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New banana-type liquid crystal with a methoxy group substituted near the central ring

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A seven-ring achiral bent core (banana-shaped) mesogen with a thermally stable ester linkage in the molecule was synthesized. The novelty of the molecular structure lies in the methoxy group laterally substituted in the *ortho* position on the phenyl ring located near the molecular centre. The compound shows two mesophases; the high temperature one can be attributed to the antiferroelectric B_2 phase, the low temperature one is a smectic phase with an in-plane ordering.

Introduction

Bent-shaped molecules are attracting much interest as they form several liquid crystalline phases with chiral structures, some of them exhibiting a dipolar order.[1,2] In contrast to liquid crystals formed by rod-like molecules the chiral polar phases are formed even in the case when the bent-shaped (banana) molecules are non-chiral. The dipolar order follows from orientation of the molecular dipoles along the transverse molecular axes and close packing of molecules within the smectic layers, which hinder their rotation along the long axes. As a result, the smectic layers exhibit spontaneous polarization. According to the mutual direction of the spontaneous polarization vector in the neighbouring layers, ferroelectric (parallel) or antiferroelectric (antiparallel) phases may exist.[2,3] So far antiferroelectric phases are more frequent especially for bent-shaped molecules without a chiral centre.

In this contribution we present the preparation of a new compound composed of achiral bent-shaped molecules with a core containing seven rings and ester linkages between mesogenic units. With increasing numbers of benzene rings in the molecule the transition temperatures increase.[4–6] Lateral substitution by a methoxy group substantially decreases the transition temperatures in both banana-like[7] and rod-like liquid crystals[8] due to increase of the molecular dipole moment. Dipolar interactions caused by the electron donating character of the methoxy group seem to be more important for molecular packing than the steric effect of the bulky methoxy groups disturbing the ordering of the molecules.[9] In contrast to ref. 7, where substitution of the methoxy group in the *meta* position relative to the central ring was used, resulting in metastable and very narrow mesophases, we chose the substitution in the *ortho* position. The mesomorphic properties of two observed thermally stable mesophases in this compound are described.

Synthesis

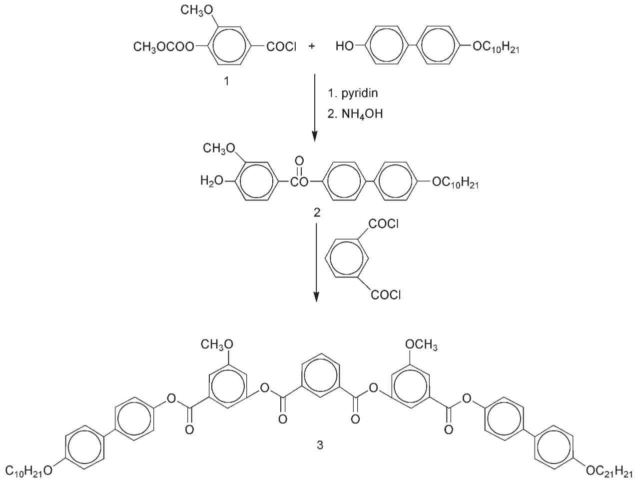
Acid chloride 1

The synthesis of the new banana-shaped molecule was carried out according to Scheme 1. 0.52 mol of vanillic acid (4-hydroxy-3-methoxybenzoic acid, Aldrich, mp 210 °C) was dissolved in a solution of 1.5 mol of NaOH in 400 ml of water. The solution was cooled with ice and 0.85 mol of methyl chloroformate (Aldrich) was slowly added under stirring in such a way that the temperature did not exceed 5 °C. The resulting slurry was stirred for 4 h and the acidity of the solution was adjusted to pH = 5 by the addition of concentrated HCl. The precipitate was filtered off and recrystallized from ethanol to give a white solid acid (yield ≈ 80%). A mixture of the acid and an excess of thionyl chloride were heated for several hours until the solid dissolved completely. The excess of thionyl chloride was removed under vacuum and solid acid chloride was obtained.

^{1}H-NMR (in ppm, 200 MHz, $CDCl_3$): 7.9 (dd, $J_1 = 8.4$, $J_2 = 1.9$, 1H, *para* to CH_3O), 7.8 (d, $J = 1.9$, 1H, *ortho* to CH_3O-), 7.25 (d, $J = 8.5$, 1H, *meta* to CH_3O-), 3.95 (s, 3H, CH_3OCOO), 3.92 (s, 3H, CH_3O).

