

Banana-shaped molecules derived from substituted isophthalic acids

H T NGUYEN, J P BEDEL, J C ROUILLON, J P MARCEROU and M F ACHARD*

Centre de Recherche Paul Pascal, CNRS/Université Bordeaux 1, Av. A. Schweitzer, F-33600 Pessac, France

*Author for correspondence.

Email: achard@crpp-bordeaux.cnrs.fr

Abstract. In this paper we present a review of five-rings banana-shaped molecules derived from isophthalic acids. This study deals with about a hundred compounds and most of them have not been published. By a combination of several linking groups and different selected substituents either on the outer rings or on the central core, several mesophases with switching properties are induced. The study of homologous series underlines the importance of the length and nature of the terminal chains. X-ray analysis reveals several new structures.

Keywords. Liquid crystals; banana-shaped compounds; isophthalic acids; X-ray diffraction.

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1. Introduction

Banana-shaped molecules are the results of a systematic research of new molecular shapes (rod, disk, polycatenar, sanidic, pyramidic, etc.) compatible with liquid crystalline properties. Since it has been shown that ferroelectricity is possible in such liquid crystalline materials composed of achiral molecules [1] the bent or ‘banana-shaped’ liquid crystals have turned into a major field of research.

Thus the extensive synthesis of new bent-shaped materials started a few years ago and investigations on their physical properties begun. The results obtained by different research groups give evidence that the molecular structure–mesomorphic properties relationships are much more complicated than that of rod-like liquid crystals and at the moment not well-understood and not universal. Nevertheless, it is now obvious that the liquid crystalline properties are very sensitive against any molecular change in these bent molecules.

The bending angle results from the central part of these molecules (1,3-phenylene or 2,7-naphthalene or 2,5-substituted heterocycle unit) and compounds with five, six or seven aromatic or heterocyclic rings have been synthesized [2]. Nonetheless, most banana-shaped liquid crystals reported up to now, correspond to five-ring mesogens with a 1,3-phenylene central unit on which two branches with two phenyl rings are fixed. Depending on the choice of central part precursor (figure 1), materials derived from resorcinol,

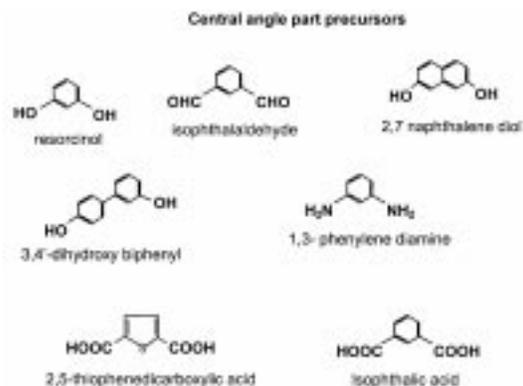


Figure 1. Different precursors inducing the bending angle of the banana-shaped molecules.

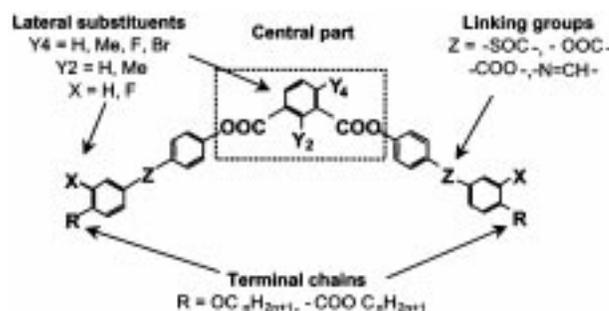


Figure 2. General formula of five phenyl rings banana-shaped molecules based on isophthalic acid. Variations of this basic chemical structure concern the linking group Z (the sense of Z is given from the center to the outer phenyl ring), the lateral substituent on the central phenyl ring (Y2 and Y4) or on the outer ring (X) and the nature and length of the terminal chains R.

isophthalaldehyde [3], 1,3-phenylene diamine or isophthalic acid are obtained. Many compounds are derived from resorcinol [2,4–9] and we reported the first examples of esters of isophthalic acid [10].

In this paper we focus on the banana-shaped molecules based on esters of isophthalic acid as central core and we explore the different possibilities of variation of the chemical structure as shown in figure 2: nature and sense of the linking groups Z, introduction of lateral substituents (Me, F, Br) positioned either on the outer rings (X in position 3) or on the central ring (Y2 in position 2, Y4 in position 4) and nature and length of the terminal chains (R). Systematic investigations on homologous series show that the chain length–polymorphism relationship is not unique in banana compounds. Thus, to leave this parameter out of account, we fixed as a first step, the number of carbon atoms in the chain to be 14.

