Polar switching in a crystalline modification of a five-ring bent-core compound†

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A new five-ring banana-shaped compound is presented which does not exhibit a mesophase but a high-temperature crystalline phase with unexpected electro-optical properties. By application of a sufficiently high electric field (15 V μm^{-1}) this solid modification can be clearly switched where the texture of the switched state is different for an opposite sign of the applied electric field. This switching is accompanied by a current response which indicates an antiferroelectric ground state. The switching polarisation was found to be 700 nC cm^{-2}. It is interesting that the polar switching takes place only below a frequency of 5 Hz. The crystalline nature of the solid modification was proved by X-ray diffraction measurements on partially oriented samples. The mechanism of the polar switching is not yet clear. It can be assumed that the switchable modification has a structure with sufficient free volume which enables the collective rotation of at least parts of the molecules.

Introduction

Polar crystals have at least one polar axis along which a macroscopic spontaneous polarization occurs. Ferroelectric crystals are the part of a variety of polar crystals in which the direction of the spontaneous polarization can be reversed by applying an electric field. Ferroelectric (or antiferroelectric) crystals are of great interest for applications in electronics and optoelectronics (materials for capacitors, light modulators, light frequency converters, *etc.*).[1] The majority of ferroelectric crystals are inorganic compounds. But among ferroelectrics there are also organic crystals (*e.g.* triglycine sulfate,[2] thiourea,[2] tanane,[3] co-crystals of phenazine and chloraniline acid[4]) as well as crystalline polymers[5] such as copolymers of vinylidene fluoride–trifluoroethylene. Ferroelectric and antiferroelectric properties can be also realized in liquid crystals, for example in smectic phases with a tilted arrangement of chiral calamitic molecules.[6–8] In 1996, it was found that achiral banana-shaped molecules can be packed in a polar fashion due to restricted rotation of the molecules about their long axes within the smectic layers. This leads to a long-range correlation of the lateral dipoles and to a spontaneous polarization, which is usually parallel to the layers.[9–12] To the best of our knowledge only two examples were reported in the literature of a mesogenic compound forming a crystalline modification which not only has a polar structure (with pyro- and piezoelectric properties) but also shows a ferroelectric switching.[13] The spontaneous polarization values were found to be about 25 nC cm^{-2} and 45 nC cm^{-2}, respectively.

Herein we present a novel bent-core compound which forms a crystalline phase with polar switching. This polar switching in the crystalline modification of a bent-core compound is being reported for the first time.

Results

The five-ring compound under study is derived from 2-methylresorcinol having ester linkage groups between the aromatic rings and *n*-hexadecyloxy chains as terminal moieties (Fig. 1).

It is seen from the DSC curves in Fig. 2 that two phases can be distinguished and that there are no significant differences for different heating or cooling rates. X-Ray investigations give clear evidence for the crystalline nature of the low- and high-temperature phases. The X-ray powder pattern shows several sharp reflections not only in the small angle region but also in the middle and wide-angle regions. To check the crystalline nature of the CrII phase in more detail we investigated samples which were aligned by cooling a drop of the isotropic liquid on a glass plate at different cooling rates. The different cooling rates (10 K min^{-1} and 0.5 K min^{-1}) were applied to approach the experimental conditions in the X-ray experiment to those of the optical studies (10 K min^{-1}

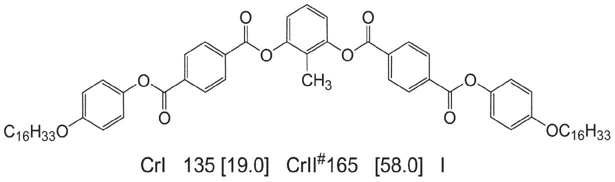

Fig. 1 Chemical structure and transition temperatures (°C) of the bent-core compound. The values in parentheses refer to the related transition enthalpies in kJ mol^{-1}. #This phase can be supercooled by about 15 K.