Mesogenic phenol 2

A solution of 50 mmol of 3-methoxy-4-(methoxycarbonyloxy)-benzoyl chloride in 100 ml of dried chloroform was added dropwise under stirring to a solution of 50 mmol of 4′-alkyloxybiphenyl-4-ol and 75 ml of pyridine in 100 ml of dry chloroform. The transparent solution was allowed to stand overnight, filtered and the solvent was removed under reduced pressure. The residue was hydrolyzed in a mixture of 50 ml of ethanol, 100 ml of chloroform and 25 ml of 25% ammonia



Scheme 1 Synthesis of the studied compound.

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for 8 h to give the solid title compound which was filtered off and dried in air. The hydrolyzing solution was added to 1 litre of water. The organic layer was separated and after filtration evaporated to dryness to give an additional amount of the mesogenic phenol.

^{1}H-NMR (in ppm, 200 MHz, $CDCl_3$): 10.5 (s, 1H, ArOH), 7.7 (dd, J_1 = 8.5, J_2 = 2.2, 1H, *para* to CH_3O), 7.55 (d, J = 2.2, 1H, *ortho* to CH_3O), 7.65 and 7.58 (m, 4H, *ortho* to Ar), 7.26 (d, J = 8.8, 2H, *ortho* to -OCO), 6.99 (d, J = 8.8, 2H, *ortho* to OR), 6.93 (d, J = 8.3, 1H, *ortho* to -OH), 3.98 (t, J = 6.5, 2H, CH_2O), 3.92 (s, 3H, CH_3O), 1.71 (quintet, J = 6.5, 2H, $OCH_2\mathit{CH_2}$), 1.15–1.5 (m, 14H, CH_2), 0.9 (m, 3H, CH_3).

Final product 3

A solution of 5 mmol of isophthalic dichloride in 50 ml of dichloromethane was added to a stirred solution of 10 mmol of mesogenic phenol **2** in 50 ml of dry dichloromethane and 20 ml of pyridine and the mixture was stirred under reflux for 20 h. The cold reaction mixture was after 3 days poured into dilute HCl and extracted with dichloromethane. The organic extract was washed twice with dilute HCl, twice with water and then dried over anhydrous sodium sulfate. The solvent was removed and the residue was purified by column chromatography on silica gel (Kieselgel 60, Merck, particle size 0.063–0.2 mm) using a mixture of dichloromethane and acetone (98 : 2) as eluent. The collected product was crystallized from acetone.

The results of elemental analysis for the final compound: found C 75.49% and H 6.81%, calc. C 75.42% and H 6.84%. **^{1}H-NMR** (in ppm, 200 MHz, $CDCl_3$): 9.1 (s, 1H, *ortho* to -COO), 8.5 (dd, J_1 = 8.0, J_2 = 1.5, 2H, *ortho* to -COO), 7.95 (dd, J_1 = 8.5, J_2 = 2.0, 2H, *para* to CH_3O-), 7.88 (d, J = 2.2, 2H, *ortho* to CH_3O-), 7.75 (t, J = 7.8, 1H, *meta* to -COO), 7.6 (m, 8H, *ortho* to -Ar), 7.3 (m, 2H, *meta* to CH_3O + 4H, *ortho* to OCOAr), 6.98 (d, J = 8.7, 4H, *ortho* to RO-), 4.0 (t, J = 6.5, 4H, CH_2OAr), 3.95 (s, 6H, CH_3O), 1.8 (quintet, J = 6.5, 4H, $\mathit{CH_2}CH_2OAr$), 1.2–1.6 (m, 28 H, CH_2), 0.9 (t, J = 6.4, 6H, CH_3).

Experimental results

The phase transition temperatures were determined by differential scanning calorimetry (DSC7, Perkin Elmer) and by observation under a polarizing microscope (Nicon Eclipse E600). During calorimetric measurements cooling and heating rates of 5 K min^{-1} were applied. The mass of the samples was about 8 mg. The samples were placed in a nitrogen atmosphere and hermetically closed in aluminium pans.

