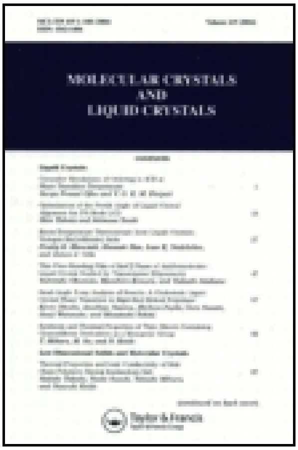

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1,3-Propandiol Bis (4-(4-Alkyloxy-Benzylideneamino)Benzoates - A New Series of Mesogenic Dimers

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1,3-Propandiol Bis (4-(4-Alkyloxy-Benzylideneamino)Benzoates - A New Series of Mesogenic Dimers

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A new homologous series of mesogenic dimers with an odd-numbered flexible spacer is presented. It is shown that the short-chained members of the series form a SmC phase, only, whereas the longer-chained homologues exhibit a SmA phase. The layer spacing of the SmC phase was found to be about the half of the molecular length. This result and the occurrence of singularities with s = 1/2 or s = 3/2 in the schlieren texture point to an intercalated structure. The electro-optical switching of the SmC phase can be attributed to a dielectric transition.

Keywords: Mesogenic dimers; smectic mesophases; X-ray measurements; electro-optical behavior

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INTRODUCTION

Dimeric liquid crystals constituted of two mesogenic units linked via a flexible spacer have attracted attention because of their unusual mesophase behavior which is clearly different of that of the corresponding monomers. In some respect these dimeric liquid crystals can be regarded as model compounds for main-chain liquid crystal polymers [1-4]. The mesophase behavior of symmetric dimeric liquid crystals not only depends on the structure of the mesogenic units and the structure and parity of the spacer, but also on the ratio between the length of the spacer and the length of the terminal chains [5-8]. The transition temperatures as well as the phase behavior is often affected by the parity of the spacer [5, 6, 9]. Remarkable is the odd-even oscillation of the mesophases (SmA, SmC_A) described for symmetric mesogenic dimers containing biphenyl units and linked by a $-COO(CH_2)_nOOC-$ spacer [5, 9]. Another interesting finding is that in dependence on the ratio between the length of the spacer and the length of the terminal chains intercalated SmC phases (layer spacing of about the half molecular length), antiferroelectric SmC phases (layer spacing of about the molecular length) or two-dimensional frustrated smectic phases can occur [9, 10, 11]. Also the length of the mesogenic unit can play a role. If three-ring mesogens are linked by a $-COO-(CH_2)_3-OOC-$spacer an inverse phase sequence SmA-SmC was found where SmA is the low temperature phase with respect to SmC [8].

It should be noted that in non-symmetric liquid-crystalline dimers the structure-property relationships are much more complicated [12-14]. In these compounds besides intercalated SmA phases also partially bilayered SmA phases, intercalated SmI, crystal B and crystal I phases [12], but also an incommensurate SmA phase were reported [14].

In this paper we present 11 members of a new homologous series of symmetric dimeric liquid crystals where the mesogenic units are linked by a $-COO-(CH_2)_3-OOC-$ spacer. We compare the mesophase behavior with that of analogous mesogenic dimers.

EXPERIMENTAL

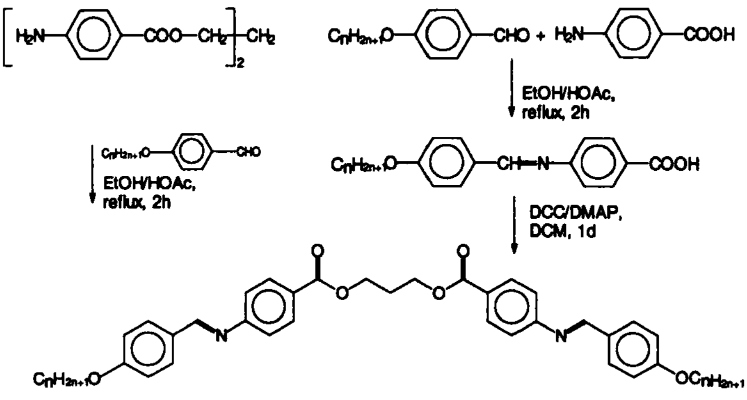
The transition temperatures were determined using a polarizing microscope (Leitz Orthoplan) equipped with a hot stage (THM 600, Linkam). For the homologues with an enantiotropic mesophase the transition enthalpies were measured by differential scanning calorimetry (DSC7, Perkin Elmer). The mesophases were identified on the base of their characteristic optical texture. Structure investigations were performed by X-ray diffraction measurements using a Guinier camera or a Guinier goniometer (Huber, Germany).

