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New Banana-Shaped Mesogens Exhibiting Switchable Phases at Relatively Low Temperatures

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New Banana-Shaped Mesogens Exhibiting Switchable Phases at Relatively Low Temperatures

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4-Chloro-1,3-phenylene bis[4-(4-n-alkylphenyliminomethyl)benzoates] have been synthesized and the mesophases were investigated by optical microscopy, X-ray diffraction measurements and electrooptical methods. Some derivatives exhibit the electrooptically switchable mesophase B_2 between 75 – 125 °C, which can be supercooled additionally by about 20 K. This existence range is very useful for further physical measurements.

Keywords: Banana-shaped mesogens; smectogenic mesophases; electrooptical behaviour; X-ray measurements

INTRODUCTION

Since Takazoe's report at the 16. International Liquid Crystal Conference, Kent 1996, banana-shaped mesogens are advanced to a highlight in the liquid crystal field [1]. Especially, the ferroelectric or antiferroelectric switching

behaviour, resp., is the main reason for manifold theoretical and experimental works [2-4]. Usually such properties are connected to optical activity resulting from chiral molecules. Therefore, it should be mentioned that the bent mesogens under discussion do not exhibit chirality themselves [2-4]. The source for the remarkable behaviour is a uniform arrangement of the angled molecules in bent direction resulting in a structure that possess a C_{2v} symmetry. Within the layers the direction of the spontaneous polarization should be in direction of the two-fold symmetry axis. Additionally, according to a model proposed by Link et al. [5] the long axis of the bent molecules are tilted with regard to the layer normal. The combination of both symmetry breaking factors allow the appearance of spontaneous polarization of non-chiral compounds.

Up to now electrooptically switchable phases at banana-shaped mesogens were reported mainly in the substance class of 1,3-phenylene bis[4-(4-subst.-phenyliminomethyl)benzoates] [2-4]. To vary the chemical constitution the central phenylene ring can be substituted in different ways [4]. Depending on the type, the number and the positions of the substituents the clearing points can be decreased or the liquid crystalline phases can disappear or, more important, novel smectogenic mesophases can be formed. Up to now, five different B-phases could be detected which have no in-plane order according to X-ray measurements [6]. However, only two of them can be electrooptically switched: the B_2 phase found in the parent series and in 4-chlorosubstituted 1,3-phenylene bisesters [7] as well as the 2-methylresorcinol derivatives which additionally exhibit the switchable B_5 phase [8]. But all the compounds described yet form the switchable phase at temperatures above 125 °C, the clearing points exist between 150 - 175 °C. Such high temperatures are of a marked disadvantage for physical measurements of the novel

mesophases, especially for longstanding investigations. These substances can show decomposition connected with an increase of the conductivity.

It should be mentioned that, recently, electrooptically switchable phases were also reported for twin-mesogens with an odd-numbered spacer [9]. Therefore, these bent twin-molecules can be related to banana-shaped liquid crystals.

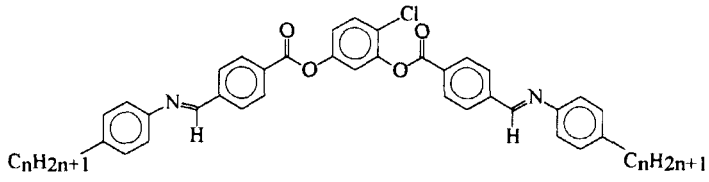
In the paper we present the synthesis, characterization and investigation of 4-chloro-1,3-phenylene bis[4-(4-n-alkylphenyliminomethyl)benzoates]. The tetradecylsubstituted derivative **4** exhibits the switchable B_2 phase in the temperature range between 68 - 127 °C, but generally this phase can be supercooled by about 20 degrees.

MATERIALS

The preparation of the 4-chloro-1,3-phenylene bis[4-(4-n-alkyl-phenyliminomethyl)benzoates] **1-4** was performed by esterification of 4-chlororesorcinol with the 4-(4-n-alkylphenyliminomethyl)benzoic acids by means of dicyclohexylcarbodiimide according to the method described for the alkyloxy derivatives [7]. The substituted benzoic acids, which exhibit liquid crystalline behaviour themselves, were synthesized by condensation of 4-n-alkylanilines with 4-formylbenzoic acid [10]. The transition temperatures (°C) and the transition enthalpies [kJmol^{-1}] are given in Table 1.