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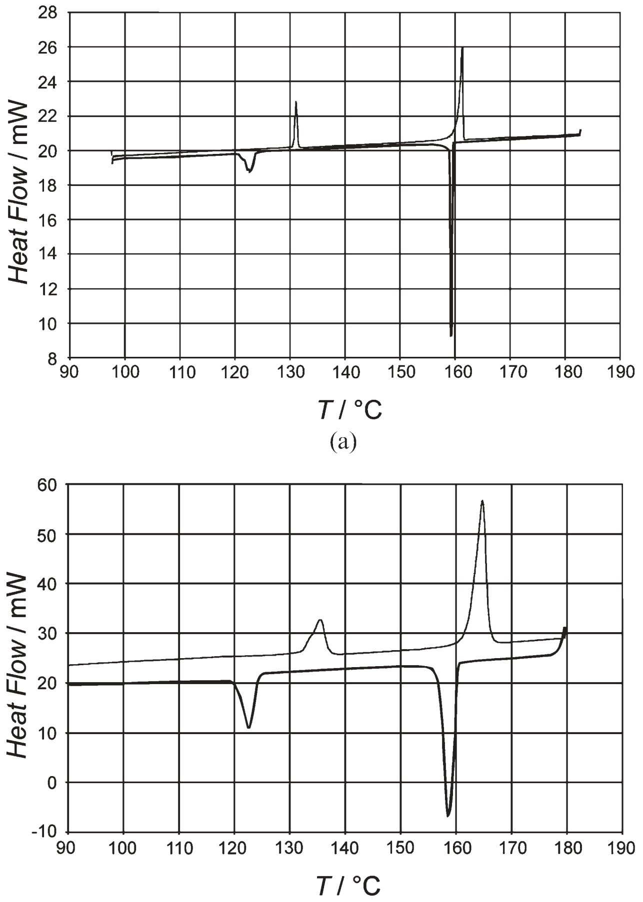


(a)

(b)

Fig. 2 DSC scans at different heating and cooling rates: (a) 1 K min^{-1} and (b) 10 K min^{-1}.

and 1 K min^{-1}) and DSC measurements (10 K min^{-1} and 1 K min^{-1}). In one case, on fast cooling from the isotropic phase a pattern of a well-developed mono-domain could be obtained which clearly demonstrates the high crystallinity of the sample (Fig. 3a).

In all other cases patterns similar to the pattern shown in Fig. 3b were obtained which were not essentially changed, neither by annealing nor by cooling the sample. The pattern again displays a lot of strong reflections in the small- as well in the wide-angle region, which characterize the phase under discussion as crystalline in nature. In the wide-angle region—in addition to the strong reflections—some diffuse scattering maxima can bee seen which point to a certain amount of disorder in the structure. The disorder is limited to short distances and does not influence the whole structure. The positions of the reflections suggest the assumption of a layer structure with a periodicity of 58 Å.

It should be noted that the transition from the high-temperature crystalline phase CrII into the low-temperature phase CrI is not only indicated by a change of the optical texture but also by the change of the X-ray scattering diagram.

On the other hand, the crystalline nature is also supported by the high enthalpy value at the transition to the isotropic phase (58 kJ mol^{-1}) whereas the clearing temperatures of the B_7 phase or columnar phases formed by bent-core compounds do not exceed 25 and 30 kJ mol^{-1}, respectively. We found that the sample of the high-temperature phase (CrII) could be slightly and irreversibly deformed by a strong shearing of the bounding glass plates.

On fast cooling the isotropic liquid, the CrII phase appears preferably as a weakly birefringent modification designated as CrIIa (Fig. 4). If the isotropic liquid is cooled very slowly (0.5 K min^{-1}) (Fig. 5a) or in the presence of a dc field (20–25 V μm^{-1}) preferably a different solid modification arises designated as CrIIb. Particularly by application of an electric field this modification adopts an unusual and exciting optical texture with colourful ribbons, circular and oval domains (see Fig. 5b).

It is remarkable that above the transition temperature to the isotropic phase (165 °C) the nucleation of this modification within the isotropic liquid can be induced by the application of a sufficiently high electric field. We found that in this way the transition temperature to the isotropic liquid can be enhanced by ≈2 K with a field of 30 V μm^{-1}. If the applied field is removed the field-induced phase disappears. The field-induced phase is retained below 165 °C on terminating the field. Since the textures of the domains on slow cooling and under the field are comparable we argue that the crystalline modification under the electric field is indeed the same as the modification obtained without field. The field-induced formation of the CrIIb modification above the melting temperature is similar to the field-induced formation of the ferroelectric SmC phase ($SmCP_F$) above the clearing temperature in some bent-core mesogens.[14,15] This effect can be interpreted by the field-induced alignment of ferroelectric clusters which already exist in the short-range order region of the isotropic liquid.[15,16]

In contrast to the weekly birefringent modification CrIIa, the modification CrIIb shows a clear electro-optical response. Above a critical field (15 V μm^{-1}) and at frequencies <5 Hz a polar switching is visible where the texture of the switched state depends on the polarity of the field. As seen in Fig. 6a and b, the colour of the circular domains changes immediately from yellow to blue and *vice versa* by the reversal of the polarity of the applied field. The texture of the switched state relaxes to a pink texture after a sufficiently long time (5–10 min), *i.e.* the colour of the circular domain in the switched state is different from that of the zero field (Fig. 6c).

