Unusual electro-optical response of an oblique columnar phase formed by a bent-core mesogen

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Mesophases formed by bent-core mesogens have attracted special attention because they can organise into fluid phases with polar order and supramolecular chirality. In this paper, a new five-ring bent-core mesogen is presented which forms a columnar mesophase. The structure is built up by layer fragments and possesses an oblique two-dimensional lattice with a layer group of the type $p112/a$. The columnar phase can be transformed into a ferroelectric SmCP phase ($SmCP_F$) by application of a sufficiently high electric field ($25 \, V \, \mu m^{-1}$). This field-induced transition was found to be reversible. The mechanism of the polar switching depends on the frequency of the applied electric field. The switching takes place in the usual way by a collective rotation of the molecules around the tilt cone. At very low frequencies (0.1 Hz and lower), the polar switching is based on a collective rotation of the molecules around their long axes. In the latter case, the switching is accompanied by an inversion of the layer chirality.

1. Introduction

Bent-core mesogens have gained considerable importance because they are able to form new mesophases with unusual physical properties. In most cases these mesophases possess a layered structure in which the (non-tilted or tilted) molecules are packed in the bent direction giving rise to polar ordered smectic phases, i.e. smectic phases with ferroelectric or antiferro-electric properties (*1–5*). Additionally, chiral structures can occur in tilted polar smectic phases with C_2 symmetry of the layers (designated as SmCP) or C_1 symmetry (designated as SmCG) although the individual molecules are achiral (*6–8*). Depending on the structural features of the bent molecules, a mismatch of the space required by the rigid cores and the flexible alkyl chains as well as polar effects can lead to a frustration of the layer organisation resulting in columnar phases of different structure in which the columns are formed by layer fragments. In these layer fragments the molecules cannot freely rotate due to their bent shape and the sterical hindrance causes an ordering of the molecular dipole moments as in polar smectic phases.

Such a columnar phase was first observed by Watanabe et al. (*9*) in bent-core mesogens with rather short alkyl chains, and has been further investigated (*2, 10, 11*). This B_1 phase has been described as a columnar phase with a rectangular lattice. The bent direction (two-fold axis respectively polar axis) is parallel to the b axis of the lattice within the columns (i.e. in the layer fragments), that means, perpendicular to the layer normal. The structure has the symmetry of the two-dimensional space group $p2mg$ and can be characterised as a Col_r phase.

Somewhat later it was shown (*12–15*) that bent-core molecules can also pack in columnar phases with another structure type in which the polar axis is parallel to the columnar axis. In this context it should be noted that Takanishi et al. (*16*) proposed an analogous structure model to explain the electro-optical behaviour in the columnar phase of twin molecules with an odd-numbered spacer. The molecules can be tilted (Col_{ob}) or non-tilted (Col_r) within the layer fragments of such a structure, leading to the layer group symmetry $p112/a$ (monoclinic/ oblique) in the first case (because of the liquid-like order within the layer fragments, the polar axis should be a two-fold axis which is assumed to be perpendicular to the a–b plane) (*17–21*) and to $pmm2$ (orthorhombic/ rectangular) in the second case (*12–15*). The B_1 phase typically does not show any switching under electric fields. In contrast, the columnar 'banana phases', in which the polar axis coincides with the columnar axis, can show polar switching which is mainly based on a collective rotation of the molecules around their long axes. Only in exceptional cases (small tilt angle and special experimental conditions) can the switching take place by rotation of the director around the tilt cone (*13–15*). This paper presents a new bent-core mesogen, shown in scheme 1, which forms a columnar phase with an oblique two-dimensional cell. It will be shown that this columnar phase exhibits an unusual electro-optical response based on the structural features of the columnar phase.

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Cr 99 [71.4] Col$_{ob}$ 122 [65.8] Is
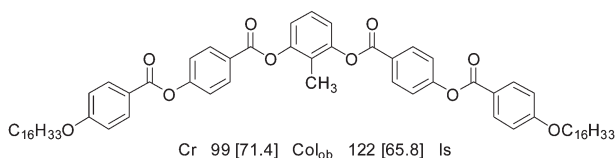
Scheme 1   Chemical structure and transition temperatures (°C) of the bent-core compound. The values in parentheses refer to the related transition enthalpies in kJ mol-1.

