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New chiral discotic triphenylene derivatives exhibiting a cholesteric blue phase and a ferroelectrically switchable columnar mesophase

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We have synthesized a number of new achiral and chiral triphenylene derivatives bearing laterally substituted phenylene units in the side chains. Their polymorphism includes the first reported discotic blue phase of a pure compound and a ferroelectrically switchable columnar mesophase.

Introduction

Chirality is known to have a major influence on the material properties of liquid crystals. It is responsible for the cholesteric twist and eventually the appearance of cholesteric blue phases. It is also essential for the presence of a spontaneous polarisation in ferroelectric liquid crystals. These observations are well established for calamitic liquid crystals.

In the last decade it was demonstrated that discotic materials may show many of the exciting properties that result from the presence of chirality such as cholesteric helix inversion,[1] discotic blue phases[2] and ferroelectricity in tilted columnar mesophases[3,4] as well.

However, it has been difficult to find suitable materials that exhibit these effects. This is demonstrated by the fact that discotic blue phases have only been observed in binary mixtures[2] so far. Moreover, it took over ten years to find a material and experimentally verify Prost's prediction[5] of ferroelectricity in tilted columnar mesophases and even today there are only a very few other examples.[6–8]

Triphenylene derivatives are easily achievable and have been used successfully for basic studies and application,[9] but there is, as yet, no ferroelectric columnar triphenylene derivative. Based on work published by Goodby *et al.*,[10,11] we have synthesized a series of chiral and achiral triphenylene derivatives bearing phenylene units in the side chain and different lateral polar and apolar substituents.

Results and discussion

Polymorphism

Phase identification was carried out by polarised microscopy; the temperature was controlled by a Linkam TMS90 hotstage. Additionally, the phase transition temperatures and enthalpies were recorded by differential scanning calorimetry (Perkin-Elmer DSC7). All but one of the compounds presented exhibit columnar mesophases (see Fig. 1 and Table 1). While Goodby *et al.* found that substitution of a hydrogen in the lateral phenyl groups by X = methyl, ethyl or isopropyl groups lowers the clearing temperature in the same achiral triphenylene system by up to 20 K, due to steric effects,[10,11] we found that substitution by a strongly polarising substituent such as a chlorine atom[12] or a nitro group leads to a considerable increase in the clearing temperature by more than 80 K with respect to the unsubstituted material (compounds **1** and **2**). Substitution by sterically very demanding groups may, however, completely suppress the formation of a mesophase *e.g.* compound **4**.

For chiral derivatives, the same effect was observed: the clearing temperature of the methoxy substituted compound **6** is higher by 17 K than the clearing temperature of the unsubstituted compound **5** (see Fig. 2). Substitution by a chlorine atom (compound **7**) leads to a clearing point more than 80 K higher than that of the unsubstituted material. Apparently, the polarising power of these substituents plays a more significant role on the mesophase formation than steric demands.

Discotic cholesteric and blue phase

To our knowledge compound **5** is the first example of a pure chiral discotic material to exhibit a cholesteric blue phase. The phase transitions N*–BP and BP–Iso could not be resolved in our DSC experiments (Fig. 2)—this has been difficult even in calamitic systems studied so far.[13]

Selective reflection spectra were recorded by a Photoresearch PR-703A diode array spectrometer mounted on a microscope operating in reflection mode. In the blue phase texture of compound **5**, only one blue phase modification was observed and it was found to be right-handed. We mainly found single crystals reflecting right circularly polarised green light. This probably originates from the (200) reflection of a [001] oriented body-centred cubic (bcc) lattice structure. A few single crystals reflecting red light, which may be due to the (110) reflection from [111] oriented bcc single crystals, were also found (see Figs. 3 and 4). The phase appeared to be a BP_DI phase with a lattice constant of approx. $a = 340$ nm.

