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Klaus J. K. Semmler; Theo J. Dingemans; Edward T. Samulski

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Biaxial smectic phases in non-linear mesogens: optical properties and phase behaviour of an oxadiazole liquid crystal

by KLAUS J. K. SEMMLER, THEO J. DINGEMANS,
EDWARD T. SAMULSKI*
Department of Chemistry CB# 3290, University of North Carolina at Chapel Hill,
Chapel Hill, NC 27514, USA

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A symmetric, low-molecular-mass liquid crystal based on the oxadiazole ring was synthesized and characterized. The symmetric position of the heterocyclic group in the centre of the liquid crystal, bis(4-hexyloxyphenyl)4,4′-(1,3,4-oxadiazole-2,5-diyl)dicarboxylate, yields a very rigid and non-linear mesogenic core. Despite this non-linear structure, a broad liquid crystalline range with a smectic C and a smectic A phase was found. Conoscopic experiments on freely suspended films revealed the existence of two optical axes in the smectic A phase, indicating a phase symmetry anticipated for either a 'McMillan' biaxial smectic phase or a biaxial (achiral) ferroelectric smectic phase.

1. Introduction

Since the seminal studies of Vorländer at the beginning of this century it has been well-established that thermotropic calamitic mesomorphism can be achieved by a wide variety of lath-shaped molecules having linear mesogenic cores [1(*a*)]. But Vorländer and Apel also noted an instance wherein a non-linear molecule—one with mesogenic azoxyanisole cores appended to a central *meta*-substituted aromatic ring—exhibited liquid crystalinity [1(*b*)]. Although Demus [2] characterizes the Vorländer–Apel mesogen to be of the type 'terminal–terminal parallel rigid', their mesogen in fact comprises two reasonably independent mesogens covalently joined via (flexible) ester linkages to a central *meta*-substituted ring; i.e. there is a flexible 120° bend in the centre of the mesogen. (A good overview of molecular geometries compatible with thermotropic liquid crystallinity has been published by Demus [2].) Several years ago we showed that symmetric molecules containing 2,5-substituted thiophene—an aromatic ring with a 148° bend between the 2,5 exocyclic bonds—yields geometries having a non-linear core and moreover, this geometry exhibits liquid crystallinity. The nonlinear mesogens exhibited both nematic and smectic A and C phases [3]. Such bent liquid crystals are currently referred to as 'banana-shaped' mesogens, and evidence for packing (achiral) banana shapes to give ferroelectric phases has been reported [4].

Both the geometry and electronic properties of liquid crystalline compounds containing heterocyclic compounds have been investigated in detail by different groups [3, 5]. In a study by Zaschke and co-workers [6] on thiadiazole and oxadiazole derivatives, a suppression of mesomorphic behaviour was found with increasing non-linearity of the mesogenic structure. Compounds having a symmetric structure with an oxadiazole unit in the centre of the mesogen did not exhibit liquid crystalline behaviour. The authors assumed that the bend (134°) associated with the exocyclic bonds in the 2- and 5-positions of the oxadiazole unit was too severe to achieve the requisite ordered packing in mesophases. If such structures could exhibit mesomorphism, the severe bend in the mesogenic core might restrict the free rotation of the mesogenic unit around its 'long dimension'. This in turn should lead to a deviation from the typical (average) rod-like mesogen symmetry towards one with an (average) biaxial shape. The properties of such non-linear mesogens might be expected to be similar to the system synthesized by Leube and Finkelmann [7], wherein mesogen rotation is hindered by lateral covalent attachment to a polymer backbone.

In this paper we present the synthesis and characterization of a strongly non-linear shaped liquid crystal, bis(4-hexyloxyphenyl)4,4′-(1,3,4-oxadiazole-2,5-diyl)-dicarboxylate (**1**). In order to obtain the very bent mesogenic core geometry, we chose 2,5-arylated oxadiazole as its central building block.

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*Author for correspondence.