The DSC graph is shown in Fig. 1. Two mesophases, the high temperature one, B_H, and the low temperature one, B_L, have been found between the isotropic phase and the crystalline phase. The phase transition peak between B_H and B_L has a very low enthalpy and is shown in detail in the inset. Phase transition temperatures and values of enthalpy have been evaluated on cooling:

$$\text{Iso–B}_H\text{: 213 °C } (\Delta H = -22.2 \text{ J g}^{-1})$$

$$\text{B}_H\text{–B}_L\text{: 173 °C } (\Delta H = -0.7 \text{ J g}^{-1})$$

$$\text{B}_L\text{–Cryst: 112 °C } (\Delta H = -11.9 \text{ J g}^{-1})$$

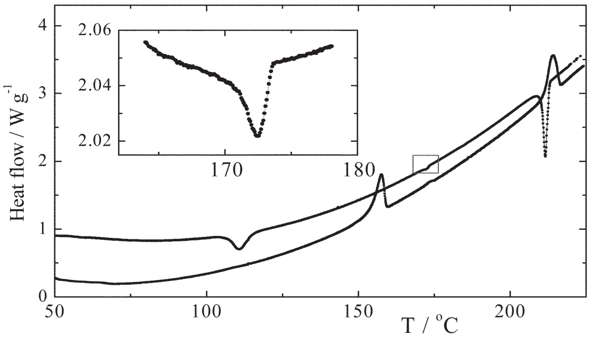

Fig. 1 DSC plots recorded on subsequent heating and cooling. The inset shows the B_H–B_L phase transition in a magnified scale.

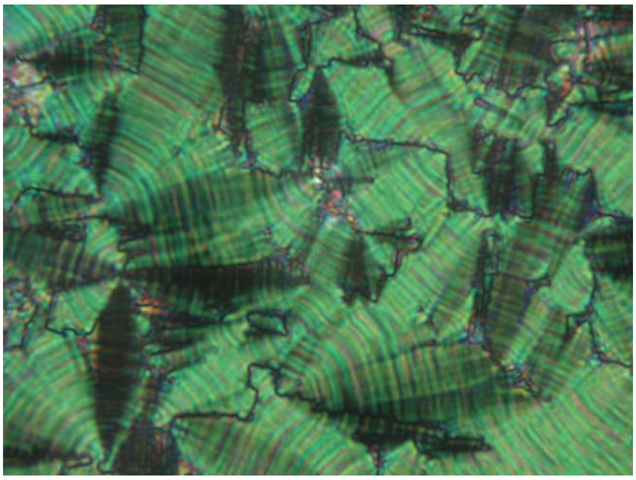

Fig. 2 Texture of the B_H phase (identified with the B_2 phase) observed at T = 187 °C under crossed polarizers with horizontal and vertical polarization directions. The width of the picture is 400 μm.

Microscopic observation and dielectric measurements were carried out on planar cells prepared from indium–tin-oxide (ITO) coated glass plates separated by mylar spacers 6 and 25 μm thick. The cells were filled in the isotropic phase. The temperature was changed and stabilized with an accuracy of ±0.1 °C on a hot stage apparatus (Linkam). In the B_H phase a schlieren texture usually appeared, which was converted to a fan-shaped texture under an ac electric field. In thin samples both schlieren and fan-shaped textures may appear spontaneously.

A typical texture of the B_H phase, observed in a planar 6 μm thick sample after the application of the electric field, is shown in Fig. 2. The occurrence of the fan-shaped texture suggests a layered (smectic) structure. The stripes are parallel to the smectic layers. The parts of the sample with stripes parallel to the directions of the light polarization (horizontal or vertical) are areas of optical extinction (see dark areas in Fig. 2). Under a dc electric field of 0.5–1 V μm^{-1} the majority of the stripes disappear. In such a structure the extinction remains the same as in the case of zero field, the optical axis being parallel to the smectic layer normal. This finding indicates the anticlinic orientation of the director in the adjacent layers.[3] Under a sufficiently high field the extinction position may deviate from the previous optical axis, symmetrically for the opposite fields. This deviation corresponds to removal of the anticlinic structure. The value of inclination represents an apparent tilt angle Θ_s of ~10–12°. In another observation the optical extinction does not change even under high electric fields.

In the low temperature phase B_L the texture is finer but fans confirming a smectic structure are still seen. The stripes represent either defects or narrow domains with different orientations of the structure (see Fig. 3).

A free standing film is easily formed in the B_H phase by spreading the material across a circular hole 3 mm in diameter made in a thin metallic plate. The film persists even on cooling below the phase transition to the B_L phase. The textures in both phases are shown in Figs. 4 and 5. In the B_H phase a schlieren texture is observed indicating a full degeneracy of the director in-plane orientation. The texture in the B_L phase suggests an in-plane ordering.