The polar character of the switching is confirmed by the current response using the triangular-wave voltage method.[17] We found only one polarization current peak per half period of the triangular voltage (Fig. 7) which points to a ferroelectric switching of the CrIIb phase. The single polarization current peak was observed even at low frequencies (<0.5 Hz) and also in the modified triangular-wave method in which there will be ample time for the molecules to relax to the ground state structure. But because the texture of the switched state is very slowly changed after removing the field we believe that the ground state structure is antiferroelectric. In this context it is important to note that above 165 °C (until about 167 °C) the application of a triangular voltage (<5 Hz) gives the same current response, which indicates that the field-induced modifications above and below 165 °C are identical.

The polar switching was observed up to 15 K below the Iso–CrIIb transition temperature, at lower temperature the

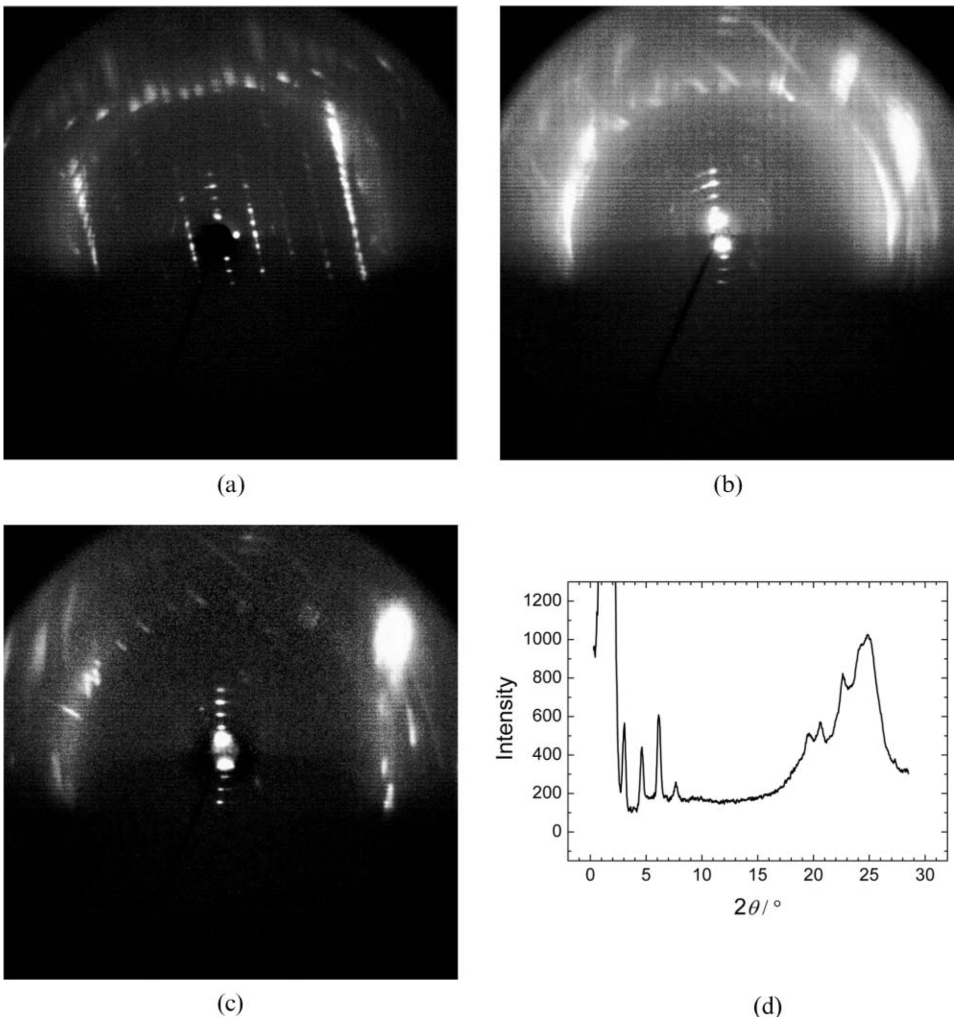


Fig. 3 (a) X-Ray pattern in the CrII phase of a sample which was cooled down from the isotropic state by 10 K min^{-1} (154 °C). (b) The pattern obtained by slow cooling, 0.5 K min^{-1} (159 °C); (c) followed by an annealing process of 20 h (d) and the related intensity *versus* 2θ profile.