Since most of the banana molecules arrange on smectic layers, we adopt the nomenclature SmCP (instead of ‘Bn’), where SmC means a fluid biaxial lamellar phase and P signifies that the phase is switchable under electric field. Additional letters complete and

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Table 1. Molecular characteristics and phase sequence for the banana-shaped compounds of this study. [] indicates a monotropic transition. K: crystalline phase; I: isotropic liquid; N: nematic; SmA: smectic A; SmC: smectic C. For other phase assignments, see text.

Sample	Z	X	Y2	Y4	R	Polymorphism
A14	SOC	H	H	H	OC ₁₄ H ₂₉	Cr 157.8°C SmC'' 160.8°C SmC' 171.1°C I
A14Me2	SOC	H	H	H	OC ₁₄ H ₂₉	Cr 132°C SmC 203°C N 222°C I
A14Me4	SOC	H	H	H	OC ₁₄ H ₂₉	Cr 149°C I
A14F3	SOC	F	H	H	OC ₁₄ H ₂₉	Cr 151°C [SmC _{hex} P 147°C] SmC''P 156°C USmCP 158.8°C SmC'P 173°C I
A13F3Me2	SOC	F	H	H	OC ₁₃ H ₂₇	Cr 128°C SmC 212°C N 214°C I
A14F3Me4	SOC	F	H	H	OC ₁₄ H ₂₉	Cr 150°C I
DB14	OOO	H	H	H	OC ₁₄ H ₂₉	Cr 150°C I
DB14Me2	OOO	H	Me	H	OC ₁₄ H ₂₉	Cr 108°C SmC 175°C N 195°C I
DB14Me4	OOO	H	H	Me	OC ₁₄ H ₂₉	Cr 138°C I
DB14F4	OOO	H	H	F	OC ₁₄ H ₂₉	Cr 152°C I
DB _{inv} 14	COO	H	H	H	OC ₁₄ H ₂₉	Cr [180°C SmC] 183°C I
DB _{inv} 14Me2	COO	H	Me	H	OC ₁₄ H ₂₉	Cr 122°C SmC 225°C SmA 232°C I
DB _{inv} 14Me4	COO	H	H	Me	OC ₁₄ H ₂₉	Cr 132°C SmCP 158°C I
DB _{inv} 14Br4	COO	H	H	Br	OC ₁₄ H ₂₉	Cr 125°C SmCP 160°C I
DB _{inv} 14F4	COO	H	H	F	OC ₁₄ H ₂₉	Cr 174°C [SmC 170°C] SmA 185°C I
BS14	N=CH	H	H	H	OC ₁₄ H ₂₉	Cr 186°C I
E14	N=CH	H	H	H	COOC ₁₄ H ₂₉	Cr 169.6°C SmC'G ₂ P 176.9°C I
E14Me2	N=CH	H	Me	H	COOC ₁₄ H ₂₉	Cr 96°C SmC 202°C SmA 217°C I
E14Me4	N=CH	H	H	Me	COOC ₁₄ H ₂₉	Cr 121°C USmC''P 134°C USmC'P 142°C I
E14F4	N=CH	H	H	F	COOC ₁₄ H ₂₉	Cr 161°C × 170°C USmX 172°C I

diversify this basic appellation [11,12]. Phase transition temperatures and phase identification were obtained by a combination of optical observations, DSC measurements and X-ray diffraction analysis on oriented samples. Results are summarized in table 1.

2. Results and discussion

2.1 Influence of the connecting groups

In banana-shaped mesogens, the influence of the type and/or the sense of the connecting groups appears very strong. For example, in the parent series in which the first 'banana' phases were discovered [1] the simple inversion of the sense of azomethine groups can lead to the disappearance of the mesophases [2].

In the case of banana compounds based on isophthalic acid, the Schiff base (Z = N=CH, BS14), and the carboxylic acid (Z = OCO, DB14) prevent the formation of mesophases. Among the tested linking groups, only the thiocarboxylic linkage (Z = SCO, A14) leads to stable mesophases. As previously observed for resorcinol-based compounds, the direction of the Z linkage is also important. Here the inversion of the sense of the carboxylic linkage (Z = COO, DB_{inv}14) induces a metastable SmC phase.

