

A novel class of non-chiral banana-shaped liquid crystals with ferroelectric properties

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The first banana-shaped molecules without Schiff-base units, with broad regions of a ferroelectric switchable liquid crystalline phase and low melting points, have been obtained.

Ferroelectricity, resulting from a spontaneous macroscopic electric polarization, is a property which was first reported by Meyer¹ to occur in a fluid, liquid crystalline phase. Until recently, ferroelectricity in liquid crystals was based on a tilted arrangement of homochiral molecules in layers (e.g. smectic C phase) which generates C_{2v} symmetry and allows the occurrence of a spontaneous electric polarization. In recent years such ferroelectric liquid crystals have attracted considerable interest because of their unique switching properties and their technical applications, for example, in fast-switching electrooptical devices.² As predicted by theory, ferroelectricity is not restricted to chiral tilted phases.^{3–5} In 1996 Niori *et al.*⁶ reported on ferroelectricity in a smectic phase formed by bow-shaped ('banana-shaped') non-chiral molecules. Later on, antiferroelectric switching behavior was found for these compounds.^{7–9} Not only is the special electrooptical behavior of these non-conventional liquid crystals of interest. These molecules also represent a new subfield of thermotropic liquid crystals, different from the classical types such as calamitic and disc-like mesogens. Up to now, all banana-shaped liquid crystals which exhibit (anti)ferroelectric switching behavior have had a rather uniform structure. They usually comprise 1,3-phenylene bisbenzoates incorporating at least one Schiff-base unit.^{6–9} Therefore, a major drawback of these compounds is their limited thermal, hydrolytic and photochemical stability. Furthermore, these special mesophases occur at rather high temperatures. Thus, the design of novel stable and low-melting materials is a topical subject in liquid crystal research.

Here we describe the first banana shaped molecules without Schiff-base units which have a ferroelectric switchable liquid crystalline phase. This was achieved by combination of an angular 3,4'-disubstituted biphenyl central unit with two phenyl benzoate rigid cores *via* ester linkages. Thus the two halves of these banana-shaped molecules are different.

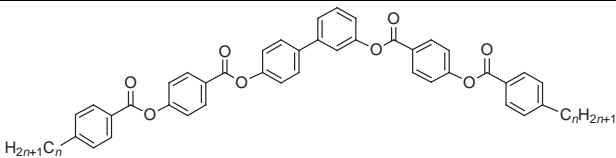
The transition temperatures of the compounds **1–5** are collected in Table 1.[†] Different mesophases were found depending on the length of the alkyl chains and the temperature. Compounds **1** and **2** with short terminal chains form only one mesophase (M_3). On cooling **1** from the isotropic liquid state at 157 °C batonnets are formed which coalesce into a mosaic-like texture. This texture is identical with that reported for some short chain banana-shaped Schiff-base derivatives,¹⁰ and is designated an X_{B1} phase.[‡] A similar texture was also observed by cooling compounds **2–4** from the isotropic liquid.

However, in the case of compound **3** two additional phase transition can be found on further cooling. At 147 °C a nonspecific texture which immediately changes into a gray schlieren texture is formed [see Fig. 2(a)]. This mesophase always shows a distinct birefringence and no pseudoisotropic regions can be obtained by shearing. Furthermore, this meso-

phase has a lower viscosity (comparable to conventional S_A and S_C phases) than the phase M_3 . On heating, it directly turns into the isotropic liquid phase at 152 °C without passing the high temperature mesophase. This means that, probably for kinetic reasons, the M_3 phase can only be observed on cooling from the isotropic state. On further cooling, at 86 °C the schlieren texture turns into a mosaic-like texture with a significant increase of the viscosity.

