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Field dependent switching angle of a columnar pyrene

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The switching behaviour of 1,3,6,8-tetrakis-((*S*)-2-(heptyloxy)propanoyloxy)pyrene was studied near room temperature in a monotropic columnar phase. The switching angle (optical tilt angle) increases linearly with the applied electric field from 0° to *c.* ± 10° at $\pm 0{\cdot}35°/(\mathrm{V}\,\mu\mathrm{m}^{-1})$, then rapidly increases to its upper limit of 22°. The electric polarization is roughly proportional to the switching angle with a maximum value of $110\,\mathrm{nC\,cm}^{-2}$ at high field strengths. At field strengths up to $10\,\mathrm{V}\,\mu\mathrm{m}^{-1}$, a voltage and temperature independent 0 to 90 per cent switching time of *c.* 650 μs was measured. The observations are explained in terms of deformation and unwinding of an intracolumnar helix.

1. Introduction

Recently, Chen and Scherowsky synthesized phenanthrene derivatives which, when suitably mixed, have an electro-optically switchable columnar phase [1]. The switching angle of these materials varies linearly with voltage at low enough field strengths. We now communicate our study of a chiral columnar pyrene exhibiting a similar behaviour. The compound investigated is 1,3,6,8-tetrakis-((*S*)-2-(heptyloxy)propanoyloxy)pyrene which we abbreviate as P4m*10 (see figure 1).

2. Synthesis

P4m*10 was assembled by reductive esterification of 3,8-dihydroxypyrene-1,6-quinone with (*S*)-*O*-heptyllactic acid chloride. The quinone was synthesized in three steps following the procedure of Vollmann *et al.* [2] (first, 1,3,6,8-tetrabromination of pyrene, second, treatment with sulphuric acid to give 2,7-dibromo-3,8-dihydroxypyrene-1,6-quinone and third, debromination with sodium hydroxide and zinc). The alkyl lactic acid chloride was obtained by etherification of ethyl lactate with heptyl iodide in the presence of silver oxide, basic saponification and treatment with thionyl chloride [3].

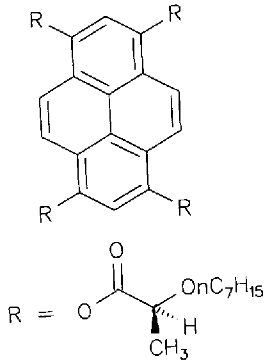

Figure 1. Molecular structure of P4m*10.

The finely powdered quinone (1 g) was suspended in 30 ml of dry THF and 10 ml of dry pyridine. Zinc dust (3 g), a trace of 4-*N*,*N*-dimethylaminopyridine and 6 g of the acid chloride were added and the mixture was stirred for 4 h. Then the mixture was diluted with 100 ml of dichloromethane, filtered and washed with 10 per cent aqueous HCl. The aqueous phase was washed with 4 × 100 ml of dichloromethane, and the organic phases were united and dried over sodium sulphate. The solvent was evaporated, and the residue was chromatographed on silica gel with a 3 : 1 mixture of hexane and ethyl acetate, recrystallized from isopropanol, chromatographed again and recrystallized again. Yield: 0·4 g of P4m*10. ^{1}H NMR ($CDCl_3/(CH_3)_4Si$, 90 MHz): $\delta = 0{\cdot}85$ (t, 6 Hz, 12 H), 1·3 (m, 32 H), 1·65 (m, 8 H), 1·7 (d, 7 Hz, 12 H), 3·65 (m, 8 H), 4·4 (q, 7 Hz, 4 H), 7·8 (s, 2 H), 8·05 (s, 4 H).

