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Preliminary communication

Dimorphism SmA-B_2 in bent-core mesogens with perfluorinated terminal chains†

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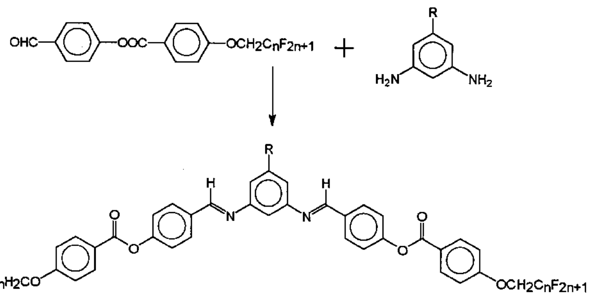
Several banana-shaped liquid crystal materials with perfluorinated terminal chains have been synthesized. A dimorphism SmA–B_2 was proved by X-ray studies and electro-optical measurements. The unusual ratio d/L (d = layer spacing, L = molecular length) and the unexpected behaviour of the layer spacing at the phase transition SmA → B_2 can be interpreted by a change of the packing of the bent molecules.

In 1996 Niori *et al.* [1] detected ferroelectricity in a smectic high temperature phase formed by achiral banana-shaped molecules. This discovery has initiated not only many electro-optical, structural and theoretical studies [2–10], but also the synthesis of a large number of new compounds with a bent molecular structure [10].

It is known that by the introduction of perfluoroalkyl chains into the terminal positions of mesogens the mesophase stability is generally increased because of the stiffness of such chains. Such a relation can also be confirmed for banana-shaped mesogens. The clearing temperatures are much higher than those of related hydrocarbon derivatives. To reduce the clearing points of bent perfluoroalkylated mesogens there are various possibilities.

(1) The perfluoroalkyl chains can be decoupled from the aromatic part of the molecules by aliphatic spacers. Recently, Shen *et al.* [11] described banana-shaped compounds designed according to this concept. They found that the formation of the switchable antiferroelectric B_2 phase is favoured.
(2) The number of aromatic rings can be reduced. Most of the bent perfluoroalkylated three-ring compounds exhibit smectic A phases unlike the related alkyloxy derivatives which are not liquid crystalline [12, 13].
(3) The transition temperatures can be decreased by the influence of lateral substituents.

In this paper we present four new banana-shaped mesogens with perfluorinated terminal chains according to the third of the above mentioned concepts. According to the reaction scheme



these compounds were prepared by condensation of the appropriate 1,3-phenylene diamines (R = H, $COOCH_3$) with 4-[4-n-(1H,1H-perfluoroalkyloxy)benzoyloxy]-benzaldehydes synthesized by esterification of 4-hydroxybenzaldehyde with the 4-n-(1H,1H-perfluoroalkyloxy)-benzoyl chlorides. Methyl 1,3-diaminobenzoate is used as commercial product.

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†This paper is dedicated by the authors to Professor Alfred Saupe on the occasion of his 75th birthday.

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Table 1. Phase transition temperatures (°C) and enthalpies (kJ mol^{-1}) of the substances studied.

Compound	*R*	*n*	Phase behaviour						
1a	H	9	Cr	198 (14.2)	B_2[a]	235 (4.0)	SmA	278 (1.6)	I
1b	H	11	Cr	200 (10.3)	B_2[a]	240 (3.1)	SmA	300 (1.8)	I
2a	$COOCH_3$	9	Cr	160 (20.6)	B_2	165 (6.7)	SmA	250 (1.8)	I
2b	$COOCH_3$	11	Cr	175 (19)	B_2	182 (8.8)	SmA	265 (1.9)	I

[a] Identified by texture investigations only.