The analytical data are given for the decylderivative **2:**
^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.59 (s, 1H, CH=N), 8.58 (s, 1H, CH=N), 8.34 (d, 2H, Ar-H, J=8.4 Hz), 8.28 (d, 2H, Ar-H, J=8.2 Hz), 8.25 (m, 1H, Ar-H), 8.06 (d, 2H, Ar-H, J=8.4 Hz), 8.05 (d, 2H, Ar-H, J=8.4), 7.47 (m, 8H, Ar-H), 2.64 (t, 4H, Ar-CH_2, J=7.6 Hz), 1.30 (m, 32H, CH_2), 0.89 (m, 6H, CH_3)
Elemental analysis: $C_{54}H_{63}ClN_2O_4$ (Mm 839.56)
calcd: C 77.25, H 7.56, N 3.34, Cl 4.22;
found: C 76.75, H 7.48, N 3.32, Cl 4.96;

TABLE I Transition behaviour of the 4-chloro-1,3-phenylene bis[4-(4-n-alkylphenyliminomethyl)benzoates] **1-4**



No.	n	Cr		B_2		I
1	8	·	98	·	119	·
			[-]		[-]	
2	10	·	74	·	125	·
			[19.0]		[14.2]	
3	12	·	75	·	127	·
			[14.7]		[14.9]	
4	14	·	68	·	127	·
			[18.6]		[15.6]	

EXPERIMENTAL RESULTS AND DISCUSSION

X-ray investigations

The homogeneous orientation of the smectic phase of compound **2** was possible by very slow cooling of a drop of the isotropic liquid placed on a glass

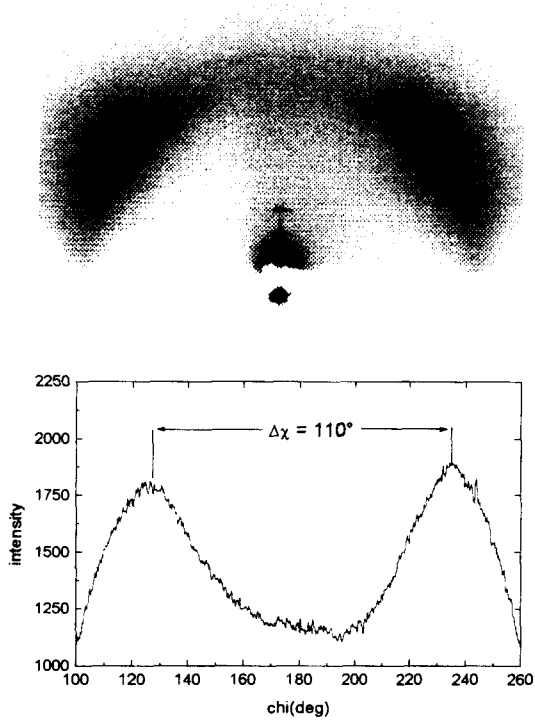


FIGURE 1: X-ray pattern of the B_2 monodomain of compound **2** (123 °C); the χ-scan is shown in the lower part of the picture

plate. By long annealing of this drop (~ 2 hours) immediately below the clearing point well-oriented monodomains were obtained. Since the X-ray beam is incident parallel to the glass surface only the scattering intensity of the upper half of the reciprocal space could be recorded. The X-ray pattern of the smectic phase shown in Figure 1 is similar to that which was reported for the

B_2 phase of other compounds [4,7,8]. The Bragg reflection and their higher orders which correspond to a layer spacing d of 4.0 nm (123 °C) lie on the meridian of the pattern. The diffuse scattering in the wide angle region indicating the liquid-like order within the smectic layers is located out of the equator of the pattern. The χ-scan between the two diffuse maxima gives an angle of 110 ° which corresponds to a tilt angle of 35 °. It should be noted that the X-ray pattern as well as the layer spacing d do not markedly change with temperature by supercooling up to 60 °C.