2.   Experimental

2.1.   *Material*

2.2.1.   2-Methyl-1,3-phenylene bis[4-(4-n-hexadecy-loxybenzoyloxy)-benzoate].

4-(4-*n*-Hexadecyloxybenzoyloxy)benzoic acid (0.5 g; 0.1 mmol) was added to a solution of 2-methylresorcinol (0.064 g; 0.05 mmol), dicyclohexylcarbodimide (DCC) (0.23 g; 0.11 mmol) and 4-dimethylaminopyridine (DMAP) (20 mg) in dry dichloromethane. The reaction mixture was stirred for 24 h at room temperature. After filtration the solvent was evaporated, and the crude product was repeatedly recrystallised from an ethanol/ethyl acetate mixture. Yield 0.41 g (39.0%).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm)=8.28 (m, 4H, Ar–H), 8.13 (m, 4H, Ar–H), 7.35 (m, 4H, Ar–H), 7.27 (t, 1H, Ar–H), 7.13 (d, 2H, Ar–H), 6.96 (m, 4H, Ar–H), 4.04 (t, ^3J=6.5 Hz, 4H, 2× –OCH$_2$), 2.11 (s, 3H, Ar–CH$_3$), 1.81–1.76 (m, 4H, 2× –CH$_2$), 1.32–1.25 (m, 48H, 24× –CH$_2$), 0.87 (t, ^3J=6.7, 6H, 2× –CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm)=164.16, 163.78, 155.58, 150.38, 132.35, 131.75, 126.68, 122.08, 121.17, 119.85, 114.52, 68.50, 31.91, 29.66, 29.62, 29.52, 29.31, 29.14, 26.00, 22.64, 14.26, 13.98; elemental analysis: calculated for C$_{67}$H$_{88}$O$_{10}$ (%): C 76.39, H 8.42; found C 75.94, H 8.38.

2.2.   *Methods*

The phase transition temperatures and transition enthalpies were determined using a differential scanning calorimeter DSC Pyris 1 (Perkin Elmer). The optical textures and the field-induced texture changes were examined using a polarising microscope DMRXP (Leica) equipped with a hot stage HT80 and an automatic temperature controller (Mettler-Toledo).

The switching polarisation was measured employing the triangular-wave voltage method (*22*). The liquid-crystalline material was loaded into commercial electro-optical cells (E.H.C.Corp, Tokyo) with a gap of 6 μm or 10 μm. The cells had 1 cm^2 indium tin oxide (ITO) electrodes coated with a rubbed polyimide layer to induce a homogeneous alignment. The cells were mounted in the heating stage of the

polarising microscope and a function synthesiser (Keithley 3910) generated the voltage of different shape.

X-ray diffraction measurements on powder-like samples were performed using a Guinier film camera (Huber Diffraktionstechnik GmbH). X-ray investigations on aligned samples were carried out with a two-dimensional detector (Siemens AG). The positions of the scattering maxima in the two-dimensional patterns were measured by the scans $I(\theta)$, χ=constant and $I(\chi)$, θ=constant where θ is the Bragg angle and χ is the angle between the scattering vector and the meridian of the pattern. The last scan was used to measure the tilt angle of the molecules with respect to an axis of the unit cell. Aligned samples of the mesophase were obtained by long annealing of a drop of the liquid crystal on a glass plate after very slow cooling of the isotropic liquid.

3.   Results

### 3.1.   *X-ray diffraction measurements*

Powder-like samples show some strong, sharp reflections in the small angle region, the *d* values of which are not multiples of each other indicating at least two-dimensional long-range order within the phase. The diffuse scattering maximum in the wide-angle region is characteristic for the liquid-like (short-range) ordered part of the structure.