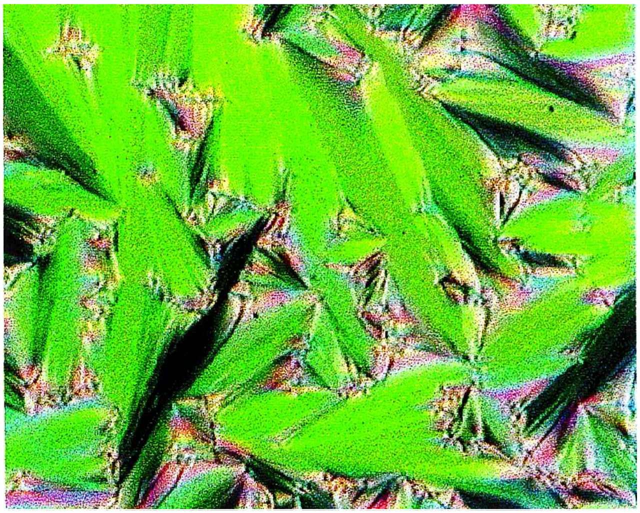
Table 1 presents the phase transition temperatures (°C) and the transition enthalpies (kJ mol^{-1}) of the substances studied. It can be seen that compounds **1a** and **1b**, having no lateral substituent at the central phenyl ring, exhibit very high transition temperatures unsuited for any physical measurements. In comparison, the analogous decyloxy derivative of compound **1a** shows the transition behaviour Cr 120 (B_1 117) I [10]. By introduction of the methoxycarbonyl group in the 5-position (compounds **2a**, **2b**) the clearing temperatures are not however decreased as strongly as might have been expected.

The temperature and enthalpy values of the phase transitions were determined by differential scanning calorimetry (DSC 7, Perkin Elmer) at a heating rate of 10 K min^{-1}. The microscopic textures were analysed by using a polarizing microscope (Leitz Orthoplan) equipped with a heating stage (Linkam THM 600/S). X-ray investigations on non-oriented samples were carried out using a Guinier goniometer and a Guinier film camera. The samples were filled into glass capillaries (Ø 1 mm). The temperature of the heating stage was controlled to better than ± 1 K. The electro-optical investigations were performed using the usual experimental set-up where the cells are heated on the hot stage of a polarizing microscope and a power supply (8116A, Hewlett-Packard) generated the voltage signals. The liquid crystals were filled into commercially available polyimide coated ITO test cells (EHC).

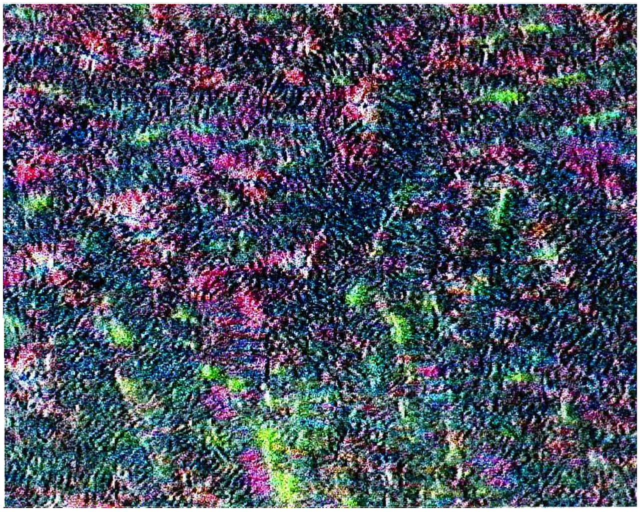
Table 2. Layer spacing of the SmA phase (d_A) and molecular length (L) deduced from the conformation shown in figure 5.

Compound	d_A[a]/nm	L/nm	$(L-d)$/nm
2a	4.7	5.7	1
2b	5.2	6.2	1

[a] d_A is found to be nearly independent of the temperature.