3. Experimental

Although we found that 1,3,6,8-tetrakis-*n*-alkanoyloxypyrenes are not mesomorphic (we prepared the nonanoyl, decanoyl and dodecanoyl derivatives, with melting points of 97, 100, and 86°C, respectively), P4m*10 exhibits a monotropic columnar phase appearing on slow cooling below 34°C. On slow heating, the mesophase clears at 39°C with a transition enthalpy of $1{\cdot}4\,\mathrm{J\,g}^{-1}$ or $1{\cdot}3\,\mathrm{kJ\,min}^{-1}$ (DSC, $3\,\mathrm{K\,min}^{-1}$). On cooling from the isotropic liquid through the mesophase at $3\,\mathrm{K\,min}^{-1}$, the crystalline phase forms at −7°C as

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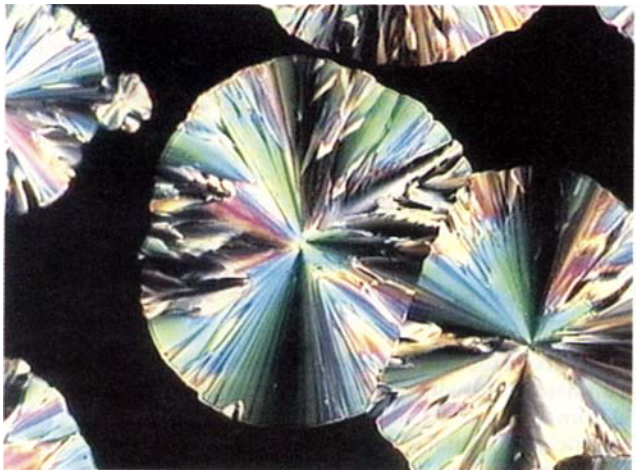


Figure 2. Flowers growing from the isotropic liquid on cooling, 10 μm cell. Field of view c. 600 μm × 800 μm.

detected by DSC. At room temperature in 4 or 10 μm thick cells, the substance usually crystallizes after several hours or overnight. The needle-shaped crystals melt at 47°C with an enthalpy of 26 J g^{-1} or 24 kJ mol^{-1}.

Between crossed polarizers, the texture of the mesophase that appears when the isotropic liquid is cooled consisted of characteristic flower-like domains (see figure 2), in which the columns form circles around the flower centre and are parallel to the glass [4]. The majority of the flowers were rich in domain boundaries and defects, exhibiting a multitude of colours in 10 μm samples between crossed polarizers. However, some of the flowers were largely free of boundaries and defects, and the birefringence colour of these well aligned areas was a uniform second order green in 10 μm samples between crossed polarizers. This green colour in 10 μm cells corresponds to a refractive index anisotropy of c. 0·07 [5]. The refractive index was maximal when the electric vector of the light was normal to the columns. Sheared samples, where the columns are oriented parallel to the shear direction [6], also showed a mixture of many colours.

When a triangular alternating electric field is applied, the four orthogonal extinction brushes originating from the flower centres rotate back and forth around these centres. This rotation is counter-clockwise when the voltage on the side of viewing changes from negative to positive, in accordance with the spontaneously ferroelectric columnar phase of another compound bearing the same chiral side chain [3]. Some cells were stable up to a field strength of 50 V μm^{-1}, but in general electrical break-down occurred around 30 V μm^{-1}. In 4 μm cells that were submitted for hours to a rectangular alternating voltage of 200 V (corresponding to 50 V μm^{-1}, a field strength that we could not apply to 10 μm cells, because the limit to the voltage was 200 V), a uniform birefringence colour (deep yellow) was established and the number of defects decreased in the course of time.

We measured the field dependence of the optical tilt angle at room temperature (26°C) using 4 μm cells, applying a triangular electric field of ± 50 V μm^{-1} with a frequency of 0·06 Hz and making video prints of a well-aligned flower at fixed time intervals. At zero field, the dark extinction brushes coincide with the polarizer cross, indicating that on average the normals to the molecular aromatic cores are parallel to the alignment of the columns [4]. The optical tilt angle increases linearly with the applied field at a rate of c. 0·35°/(V μm^{-1}) before it reaches 10° near 30 V μm^{-1} and then increases rapidly to 22°. Beyond 40 V μm^{-1}, no further increase in this angle was observed. The data plotted in figure 3 show a slight 'hysteresis' which is due to the finite switching time (see below).

In 4 μm cells, the birefringence colour changes from pale yellow to deep yellow during the steep rise of the tilt angle. At field strengths of c. 30 V μm^{-1}, the switching of the black brushes takes place in two steps. Most of the rotation occurs inperceptibly fast, but then the brushes continue to rotate at a speed low enough to be followed by eye, before the rotation ends after about a second. Whereas this slower part of the process seems to be negligible at low voltages, it becomes important when the field strength approaches 30 V μm^{-1}. No slow second part of the switching process is observed above 40 V μm^{-1}. Also, there is no slow component when the voltage is turned off.