The scattering diagram for a surface-aligned sample, presented in Figure 1 (a), proves the formation of a monodomain in the whole irradiated volume. Only one pair of diffuse crescents can be seen, so that the tilt direction of the molecules is synclinic. This monodomain is grown near the sample-air-interface of a drop of the sample on a glass-surface, which explains the inclined arrangement of the vectors with respect to the substrate plane (parallel to the equator of the pattern).

The reflections in the small angle region could be indexed by a two-dimensional oblique cell, according to the squared Bragg equation

$$\sin^2 \theta = \frac{\lambda^2}{4 \sin \gamma} \left\{ \left(\frac{h}{a} \right)^2 + \left(\frac{k}{b} \right)^2 - \frac{2hk \cos \gamma}{ab} \right\}. \quad (1)$$

Table 1 lists these indices and the θ values for the observed reflections. The calculated cell parameters are a=25.4 Å, b=44.7 Å and γ=106°. The angle between the direction of the molecular long axes and the axis *b* of the unit cell can be derived from the angle between the *b** axis of the reciprocal lattice, the angle γ and the position of the outer diffuse scattering (Figure 1 (b)). The molecules are tilted with respect to the *b* axis by an angle of 22°.
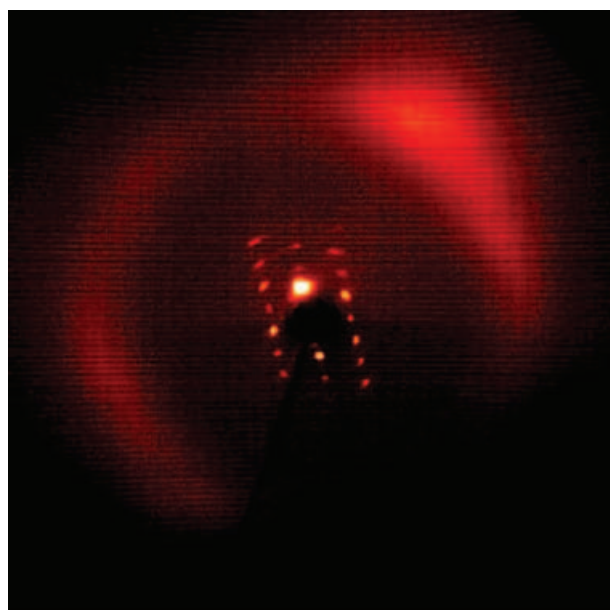
(a)
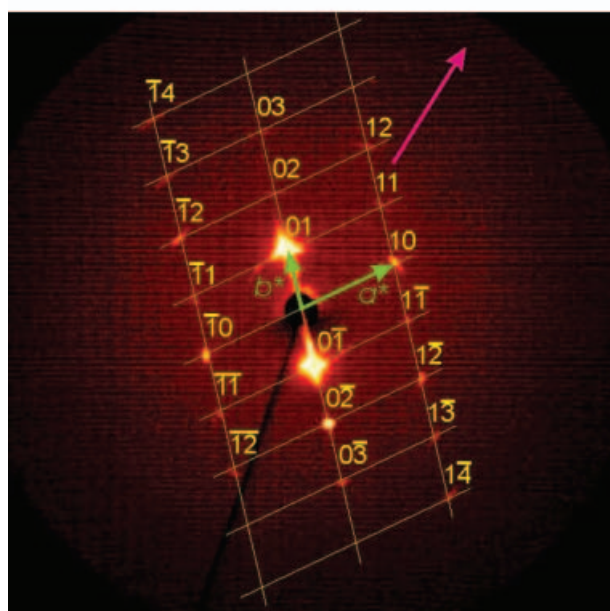
(b)

Figure 1. X-ray diffraction pattern of a well-aligned sample of the columnar phase, $T=110°C$ (a) Wide-angle scattering. (b) Small-angle scattering with indices for the observed reflections. The lines represent the reciprocal lattice, the magenta arrow illustrates the direction to the maxima of the diffuse scattering (b).