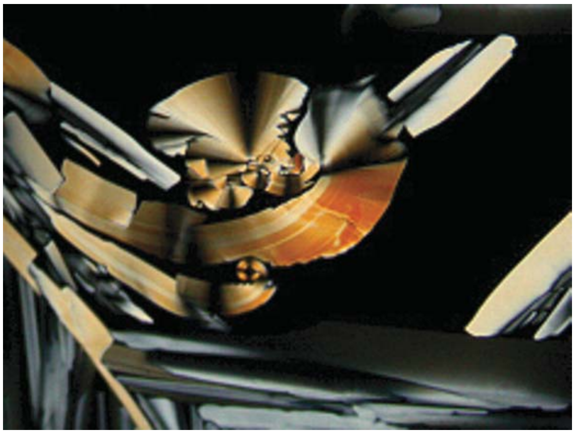
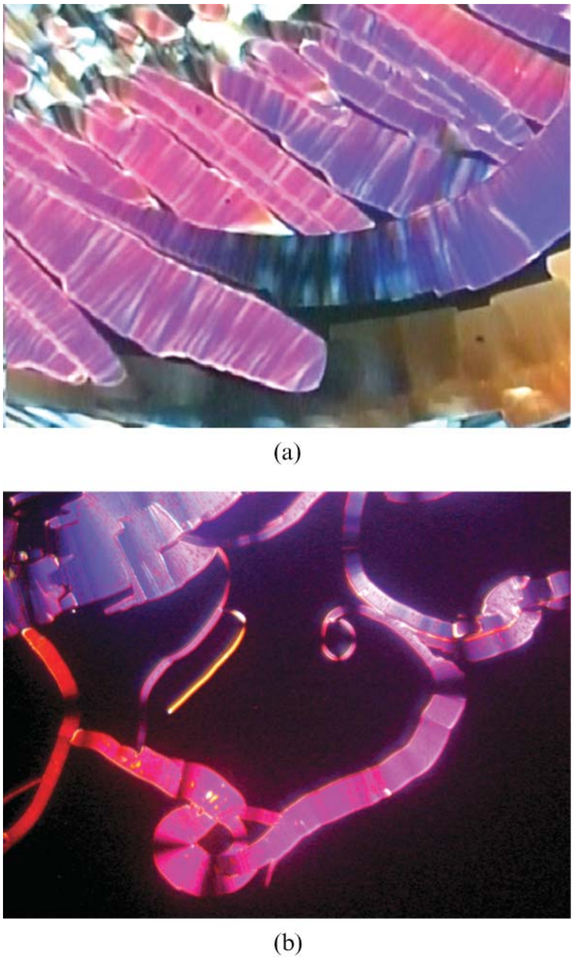


Fig. 4 Optical photomicrograph of the texture of the CrIIa modification growing on fast cooling from the isotropic phase (10 K min^{-1}).

switching of the domains as well as the polarization current peak disappear. The switching polarization P_S obtained by integrating the area under the current peak was found to be 700 nC cm^{-2}.

As mentioned before the switching process in the solid modification CrIIb can be only observed when the frequency of the applied field is below 5 Hz. It is remarkable that by application of a sufficiently high electric field (30 V μm^{-1}) below a frequency of 5 Hz the non-switchable CrIIa modification can be completely transformed into the colourful switchable modification CrIIb. If the frequency is increased to >5 Hz under the same conditions the reverse transition CrIIb → CrIIa can be realized (see Fig. 8b → c).