Switching times were measured with a photomultiplier for a 20 μm thick sample uniformly oriented by shearing. Applying a rectangular alternating field and setting the polarizer directions at + 22·5° and − 67·5° from the shear direction, we measured the times for a 0 to 90 per cent change of the photomultiplier current. This method yields only the time for the fast part of the switching process, as

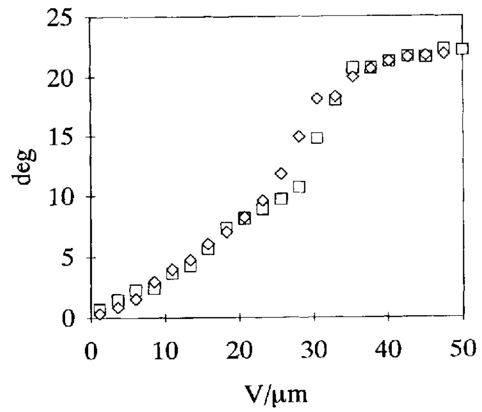


Figure 3. Optical tilt angle versus electric field strength: (□) increasing field strength, (◇) decreasing field strength, 26°C, triangular voltage, ± 12 (V μm^{-1})/s.

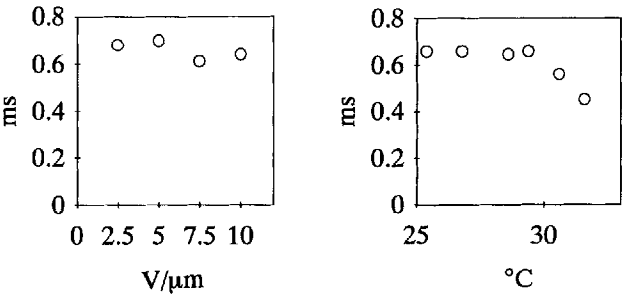


Figure 4. Optical 0–90 per cent switching time versus electric field strength (left, 26°C) and temperature (right, $12{\cdot}5\,\mathrm{V}\,\mu\mathrm{m}^{-1}$).

the very slow change of the multiplier current caused by the second part was not resolved. At field strengths below the steep rise of the optical tilt angle, a switching time of c. 650 μs was observed (see figure 4). At higher fields, the change of the birefringence colour during the switching made exact determinations of 0 to 90 per cent times impossible. However, comparing the times for a 50 per cent change of the photomultiplier current, we found switching at $50\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ to be roughly five times slower than below $25\,\mathrm{V}\,\mu\mathrm{m}^{-1}$.

Above 30°C, the texture disintegrates quickly when a field is applied, making it difficult to measure switching angles and times. Traces of isotropic liquid seem to be present at these temperatures near the clearing point. At low field strengths, neither the switching time nor the switching angle varied noticeably with temperature in the narrow range from 25 to 30°C where systematic measurements were made (see figure 4 and 5).

The current produced by a triangular field shows two polarization peaks while the field passes from -50 to $+50\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ or vice versa (see figure 6). The base line between these peaks is higher than at very high field strengths, indicating a continuous flow of polarization current between the two maxima. Both peaks begin at c. $34\,\mathrm{V}\,\mu\mathrm{m}^{-1}$, the maxima being at 29 and $39\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ for decreasing and increasing field strength, respectively. With increasing frequency, the peaks broaden with respect to voltage, but still begin at roughly the same field strength. At higher frequencies, the peak at increasing field strength is broader than the peak at decreasing field strength (see figure 6 (*b*)). Both peak areas correspond to $60\,\mathrm{nC}\,\mathrm{cm}^{-2}$, regardless of frequency, and the area between peaks that is bordered by the actual current and the baseline, representing capacitive currents, corresponds to c. $100\,\mathrm{nC}\,\mathrm{cm}^{-2}$ ($= 2 \times 50\,\mathrm{nC}\,\mathrm{cm}^{-2}$) (see figure 6 (*a*)). Accordingly, the maximum polarization is c. $110\,\mathrm{nC}\,\mathrm{cm}^{-2}$. No peaks are observed between voltage reversals when a rectangular field is applied.