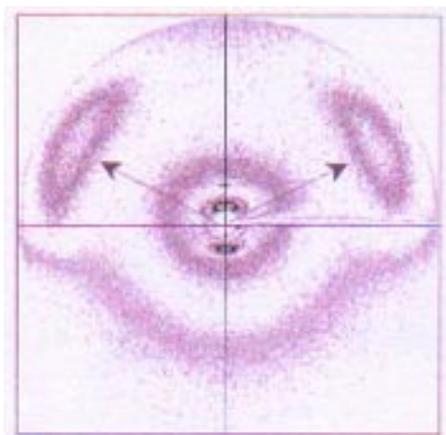


Figure 3. Typical X-ray pattern of oriented fluid lamellar phase. Orientation was obtained by slow cooling of a drop of the isotropic liquid. In the small-angle region the strong Bragg reflection with its higher order reflections located on the meridian indicate a smectic layer structure. In the wide-angle region, the diffuse scattering maxima situated out of the equator indicate a liquid-like order within the layer and the tilt of the molecules with respect to the layer normal. Note that the free droplet geometry prevents access to the lower part of the pattern at wide angle.

At the moment, the reason for the importance of the nature and the sense of the linking groups is not clear. The packing of bent-shaped molecules, more or less rigid and bearing long terminal chains, is not easy and probably is the result of a subtle balance between steric hindrance, electrostatic and Van der Waal's forces. In this sense, we noted that molecular formula corresponding to an alternating distribution of the electronic density throughout the molecules favours the packing of the bent-shaped molecules and thus the liquid crystalline properties [8,10]. Thus the whole chemical formula has to be considered and it is difficult to isolate and predict the effect of a specific part of the banana molecule.

2.2 Influence of lateral substituent on the outer rings X

The mesomorphic behavior of thioester series is strongly affected by the introduction of a fluorine atom on the outer rings. The unsubstituted materials form nematic for short terminal chains and smectic C phases for longer chains (A14) and no electric field response has been evidenced. By the introduction of a fluorine atom in the outer rings, the nematic phase disappears, the short chain homologues exhibit a rectangular columnar phase (B1 type) and the long chain homologues of the series (e.g. A14F3) form up to four smectic phases (figure 4). All are tilted lamellar phases and are switchable under electric field. These mesophases thus belong to the general class SmCP. Oriented X-ray patterns (figure 3) show a fluid smectic C at high temperature (SmC'P), followed by a fluid smectic C with undulated layers (USmCP) on further cooling and again by a fluid smectic C (SmC''P). As shown in figure 5 the layer thickness is quasi-constant within the temperature range of these three high temperature mesophases and only the low temperature phase can be distinguished

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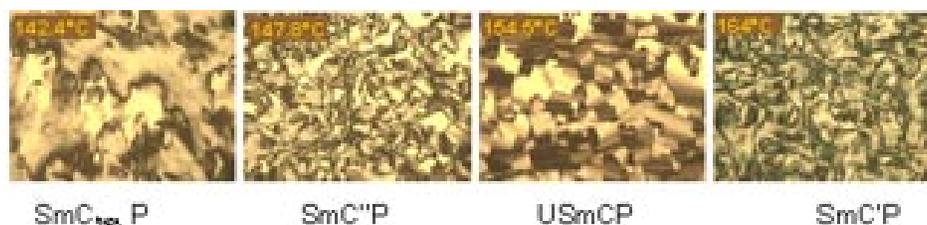


Figure 4. Photomicrographs of the textures observed for the four phases of the A14F3 compound.

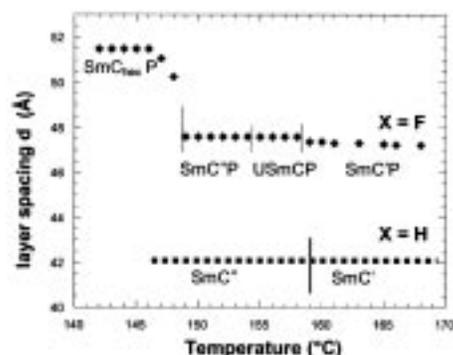


Figure 5. Influence of a lateral fluorine substituent on the outer rings on the layer spacing in thiobenzoate compounds (A14 with no substituent and fluorine substituted compound A14F3).

by the layer parameter. For this phase the wide angle maxima are narrower indicating a short range order within the layers and a tilted hexatic phase ($\text{SmC}_{\text{hex}}\text{P}$). The increase of the layer parameter at the $\text{SmC}''\text{P}$ – $\text{SmC}_{\text{hex}}\text{P}$ transition most probably originates from a decrease of the tilt of the aliphatic chains (unpublished results).