Table 1. Observed reflections with indexing and the measured and calculated values of the Bragg angle θ.

h	k	θ (measured)/°	θ (calculated)/°
0	1	1.025	1.026
0	2	2.05	2.053
0	3	3.10	3.080
1	0	1.80	1.802
1	1	2.30	2.306
1	2	3.05	3.082
1	-1	1.85	1.813
1	-2	2.425	2.330
1	-3	3.225	3.113
1	-4	4.15	4.008

An estimate of three, for the number of molecules in the cross section of the layer fragments within the Col_{ob} phase, can be given using crystal volume increments (Immirzi and Perini (23)) to calculate $V_{mol,cr}=1512.2\,\text{Å}^3$ (molecular volume in the crystal with an average packing coefficient $k=0.7$ according to Kitaigorodski (24)), $V_{mol,is}=1924.6\,\text{Å}^3$ (molecular volume in the isotropic liquid, average packing coefficient $k=0.55$), $V_{cell}=a\cdot b\cdot h\cdot\sin\gamma=5675.3\,\text{Å}^3$ (unit cell volume obtained from the lattice parameters a, b, γ and assuming a height of $h=5.2\,\text{Å}$ for a stacking in bend direction of molecules with a bend angle of $120°$), the number of molecules in a unit cell with crystal-like density according to $n_{cell,cr}=V_{cell}/V_{mol,cr}=3.8$, with liquid-like density according to $n_{cell,is}=n_{cell,cr}\cdot0.55/0.7=2.9$, and in the liquid-crystalline phase $n_{cell,LC}\approx3$ estimated as an intermediate between that in the crystalline and the liquid phase.

3.2. Polarising microscopy and electro-optical investigations

On cooling the isotropic liquid, the liquid-crystalline phase appears with a mosaic texture which indicates a columnar phase (Figure 2). If an alternating electric field is applied above a threshold $(25\,\text{V}\,\mu\text{m}^{-1}$; 10 Hz) the original texture is transformed into a texture with small fan-like domains (Figure 3 (a)). Simultaneously, a current response with two peaks per half period of the applied triangular voltage is observed (Figure 3 (b)) indicating the switching of an antiferroelectric ground state into corresponding ferroelectric states. If the field is removed a non-specific texture occurs.

On cooling the isotropic liquid in the presence of an alternating field $(\approx15\,\text{V}\,\mu\text{m}^{-1}$; 10 Hz), the columnar phase grows as well-developed mosaic domains. When just below the clearing temperature the field overcomes the threshold $(25\,\text{V}\,\mu\text{m}^{-1})$, the isotropic liquid forms at first a fan-like texture similar to that shown in Figure 3 (a). Nearly simultaneously the mosaic domains adopt the same fan-like texture. In addition, an antiferroelectric switching can be observed by current response measurements. These experimental findings are a clear hint for the field-induced transition of the columnar phase into the polar (ferroelectric) SmC phase designated as $SmCP_F$.