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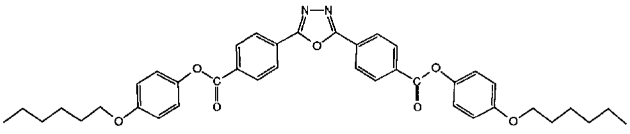

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In contrast to other systems containing the oxadiazole unit, the direct linkage between the heterocyclic group and the phenyl rings ensures a bend of 134° in the overall (average) shape of the mesogenic core, a shape more akin to that of a 'boomerang'. The phase symmetry exhibited by **1** was investigated by interference microscopy (conoscopy).

2. Experimental

2.1. *Synthesis*

A 100 ml flask was charged with 4 mmol of 4,4′-(1,3,4-oxadiazole-2,5-diyl)bisbenzoic acid, 25 ml of $SOCl_2$, and three drops of dimethylformamide (DMF). After refluxing this mixture for 4 h, the excess thionyl chloride was removed under vacuum. 40 ml of dried pyridine, followed by 9 mmol of 4-hexyloxyphenol, were added and the solution was stirred under reflux for 20 h. After cooling the reaction mixture to room temperature, 100 ml of water was added and the resulting precipitate was filtered and washed successively with water, 1M Na_2CO_3, and water. The resulting product was dried under vacuum at 60°C and recrystallized from chloroform; an 88% yield of the title compound was obtained. ^{1}H NMR ($CDCl_3$/TMS): δ in ppm: 0·90 (t, 6H, $-C\underline{H}_3$; 1·24–1·55 (m, 12H, $-(C\underline{H})_2-CH_3$); 1·70–1·86 (m, 4H, $-C\underline{H}_2-CH_2-O$); 3·95 (t, 4H, $-C\underline{H}_2-O$); 6·92, 7·12 (dd, 8H, –COO–Ar$\underline{H}$); 8·28, 8·35 (dd, 8H, –OOC–Ar$\underline{H}$)

The 4,4′-(1,3,4-oxadiazole-2,5-diyl)bisbenzoic acid was provided by Hoechst Celanese Corporation and used without further purification.

2.2. *Measurements*

X-ray measurements were performed on aligned samples with monochromatic CuK_α radiation ($\lambda = 1{\cdot}54$ Å) in the Kiessig geometry. The DSC data were recorded with a Seiko DSC 120. For the conoscopic and orthoscopic investigations a Nikon (Microphot FX) microscope was used. The freely suspended films were prepared according to literature on silica plates with circular openings (diameter = 2·5 mm) [8, 9]. The electrodes were prepared either by depositing gold on the silica, or by introducing two thin wires into the freely suspended films. The d.c. voltage was applied by a HP (6211 A) power supply and the temperature was controlled by using a Linkam (TMS 90) hot stage without any glass or silica covers.

3. Results and discussion

The phase behaviour of compound **1** was determined by polarization microscopy (orthoscopy), differential scanning calorimetry (DSC) and X-ray scattering. On heating, (10°C min^{-1}) the DSC reveals a crystal-to-crystal transition at 156·8°C and a melting peak at 220·2°C. The clearing temperature, T_{cl}, is 295·7°C. These phase transformations were confirmed by observations in the polarizing microscope (figure 1). On cooling from the isotropic melt the system displays a bâttonet texture below T_{cl}; in thick samples a schlieren texture can be seen. Both textures evolve into a focal-conic texture indicating an isotropic to smectic A (SmA) transition. At 235°C a transition to a broken focal-conic texture is suggestive of the formation of a smectic C (SmC) phase. The sample recrystallizes at 220°C. The layering in the first phase (SmA) and phase transformation from the untilted layered structure to the tilted SmC phase was confirmed by X-ray scattering. In addition to the broad wide-angle reflection stemming from the mean lateral intermolecular distance, the scattering pattern reveals a reflection in the small-angle region corresponding to a layer periodicity of 44 Å in the SmA phase. In the SmC phase (at 223°), the layer thickness is 42 Å and corresponds to an ideal tilt of the 'all trans' mesogenic unit relative to the layer normal of 17·5°.