In order to get information about the dynamics of polar units (molecules, parts of molecules or even aggregates) dielectric measurements were performed on the crystalline modification CrII. The measurements were carried out with an alternating voltage of 1 V in a cell of 50 μm thickness (for experimental details see ref. 18). Different experimental runs were: the first during fast cooling from the isotropic liquid, the second in the same way by slow cooling and the third directly after the second on heating. In the first run no relaxation and only a decrease of the dielectric constant is observed at the Isotropic–CrII phase transition (Fig. 9a). Such behaviour is typical for a true solid. But in the second and third runs a broad and less intensive dielectric relaxation range with a

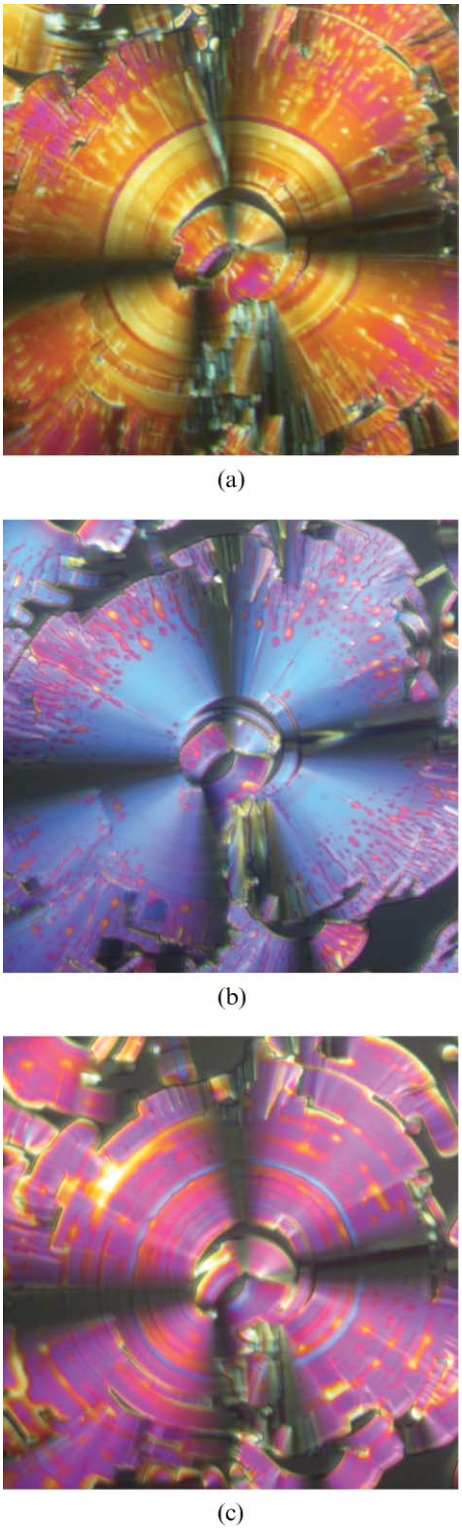

(a)

(b)

Fig. 5 Textures of the switchable solid modification CrIIb growing on slow cooling of the isotropic liquid: (a) without field and (b) in the presence of a dc field of 15 V μm^{-1}.

relaxation frequency of about 1.5 kHz was detected (Fig. 9b). The high frequency limit of the dielectric constant agrees well with that seen in the first run. Assuming that the observed dynamics is related to a slow crystallization process (two phase range, Maxwell–Wagner relaxation), then the low frequency limit of the dielectric function ε_0 should further decrease during the heating run due to faster crystallization. This is not observed. It should be emphasized that the relaxation frequency and the applied voltage (1 V in a 50 μm cell) do not agree with the frequency scale of the electro-optical experiments. Probably the linear method is sensitive to the dynamics of small polar groups whereas for the collective reorientation of the ferroelectric units a considerably higher electric field is necessary. Anyway, from the results of dielectric measurements we can argue that the sample shows two high-temperature modifications, one without dynamics and a second one in which the free volume does allow a linear response of polar units.

Now the question arises: what is the origin of the ferroelectricity (polar properties) in the CrIIb phase? We can exclude the displacive type as found for the inorganic[1] and a few organic crystals.[2–4] Unfortunately, we do not know the detailed structure of the CrIIb phase but it is reasonable to assume that the polar structure and the polar switching of the crystalline layered structure are in any way related to the polar packing of the bent molecules as known for switchable


(a)

(b)

(c)

Fig. 6 Switching behaviour of the CrIIb phase. Texture in a circular domain: (a) at −16 V μm^{-1}, (b) +16 V μm^{-1}, (c) at 0 V μm^{-1} after 10 min (temperature: 160 °C; cell gap: 6 μm).