(*a*)



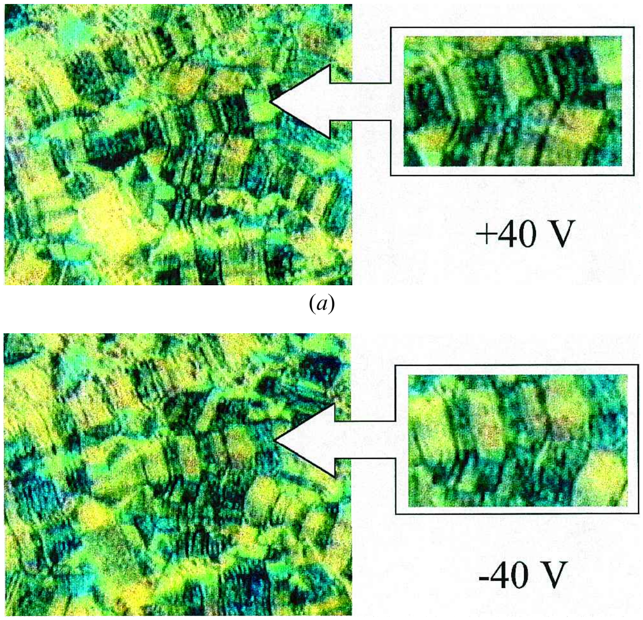
(*b*)

Figure 1. (*a*) Fan-shaped texture of the SmA phase of compound **2a**; (*b*) unspecific grainy texture of the B_2 phase of compound **2a**.

The SmA phase of compounds **2a** and **2b** could be clearly identified by its optical texture. On cooling the isotropic liquid, bâtonnets developed which coalesced to form a characteristic fan-shaped texture coexisting with regions of non-birefringent homeotropic texture, see figure 1 (*a*). The low-temperature smectic phase forms a non-specific 'grainy' texture, figure 1 (*b*); whereas the homeotropic SmA regions are transformed into a schlieren texture.

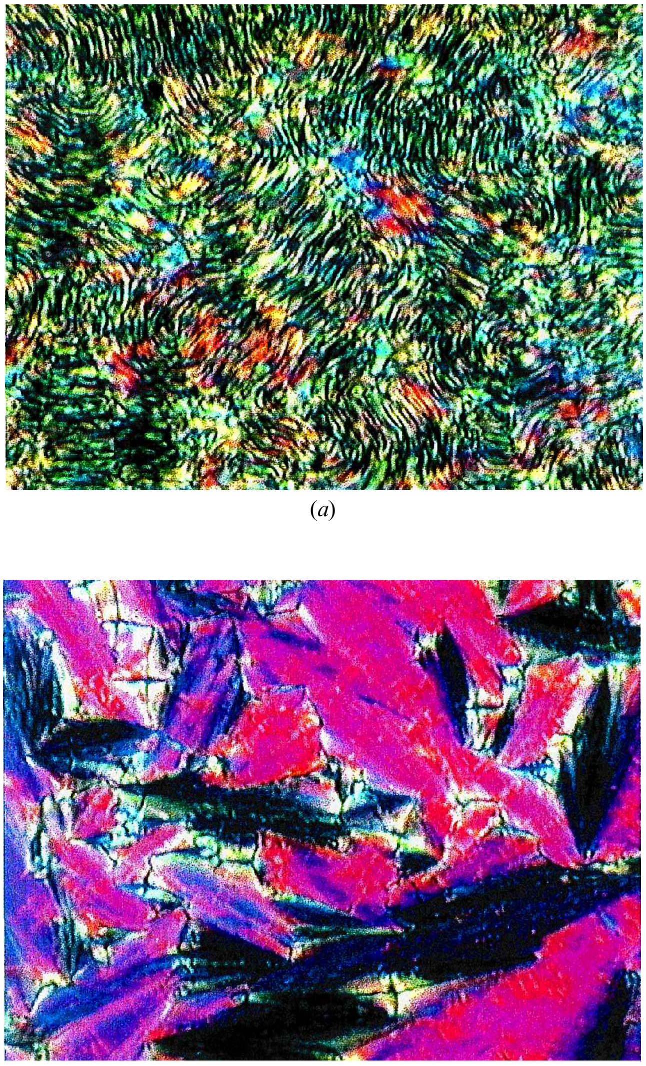
The electro-optical investigations were strongly affected by the relatively high clearing temperatures. Well developed monodomains of the low temperature phase could be obtained only by cooling the SmA fan-shaped texture which was generated by slow cooling of the isotropic liquid. By this procedure some decomposition of the sample could not be avoided, giving rise to unwelcome electrohydrodynamic (EHD) processes. But in spite of the disturbing EHD processes, the electro-optical investigations performed on the smectic low temperature phase point clearly to a ferroelectric or antiferroelectric switching behaviour. On applying an electric field, stripes parallel to the smectic layers first occur as known for B_2 phases. Furthermore, it is obvious from figure 2 that the switched states depend on the polarity of the applied field, indicating homochiral domains. On the other hand, we also found domains where the switched states are independent of the sign of the field, indicating racemic domains (figure 3). Unfortunately, we cannot distinguish between a ferroelectric or antiferroelectric ground state, because the current response could not be measured due to the high electrical conductivity caused by the alignment procedure. But considering the present knowledge about switchable phases of banana-shaped liquid crystal materials, we assume an antiferroelectric ground state typical for B_2 phases. This would mean that the molecules in the smectic low temperature phase are bent and tilted with respect to the layer normal, giving rise to a polar order of the achiral molecules.