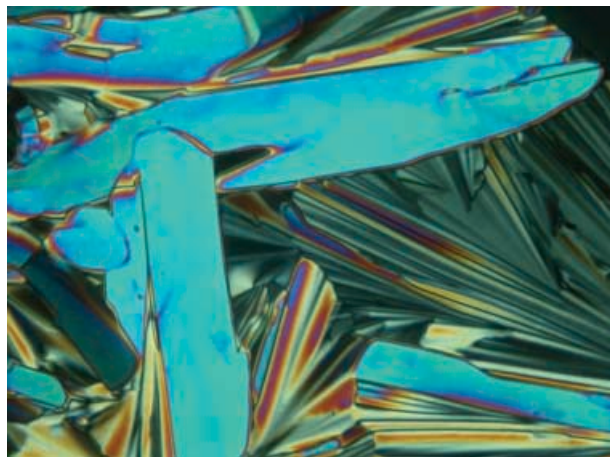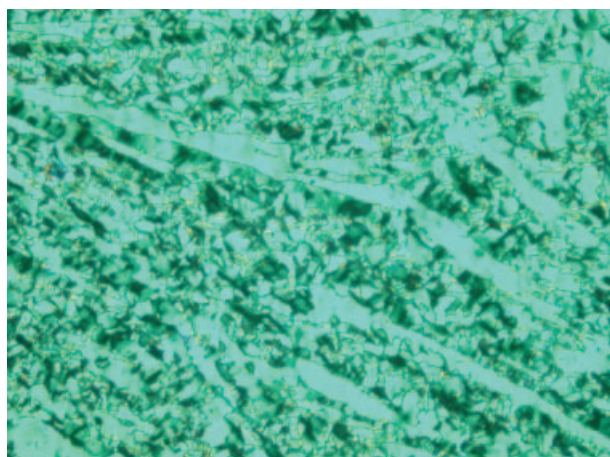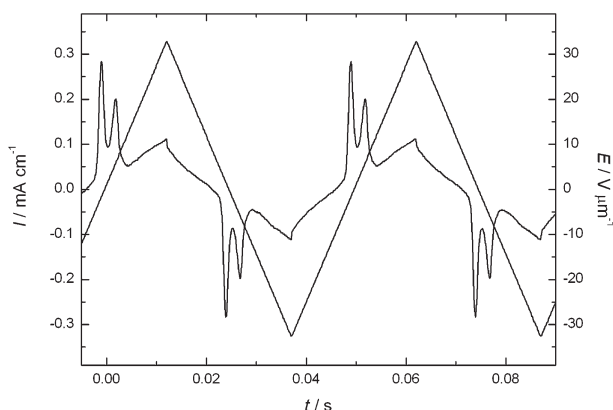If the isotropic liquid is cooled in the presence of a d.c. field above the threshold at first small circular

Figure 2. Mosaic texture of the Col$_{ob}$ phase (T=110°C).

(a)

(b)

Figure 3. (a) Fan-like texture of the field-induced SmCP$_F$ phase, T=112°C and E=30 V µm^{-1}. (b) Switching current response of the SmCP phase obtained by applying a triangular wave voltage, E=±32 V µm^{-1}, P_S=370 nC cm^{-2}.

domains nucleate already above the clearing temperature which coalesce to the texture which is shown in Figure 4, that is the mesophase is stabilized above the liquid crystal-isotropic transition temperature by means of the electric field. The extinction crosses of the circular domains are tilted by nearly 45° with respect to the crossed polarisers indicating a tilt angle of molecules in the smectic layers (or layer fragments). If the field is removed very slowly the extinction crosses as well as the birefringence do not markedly change. The same effect is observed if an alternating field of very low frequency is applied (0.01 Hz). In contrast, if the field is removed very quickly the extinction crosses rotate for a short time in a position parallel to the crossed polarisers and simultaneously the birefringence becomes very low. However, after a few seconds the birefringence again increases and the extinction crosses rotate into the original tilted position.

4. Discussion

It was mentioned in the introduction that the Col$_r$ phases formed by bent-core molecules are mostly insensitive to electric fields (*2, 9–11*). There are cases where the Col$_r$ (*13–15, 19, 20*) and the Col$_{ob}$ phase (*17, 20*) show polar (ferroelectric or antiferroelectric) switching. It is also possible that a non-switchable Col phase can be transformed into a SmCP$_F$ phase. Such electro-optical behaviour was first observed for a Col$_r$ phase (*25*). In this case this transition was found to be reversible, i.e. the columnar structure is recovered upon removal of the field. But there are also cases where the field-induced transition Col$_r$ to SmCP$_F$ and Col$_{ob}$ to SmCP$_F$ (*26*) is irreversible. Interesting bent-core compounds were reported by
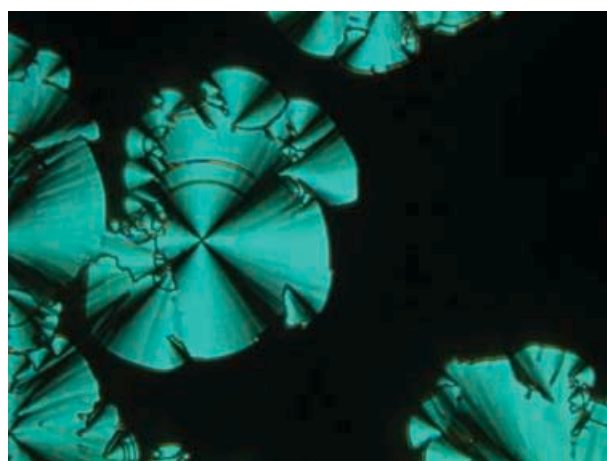