The same trimorphism was also found for **4**, but only the mesophases M_1 and M_2 were detected for the long chain compound **5**. Here, the M_2 phase grows directly from the isotropic liquid as spherulites with a fringe pattern, characteristic of a helical structure [see Fig. 2(b)]. This texture is very similar to the texture of the (anti)ferroelectrically switchable mesophase (X_{B2} phase[‡]) of the banana-shaped Schiff-base derivatives. Slight shearing of the sample gives rise to the same

Table 1 Phase transition temperatures of **1–5**. Abbreviations: Cr = crystalline solid, M_1 = smectic low-temperature mesophase (probably S_G or S_H), M_2 = ferroelectrically switchable mesophase [X_{B2} -phase,[‡] probably arrangement shown in Fig. 1(a)], M_3 = two-dimensionally ordered (modulated smectic) mesophase [X_{B1} -phase,[‡] see arrangement in Fig. 1(c)], Iso = isotropic liquid.^a



Compound	n	T/°C					
1	4 Cr	161					(M_3 157) Iso
2	6 Cr	119					M_3 158 Iso
3	8 Cr	85	M_1 86	M_2 152			Iso
				(M_2 147	M_3 152		Iso) ^a
4	10 ^b		M_1 79	M_2 148			Iso
				(M_2 147	M_3 148		Iso) ^a
5	12 ^b		M_1 78	M_2 156			Iso

^a The phase sequence in parentheses is only observed on cooling (determined by polarizing microscopy). ^b No crystalline phases have been found yet.

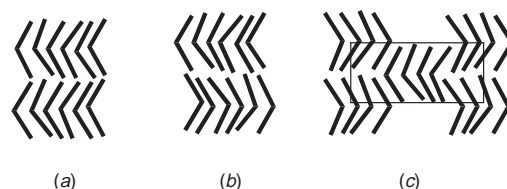


Fig. 1 Selected possible arrangements of banana shaped molecules in their mesophases: (a) polar biaxial smectic phases with ferroelectric alignment of the layers, (b) antiferroelectric alignment of the layers, and (c) modulated layer structure (ribbon phase). The molecules can be arranged perpendicular to the layer plane (S_A -like) or tilted (S_C -like).

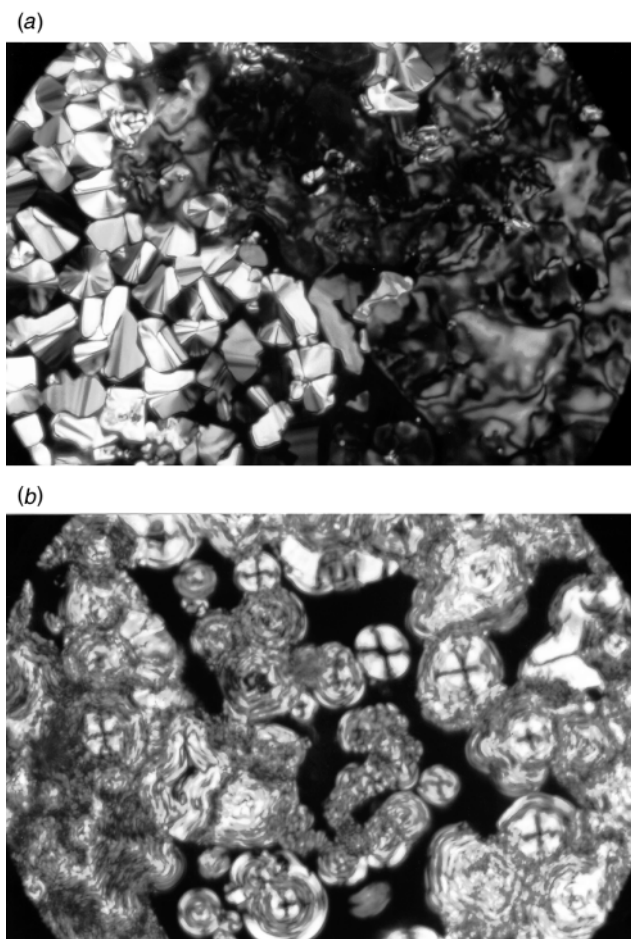


Fig. 2 Optical photomicrographs (crossed polarizers): (a) of **3** at the transition from the high temperature mesophase M_3 (left hand side) to the M_2 phase (schlieren-texture at the right hand side) at 147 °C; (b) of **5** at the transition from the isotropic liquid to the M_2 phase at 156 °C.

gray schlieren texture as observed for the M_2 phases of **3** and **4**.