With rectangular alternating voltages, we measured the polarization at field strengths up to $20\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ by integrating the exponentially decaying current peak that follows each field reversal. As this current includes also a part not caused by the polarization of the mesophase, but by the cell capacitance, we subtracted the value obtained with the same sample at the same temperature (26°C) when the measurement was repeated after crystallization. We assume that this capacitive current is roughly independent of the phase of the substance. The polarization is found to increase linearly with the field strength at a rate of $1{\cdot}6\,(\mathrm{nC}\,\mathrm{cm}^{-2})/(\mathrm{V}\,\mu\mathrm{m}^{-1})$ (see figure 7). Dividing this by the rate of increase of the optical tilt angle in the linear range, $0{\cdot}35^\circ/(\mathrm{V}\,\mu\mathrm{m}^{-1})$ (see above), we obtain $4{\cdot}6\,(\mathrm{nC}\,\mathrm{cm}^{-2})/^\circ$. The ratio of rates agrees well with the ratio of the maximum values of polarization and optical tilt angle, $110\,\mathrm{nC}\,\mathrm{cm}^{-2}$ and 22°, which is $5\,(\mathrm{nC}\,\mathrm{cm}^{-2})/^\circ$.

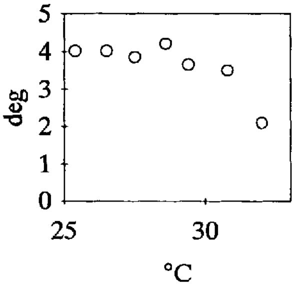
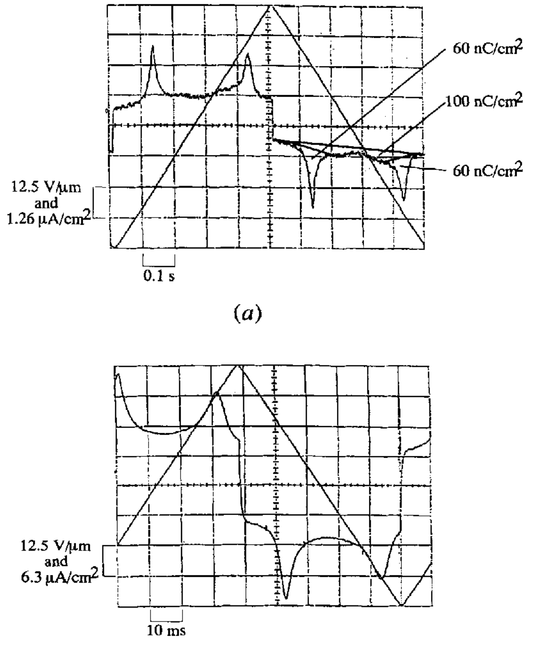


Figure 5. Switching angle versus temperature, $12{\cdot}5\,\mathrm{V}\,\mu\mathrm{m}^{-1}$.



(*a*)

(*b*)

Figure 6. Oscilloscope traces of triangular voltage ($100\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ peak to peak) and current density versus time, 26°C; (*a*) 1 Hz, (*b*) 10 Hz.

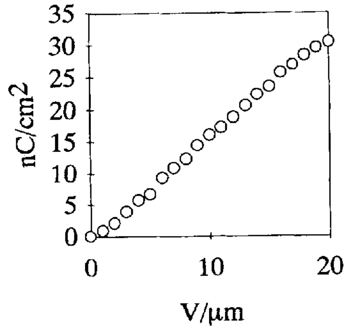


Figure 7. Polarization versus electric field strength, 26°C.

Especially in 10 μm cells near 20 V μm^{-1}, another weak effect was sometimes observed. During the slow and comparatively very weak second part of the switching about very small additional angles, the initially dark extinction brushes become pale, a process starting from the rims and the centres of the flowers, and faint tangential defect lines appear in the deeply coloured areas of the flowers. After completion of the rotation of the extinction brushes, these defects disappear again. The effect is not visible in well oriented uniformly green areas, but only in some areas of reduced birefringence.