One can also note that the switchable $\text{SmC}'\text{P}$ of A14F3 and the high temperature SmC' (non-polar phase) of the non-substituted compound (A14) are miscible: this observation underlines the fact that the behaviour under electric field is not characteristic of the mesophase at zero field. In addition the lower layer spacing in A14 may be due to a possible interpenetration of the molecules.

The molecular characteristics of this series (sense of the carboxylate and thio-carboxylate groups, presence of a sulphur atom and of a fluorine substituent in meta position of the outer rings) result in a large number of possible conformations.

2.3 Influence of lateral substituent on the central ring Y2 or Y4

Resorcinol-based banana-shaped molecules are very sensitive to the introduction of substituents in the central 1,3-phenylene unit [4]. The effect on the liquid crystalline properties is peculiarly strong and depends on the nature and position of the substituted group on the central ring.

2.3.1 *Derivatives of the 2-methyl isophthalic acid.* For materials based on isophthalic acid, a methyl group in position 2 favours and enhances the liquid crystalline potential, however, only nematic, smectic A and C phases are observed (A14Me2, A14F3Me2, DB14Me2, DB_{inv}14Me2, E14Me2). These smectic phases are not switchable under electric field. It is possible that the bending angle between the two branches of the molecules was increased by the presence of a methyl group in the obtuse angle and in this case it would be not surprising to observe classical mesophases.

Nevertheless two points are remarkable in these methyl 2-substituted materials. The first one concerns the evolution of the layer spacing in DB_{inv}14Me2: the high temperature phase spontaneously aligns homeotropically and this observation is compatible with a uniaxial phase; either a SmA phase or a compensated tilted smectic phase. On decreasing the temperature, the transition to the lower temperature phase corresponds to an increase of the layer spacing (figure 6) which is rather unusual for a smectic C phase! Similar observations have been done in fluorinated tail compounds [13].

The second point concerns the unusual behaviour of the nematic phase of DB14Me2. Figure 7 shows the oriented pattern in the small angle region. Experiments are performed on free droplets and a spontaneous orientation is observed in the nematic phase. The

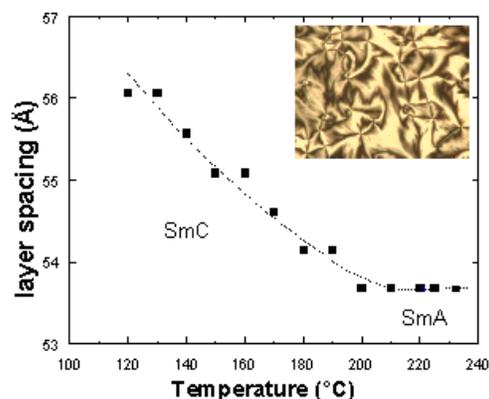


Figure 6. Evolution of the layer spacing of the DB_{inv}14Me2. The inset shows the texture of the smectic C phase.

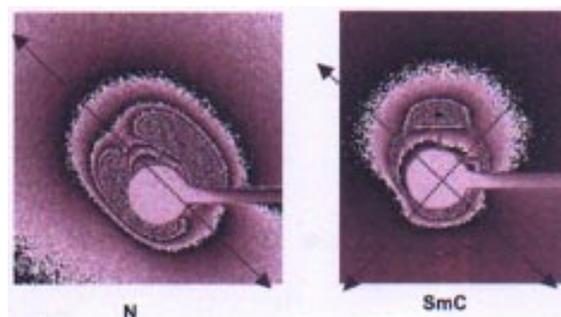


Figure 7. X-ray patterns in the small angle region in the nematic and smectic C phases of DB14Me2. The arrows indicate the direction of the diffuse maxima at wide angles.

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arrows indicate the direction of the diffuse maxima at wide angles. Four maxima are observed in the small angle region. They are present in the whole nematic range and also exist for short chain homologues which only exhibit a nematic phase. Similar observations have been done in 1,3,4-oxadiazole derivatives [14] suggesting the possibility of a biaxial nematic phase. At the nematic–smectic C transition, the sample is spontaneously reorganized and the layer spacing (41.3 Å) is clearly lower than the parameter corresponding to the four spots in the nematic phase (44.8 Å). Thus these spots do not correspond to cybotactic groups. A previous study on side-on fixed liquid crystalline polymers showed that similar spots in nematic phase are connected to short range correlations of the aliphatic chains [15].

