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Broadening Of Mesophase Temperature Range Induced By Doping Calamitic Mesogen With Banana-Shaped Mesogen

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Abstract. We have investigated three binary mixtures composed of selected banana-shaped dopant in low concentrations and calamitic mesogen in high. Banana-shaped dopant forms a B7 phase, while the calamitic mesogen exhibit nematic and smectic SmA and SmC phases. The occurring mesophases have been identified by their optical textures. At dopant concentrations of 2.2 and 3.1 mol%, there is evident broadening of nematic and smectic SmA temperature ranges in respect to the pure calamitic compound. Yet, the mixture with dopant concentration of 7 mol% exhibits narrower temperature ranges of mesophases. Increasing dopant concentration caused lowering of all phase transitions temperatures ($T_{I\text{-}N}$, $T_{N\text{-}SmA}$, $T_{SmA\text{-}SmC}$) in all investigated mixtures. Therefore, mixing classic calamitic compounds with novel banana-shaped compound in low concentrations is viable way to attain useful mesophase range for application in industry.

INTRODUCTION

Classic calamitic mesogens were cornerstone of the industry of liquid crystalline displays since its inceptions. Their importance is evident from the sheer number of newly synthesized compounds. Even so, required characteristics for industrial application are more easily achieved by mixing classic calamitic mesogens with other diversely shaped compounds than by synthesis alone.

Owing to their unusual architecture and physico-chemical properties, banana-shaped mesogens attracted much attention during the last decade. Initially, research interest in banana-shaped compounds was fueled by pursuit of elusive biaxial nematic phase[1, 2]. Nonetheless, their most important characteristics are existence of switchable ferroelectric phases and supramolecular chirality in absence of molecular chirality[3]. Among the peculiar mesophases expressed by banana-shaped compounds, B7 mesophase stands out due to its electro-switching properties[4] and the formation of distinctive optical textures[5, 6].

The objective of the present paper is to study miscibility and mesophase behaviour of banana-shaped compound exhibiting B7 mesophase 2-Nitro-1,3-phenylene bis[4'-(9-decen-1-yloxy)-4-biphenylcarboxylate][7] (Compound **I**, Fig.1(a)) with nematogenic calamitic compound 4-hexyloxyphenyl 4'-decyloxybenzoate[8] (Compound **II**, Fig.1(b)).

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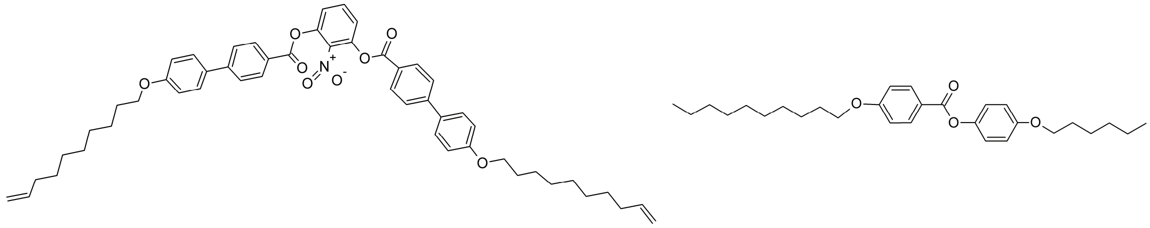


(a) (b)

FIGURE 1. Structural formula of: (a) Banana-shaped compound **I**, (b) Calamitic compound **II**

EXPERIMENTAL

Sequences of phases and phase-transition temperatures were determined on cooling from the isotropic phase from characteristic textures and their changes observed on planar cells in the polarizing microscopes. A hot-stage with platinum–rhodium thermocouple was employed for controlled heating and cooling of the sample.

In order to obtain more structural information and with the intention of affirming or refuting previously reported sequences of phases, non-oriented samples were investigated by X-ray diffraction in Brag–Brentano $\theta : 2\theta$ geometry using a conventional powder diffractmeter, Seifert V-14, at Cu*K*α radiation (λ=1.5406Å), with an automatic high-temperature kit Paar HTK-10. Calibration was performed employing the two most intense platinum lines. Continual scanning was employed with a scanning speed of $1°2\theta \text{min}^{-1}$.

RESULTS AND DISCUSSION

The goal of the present work was to test the miscibility of the banana-shaped dopant **I** with the calamitic compound **II**, and to investigate the mesomorphic behaviour of their binary mixtures. For the detailed study, three mixtures, **M1** to **M3**, have been prepared with 2.2, 3.1 and 7.0 mol% (3.9, 5.5 and 12 wt% respectively) of the banana-shaped dopant **I**, respectively. Rich polymorphism of starting compound **II** is preseved in all mixtures (Table 1, Fig.2.).

TABLE 1. Sequence of phases and phase transition temperatures *T* [ºC] obtained by POM in cooling (• the phase exists, phases: isotropic – I, banana B7 – B7, nematic – N, Smectic SmA – A, smectic SmC – C, unknown tilted smectic SmX – X).

	mol% I	I	*T*	B7	*T*	N	*T*	A	*T*	C	*T*	X
I	100%	•	113.2	•								
M3	7%	•			87.5	•	86.0	•	76.0	•	73.0	•
M2	3.1%	•			88.0	•	85.2	•	77.3	•	72.2	•
M1	2.2%	•			89.1	•	84.7	•	77.1	•	68.8	•
II	0%	•			89.5	•	83.5	•	77.4	•	64.5	•

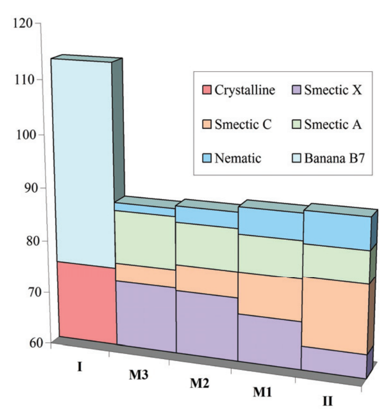


FIGURE 2. Phase diagram of investigated samples

Smectic SmA and SmX temperature ranges broadened with increasing concentration of dopant **I**, reaching temperature width of 10°C for SmA phase of **M3**. This phase broadening occured at the expense of narrowing of smectic SmC and nematic phases' temperature ranges. Clearing temperatures show slight decreasing trend.