Electro-optical investigations were carried out using commercial test cells (E.H.C. Co, Japan) with a cell spacing of 5 μm.

MATERIALS

The substances were prepared by two different routes. The first route was used to synthesize homologous compounds possessing alkyl wings with more than 6 carbon atoms. It consists of a condensation of two parts alkyloxybenzaldehyde with one part 1,3-propandiol bis(4-aminobenzoate) by heating in ethanolic solution under acetic acidic conditions. It had to be recognized that shorter wing compounds could not be synthesized using this route because of difficulties of working up the products. Therefore a second route was established starting with the condensation of an alkyloxybenzaldehyde and 4-aminobenzoic acid catalyzed by acetic acid in an ethanolic solution followed by an esterification of the developed 4-(4-alkyloxybenzylideneamino) benzoic acid with 1,3-propandiol in DCM by DCC/DMAP. The crude products were recrystallized at least four times from a slightly basic (by addition of some drops of TEA to prevent hydrolysis of *Schiff* bases) ethanol/DMF mixture (~10:1). The materials were obtained as colorless or white plates or scales.

Synthetic route:



The transition temperatures of the homologous compounds are listed in Table 1

TABLE 1 Transition temperatures of the homologous compounds (°C)

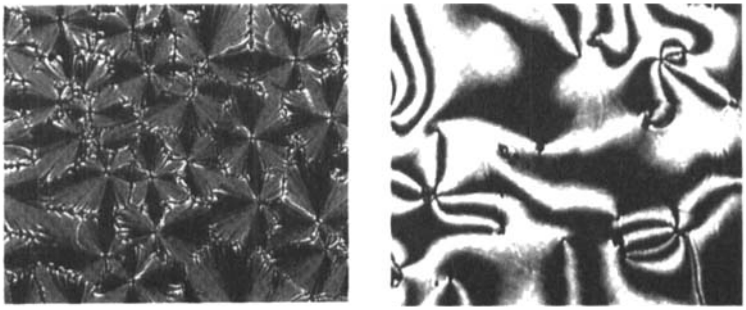
Nr.	n	Cr		SmA		SmC		I
1	1	•	165.5		-		-	•
2	2	•	154		-	(•	144.5)	•
3	3	•	127		-	•	141	•
4	4	•	142		-	•	143	•
5	5	•	137.5		-	(•	129)	•
6	6	•	135		-	(•	121.5)	•
7	7	•	122		-	(•	108)	•
8	8	•	119		-	(•	104)	•
9	9	•	121	(•	97.5)		-	•
10	10	•	120.5	(•	97.5)		-	•
12	12	•	123	(•	100.5)		-	•

Parentheses indicate monotropic transitions

RESULTS AND DISCUSSION

It is seen from Table 1 that only two homologues with short terminal chains (**3**, **4**) form an enantiotropic mesophase, whereas the long-chained members (**5-12**) of the series form monotropic mesophases.

On cooling the isotropic liquid the mesophase of the compounds **2..8** preferably grows in form of circular nuclei which coalesce to a fan-shaped texture which is reminiscent of SmA (Figure 1a).



a) b)

FIGURE 1 Microscopic pictures of the SmC phase of compound **3** (134 °C); a) Fan-shaped texture , b) Schlieren texture

See Color Plate XVII at the back of this issue.

But a SmA phase can be excluded because this phase forms a schlieren texture (Figure 1b) which points to a tilted arrangement of the molecules within the smectic layers.

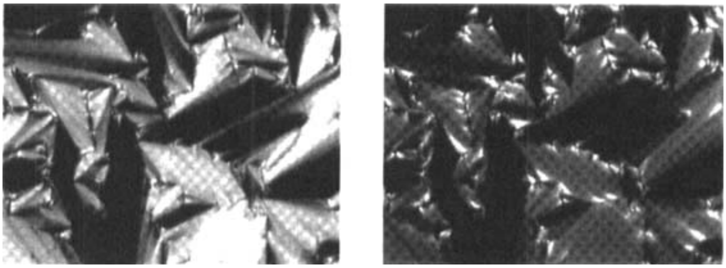
The schlieren texture shows not only singularities with four brushes ($s = 1$) which are typical for SmC phases. But in addition, we observe singularities with two ($s = 1/2$) and six brushes ($s = 3/2$). Such singularities were found in SmC$_A$ phases [15] and intercalated SmC phases of mesogenic twins [5, 9, 12, 16]. The occurrence of these singularities is the consequence of an alternating tilt of the mesogens and can be interpreted by combination of a disclination and a screw dislocation [12, 15, 16].