Dielectric measurements were performed during cooling in

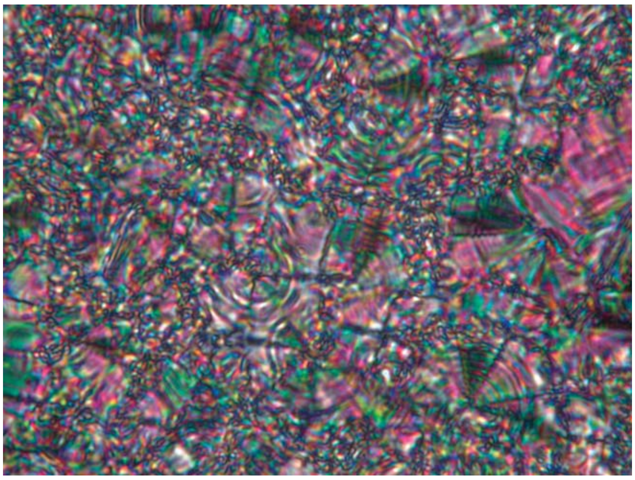

Fig. 3 Texture of the B_L phase (identified with the B_3 phase) at T = 148 °C. The width of the picture is 400 µm.

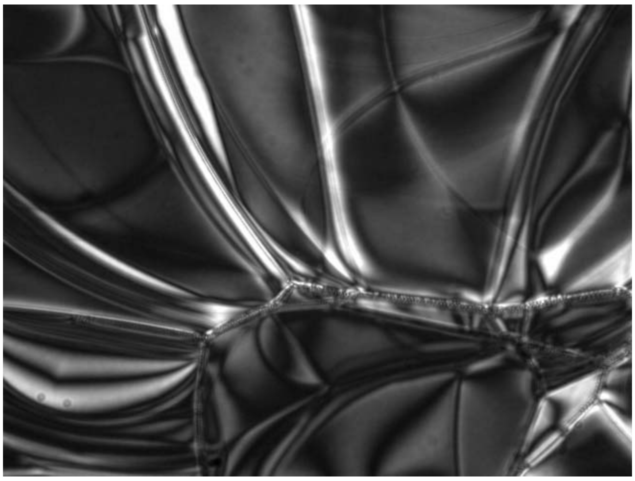

Fig. 4 Texture of the B_H phase (identified with the B_2 phase) in free standing film at T = 189 °C. The width of the picture is 300 µm.

Fig. 5 Texture of the B_L phase (identified with the B_3 phase) in free standing film at T = 150 °C. The width of the picture is 300 µm.

the temperature interval 210–100 °C using a Schlumberger 1260 impedance analyzer in the frequency range 100 Hz–1 MHz for a 25 µm thick cell. The dispersion data were analyzed using the Cole–Cole formula:

$$\varepsilon^*(f) - \varepsilon_\infty = \frac{\Delta\varepsilon}{1 + (if/f_r)^{(1-\alpha)}} - \frac{\sigma^n}{2\pi\varepsilon_0 f} \tag{1}$$

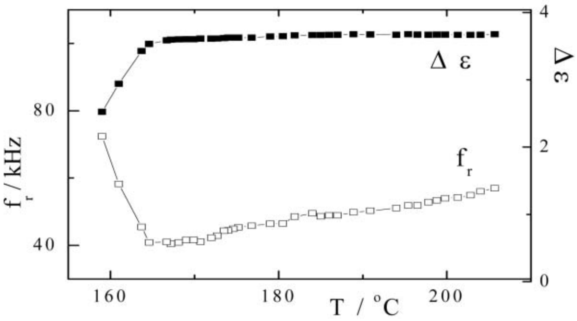

Fig. 6 The fitted relaxation frequency and relative permittivity in the B_H phase. The jump in plotted values represents the B_H–B_L phase transition.

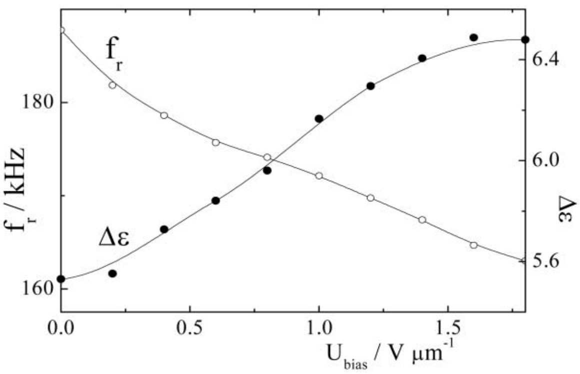

Fig. 7 Relative permittivity, $\Delta\varepsilon$, and relaxation frequency, f_r, plotted as a function of an applied dc bias field in the B_H phase at the temperature T = 187 °C.

f_r, $\Delta\varepsilon$, α, σ, and n are relaxation frequency, dielectric strength, distribution parameter, conductivity, and exponent, respectively. The relaxation frequency and relative permittivity are shown in Fig. 6. In the B_H phase $\Delta\varepsilon$ is about 3.5 and f_r is between 40 and 50 kHz. The values of both quantities are compatible with the antiferroelectric phase. At the phase transition to the B_L phase $\Delta\varepsilon$ exhibits a jump down and f_r is sharply increased. On further cooling in B_L phase no mode is detected below 160 °C.