2.3.2 Derivatives of the 4-methyl-, 4-bromo- or 4-fluoro-isophthalic acid. The introduction of a methyl group in position 4 of the central ring suppresses the liquid crystalline properties in the case of thiobenzoates ($Z = \text{SOC}$, A14Me4 and A14F3Me4) and dibenzoate compounds ($Z = \text{OOC}$, DB14Me4). For $Z = \text{COO}$ and $\text{N}=\text{CH}$, both the melting and clearing temperatures are lowered without loss of the mesophases. A switchable SmCP phase is observed for the dibenzoates with $Z = \text{COO}$: this phase presents textures and electro-optic response (figure 8) similar to the ‘B2’ group of the parent series.

For bromine-substituted central core, the properties are not markedly changed in comparison with the methyl-substituted compound [16]. Thus, the influence of a lateral substituent in position 4 seems more connected to the steric hindrance than to the donor or acceptor character. On the other hand a fluorine atom in position 4 does not modify the mesomorphic domain and the phase sequence in comparison to the compounds free of substituent.

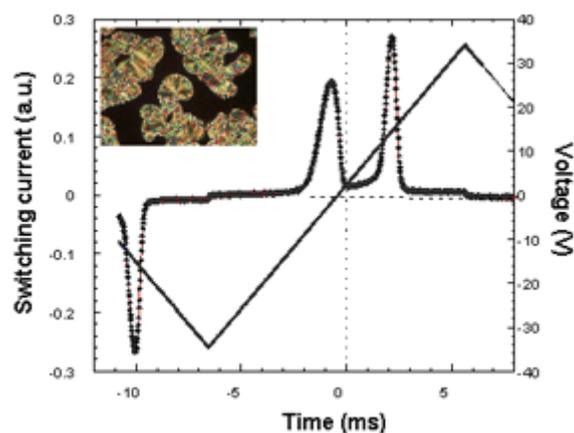


Figure 8. Switching current response in the SmCP phase for the DB_{inv}14Me4 applying a triangular voltage (± 40 V). Sample thickness $5.2 \mu\text{m}$, temperature 145°C . The apparent saturated polarization P_s is 470 nC cm^{-2} . The inset shows the texture of the mesophase growing from the isotropic liquid.

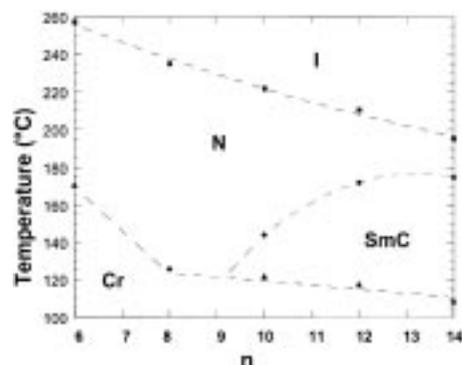


Figure 9. Evolution of the melting and clearing temperatures and of the polymorphism vs. the number n of carbon atoms in the terminal chain of the DBMe2 series ($Z = \text{OOC}$ and $Y2 = \text{Me}$).

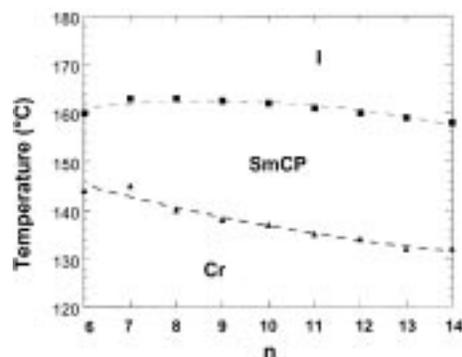


Figure 10. Evolution of the melting and clearing temperatures and of the polymorphism vs. the number n of carbon atoms in the terminal chain of the DB_{inv}Me4 series ($Z = \text{COO}$ and $Y4 = \text{Me}$).

