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New diastereomeric compound with cholesteric twist inversion

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The synthesis and characterization of a new diastereomeric compound are reported; this exhibits a temperature induced inversion of the cholesteric twist. Measurements of the cholesteric pitch and handedness are presented and qualitatively discussed in terms of the nature of the cholesteric twist inversion in pure compounds. Preliminary measurements of properties of the ferroelectric S_C^* phase of this compound are also reported.

1. Introduction

The phenomenon of a cholesteric twist inversion with temperature in pure compounds is quite new and has only been observed for a few substances [1-7]. The inversion is characterized by a change of the handedness of the helicoidal structure of the cholesteric phase when the temperature is varied. At some specific inversion temperature T_i the pitch P of the helix diverges, thus exhibiting a nematic director configuration with twisting power $1/P$ equal to zero.

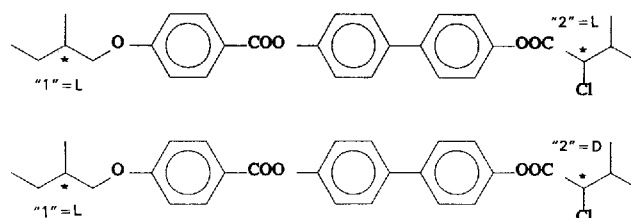
The nature of the twist inversion has not yet been clarified. There are two basic hypotheses to describe this phenomenon qualitatively, but neither of them has been verified experimentally. One was proposed by Goodby *et al.* [3, 5], and relies on a temperature dependent equilibrium between different conformers of a molecule. Another possible explanation [1, 4] attributes a specific twisting power with specific handedness and temperature dependence to each individual chiral element of the molecule; these then add up to a macroscopically observable twisting power of the cholesteric phase. The elements of chirality do not necessarily have to be chiral centres, such as asymmetrically substituted carbon atoms. In fact, an example of a twist inversion of a cholesteric phase consisting of molecules with a chiral centre and a chiral axis is known [6].

To support the conformer hypothesis, the average concentration of each conformer of a molecule has to be experimentally determined as a function of temperature. This goal has not yet been achieved, although first experiments on nematic systems doped with a small fraction of a chiral dopant (induced cholesteric phases)

have been performed [8]. To verify experimentally the second hypothesis, molecules have to be available for which the configuration of the chiral elements can be changed independently. Liquid crystalline diastereomers of this kind, exhibiting a cholesteric twist inversion, have not been reported in literature. The compound presented here is the first of this kind.

2. Experimental

The compound M96



was synthesized in two configurations, (L,L) and (L,D). Information on the synthesis and analytical data are given in the appendix.

Calorimetric (Perkin-Elmer DSC 7) and polarizing microscopic investigations (Olympus BH-2 equipped with a Mettler hot stage FP 52) suggest the following phase sequence for M96 (L,L):

I	163 N*	105.3 S _C [*]	76.4 S _X [*]	30 C
$\Delta H/kJ mol^{-1}$	(0.3)	(1.9)	(2.9)	(1.3)

The helix inversion is found microscopically at about 114°C and cannot be detected by DSC measurements. The compound M96(L,D) exhibits the phase sequence:

I	159.6 BP	158.3 N*	100.8 S _C [*]	70.8 S _X [*]	30 C
$\Delta H/kJ mol^{-1}$		(0.4)	(1.6)	(2.8)	(1.1)

* Author for correspondence.

Numbers in parentheses indicate the transition enthalpy in kJ mol^{-1} . The DSC cooling traces for both configurations are depicted in figure 1. Figure 2 shows typical textures of the mesophases observed for M96(L,D): the platelet texture of the blue phase (see figure 2(a)), a cholesteric fan-shaped texture (see figure 2(b)), the fan-shaped S_C^* texture (see figure 2(c)) and the mosaic texture of the unidentified mesophase (see figure 2(d)). This phase, denoted with S_X^* , is a higher ordered smectic phase, presumably crystal G^* or H^* . The phase belongs to the tilted type, because of a switchable director in an electric field, although saturated switching is not achieved even for very high electric field strengths. This behaviour indicates a tilted crystalline smectic phase.