The reflections of red circularly polarised light may be accounted for by transmission through [111] oriented BP_DI single crystals in combination with reflection by the lower glass

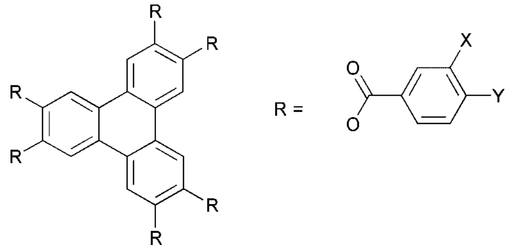

Fig. 1 Triphenylene derivatives substitution pattern.

Table 1 New materials, phase sequences and transition temperatures. The exact nature of the columnar phases is, as yet, not established. Both enantiomers of **6** have identical transition temperatures within 1 K

Compound	X in Fig. 1	Y in Fig. 1	Phase sequence
1	Cl	$OC_{10}H_{21}$	Col >300 Iso? (see Ref. 12)
2	NO_2	$OC_{10}H_{21}$	Col >300 Iso?
3	OCH_3	$OC_{10}H_{21}$	Col 265 Iso
4	$OC_{10}H_{21}$	$OC_{10}H_{21}$	Cr 79 Iso
5	H	$OC^*H(CH_3)C_6H_{13}$	Cr 161 Col 213 N* 216 BP 220 Iso
6	OCH_3	$OC^*H(CH_3)C_6H_{13}$	Cr 120 Col 237 Iso
7	Cl	$OC^*H(CH_3)C_6H_{13}$	Col >300 Iso?

substrate. According to the selection rules, no Bragg reflection will appear on the (111) set of planes but will occur on (110) planes in the direction of 35.26° with respect to the C_3 axis which is parallel to the incident light.[14] The wavelength of the laterally scattered light is $\lambda(110) = 2\,n\,a/\sqrt{3}$ according to Bragg's law (n being the mean refractive index). Since $\lambda(200) = n\,a$, the ratio of the two wavelengths is $2/\sqrt{3} \approx 1.155$, which—considering imperfect orientation of the single crystals—is in good agreement with the observed ratio $\lambda(110)/\lambda(200) = 1.175$.

Detailed studies of the blue phase lattice structure by application of the Kossel method are difficult to carry out due to the high temperature range in which it occurs.

Contact preparations established a continuous miscibility of the cholesteric phase of **5** with two achiral discotic nematics: a radial pentayne (hereafter abbreviated to La0, structure see Fig. 5) and a triphenylene derivative ($X = H$, $Y = OC_8H_{17}$, Cr 145 Col 158 N 225 Iso, *cf.* Destrade *et al.*[15]). As expected, the blue phase disappeared at lower concentrations of the chiral component.

While the mixtures with the triphenylene derivative showed a monotonic variation of the cholesteric pitch *vs.* concentration, a helix inversion occurred at a certain concentration and temperature in the binary mixtures of compound **5** with the pentayne derivative La0. The helical pitch measured in a mixture with low concentration of **5** was left-handed as opposed to pure **5** which was right-handed (see Fig. 5). Obviously, the helical twist in this system is strongly dependent on the interaction of guest and host molecules. Under certain conditions the helix is even suppressed which leads to a helix inversion.

Ferroelectric columnar mesophases

Among the chiral materials **5**, **6**, and **7**, only compound **6** was found to be electrooptically switchable. The DSC curves of compounds **5** and **6** are given in Fig. 2.

The response of the columnar mesophase of **6** to external electric fields was typical for ferroelectric materials. Samples were prepared in commercially available ITO cells from E.H.C. or home-made shear-aligned cells. By means of the Diamant bridge setup, we observed the typical hysteresis in the electrical answer to an applied sinusoidal wave (see Fig. 6). Unfortunately, the spontaneous polarisation P could not be measured reproducibly. This may have been due to ionic impurities present in the sample. From shear-aligned samples, we observed the typical bistable switching (see Fig. 7).

The switching angle was determined from "Maltese cross" texture observations of the columnar liquid crystal sandwiched in commercially available ITO cells (E.H.C. Co., Japan): Photographs were taken at positive and negative dc fields and the switching angle was determined from the direction of the extinction brushes. The tilt θ (half the switching angle) was found to be approx. 24° independent of field and temperature below approx. 205 °C. Above this temperature it was found to vary linearly with the electric field (see Fig. 8).