4. Discussion

4.1. *Mechanism of field-induced ferroelectric polarization and biaxiality*

There are three possible mechanisms which, in principle, can explain the linear and non-hysteretic increase of ferroelectic polarization and optical tilt angle with the strength of an electric field. These are, first the electroclinic effect, second, the field-induced rotation of columns of tilted molecules opposed by elastic restoring forces and, third, the deformation of a helical arrangement of the molecules within the columns.

All of them require the disc-like molecules to be chiral and are optimal when the columns are parallel to the conducting glass plates of the sample cells. The first mechanism and the third are known from smectic liquid crystals. We will show next why the first and the second are unlikely candidates in the present case.

In the case of the electroclinic effect, an electric field parallel to the layers of S_A generates a collective tilt of the typically rod-like molecules, resulting in a structure like S_C with an optical tilt angle. The columnar analogue would be a tilt of the normals to the disc-like molecules away from the centre line of the columns. For columns parallel to the electrodes, the tilt direction, the field and the centre line are orthogonal. The electroclinic effect is improbable in the present case because the sensitivity of the optical tilt angle to field strength is too high. In smectics, such a sensitivity is possible only near a thermal phase transition from S_A to S_C^*. The nearness implies a strong dependence of the induced tilt on temperature, while there is little or no dependence in our system. Moreover, we did not observe any field dependence of the optical tilt angle within either phase of a spontaneously ferroelectric columnar liquid crystal which on the other hand, was electrically switchable in its high and low field phases [3].

An optical tilt angle proportional to the electric field could also arise from a field-induced rotation of spontaneously polarized columns which is opposed by elastic restoring forces of their two-dimensional lattice. In the antiferroelectric arrangement of the columns needed in our case, the dipole moments of the columns neutralize each other when no electric field is applied. A field-induced rotation of the columns that is weak enough not to transform their lattice may also occur in truly ferroelectric columnar phases, but can be excluded, like the electroclinic effect, for the only known example of such a system [3]. One could argue that the elastic restoring force may be smaller in other ferro- or antiferro-electric phases with more nearly circular columns. The cross section of the columns of P4m*10 should, in fact, be close to a circle, since the maximum optical tilt angle of 22° is rather low. However, a nearly circular cross-section also facilitates twist within the columns, which underlies the third mechanism. Another reason to doubt the rotation of the columns is the wide range between ± 10° over which the optical tilt angle is proportional to the electric field strength—almost half the total range bounded by ± 22°.

The steep rise, nearly a jump, of the optical tilt angle at the limit of its proportionality to voltage is likely to represent the final, rapid unwinding of a helix. Alternatively, it could indicate a field-induced phase transition to a ferroelectric state of the columnar liquid crystal. Because of this ambiguity, the jump by itself does not discriminate between the three mechanisms. The same lack of discrimination applies to the field independence of the switching time. However, a detailed analysis will show that the third mechanism provides a rather consistent description of the experimental data.

A single column, i.e. a stack of tilted chiral disc-like molecules, is capable of forming a helix that exhibits two rotations of equal pitch. The tilt direction of the molecules will be twisted around the central line of the column and, at the same time, this line will form a helix in three-dimensional space (see figure 8). An attractive packing of straight columns with a rotating, slightly elliptical cross-section is the trigonal lattice. Apart from the rotation (which makes the ordering three-dimensional), the lattice of columns is hexagonal in this case, since the unit cell is made up of three twisted columns differing in 120° phase shifts. Such a lattice should minimize the mutual obstruction of the not entirely cylindrical columns. Interestingly, the competition of the three equally spaced phase angles should suppress a spatial helix, thus keeping the columns

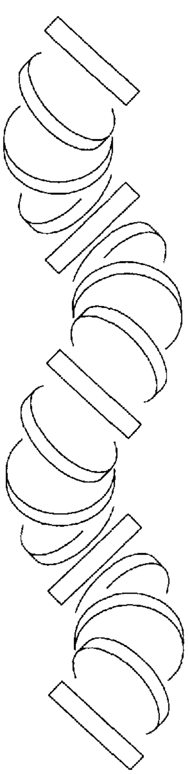


Figure 8. Sketch of a helical column of disc-like chiral molecules. The spatial helix, but not the twist of the molecular tilt, may be suppressed in the liquid crystal.

practically straight. Straight columns appear to be a prerequisite for rapid switching. They also permit us to use, as a first approximation, the theory of helix unwinding developed for S_C^* phases. [7–9].