Measurements of the temperature dependence of the cholesteric pitch for M96(L,L) were performed according to the method described in [4] with commercially available LC cells (E.H.C. Ltd.) of cell gap $4\ \mu\text{m}$ and $10\ \mu\text{m}$ and checked by the Cano-Grandjean method [9, 10]. The temperature dependence of the cholesteric pitch for the (L,D)-configured system was obtained by the wavelength of the selective reflection, recording the transmission spectra (EG+G Princeton Applied Research Model 1235 Digital Triple Grating Spectrograph with EG+G Optical Multichannel Analyser Parc 1420) of a $10\ \mu\text{m}$ sample with the Grandjean texture (helical axis parallel to the incident light beam). The wavelength of the selective reflection λ_0 , which is proportional to the cholesteric pitch, was determined as the minimum of the transmitted intensity [11]. The handedness of the cholesteric helix was determined by the method introduced in [12] and confirmed by measurements of the optical rotatory power. Measurements of the spontaneous polarization of the ferroelectric S_C^* phase were carried out using the triangular wave method

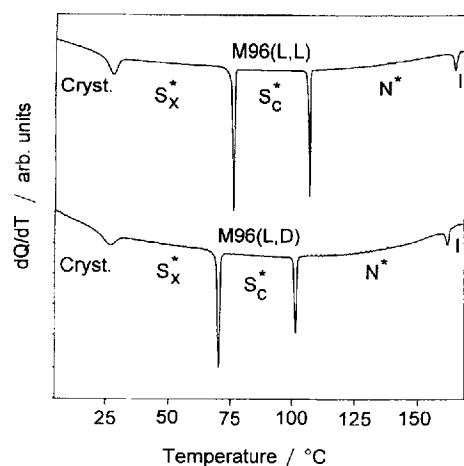


Figure 1. DSC cooling traces of the compounds M96(L,L) and M96(L,D) at a cooling rate of 5°C min^{-1} .

[13] with an electric field strength $E=5\ \text{MV m}^{-1}$ and a frequency $f=200\ \text{Hz}$. As the compounds exhibit electric field induced formation of domains [14, 15], the temperature dependence of the tilt angle θ cannot be determined very accurately. The tilt angle was estimated by observation of field induced domain textures with disclination lines due to the helical S_C^* director configuration [14, 15].

3. Experimental results

3.1. The cholesteric phase

Although the cholesteric twist inversion of M96(L,L) cannot be detected by DSC measurements, it can clearly be observed by polarizing microscopy, as depicted in figure 3, when the sample is prepared between two untreated glass slides, and in figure 4, when prepared in a LC cell with $10\ \mu\text{m}$ gap. Figure 3(a) shows a typical cholesteric fingerprint texture [16] at temperature $\vartheta=120^\circ\text{C}$ with lines due to the cholesteric helix. Slowly lowering the temperature, a nematic Schlieren texture [16] appears at $\vartheta=114.5^\circ\text{C}$ (see figure 3(b)), indicating a nematic director configuration with zero twisting power. Further cooling then results in the re-formation of the cholesteric texture (see figure 3(c), $\vartheta=107^\circ\text{C}$). Preparation of the sample in a $10\ \mu\text{m}$ LC cell produces a nearly defect free Grandjean texture with the optical axis (helical axis) parallel to the incident light beam and perpendicular to the substrate plates. In the cholesteric state, no variation in intensity or colour occurs when rotating the sample between crossed polarizers. At the

Figure 2. Texture photographs of M96(L,D). (a) Platelet texture of the blue phase, prepared between untreated glass plates at $\vartheta=158.4^\circ\text{C}$, (b) cholesteric fan-shaped texture, prepared between untreated glass plates at $\vartheta=156.7^\circ\text{C}$, (c) fan-shaped texture of the unoriented S_C^* phase prepared in a $4\ \mu\text{m}$ LC cell at $\vartheta=100^\circ\text{C}$ and (d) mosaic texture of the unidentified higher-ordered smectic S_X^* , prepared in a $4\ \mu\text{m}$ cell at $\vartheta=50^\circ\text{C}$ (10 scale units $\Delta 70\ \mu\text{m}$).

Figure 3. Textures of M96(L,L), prepared between two untreated glass slides. (a) Typical cholesteric fingerprint texture with lines due to the helical structure, $\vartheta=120^\circ\text{C}$, (b) photograph at the inversion temperature $\vartheta_i=114.5^\circ\text{C}$ depicting a typical nematic Schlieren texture and (c) reformed cholesteric line texture at $\vartheta=107^\circ\text{C}$ (10 scale units $\Delta 70\ \mu\text{m}$).