We filled a test cell with the two enantiomers of compound **6** by capillary action in the isotropic phase from opposite ends of the cell. This way we obtained a contact preparation in the cell, so we could observe the components under identical conditions and found that the switching process in the columnar phase of **6** is clearly related to chirality: The apparent rotation of Maltese crosses after field reversal is opposite in enantiomeric compounds (clockwise *vs.* counterclockwise).

In order to determine optical response times, we constructed shear-aligned cells from ITO coated glass substrates. By shearing the sample manually during cooling from the isotropic to the columnar phase, we obtained well-aligned samples. Transmission between crossed polarisers was recorded by a storage oscilloscope *via* a photomultiplier. Optical response times $\tau_{10\text{–}90}$ (10–90% transmission) were of the order of milliseconds with a minimum of 30 µs just below the clearing temperature. In the low temperature range the optical response time was proportional to the reciprocal field strength (see Fig. 9). This behaviour is common for SmC* phases[16] but different from a previous observation in a columnar liquid crystal.[17] The temperature dependence was characterised by an Arrhenius-type behaviour (see Fig. 10) with an apparent activation energy of approx. 150 kJ mol^{-1}. The slope decreased slightly above 205 °C. This coincides with the change between bistable and continuous switching and may result from a phase transition.

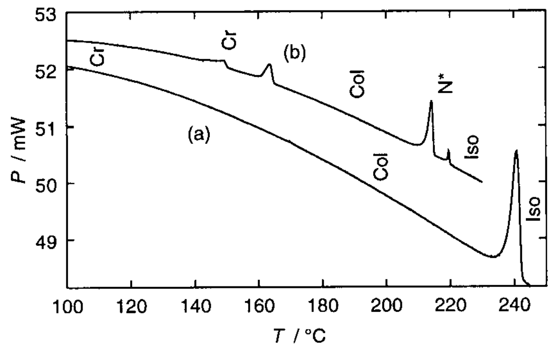

Fig. 2 DSC curves of compounds (a) **6** and (b) **5** recorded at 3 K min^{-1}. The blue phase of **5** could not be resolved in this experiment.

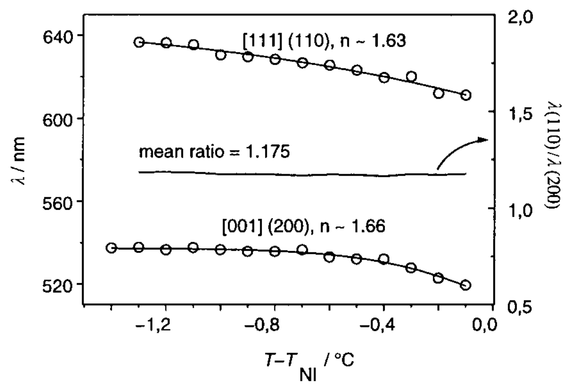

Fig. 3 Maximum wavelength of the selective reflection of BP single crystals of **5** at normal incidence (200) and 45° incidence (110).

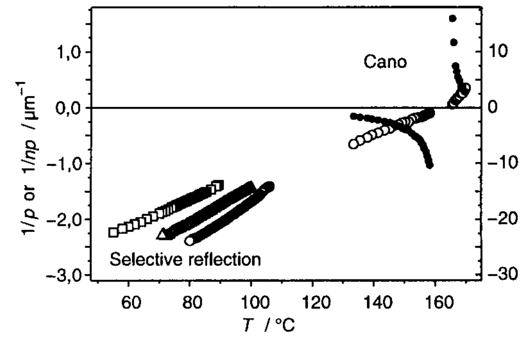

Fig. 4 Temperature dependence of the cholesteric pitch (closed symbols) and reciprocal pitch (open symbols) of different mixtures of **5** (□ 30 wt%; △ 50 wt%; ○, ●, 60 wt%) with La0 determined from selective reflection (*np*) and pitch measurements with the Cano method[21](*p*) respectively.