2.4 Influence of terminal chains

When the terminal chain length is varied, the evolution of the clearing temperature as well as of the phase sequence strongly depends on the series of banana materials. With a growing number of carbon atoms (n) in the alkoxy chain, the clearing temperature can regularly decrease: this is the case of the DB n Me2 series where a nematic phase exists in the whole series and a nematic–smectic C sequence is observed for long chains (figure 9). In other series like DB_{inv} n Me4, the clearing temperature remains quasi-constant and the same switchable SmCP mesophase exists from $n = 6$ to 14 (figure 10). Other systems present a non-regular evolution of the temperatures and of the polymorphism vs. the length or the nature of the terminal chains. In A n F3 series, the clearing temperature presents a minimum with n and two regimes are observed: a columnar mesophase (B1) for short terminal chains and a SmCP polymorphism for longer homologues (as for A14F3). More surprising is the case of BS14 series which presents no mesophase for alkoxy chains while a carboxylate linkage (En series) induces a rich polymorphism with five original mesophases. They

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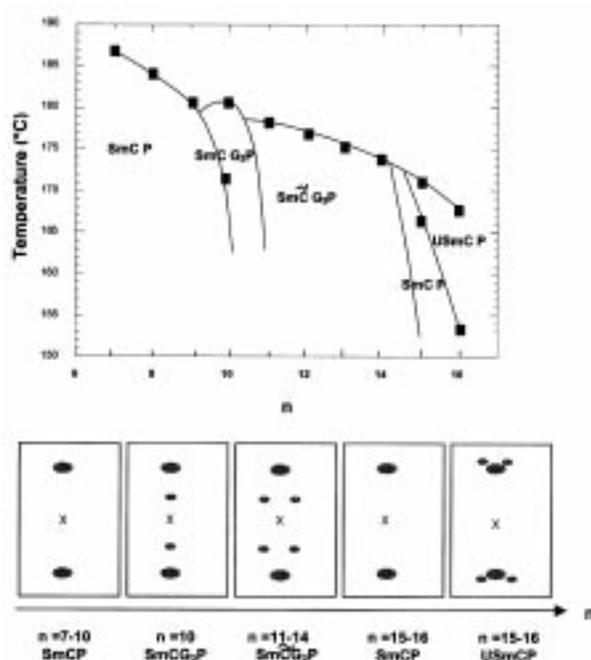


Figure 11. Evolution of clearing temperatures and of the polymorphism vs. the number n of carbon atoms in the terminal chain of the E_n series ($Z = N=CH$ and $R = COOC_nH_{2n+1}$). A schematic of the oriented X-ray patterns in the small angle region are drawn for different mesophases.

are all fluid tilted layered structures and they all present switchable properties. A detailed study of this series and of its variants will be published elsewhere [17]. As shown in figure 11, the phase diagram summarizes the evolution of the polymorphism vs. the length of the terminal chains.

The phase identification is mainly based on X-ray studies and a very schematic representation of the oriented patterns is shown in figure 11. For short chains ($n = 7-10$), a SmCP phase is observed. More interestingly, a bilayered smectic phase is detected in the decyl compound [18]. A bilayer–monolayer transition is evidenced in this material. Several arguments are in favour of a structure based on SmCG (G for generalized, which means that none of the axes of the banana molecule lies in the layer plane or is parallel to the layer normal) [19]. The association of two different SmCG leads to a bilayer smectic called SmCG₂P. Longer homologues ($n = 11-14$) present the same bilayer structure but with a 2D-modulation in the layers corresponding to an antiphase or ribbon phase [20]. At last for longer homologues ($n = 15-16$), an undulated monolayer phase (USmCP) is observed followed by a SmCP.

3. Conclusion

Isophthalic acid as central part precursor seems *a priori* less favourable to generate a packing of bent-shaped molecules. Indeed, contrary to resorcinol, the central part based on

isophthalic acid is rigid due to the conjugation and the first conformational freedom is rejected at the level of the intermediate rings of the branches. Nevertheless, this study shows that a suitable choice of linking groups and lateral substituents can induce mesophases with electro-optic properties. This is the case of thioester linkage with a fluorine substituent in position 3 on the outer rings, of a benzoate linkage with a 4-methyl and 4-bromine substituted central ring and of a Schiff's base linkage with carboxylate terminal chains. This study also underlines the complexity of the molecular structure–mesomorphic properties relationship in banana-shaped molecules. It is obvious that the influence of each part of the chemical formula cannot be isolated and that the whole molecule has to be considered. This study also gives emphasis on the essential role of the terminal chains in banana compounds.

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