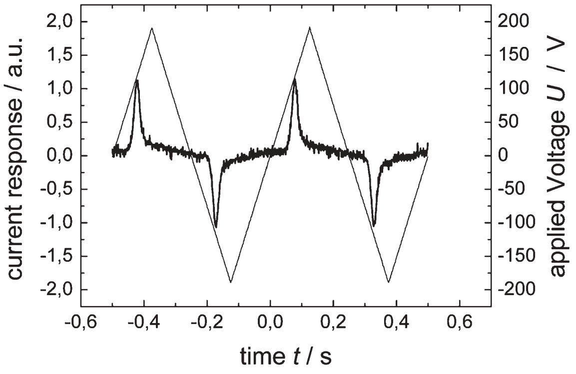


Fig. 7 Switching current response obtained in the CrIIb phase under an applied triangular wave field of 30 V µm^{-1} at 160 °C; frequency: 3 Hz.

"banana mesophases".[9–12] This assumption is based on several experimental observations.

1. In resemblance to some SmCP$_A$ phases the transition of the CrIIb phase into the isotropic liquid can be enhanced by a few degrees by applying a sufficiently high electric field. This effect can be understood if already in the isotropic liquid ferroelectric clusters in the short range exist.[15,16]

2. Furthermore, the switching polarization of the CrIIb phase was found to be of the same order of magnitude as found for "banana mesophases" (SmAP, SmCP, ColP).[12,19]

3. The nucleation on cooling the isotropic liquid and the optical appearance of the field-induced switching (also its dependence on the polarity of the field) is in a sense reminiscent of "banana phases".

At the present stage of research we are not able to present a convincing model of the polar switching in the CrIIb modification. But in this context it should be mentioned that in some solid phases flips of the aromatic rings as well as reorientation of elongated molecules around their *para* axis are–in principle–possible.[20–22] On the basis of the results of our dielectric and electro-optical measurements we can assume that in the CrIIb modification the collective motion of at least bigger parts of the molecules is possible because the field-induced change of the birefringence is relatively large. On the other hand, the optical response of the CrIIb modification is clearly different compared with polar "banana phases". We can only speculate that the arrangement of the molecules in the