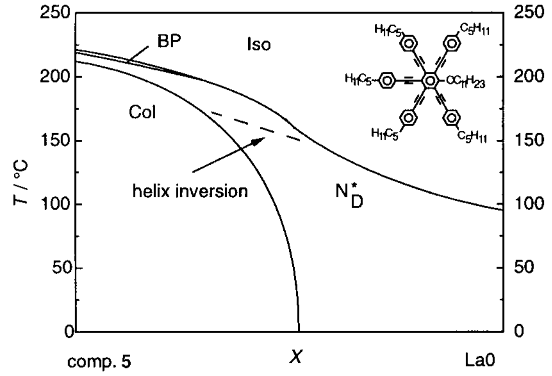

Fig. 5 Schematic phase diagram observed in a contact preparation of the chiral compound **5** and an achiral discotic nematic pentayne. The helix inversion was not observed when we substituted the pentayne host with a nematic triphenylene derivative.

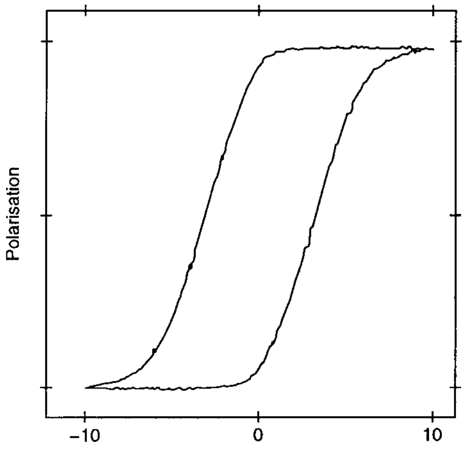

Fig. 6 Hysteresis of polarisation *versus* applied field of compound **6** measured by means of the diamant bridge setup at 175 °C and 15 Hz.

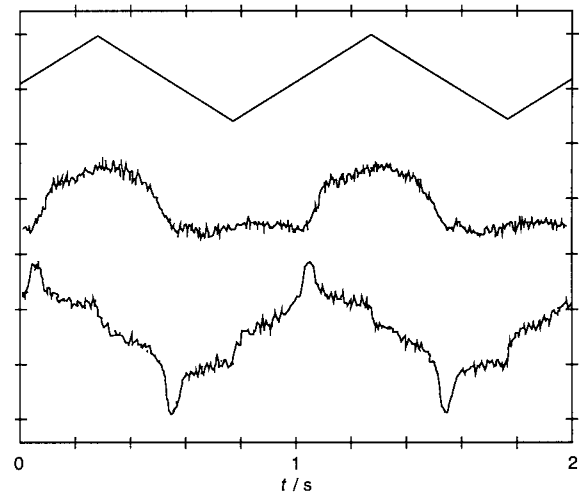

Fig. 7 Oscilloscope traces of the response of a shear aligned cell filled with compound **6** to a triangular electric field: Oscilloscope traces of the electric field (top, ±10 V µm^{-1}), transmission of white light between crossed polarisers (middle) and current through the cell (bottom) at 175 °C.

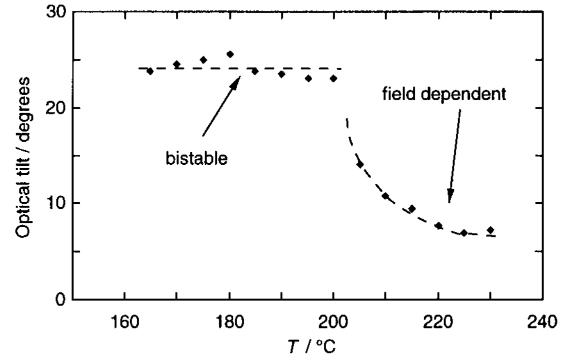

Fig. 8 Temperature dependence of the optical tilt of compound **6** at constant electric field of 10 V µm^{-1}. Dashed lines are guides for the eye.