Electrooptical investigations

Figure 2 shows the current response of the B_2 phase of compound 4 to a

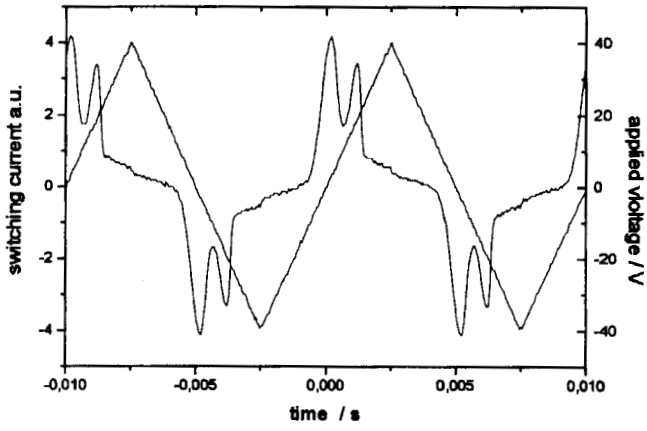


Figure 2: Switching current response in the B_2 phase of compound 4 obtained by applying a triangular voltage (± 40 Volts, 100 Hz)

triangular voltage (100 Hz, ± 40 Volts). The two current peaks during a half period give evidence for the antiferroelectric switching behaviour which was also observed for the other homologues. The spontaneous polarization derived from the switching current peaks is found to be 500 $nCcm^{-2}$. The switching behaviour of the B_2 phase depends on the treatment of the samples. On cooling of the isotropic liquid usually the grainy racemic texture is formed. Applying a sufficiently high electric field the fringes parallel to the smectic layers caused by the coexistence of domains with alternating tilt directions disappear above a threshold. If the voltage is switched off very fast a fan-shaped texture appears where the stripes reappear with some relaxation. In this case the texture of the switched state is independent of the polarity of the field indicating the „racemic" original state which is characterized by an alternating polarization and a synclinic director tilt [5,11]. If the isotropic liquid is cooled down very slowly (0.3 °C/min.) into the B_2 phase under an extended application of a strong a.c. voltage (45Vpp) a fan-shaped texture with a number of circular domains is obtained.

It is shown in Figure 3 that for this texture the switched state depends on the polarity of the applied electric field., e.g. the extinction cross rotates clock-wise or anti-clock-wise for a voltage of opposite sign. This behaviour points to a „homochiral" ground state characterized by an alternating tilt and an alternating polarization direction [5]. The maximum rotation angle of the extinction cross between the switched ferroelectric states (± 40 Volts) was found to be 80 ° which corresponds to twice the tilt angle of the molecules. A tilt angle of about 40 ° is in the same order of magnitude as found by X-ray investigations. It is seen in Figure 3 (at ±22 Volts) that in the centre and in the outer regions of the circular domain the handeness of homochiral state is different which is indicated by the opposite rotation of the extinction crosses.

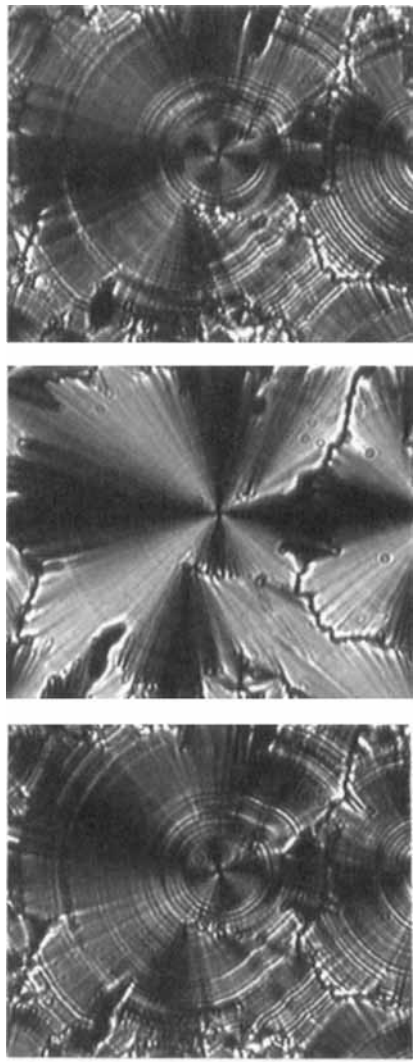


FIGURE 3: Switching behaviour observed in the B_2 phase of compound 3 in dependence on the polarity of the applied field
(See color plate II at the back of this issue)

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