The very high clearing temperatures also prevent the preparation of monodomains for X-ray studies. Therefore only non-oriented samples have been studied



(*b*)

Figure 2. Texture of the B_2 phase of compound **2a** after applying (*a*) +40 V, (*b*) − 40 V—see the text. Sample thickness 6 μm, temperature 153°C.



(*a*)

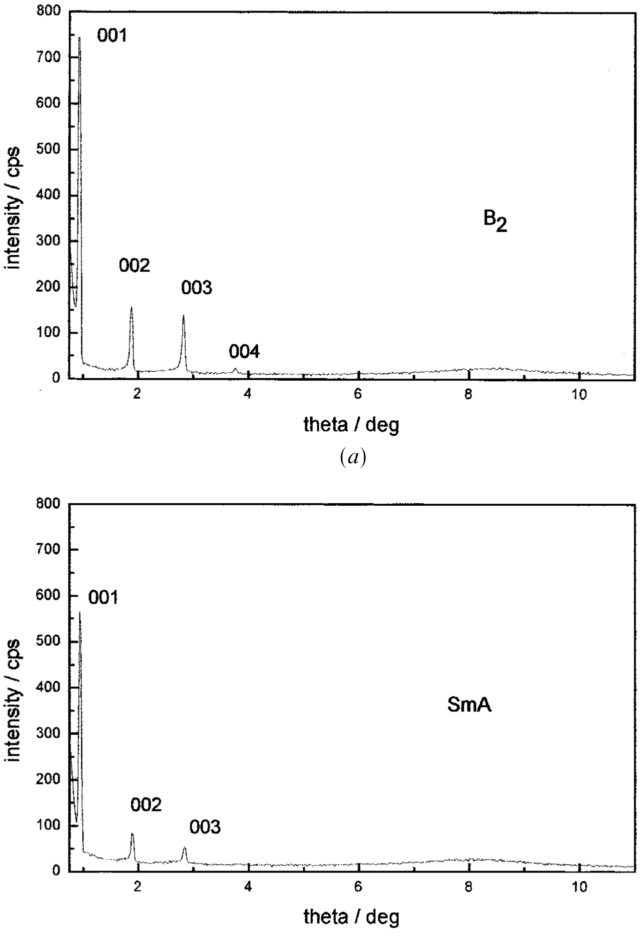
(*b*)

Figure 3. (*a*) Grainy texture of the B_2 phase of compound **2a**; (*b*) fan-shaped texture after applying a voltage of +80 V or − 80 V—see the text. Sample thickness 6 μm, temperature 150°C.

by X-ray diffraction. Figure 4 displays the scattering diagrams of the SmA and B_2 phases which lead to two remarkable results. First, the layer spacing remains nearly constant at the transition from the SmA phase into the B_2 phase although the banana-shaped molecules must be tilted, according to the results of electro-optical measurements. A small continuous increase of about 0.1 nm is observed instead of the expected decrease. Furthermore, there is only a small difference of the relative intensity of the higher orders. Second, the *d* values are essentially smaller than the length of the molecules determined from a model shown in figure 5. The conformation of the middle part of the molecules is indicated by NMR measurements of an analogous three-ring compound (see figure 6).