The microscopy and X-ray experiments lead to the following phase transition map for compound **1**:

$$\mathrm{Cr} \xrightarrow{220^\circ\mathrm{C}} \mathrm{SmC} \xrightarrow{235^\circ\mathrm{C}} \mathrm{SmA} \xrightarrow{295^\circ\mathrm{C}} \mathrm{I}$$

While it can be anticipated that distorting the linearity of the mesogen core geometry will alter the symmetry of the mesogenic unit (e.g. $C_{2h} \rightarrow C_{2v}$), the motionally averaged 'boomerang' shape of non-linear mesogens may also in turn influence the symmetry of the phase itself. In the case of the non-linear mesogen **1** with average C_{2v} symmetry this could, for example, lead to optical biaxiality in the SmA phase, a phase which is typically uniaxial for linear calamitics. For this reason we performed conoscopic experiments in order to investigate the optical behaviour of the oxadiazole derivative in the temperature range 235 to 295°C.

Conoscopy requires a macroscopically aligned monodomain, and in the case of a biaxial phase, both directors have to be uniformly aligned. A homeotropic orientation of the mesogen's long axes is usually achieved by treating glass slides with lecithin or silanes [10, 11]. However, the decomposition of such coatings in the temperature range of the SmA phase ($T > 235$°C) precluded alignment between glass slides, and such experiments failed to give uniform samples.

Freely suspended films offer the unique opportunity to achieve a uniform homeotropic orientation in the

SmA phase without a sample–glass interface. Moreover, the latter interface sometimes leads to anchoring artifacts that result in biaxial interference patterns. The textures of the freely suspended film of **1** (figure 2) are consonant with the phase behaviour determined by X-ray and microscopy; the textures reveal a homeotropic alignment of the mesogen's long axes normal to the plane of the suspended film in the SmA phase. The conoscopic experiment in the SmA phase exhibits the usual uniaxial interference pattern (maltese cross) for all orientations of the specimen as it is rotated around the surface/layer normal. This result is expected, since no effort has been expended to align macroscopically an in-plane second director in the experimental set-up (figure 3). In order to accomplish the latter and thereby achieve uniform biaxial orientation in the suspended film, a field has to be applied orthogonal to the primary director (layer normal). The non-linear geometry of **1** and its associated asymmetric charge distribution (due to the hetero-atoms in the centre of the oxadiazole mesogen) suggests that the mesophase should exhibit a negative dielectric anisotropy ($\Delta\varepsilon < 0$). We examined the possibility that an electric field in the plane of the suspended film would uniformly align the second director. As described in the experimental section, we applied an electric field of 60 V in the plane of the freely suspended film for 10 min. The sample was either poled in the SmC phase (233°C) and then slowly heated to the SmA phase (240–280°C), or directly poled in the smectic A phase. In both cases the conoscopic experiment revealed an opening of the isogyres with the rotation of the sample (figure 4). This result indicates the existence of two optic axes in the SmA phase. The sample retains this biaxial orientation without the applied field until either decomposition occurs (~30 min), or the sample is heated close to the clearing temperature. (The freely suspended films were not stable in the isotropic phase.) Occasionally, if a particulate contaminant was suspended in the film, we would observe macroscopic 'phase-winding' in the SmC phase which produced 'spiral' and 'target' patterns in the freely suspended films [12]. Presumably the gradients in the applied field and the asymmetry of suspended droplet shapes contributed to these observations.

4. Conclusions

The results presented here reconfirm Vorländer's hypothesis: liquid crystallinity can be realized even in the case of strong non-linearity in the centre of the mesogenic unit. The rigidity and large delocalized charge through the aromatic rings in the oxadiazole mesogenic unit leads to high transition temperatures in this 'boomerang'-shaped mesogen. This in turn makes the investigation of the phase behaviour and symmetry rather difficult, especially because of the decomposition of compound **1** in the presence of oxygen. Structural variations of **1** aimed at lowering transition temperatures are in progress; reversing the sense of the ester moiety dramatically influences the transition temperatures [13]. We showed by conoscopy that the optical properties of the oxadiazole derivative **1** in the untilted phase is not consistent with the uniaxial smectic A phase. Rather the existence of two optical axes indicates a biaxial smectic phase. However, the current findings do not distinguish between the biaxial phases schematically illustrated in