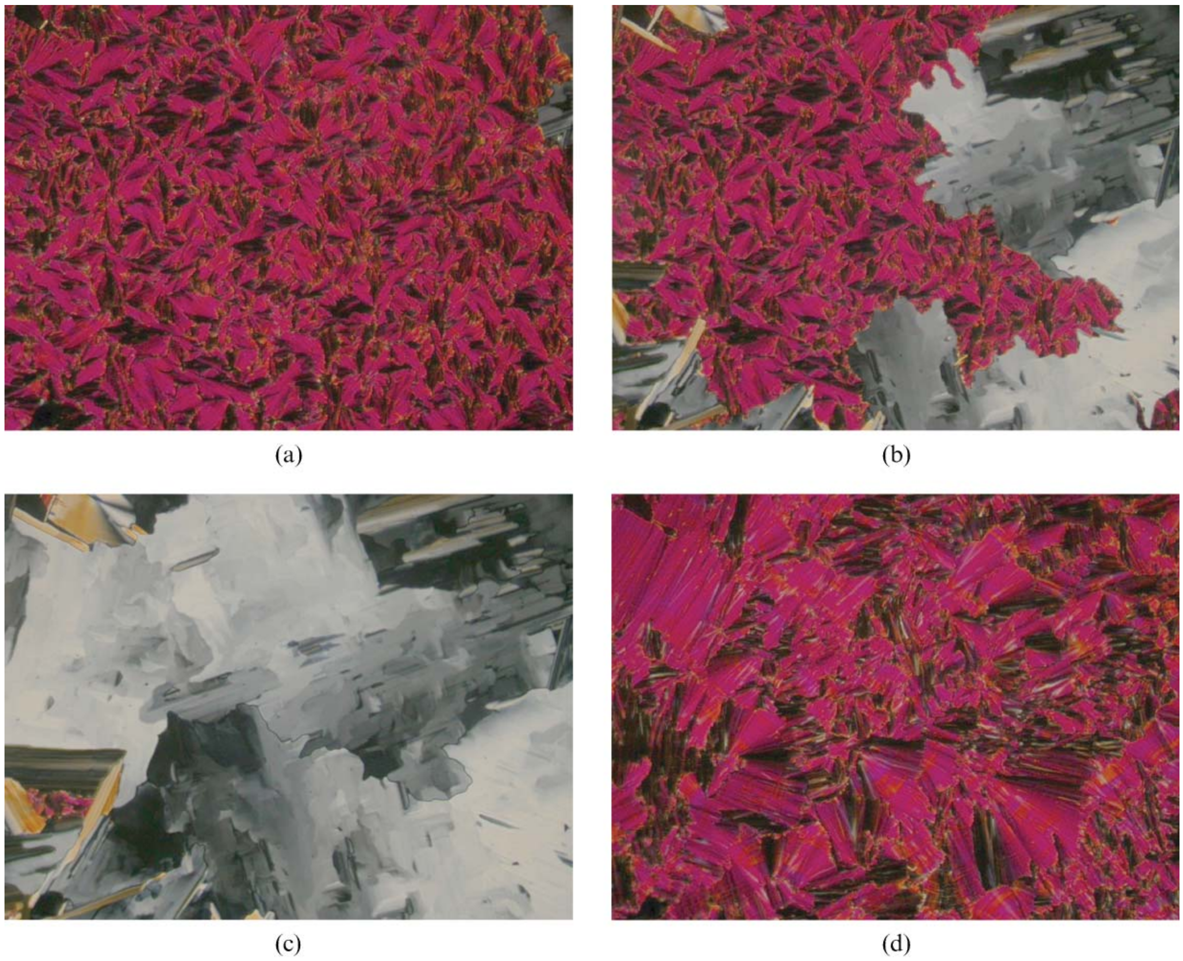

(a) (b) (c) (d)

Fig. 8 Frequency dependence of the transition of the switchable high-birefringent CrIIb modification into the non-switchable modification CrIIa at a field of 30 V µm^{-1} (temperature: 160 °C): (a) 3 Hz (CrIIb); (b) 7 Hz (after 15 s; CrIIb + CrIIa); (c) 7 Hz (after 20 s; CrIIa), and (d) again 3 Hz (after 15 s; CrIIb).

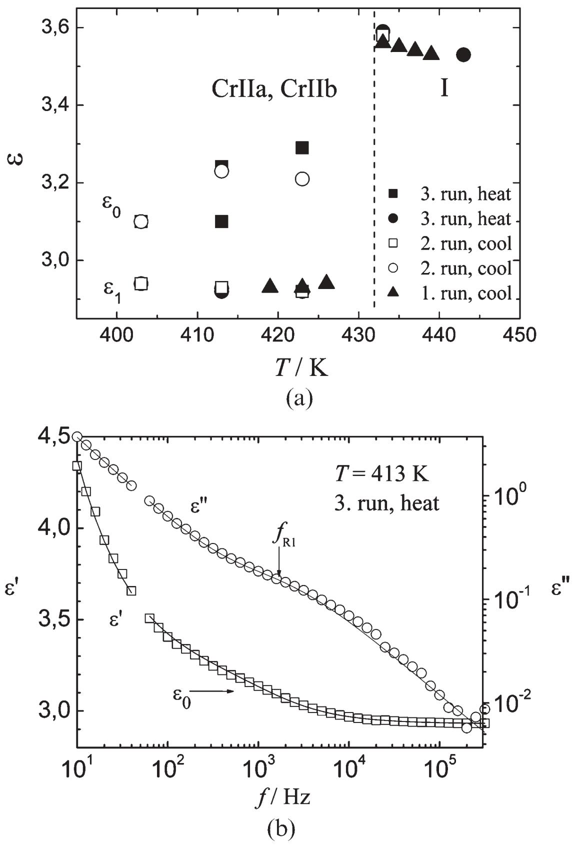


Fig. 9 (a) Limits of the dielectric function obtained from the fit to a Cole–Cole mechanism.[18] The curve of the first run is related to the CrIIa modification and the other curves correspond to the CrIIb modification. (b) The complex dielectric function curve measured for the CrIIb modification during heating (third run) and the fitted curve.

switchable CrIIb modification is more complicated than in simple "banana phases" (possibly there is not only one polar axis) which allows, nevertheless, a partial rotation of the molecules or bigger parts of them on applying an electric field.

Conclusions

In summary, the search for new ferroelectric or antiferroelectric materials is not only interesting from the basic scientific point of view but also with respect to possible practical application for example as materials with high NLO coefficients. Here we presented for the first time a new variant of crystalline organic ferroelectrics formed by bent-core molecules whereby the switching mechanism seems to be in a sense similar to that of polar "banana" mesophases.