Figure 4. Texture with circular domains obtained by slow cooling in presence of a d. c. field of E=25 V µm^{-1}. T=123°C.

Bedel et al. (*18*) which exhibit a Col$_{ob}$ phase of unusual structure. It consists of SmCG double-layer fragments and shows antiferroelectric switching. Also, it can be transformed into a SmCP$_F$ phase at sufficiently high electric fields.

It follows from the X-ray diffraction measurements for the bent mesogen presented here that the mesophase is a columnar phase with an oblique two-dimensional cell; the molecules in the layer fragments adopt a uniform tilt direction (synclinic tilt). The properties of the structure obtainable by X-ray diffraction can be described by the two-dimensional space group $p2$. But the knowledge gained from the electro-optical investigations proves that this model is definitely not sufficient. The postulated model has to reflect the polar character of the structure. Therefore the symmetry of the structure is characterised by one of the 80 layer groups (*12*). To realise the antiferroelectric ground state several arrangements of neighbouring layer fragments are possible each of them possessing a different symmetry (Figure 5) (*3, 27*). In each case the unit cell area, i.e. one of the above calculated lattice parameters a or b, must be doubled to give the unit cell of the appropriate layer group. These different arrangements cannot be distinguished using our experimental techniques.

The application of a sufficiently high electric field ($25\,V\,\mu m^{-1}$; 10 Hz) leads to a transition of the Col$_{ob}$ phase into the ferroelectric SmCP phase (see Figure 6) which can be recognised by a characteristic fan-like texture. It should be noted that unambigious evidence for a field-induced transition from the columnar to a smectic phase can only be obtained using a X-ray diffraction technique under electric field which is unfortunately above our present experimental capabilities. But we found that both phases could also be distinguished by the different behaviour in the electric field. If, during the slow nucleation of the mosaic
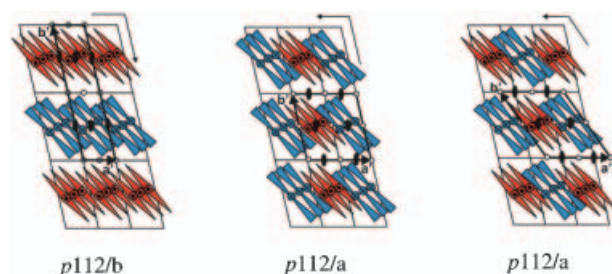

Figure 5. Three possible periodical arrangements of neighbouring layer fragments in the Col$_{ob}$ phase with symmetry elements and corresponding layer groups. (Thin lines: two-dimensional oblique lattice as obtained from X-ray diffraction, heavy lines: unit cell of the layer group with axes a' and b', red and blue molecular symbols represent the two opposite orientations of the polar axes).
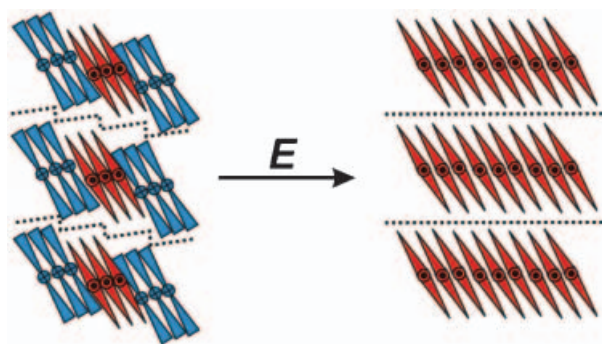