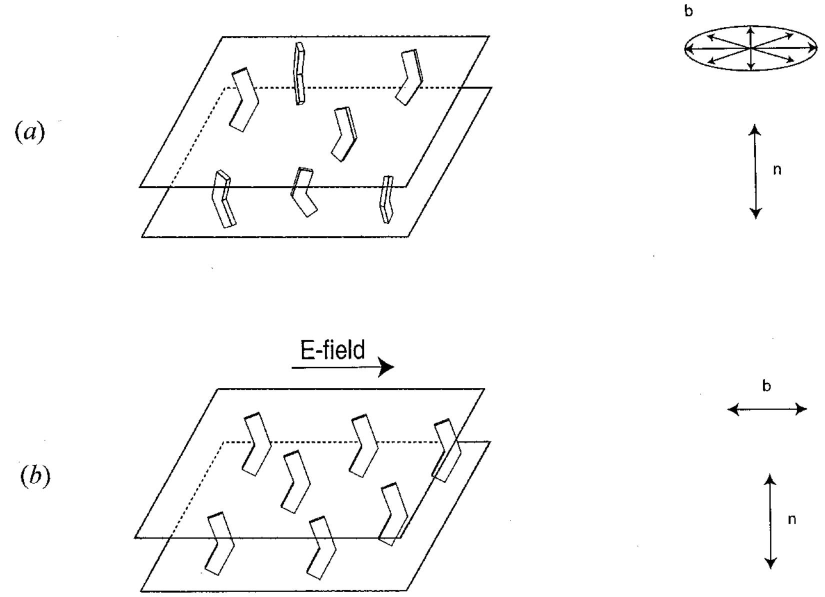

Figure 3. Schematic illustration of the orientation of boomerang-shaped mesogens and macroscopic directors in the freely suspended film in the smectic A phase: (*a*) without electric field; (*b*) with electric field.

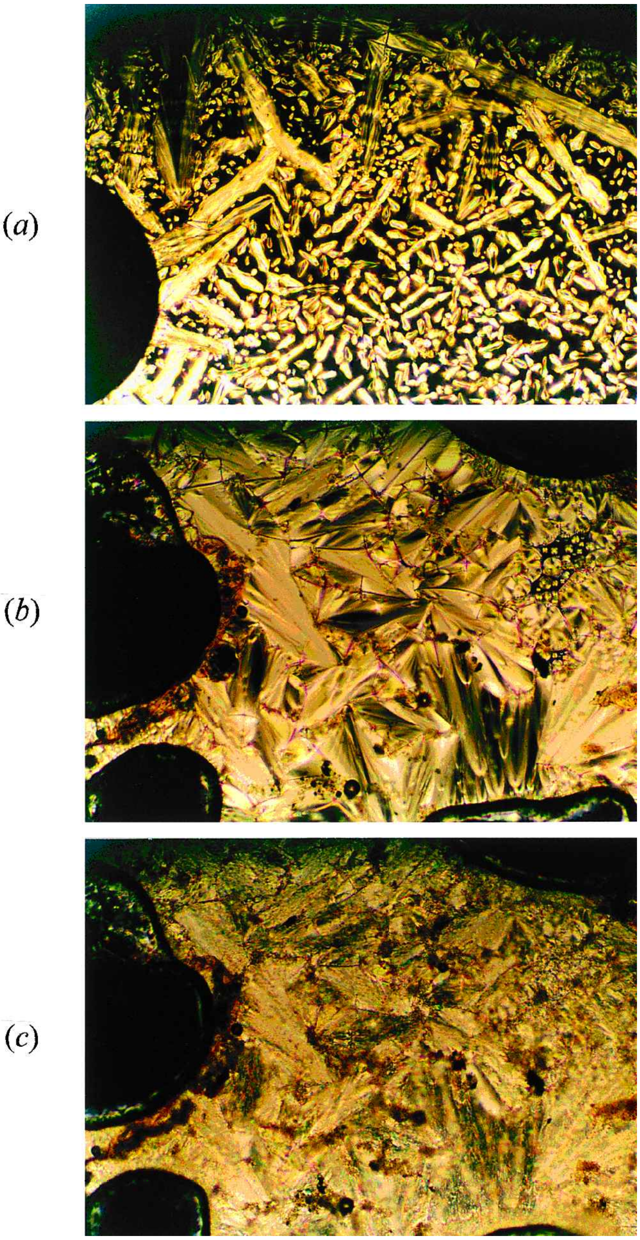

Figure 1. Photomicrographs of the liquid crystalline phases of bis(4-hexyloxyphenyl)4,4′-(oxadiazole-2,5-diyl)dicarboxylate (**1**): (*a*) I–SmA transition (288°C); (*b*) focal-conic texture of **1** (285°C); (*c*) broken focal-conic texture (232°C).

figure 5: the smectic proposed by McMillan and denoted SCM by de Gennes [14] or the ferroelectric arrangement of the bent mesogens advanced by Niori *et al.* [4].

