in figure 7 that the C1010 layer spacing in Sm? is about 36.7 Å which is less than the elongated molecule length. For the C0910, the figure 6 displays that the ratio q_1/q_0 is not constant in the Col?

phase, it increases with temperature, and it is not close to a classical ratio for higher ordered smectic phases. This result confirms that the phase is not a classical smectic phase, but probably another ordered phase such as a two-dimensional phase. It will be necessary to carry out X-ray diffraction experiments using well oriented samples to know more precisely the Col? structure.

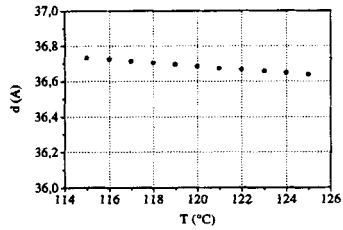


FIGURE 7: C1010 layer spacing of Sm?

ELECTRO-OPTICAL STUDY:

An electro-optic characterization, in the surface stabilized ferroelectric liquid crystal (SSFLC) configuration, has been performed on the C1412 which exhibits the Sm? phase, and on the C0810 which exhibits the Col? one. The samples were introduced by capillary action in the isotropic phase in 6 μm thick commercial test cells from E.H.C with the inner faces covered with an insulation layer and a rubbed polyimide. The insulation layer function is to avoid the short-circuits. Aging of the cell make them to occur anyway after a few hours of experiments. This phenomenon is probably due to a degradation of the material submitted to high voltages and high temperatures. The role of the rubbed polyimide is to promote the planar alignment in the SSFLC geometry. Though there was no uniform alignment in any sample. A clear trend to planar alignment was observed for the Sm? phase. It is enhanced by the electric field. The Col? phase alignment is

influenced neither by the polyimide nor by the electric field. In order to avoid a decay of the sample purity, the preparation and measurement processes were done under dry nitrogen atmosphere. A triangular voltage wave is applied to the samples. Switching current curves were obtained, which are shown in figures 8 and 9 for Sm? and Col? phases.

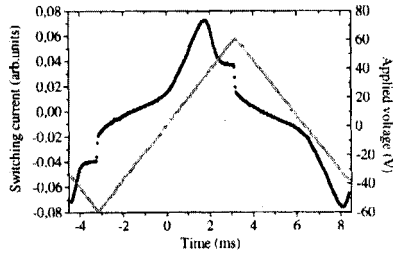


FIGURE 8: Switching current curve obtained by applying a triangular voltage wave (± 10 V/µm, 80Hz) at 124°C in the smectic phase of C1412. The spontaneous polarization was estimated to be about **95 nC cm^{-2}**.

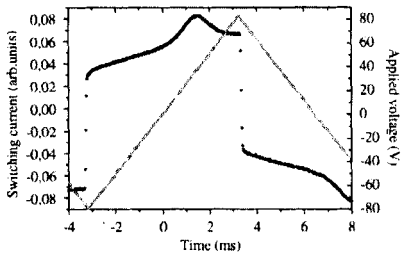


FIGURE 9: Switching current curve obtained by applying a triangular voltage wave (± 13,3 V/µm, 80Hz) at 127°C in the liquid crystal phase of C0810. The spontaneous polarization was estimated to be about **10 nC cm^{-2}**.

A single switching current peak is clearly observed when the polarity of the electric field changes. Thus both Sm? and Col? are ferroelectric phases. As for the series of Niori et al.[1], this ferroelectricity is due to the tip of the bent molecules orienting parallel to the electric field and reversing its orientation on reversal of the field polarity. The spontaneous polarization, when

saturated, was estimated measuring the switching current peak area. The very low spontaneous polarization of the Col? phase could be explained by a poor alignment in the SSFLC geometry. In this way an important part of the dipoles are not oriented parallel to the electric field, thus a part of the spontaneous polarization is concealed. However because the applied voltage is relatively high, this polarization peak could be an artefact caused by the conductivity (no texture change is connected to the peak in figure 9).

CONCLUSION:

We synthesized the first series of non symmetric banana-shaped molecules. Each of these compounds displays a liquid crystal phase. Nevertheless the phase is not the same all over the series, but depends on the whole number of carbons in the alkyl chains. The phase is smectic (Sm?) for a carbon number superior or equal to 20 and probably two-dimensional (Col?) for a carbon number inferior or equal to 19. None of the compound exhibits the two phases but binary mixtures do so, such as: C0910 with 75 wt% C1010. Sm? and Col? are ferrolectric mesophases.

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