4.2. *Comparison with theory*

Let us now analyse our data in terms of the third mechanism, assuming a hexagonal lattice of straight twisted columns. The theory of the S_C^* phase predicts the critical electric field strength of helix unwinding to be [7–9]

$$E_c = \frac{\pi^2}{16}\frac{kt_0^2}{P_{max}}. \qquad (1)$$

Here $t_0 = 2\pi/p$ is the spontaneous twist, p is the pitch of the helix, P_{max} is the ferroelectric polarization of the unwound liquid crystal, and k is an elastic modulus with the dimension of force. Inserting $P_{max} = 110\,\mathrm{nC\,cm^{-2}}$ as measured, $E_c = 30\,\mathrm{V\,\mu m^{-1}}$ as relevant to the 'jump' of the optical tilt angle (see figure 3), and assuming $k = 5 \times 10^{-12}\,\mathrm{N}$ (typical of nematic liquid crystals), we obtain from equation (1) the pitch $p = 61$ nm. This value is about three times less than the smallest pitches measured for S_C^*. However, a strong twist seems natural, because molecules with flat aromatic cores and four pronounced chiral groups are stacked on each other in the columns. Incidentally, this kind of stacking may also increase the elastic modulus k and, thus, the estimate of the pitch p.

A central formula in the theory of helix unwinding in S_C^* [7–9] is the first integral of the torque balance,

$$\frac{d\alpha}{dz} = \pm\sqrt{\left(C^2 - \frac{2P_{max}E}{k}\cos\alpha\right)}, \qquad (2)$$

where C is a constant with the dimension of inverse length. The angle α denotes the local direction of the ferroelectric dipole moments of the tilted chiral molecules. It vanishes where the dipole moments are parallel to the electric field. Both the dipole moments and the field are parallel to the smectic layers, while the coordinate z is the normal to the layers. The theory predicts that the main effect of weak electric fields is a distortion of the helix at almost constant pitch. Only when E approaches E_c as given by equation (1), does the pitch rise rapidly and finally diverge. In the range of almost constant pitch, the angular distribution function $f(\alpha)$ of the molecular dipole moments can be obtained from a first order expansion of equation (2) for $C = t_0$. The result is [8]

$$f(\alpha) = 1 + \frac{P_{max}E}{kt_0^2}\cos\alpha, \qquad (3)$$

with $f(\alpha)$ satisfying

$$\frac{1}{2\pi}\int_0^{2\pi} f(\alpha)\,d\alpha = 1.$$

The distribution function (3) leads directly to the ferroelectric polarization as a function of field strength in the range of proportionality. From the integral

$$P = P_{max}\frac{1}{2\pi}\int f(\alpha)\cos\alpha\,d\alpha$$

and equation (1) one obtains

$$P = \frac{\pi^2}{32}P_{max}\frac{E}{E_c} = 0{\cdot}31P_{max}\frac{E}{E_c}.$$

The relationship agrees fairly well with the experimental data of figure 3 which together with $E_c = 30\,\mathrm{V\,\mu m^{-1}}$ give 0·41 for the numerical factor.

On the basis of the theory for S_C^*, it is also possible to derive a formula for the linear rise of the optical tilt angle with electric field strength. For this purpose, it is convenient to approximate the dielectric tensor of a uniformly tilted columnar liquid crystal by an isotropic part ε_{is} and a much smaller and negative uniaxial part ε_{ax} parallel to the direction of the core normal [3]. Using a right-handed x, y, z coordinate system with z parallel to the columns and y parallel to the applied field, we need the elements ε_{zz}, ε_{xx} and ε_{zx} of the optical dielectric tensor. For the twisted phase at zero field strength we have

$$\left.\begin{aligned} \varepsilon_{zz} &= \varepsilon_{is} + \varepsilon_{ax}\cos^2\vartheta, \\ \varepsilon_{xx} &= \varepsilon_{is} + \tfrac{1}{2}\varepsilon_{ax}\sin^2\vartheta, \\ \varepsilon_{zx} &= 0, \end{aligned}\right\} \qquad (4)$$