Figure 6. Schematic representation of the field induced transformation from the Col$_{ob}$ phase into the SmCP$_F$ phase (right).

domains of the columnar phase within the isotropic liquid (where both phases coexist), an electric field is applied above the threshold ($25\,V\,\mu m^{-1}$) at first regions of a fan-like texture appear within the isotropic liquid which show antiferroelectric switching. Afterwards, the mosaic texture gradually transforms also into the switchable fan-like texture of the SmCP phase. This is caused by an interesting electro-optical effect: in the isotropic liquid near to the clearing temperature the mesophase can be stabilised, corresponding to a field-induced enhancement of the clearing temperature. In the compound under discussion this enhancement was found to be 3 K for an electric field of $30\,V\,\mu m^{-1}$. The effect of this field-induced stabilisation of a SmCP phase above the clearing temperature is not unusual for bent-core mesogens and can be explained by an alignment of polar clusters which exist already in the isotropic liquid (*28*).

The experimental finding that the formation of the switchable fan-like texture begins in the isotropic liquid and later in the mosaic domains is an important argument for the existence of distinct mesophases. The field-induced enhancement of the clearing temperature is also obvious when a d.c. field greater than $25\,V\,\mu m^{-1}$ is applied during the cooling from the isotropic liquid. In this case the mesophase appears above the clearing temperature and forms preferably circular domains (Figure 4) in which the smectic layers are arranged cylindrically around the centre of the domains. The tilt of the extinction crosses, at about $45°$ with respect to the crossed polariser directions, gives evidence for a synclinic SmCP phase (SmC$_S$P$_F$) with a tilt angle of $45°$.

When the electric field is removed very slowly (or if the frequency of the applied field is very low) the extinction crosses do not change whereas the birefringence slightly decreases. Also by the reversal of the sign of the field the extinction crosses remain unchanged. Since a polar current response is

detectable by application of a triangular field we can assume that in the SmCP phase the mechanism of the polar switching is based on the collective rotation of the molecules around their long axes (*13–15, 17, 18, 20, 29–33*).

The dependence of switching mechanism of SmCP phases on the frequency of the applied field has been described (*29, 30*). This switching mechanism is accompanied by a reversal of the handedness of the smectic layers. This also means that under these experimental conditions the columnar phase exhibits a paramorphotic texture in which the synclinic smectic layers remain also in the two-dimensional arrangement of the layer fragments in the columnar phase. It is obvious that in this way the transition from Col_{ob} to SmCP and vice versa requires a minimal structural reorganisation (see Figure 6).

The situation is a little bit more complicated when the applied field is switched off very fast (or if the frequency of the applied electric field is greater 5 Hz). In this case the extinction crosses rotate for a short time in the position parallel to the crossed polarisers. This indicates a change from synclinic into anticlinic layers which takes place by the rotation of the director around the tilt cone. The rotation of the extinction crosses is hard to recognise because simultaneously the texture becomes dark. The low birefringence of the dark texture is the consequence of the anticlinic arrangement with a tilt angle near to $45°$ which corresponds to an orthoconic situation (*34*).

It is remarkable that this state is not stable. After a few seconds the extinction crosses come back into the original tilted position and the birefringence again increases. This indicates that the anticlinic packing of the molecules in the layer fragments of the columnar phase is unfavourable.

To summarise, the phase structure and the electro-optical properties of a new bent-core mesogen derived from 2-methylresorcinol were studied. X-ray diffraction measurements prove an oblique columnar phase. Application of a sufficiently high electric field leads to a transition of the Col_{ob} phase into a $SmCP_F$ phase. The process is reversible. The mechanism of the polar switching depends on the frequency of the applied field that means a collective rotation around the molecular long axis is observed at very low frequencies and the rotation around the tilt cone at higher frequencies. Furthermore, an enhancement of the clearing temperature of 3K was found on applying an electric field of $30\,V\,\mu m^{-1}$ to the isotropic liquid.

Acknowledgment

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