Dielectric spectra were recorded in a frequency range between 5 Hz and 13 MHz by means of a Hewlett Packard 4192A impedance analyser. Sample preparation was identical to that for the tilt measurements. This way, we observed the relative permittivity perpendicular to the director. In chiral smectic liquid crystals, a divergence of the relative permittivity is observed at the phase transition between the continuously switchable paraelectric SmA and the ferroelectrically switchable SmC* phase.[18] However, this behavior was not observed here.

We observed two relaxation processes in the columnar phase (see Fig. 11): Due to the conductivity of the sample, one of them was only detected close to the phase transition to the isotropic phase, the other one occurred at lower temperatures. Both could be suppressed by application of a low dc bias voltage. The relaxation times were not affected by the bias voltage.

Both the electrooptic response time and the dielectric relaxation time depend on viscosity. For the ferroelectric switching process and the Goldstone mode in the SmC* phase the following eqns.[19] (1) and (2) describe the viscosity γ:

$$\gamma = \frac{\tau_{10\text{–}90}PE}{1.76\sin^2\theta}\ \text{(electrooptic)} \qquad (1)$$

and

$$\gamma = \frac{1}{4\pi\varepsilon_0}\cdot\frac{P^2}{\theta^2\cdot\Delta\varepsilon\cdot f_{\text{relax}}}\ \text{(dielectric)} \qquad (2)$$

We tentatively applied these equations to our data in order to obtain an estimated value for the spontaneous polarisation P and a preliminary assignment of one of the observed dielectric modes to the switching process: taking the experimental data at 175 °C for the higher frequency dielectric mode, we got a value of approx. $P = 10^4$ nC cm^2. Since the low frequency mode was only observed at high temperature, we had to take the data at 230 °C and obtained a value of approx. $P = 20$ nC cm^{-1}.[2] This is in the typical range of values for ferroelectrically switchable liquid crystals. If there is a Goldstone-like mode in the system, it should be the low frequency mode. Since it is based on assumptions originally made for smectic phases, this result is to

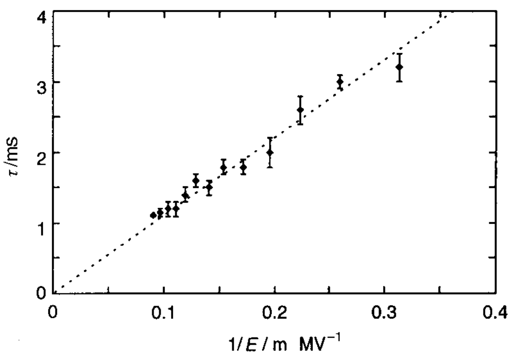

Fig. 9 Dependence of the optical response time on the reciprocal field strength of compound **6** at 175 °C.

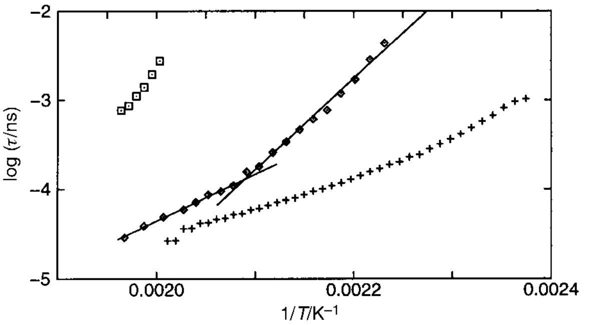

Fig. 10 Arrhenius plot of the optical response time (◇) and the dielectric relaxation times (+, □) *versus* the inverse temperature (compound **6**, 10 V μm^{-1}).