Experimental

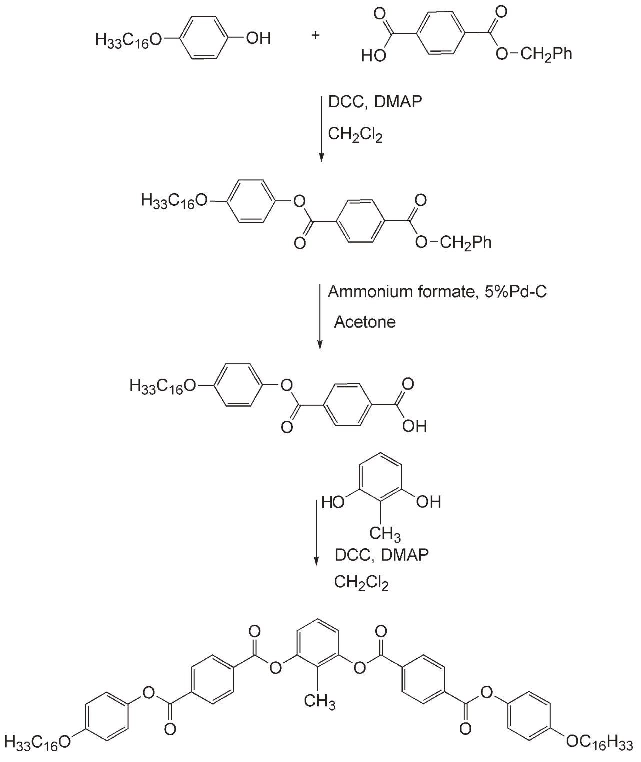
The compound was characterized by a combination of polarized light microscopy, X-ray diffraction, dielectric and electro-optical measurements. The transition temperatures and transition enthalpies were determined using a Perkin-Elmer Pyris 1 differential scanning calorimeter. The optical textures and the field-induced texture changes were examined using a polarizing microscope (Leitz Laborlux) equipped with a Linkam hotstage (THM 600/S). X-Ray diffraction measurements on powder-like samples were performed with a Guinier film camera. X-Ray studies on partially oriented samples were carried out by means of a 2D detector (HI-Star, Siemens AG). Partially oriented samples were obtained by cooling a drop of the isotropic liquid on a glass plate. Electro-optical measurements were carried out in commercial ITO cells (E. H. C. Corp.; spacing: 5 μm or 6 μm). The switching polarization was measured by means of the triangular wave voltage method.[17] Dielectric measurements were performed with a Solartron Schlumberger Impedance Analyzer SI1260 in combination with a Chelsea interface.

The synthetic path to obtain the target compound is shown in Scheme 1. The spectral and the analytical data for the compound are given below.

2-Methyl-1,3-phenylene bis[4-(4-n-hexadecyloxyphenyloxycarbonyl)benzoate]

4-(4-*n*-Hexadecyloxyphenyloxycarbonyl)benzoic acid (0.5 g; 0.1 mmol) was added to a solution of 2-methylresorcinol (0.064 g; 0.05mmol), DCC (0.23 g; 0.11 mmol) and DMAP (20 mg) in about 20 ml of dry dichloromethane. The reaction mixture was stirred for 24 h at room temperature. The solvent was evaporated, and the crude product was repeatedly recrystallised from DMF–ethanol. Yield: 0.3 g (54.0%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.32 (s, 8H, ArH), 7.33 (t, ^3J = 8.0 Hz, 1H, Ar–H), 7.17 (d, ^3J = 8.0 Hz, 2H, Ar–H), 7.11 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 4H, Ar–H), 6.93 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 4H, Ar–H), 3.95 (t, ^3J = 6.4 Hz, 4H, –OCH_2), 2.12 (s, 3H, Ar–CH_3), 1.80–1.74 (m, 4H, –CH_2), 1.52–1.41 (m, 4H, –CH_2), 1.33–1.23 (m, 48H, CH_2), 0.87 (t,



Scheme 1 Synthetic route to prepare the bent-core compound.

^3J = 6.8 Hz, 6H, CH_3); *m*/*z*: 1050 (M + 1 peak); elemental analysis: calculated for $C_{67}H_{88}O_{10}$ (%): C 76.39, H 8.42; found C 76.67, H 8.24.

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