where ϑ is the polar angle that the core normals make with the z axis. A weak electric field affects to first order only ε_{ZX}. Replacing $f(\alpha)$ by the phase shifted distribution function

$$g(\alpha) = 1 + \frac{P_{\max}E}{kt_0^2}\sin\alpha,$$

and using

$$\varepsilon_{zx} = \frac{1}{2\pi}\int \varepsilon_{ax}\cos\vartheta\sin\vartheta\sin\alpha\, g(\alpha)\, d\alpha,$$

we find

$$\varepsilon_{zx} = \frac{1}{2}\frac{P_{\max}E}{kt_0^2}\varepsilon_{ax}\cos\vartheta\sin\vartheta.$$

The optical tilt angle χ is one of the solutions of

$$\frac{\cos\chi\sin\chi}{\cos^2\chi - \sin^2\chi} = \frac{\varepsilon_{zx}}{\varepsilon_{zz} - \varepsilon_{xx}}.$$

Linearizing the left-hand side of this equation, we obtain for small χ

$$\chi = \frac{1}{2}\frac{P_{\max}E}{kt_0^2}\frac{\cos\vartheta\sin\vartheta}{\cos^2\vartheta - \frac{1}{2}\sin^2\vartheta}.$$

Assuming $\vartheta = 22°$ and inserting equation (1), we arrive at

$$\frac{\chi}{\vartheta} = 0{\cdot}35\frac{E}{E_c}.$$

The numerical factor read from the experimental data in figure 7 is 0·45.

Modelling the columnar liquid crystal on S_C^* implies that the final state at $E > E_c$ is uniformly tilted, the tilt angle of the core normals being 22° in our system. However, we do not know whether the high field phase into which the twisted state transforms at $30\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ has this simple structure or, perhaps, another with unequally tilted columns. If the assumption of one column per unit cell of the two-dimensional lattice is correct, the dielectric anisotropy, i.e. the difference between the largest and the smallest dielectric constant in the z, x plane, should be $\Delta E|_{\text{high field}} = \varepsilon_{ax}$ at $E > E_c$, and (see equation (4)) $\Delta E|_{\text{zero field}} = \varepsilon_{ax}\cos^2\vartheta - \frac{1}{2}\varepsilon_{ax}\sin^2\vartheta$ at $E = 0$. The ratio of the two quantities is, for $\vartheta = 22°$, $\Delta E|_{\text{high field}}/\Delta E|_{\text{zero field}} = 1{\cdot}27$. The same ratio should apply to the birefringences, because of $|\varepsilon_{ax}| \ll \varepsilon_{is}$. A preliminary measurement of the birefringences, based on the primitive method of colours [5], showed the ratio to be 1·5 or slightly less. This seems to support the simple structure, since all others should give ratios below 1·27.

The electro-optical switching time of $650\,\mu\mathrm{s}$ in the twisted state refers to a 90 per cent adjustment of the helix to a voltage change in the range of weak deformations. The corresponding relaxation time of an exponential time dependence, $\tau = 280\,\mu\mathrm{s}$, allows us to calculate the rotational viscosity γ of the tilt director by means of the formula

$$\tau = \frac{\gamma p^2}{4\pi^2 k},$$

well known from cholesteric and S_C^* liquid crystals. Combination of this equation with (1) to eliminate p^2/k yields

$$\gamma = \frac{16}{\pi^2}E_c P_{\max}\tau.$$

Inserting $E_c = 30\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ and $P_{\max} = 110\,\mathrm{nC\,cm}^{-2}$, in addition to $\tau = 280\,\mu\mathrm{s}$, one arrives at $\gamma = 15\,\mathrm{kg\,ms}^{-1} = 150$ Poise. The result is a hundred times larger than typical values of the analogous rotational viscosity in S_C^*. A relatively high viscosity may be expected because of the comparatively large size of the disc-like molecules in the columnar phase. However, the magnitude of the actual difference is hard to understand and may point to some special effects in columnar liquid crystals.