Figure 4. Polarizing micrograph of the nematic state (left hand side) and the cholesteric state next to it (right hand side) between crossed polarizers at angles (a) 0° and (b) 10° away from crossed position. The sample was prepared in a LC cell of cell gap $10\ \mu\text{m}$, $\vartheta=114.5^\circ\text{C}$ (10 scale units $\Delta 70\ \mu\text{m}$).

Figure 8. Photographs of the N^* phase taken in reflection. (a) $\vartheta=115^\circ\text{C}$, $\lambda_0=635\ \text{nm}$. (b) $\vartheta=120^\circ\text{C}$, $\lambda_0=580\ \text{nm}$. (c) $\vartheta=130^\circ\text{C}$, $\lambda_0=515\ \text{nm}$ and (d) $\vartheta=140^\circ\text{C}$, $\lambda_0=470\ \text{nm}$.

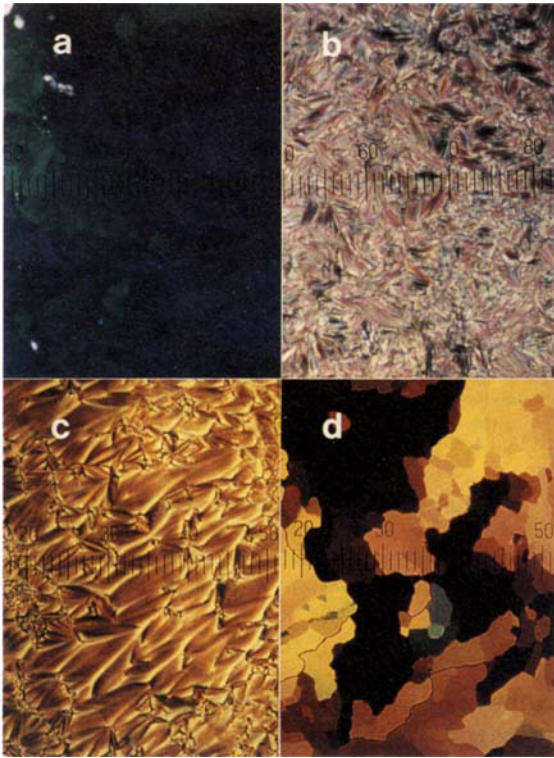


Figure 2.

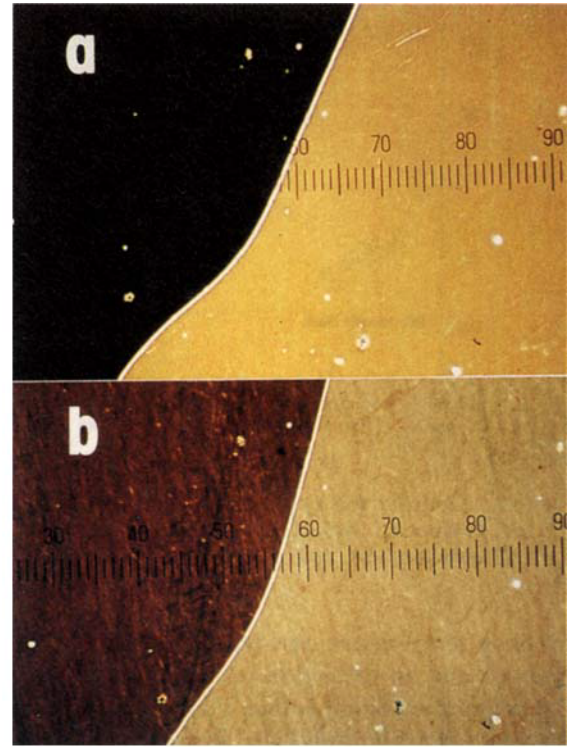


Figure 4.