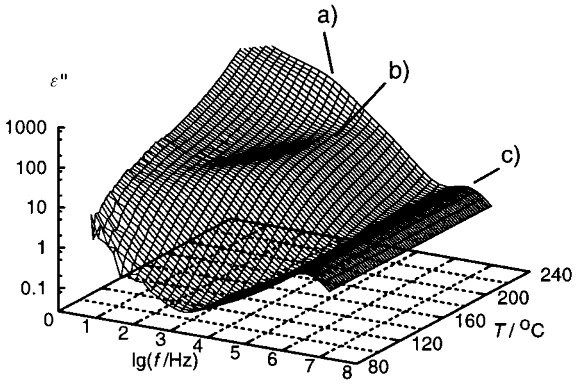

Fig. 11 Spectrum of the dielectric loss ε″ of compound **6** (0.25 V bias): There are two modes assigned to the sample: (a) and (b); the mode (c) is due to the cell relaxation.

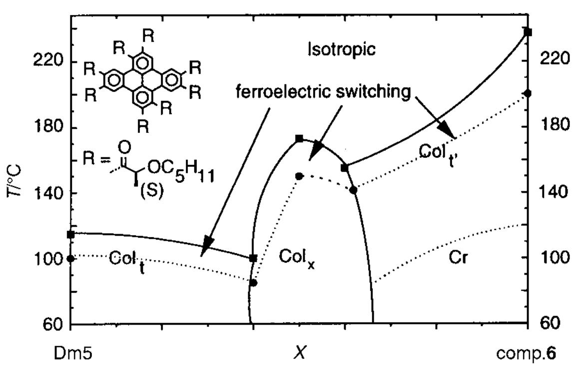

Fig. 12 Schematic phase diagram established from a contact preparation of the ferroelectrically switchable compounds **6** and the dibenzopyrene derivative indicated: a further switchable phase is induced in the middle.

be treated with caution, though. We still lack a precise model for the interpretation of the two modes, especially the high frequency mode. It is interesting to note that we also observed the occurrence of two switching modes in the columnar phase of the dibenzopyrene derivative presented by Bock and Helfrich,[3] so it may be a general feature of ferroelectrically switchable columnar phases.

In order to compare the switching behavior of different compounds we established some contact preparations in test cells. E.H.C. cells were filled with the components from opposite sides until the materials were in good contact with each other.

In mixtures of the triphenylene derivative **6** and the chiral dibenzopyrene derivative[20] Dm5—which are both ferroelectrically switchable—we observed no continuous miscibility but the induction of another columnar mesophase (see Fig. 12) which is also switchable. This suggests that there are different types of columnar mesophases that allow for ferroelectric switching.

Conclusion

We have synthesized a number of new symmetrically substituted triphenylene derivatives with interesting properties based on chirality: the first pure discotic material with a cholesteric blue phase and a compound with a ferroelectrically switchable columnar phase. According to the measurements, the latter seems to exhibit an additional phase transition around 200–205 °C which could not be detected by either thermoanalysis or polarised microscopy.

Extending the results of Goodby *et al.* concerning alkyl substituents, we found that the mesophase range of the columnar phase may also be effectively tuned with suitable polarising substituents.

The exact structure of the columnar mesophases we observed will have to be revealed by *e.g.* X-ray investigations. Since one of the compounds we presented exhibits the rarely observed phase transition between a columnar and a cholesteric phase, it will be interesting to elucidate the way the columnar packing of the molecules changes to the chiral nematic arrangement. Is there a discotic analogue to TGB phases?

Experimental

The triphenylene materials were synthesized according to procedures published by Goodby *et al.*[10,11] Product identity of some compounds was confirmed by^{1}H NMR spectroscopy. There was not enough of the chiral materials to measure the specific rotation. However, from the study of some properties of enantiomeric materials it is clear that they have approximately equal optical purity.

5: δ_H(CDCl$_3$/TMS, ppm): 0.9 (3H, t), 1.3 (10H, m), 1.55 (3H, s), 4.4 (1H, q), 6.8 (2H, d), 8.0 (2H, d), 8.5 (1H, s).

6: δ_H(CDCl$_3$/TMS, ppm): 0.9 (3H, t), 1.3 (10H, m), 1.55 (3H, s), 3.75 (3H, s), 4.45 (1H, q), 6.8 (1H, d), 7.6 (1H, s), 7.75 (1H, d), 8.55 (1H, s).

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