The two peculiarities observed in electro-optical switching, the slow component around $30\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ and the accompanying fading of the extinction brushes, were noted at rising field strength only. Therefore, they seem to indicate that unwinding the helix is more difficult than winding it up. This asymmetry is known from S_C^* and can probably be explained as follows. A strongly deformed helix will exert little torque on a barrier opposing its unwinding, i.e. the increase of its pitch, since it resembles a sequence of nearly non-interacting inversion walls. In contrast, the unwound state will exert a relatively large torque on a barrier to helix formation. Although the slow effect takes place after most of the transformation is finished, the differences between the two directions of switching may still be substantial enough to make slow switching visible only at rising field strength. The temporary fading of the extinction brushes points to an enhanced scattering that depolarizes the transmitted light. The scattering could be a consequence of disorder in the twisted columnar state concerning the phase angles of the columns. It is unclear why it was seen only in some poorly aligned regions of the columnar state.

5. Conclusions

The pyrene investigated in the present work is very similar to the dibenzopyrene which we studied earlier [3].

The molecules differ only by the number of carbon rings, four versus six, and the number of identical side chains, four versus eight, attached to the aromatic cores. Not surprisingly, the smaller molecule has its columnar state at lower temperatures (clearing point: 39°C) than the larger one (clearing point: 115°C). It seems also natural that the molecular tilt angle in the columns increases with the ratio of the number of chains to the number of carbon rings, i.e. the area of the aromatic core. However, an increase from 22° to 44° [3] is; perhaps disproportionate.

Since both molecules are fairly circular discs, normal cross-sections through a column should be circular in the absence of tilt, but will become elliptic as the molecules are tilted. The eccentricity, in turn, appears to control whether or not twist of the tilt direction is preferred at zero electric field. Evidently, the columns can assume their spontaneous twist only if they do not too much obstruct each other through their elliptic cross sections rotating with the twist.

The present study shows that the 'deformed helix ferroelectric effect' and the unwinding of the helix occur in a columnar liquid crystal. Within experimental accuracy the new material obeys the theory developed for ferroelectric smectic liquid crystals. However, our columnar liquid crystal switches more slowly, by up to a factor of 100, than typical ferroelectric smectics. It will be interesting to find out the reason for this difference. The structure of the twisted columnar phase, representing a three-dimensional order, is possibly rather complex and remains to be determined.

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Note added in proof

A mistake was made when measuring the optical switching time because the input resistance of the photomultiplier was too high. Correct measurements show the true 0 to 90 per cent switching time to be *c.* 50 μs (instead of 650 μs). This yields a rotational viscosity of 12 poise (instead of 150 poise). All other observations and interpretations remain unchanged.

We thank Daniel Krüerke and Mario Müller for assisting us in finding the fault and correcting it.

References

[1] Scherowsky, G., and Chen, X., 1994, *Liq. Crystals*, **17,** 803.
[2] Vollmann, H., Becker, H., Corell, M., and Streeck, H., 1937, *Justus Liebigs Annalen der Chemie*, **531,** 1.
[3] Bock, H., and Helfrich, W., 1995, *Liq. Crystals*, **18,** 387.
[4] Frank, F. C., and Chandrasekhar, S., 1980, *J. Phys., Paris*, **41,** 1285.
[5] Patzelt, V., 1950, *Das Mikroskop und seine Nebenapparate* (Verlag G. Fromme and Co.).
[6] Itoh, I., Tanaka, A., Fukuda, F., and Miyamoto, T., 1991. *Liq. Crystals.*, **9,** 221.
[7] (a) Ostrovskiy, B. I., Rabinovich, A. Z., Sonin, A. S., and Strukov, B. A., 1978, *Zh. éksper. Teor. Fiz.*, **74,** 1748. (b) Ostrovskiy, B. I., and Chigrinov, V. G., 1980, *Kristallogr.*, **25,** 560, (c) Ostrovskiy, B. I., Rabinovich, A. Z., and Chigrinov, V. G., 1980, *Advances of Liquid Crystal Research and Applications*, edited by L. Bata (Pergamon Press), p. 469.
[8] Beresnev, L. A., Chigrinov, V. G., Dergachev, D. I., Poshidaev, E. P., Fünfschilling, J., and Schadt, M., 1989, *Liq. Crystals*, **5,** 1171.
[9] Blinov, L. M., and Chigrinov, V. G., 1994, *Electrooptic Effects in Liquid Crystal Materials* (Springer-Verlag).