Photomicrograph of **M2** at different temperatures are shown on Fig. 3. Nematic phase of **M2** is characterized by schlieren texture, as on Fig.3(a). Its main features are uneven curved shapes, whose meeting points correspond to singularities (disclinations) in the structure. Dominant texture in smectic SmA phase was simple fan-shaped texture, shown on Fig.3(b). Due to the additional discontinuities appearing in SmC phase, its corresponding texture was broken fan-shaped texture shown on Fig.3(c). Considering that it was inherited from SmC phase (polymorphotic fan shaped texture), SmX phase's texture was almost indentical to the texture of SmC phase.

(a) (b) (c)

FIGURE 3. Micrographs of **M2** in: (a) nematic phase at 87°C, (b) smectic SmA phase at 80°C and (c) SmC phase at 73°C

All prepared binary mixtures and pure compounds were investigated by X-ray diffraction. Diffractograms at low Bragg angles of **M2** are presented in Fig.4.

Low angle peak at 2θ=2.81° at 80°C and 83°C corresponds to SmA layer spacing of d=3.14nm. This value correlates well with calculated length of compound **II**, which is 3.12nm. Subsequent shift of this peak to higher Bragg angle (77.5°C, 2θ=2.97°, d=2.97nm) indicates SmC phase with molecular tilt of 18.86° to the layer normal. Further cooling to 72°C gave rise to another tilted smectic phase, yet with short-range hexagonal order of unknown orientation of short molecular axis (SmX)[9]. This phase is characterized by inherited low angle peak from SmC phase, additional low angle peak and few sharp high angle reflections (not shown on Fig.4.).

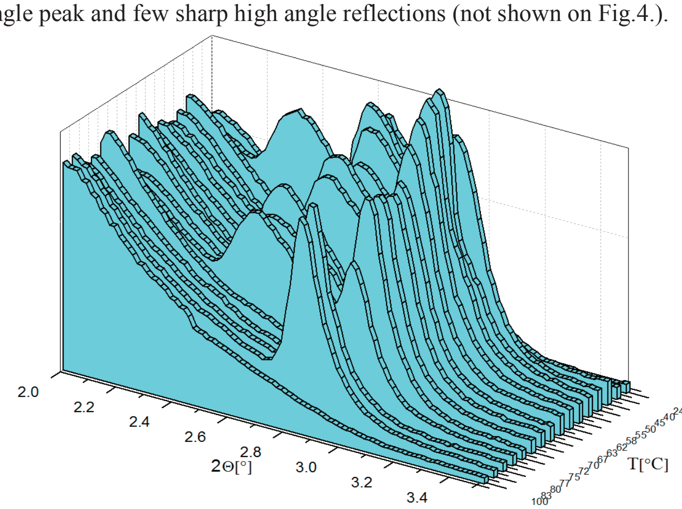
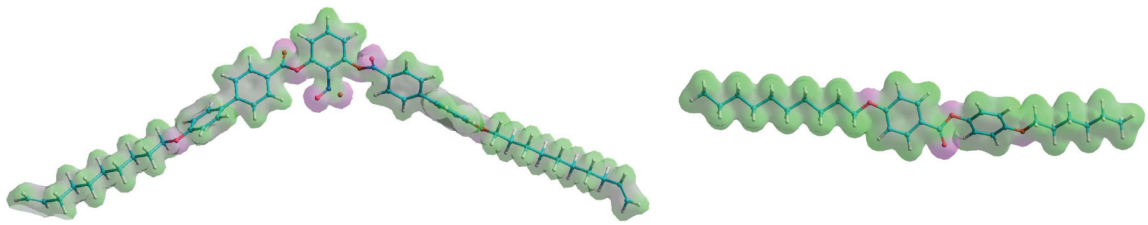


FIGURE 4. Low angle segment of X-ray diffractograms of **M2** at different temperatures

Molecular models were calculated to obtain insight on molecular self-assembly in mesophase. Owing to large number of non-hydrogen atoms in studied molecules, computationally light semi-empirical methods are often utilized to calculate molecular parameters[10, 11]. Among them, RM1 method yields minor average errors for both bond lengths and bond angles[12].



(a) (b)

FIGURE 5.The electrostatic potential map of optimized geometry of: (a) compound **I** and (b) compound **II**

The electrostatic potential map of compound **I** is shown in Fig.5(a) and of compound **II** in Fig.5(b). Length of banana-shaped dopant **I** is 4.5nm and of calamitic compound **II** is 3.12nm.

CONCLUSION

All mixtures preserved polymorphism of starting compound **II**. SmA and SmX phase temperature range broadened with increasing dopant concentration. Therefore, doping conventional calamitic mesogens with novel banana-shaped dopants is viable way to attain desirable mesophase behaviour of resulting mixtures.

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