X-Ray studies of non-oriented samples of compound **3** have been performed to support the phase characterization. The diffraction pattern of the high temperature phase M_3 ($T = 150$ °C) shows two reflections with $d_1 = 3.24$ and $d_2 = 2.37$ nm, in addition to the diffuse outer scattering. These reflections point to an undulated structure, which is already found in some banana-shaped molecules and is designated as an X_{B1} phase.[‡] In the case of compound **1**, monodomains of the M_3 phase were obtained. On the basis of these oriented samples we can deduce a two-dimensional rectangular centered cell for this phase [see Fig. 1(c)]. Since the positions of the reflections in the M_3 phase are a linear function of the chain length, the high temperature phases of compounds **1–4** can be assumed to belong to the same type.

The phase transition from the M_3 phase to the M_2 phase is indicated by an alternation of the pattern in the small angle region. The positions of the two reflections fit now the ratio $d_1:d_2 = 1:0.5$ ($d_1 = 2d_2 = 3.74$ nm, $T = 120$ °C), proving a layer structure. The d value is essentially smaller than the length of the molecule ($L = 5.0$ nm), describing a V-shaped molecule with an angle of about 120° between the two half parts and an all-*trans* conformation of the alkyl chains. This difference leads to a tilt angle of about 41°. However a deviation of the chains from the fully stretched conformation must be assumed, so that the real tilt angle should be smaller than the estimated one. With respect to this preliminary structure the phase under consideration can belong to the type X_{B2} as reported for the Schiff-base derivatives.[‡] At further cooling into the low temperature phase M_1 the layer reflections are shifted only a very little, but in the wide angle region several reflections appear. This pattern is maintained down to room temperature. The kind of reflections

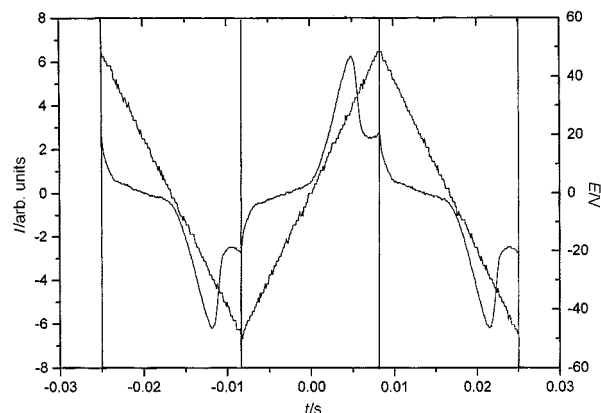


Fig. 3 Switching current response in the M_2 phase of **4** obtained by applying a triangular voltage (± 50 V, 30 Hz, 125 °C).

(number, position and intensity) resembles to those of highly ordered smectic phases (S_G or S_H), but further studies are necessary to prove this analogy. Remarkably, after the first melting this compound does not crystallizes again, even after storage for several weeks at room temperature. No crystalline phases have been detected for **4** and **5**.

Preliminary investigations of the switching behavior of the M_2 phase were performed with **4**. The switching current was examined in a 5 μm thick cell by the triangular wave method. Fig. 3 shows the electric response (30 Hz) obtained in the M_2 phase at 125 °C. It can be seen that only one current peak is recorded during a half period, pointing to ferroelectric behavior. This points to the phase structure shown in Fig. 1(a), but it should be noted that only a schlieren texture can be obtained between the glass surfaces of the cell. Therefore more detailed electrooptical investigations with uniformly aligned samples are necessary to confirm the precise structures of the switchable mesophases.

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Notes and references

[†] The synthesis will be reported in a separate paper, satisfactory C,H analyses and ¹H NMR spectra were obtained. *Selected data for 3*: δ_{H} (200 MHz, CDCl_3 , 25 °C, SiMe_4) 0.89 (2t, 6H, CH_3), 1.2–1.8 (m, 24H, CH_2), 2.72 (t, J 7.7, 4H, Ar- CH_2), 7.2–7.6 (m, 14H, aromatic H), 7.68 (d, J 8.6, 2H, aromatic H), 8.14 (d, 4H, J 8.2, aromatic H), 8.32 (d, 4H, J 8.6, aromatic H).

[‡] The nomenclature X_{B1} , X_{B2} follows the recommendations given at the Workshop 'Banana-Shaped Liquid Crystals: Chirality by Achiral Molecules', December 1997, Berlin.

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