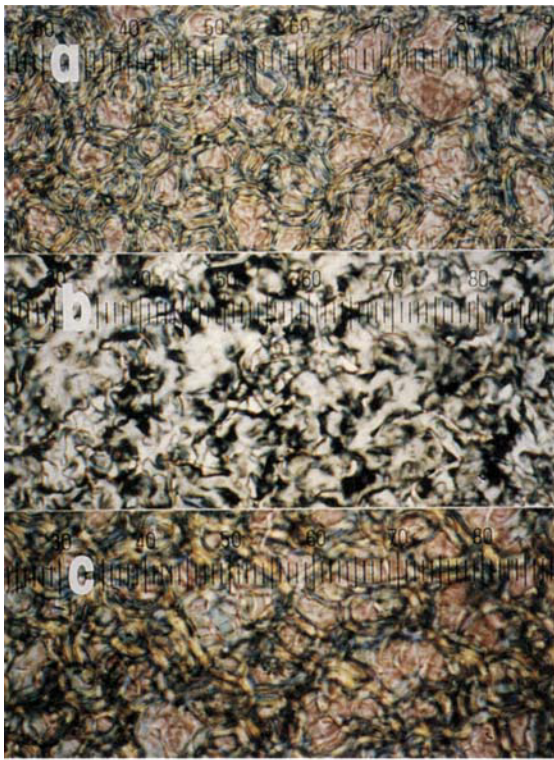


Figure 3.

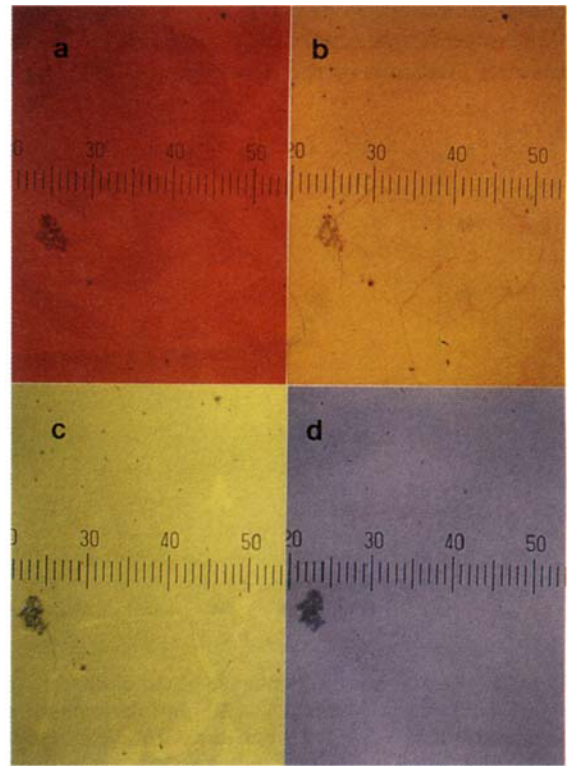


Figure 8.

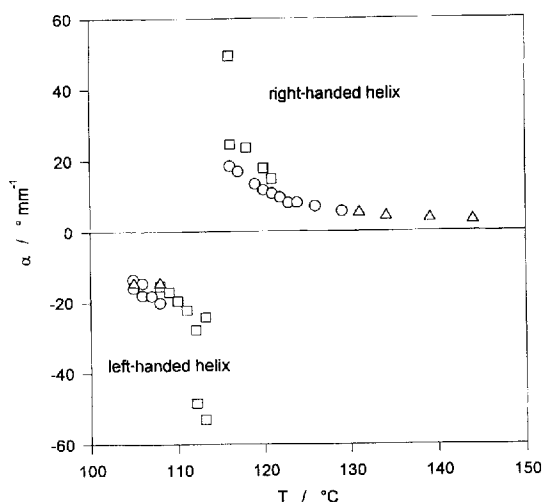


Figure 5. Optical rotatory power as a function of temperature for compound M96(L,L) for wavelength $\lambda = 590$ nm. Different symbols indicate different measurement series.

inversion temperature, the typical nematic flickering is observed and an extinction position can be found (left side in figure 4). Slight colour changes of the cholesteric structures neighbouring the nematic state (right of figure 4) can be accounted for by waveguiding effects. A behaviour of this kind, that is a twist inversion with temperature, cannot be observed for the (L,D)-configured system M96(L,D).

The microscopic observations on M96(L,L) do not yet prove an inversion of the handedness of the cholesteric

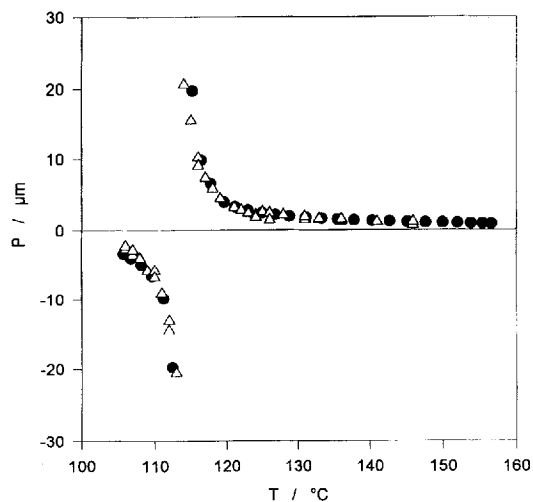


Figure 6. Temperature dependence of the cholesteric pitch P of compound M96(L,L). (●) by the colour change method and (Δ) by the Cano-Grandjean method. A positive pitch indicates a right-handed, a negative pitch a left-handed helicoidal structure.