For the compound in figure 6, a bending angle (180°-2α) of 125° follows from anisotropic ^{13}C shift measurements [14], whereas the perfluorinated chains are parallel to the molecular long axis. It should be noted that this bent three-ring compound with $-OCH_2C_9F_{19}$ terminal chains also forms a SmA phase which is proved by X-ray measurements on oriented samples [12]. Also in this case, the layer spacing *d* (3.6 nm) is clearly lower than the molecular length *L* (4.2 nm), indicating a partial interdigitation of the perfluorinated chains [12].

On the basis of the experimental data, we assume a structural model of the SmA phase in which the perfluorinated chains are more or less interdigitated, figure 7 (*a*). At the transition into the B_2 phase, the interdigitation is lost and the bent molecules are now tilted, figure 7 (*b*); using $\cos^{-1} \beta/L$, a tilt angle β of 33° can be estimated.



(*a*)

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Figure 4. X-ray diffraction pattern of (*a*) the B_2 phase (*b*) the SmA phase of compound **2a**.

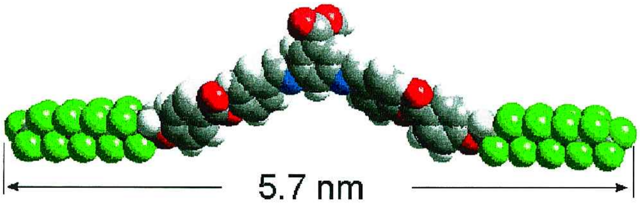


Figure 5. Molecular model of compound **2a**.

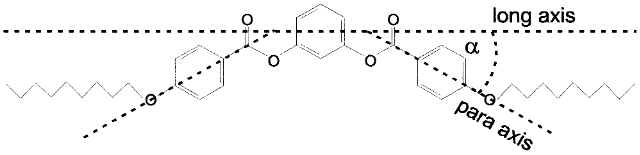
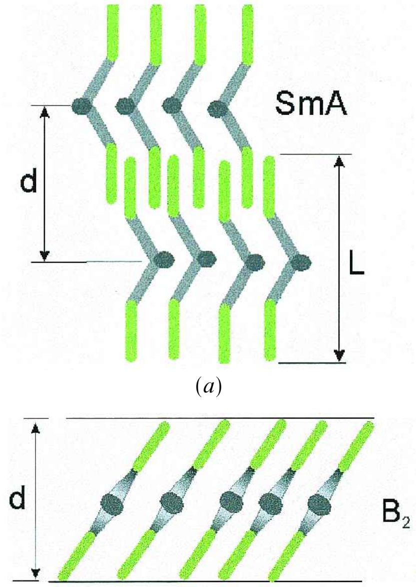


Figure 6. Molecular conformation of an analogous three-ring compound determined by NMR measurements.



(*a*)

(*b*)

Figure 7. Structural model of (*a*) the SmA phase, (*b*) the B_2 phase.

To our knowledge, the compounds under discussion are the first examples showing that a B_2 phase, characteristic for a bent molecular shape, and a SmA phase occur for the same substance. This behaviour can be interpreted by a different packing of the molecules within the smectic layers. The results of calorimetric measurements point to a distinct structural change at the transition $B_2 \rightarrow$ SmA. As seen from table 1, the transition enthalpies are rather high (3–9 kJ mol^{-1}) taking into consideration that both smectic phases have no in-plane order.

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