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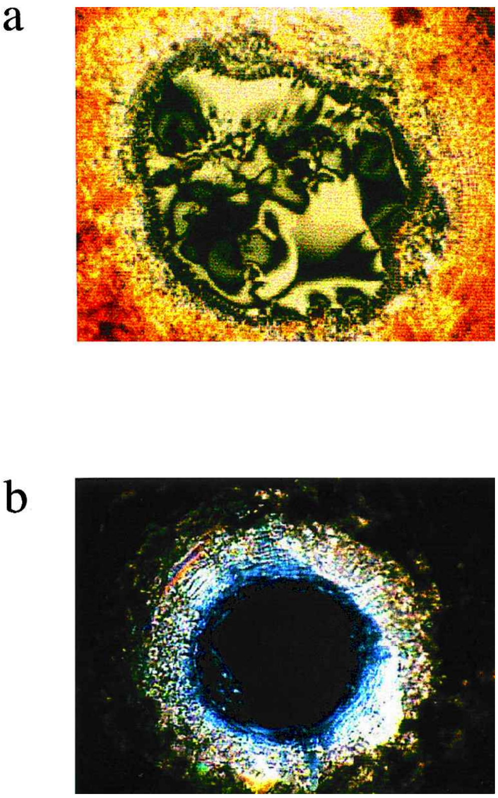

Figure 2. Textures of freely suspended film of I: (*a*) schlieren texture of the SmC phase ($T = 225°C$); (*b*) homeotropic orientation of the SmA phase ($T = 260°C$).

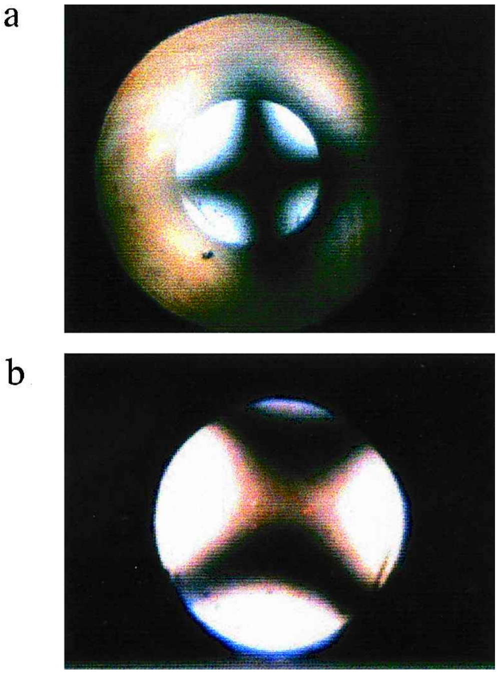

Figure 4. Observed change in conoscopic interference pattern with rotation around the film normal: (*a*) normal position; (*b*) diagonal position.

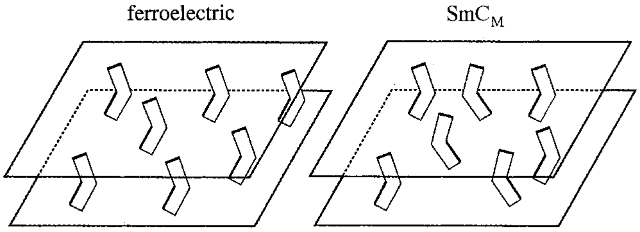

Figure 5. Biaxial smectic phases comprising non-linear (boomerang) mesogens with C_{2v} symmetry: (left) ferroelectric phase; (right) SmC$_M$ phase. The principal axis is aligned normal to the indicated layers and the second axis is aligned in the horizontal direction.

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