When applying a bias electric field in the B_H phase the relaxation frequency decreases and $\Delta\varepsilon$ increases as is shown in Fig. 7. This behaviour indicates field-induced deviations from the antiferroelectric ordering in this phase.[10]

Antiferroelectric switching was observed in the B_H phase under a triangular wave field 15 V_{pp} μm^{-1}, 20 Hz. Two distinct peaks in the polarization reversal current are clearly seen, which indicates antiferroelectricity. In Fig. 8 the corresponding triple hysteresis loop is shown. The spontaneous polarization

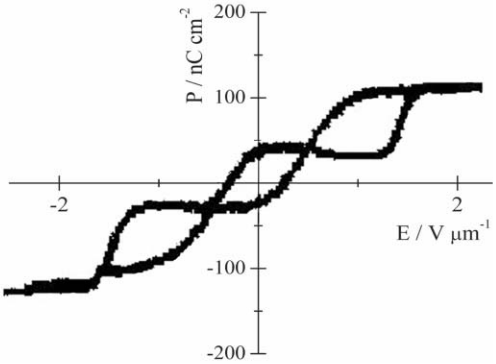

Fig. 8 Hysteresis loop detected in the B_H phase at the temperature T = 189 °C.

P_s measured in the B_H phase has been evaluated as 100–120 nC cm^{-2}.

In the B_L phase the electrooptic response has been observed only near below the B_H–B_L phase transition.

Discussion and conclusions

We prepared a new liquid crystalline material composed of seven-ring banana-shaped molecules without Schiff's base units having a lateral methoxy group in the *ortho* position on the ring next to the central phenyl. The DSC study reveals two mesophases in this compound, which are stable and exist over a very broad temperature range. The texture of the high temperature phase observed in planar samples indicates a smectic phase. The schlieren texture in the free standing films gives evidence of the absence of order in the smectic layers. The low permittivity as well as the hysteresis loop indicates an antiferroelectric structure. In the notation defined in ref. 5 this phase is the antiferroelectric B_2 phase.

As the optical axis is parallel to the smectic layer normal, the structure should be generally anticlinic. In the case of antiferroelectric ordering it corresponds to a homogeneously chiral structure denoted[3] as SmC_AP_A*. Under the assumption that the chirality is not changed under the field, such a structure is switched to the unipolar synclinic structure[3] SmC_SP_F*, with the optical axis deviating from the layer normal by the tilt angle. We observed such a behavior, but the detected deviation of the optical axis was significantly lower than the usual tilt angle in banana structures.[10,11] This behavior can be explained by a low tilt angle in the material under study or by compensation of the apparent tilt angle by mixing of domains with the opposite chirality.[10,11] In some experiments the optical axis remained parallel to the layer normal even under a high electric field. It gives evidence[11] of the racemic synclinic structure with domains of opposite direction of tilt, which is switched to the anticlinic structure under the field.[3]

The stripes observed without an electric field might represent very narrow domains. As they have the same electric energy in the applied electric field, their disappearance under the electric field is hardly expected. It is valid for both observed cases, namely for the homogeneously chiral, or the racemic structures described above. One might accept that a molecular chirality can play a role in forming a continuous helix in the sample bulk or promote the formation of domains. The chirality in molecules without the asymmetric carbon can be only of conformational character. Particular twisting of the ester groups connected to the central phenyl may lower the molecular symmetry and generate chirality.[11] When the chirality is taken into account the behavior of the structure could be more complicated and is currently the subject of a detailed study.

The texture of the free standing film observed in the low temperature phase suggests an order in the smectic layers, which indicates a B_3 or B_4 phase.[6] A characteristic feature of the B_4 phase texture is an intense blue color,[2] which we did not find in the B_L phase reported here. For this reason we identify the B_L phase with the B_3 phase. The existence of an electrooptic response just below the B_H–B_L phase transition[5] supports this conclusion.

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