In the homologous series under discussion the mesophase of the long-chained members (**9**-**12**) appears as a homeotropic texture or a fan-shaped texture which unambiguously points to a SmA phase.

X-ray investigations were performed on the SmC phase of compound **3**. In the small-angle region the X-ray pattern of the powder-like sample displays a Bragg reflection and its second order and a diffuse scattering maximum in the wide angle region (~10°). Such a pattern is characteristic for a smectic phase without in-plane order. From the small angle reflection a layer spacing d of 17.3 Å could be determined which is about the half molecular length obtained for a bent conformation (36 Å). This finding indicates an intercalated structure with a random mixing of the terminal chains and the spacer and an alternating tilt of the mesogenic units which was also described in refs. [5, 9, 12, 16]. The alternating tilt also explains the absence of a broken fan-shaped texture which is characteristic for a SmC phase.

Unfortunately, up to now X-ray measurements on the SmA phase of the longer-chained homologues were impossible because it crystallizes immediately after formation. But we found in binary mixtures of the system **3**/**10** that in a concentration range between 75 and 40 mole % **10** the metastable SmA phase is always the high-temperature phase with respect to the SmC phase. This finding suggests that also the SmA phase is an intercalated one.

Electro-optical investigations were performed on the SmC phase which exhibits a fan-shaped texture with circular domains. Applying an electric field the initially green colored fan-shaped texture is transformed into a red-colored one indicating an increase of birefringence (see Figure 2.)



a) b)

FIGURE 2 **Fan-shaped texture with circular domains of the SmC phase of compound 3, Sample thickness: 5 μm, temperature 128 °C; a) without field, b) ± 12 Volts**
See Color Plate XVIII at the back of this issue.

The threshold voltage is 4 Volts for the compound **3** and 7 Volts for the compound **8**. The switched state is independent of the polarity of the field. Furthermore, the extinction direction between crossed polarizers does not change. The same switching behavior can be observed using an ac-voltage up to a frequency of 10 kHz. On the other hand, no current peak could be detected on applying a triangular voltage. These experimental findings exclude a ferroelectric switching and point to a dielectric reorientation. We can conclude from these results that the bent-shaped molecules do not tilt with respect to the layer normal – in contrast to the B_2 and B_6 phase of banana-shaped molecules [17]. It should be noted that a similar switching behavior was described for the smectic phase of mesogenic dimers with flexible spacer but this phase is a frustrated two-dimensional smectic phase [11, 18]. The increase of the birefringence on applying the field suggests that the molecules reorient so that their bending planes becomes perpendicular to the substrate [18].

For one member of the series (compound **9**) the solid phase shows an intensive blue color. This behavior is strongly reminiscent of that of the B_4 phase observed for several banana-shaped compounds [19-21]. We found that weakly birefringent dark and light domains appear if on observation between crossed polarizer and analyzer the latter is rotated by a small angle. Rotating the analyzer in opposite direction this effect is inversed, the previously dark domains now appear light and vice versa (see Figure 3).


a) b)

FIGURE 3 Domains of the solid state of compound **9** observed by rotating the analyzer; a) 10° clockwise and b) 10° anticlockwise from the initially crossed position (80 °C)

Obviously these domains rotate the polarized light clockwise or anticlockwise indicating a helical superstructure.

CONCLUSIONS

The formation of a tilted intercalated smectic C phase in the investigated compounds is a characteristic feature of mesogenic dimers with an odd-numbered spacer. But it is not clear why the longer-chained homologues exhibit a SmA phase where the molecules are, on average, perpendicular to the layer planes. Unfortunately, X-ray diffraction measurements were impossible for the metastable SmA phase. It can be assumed that the molecules in the SmA phase adopt a more stretched conformation if the terminal chains become longer. We found that the electro-optical behavior of the SmC phase corresponds to a dielectric reorientation of the Freedericksz type. That means, that in this case the intercalation of molecules does not prevent the field-induced reorientation of the molecules.

Another surprising finding is the occurrence of a "blue" solid phase for the homologue **9**. Such solid modification was first described for several banana-shaped compounds [19-21]. Although the structure of this peculiar solid modification is not yet known it seems that the bent shape of the molecules is a presumption for the formation of this chiral solid phase.

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