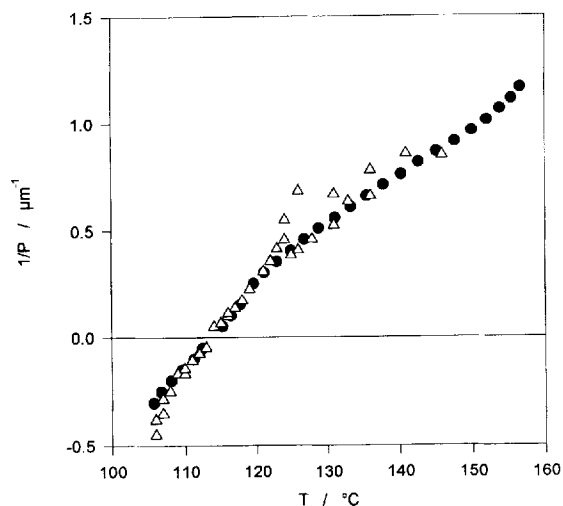


Figure 7. Twisting power $1/P$ as a function of temperature for M96(L,L) (●) by the colour change method and (Δ) by the Cano-Grandjean method. Negative values indicate a left-handed, positive values a right-handed helicoidal structure.

structure, but only indicate a diverging pitch at a certain temperature and a re-formation of the cholesteric structure at lower temperatures. For this reason, measurements of the optical rotatory power have been performed as a function of temperature for a given wavelength $\lambda = 590$ nm below the reflection wavelength λ_0 (see figure 5) and clearly verify the twist inversion for compound M96(L,L). The temperature dependence of the chole-

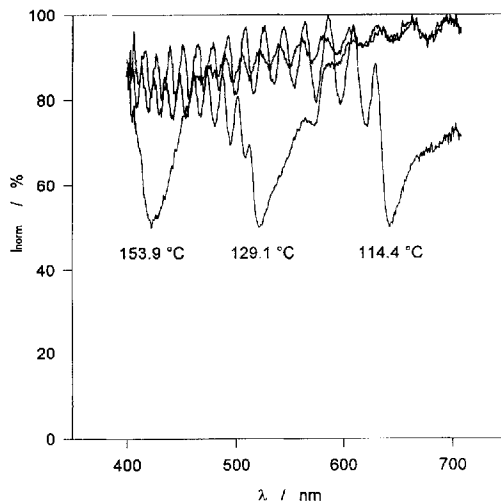


Figure 9. Some selected spectra of the normalized transmission of M96(L,D) recorded for various temperatures without analyser allowing the determination of the wavelength of the selective reflexion λ_0 , which is proportional to the cholesteric pitch. The superimposed maxima and minima are due to the cell interference.

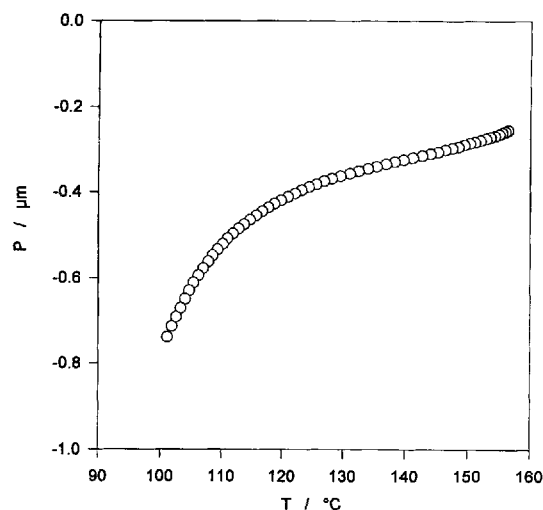


Figure 10. Temperature dependence of the cholesteric pitch P for M96(L,D). The negative values indicate a left-handed helicoidal structure.

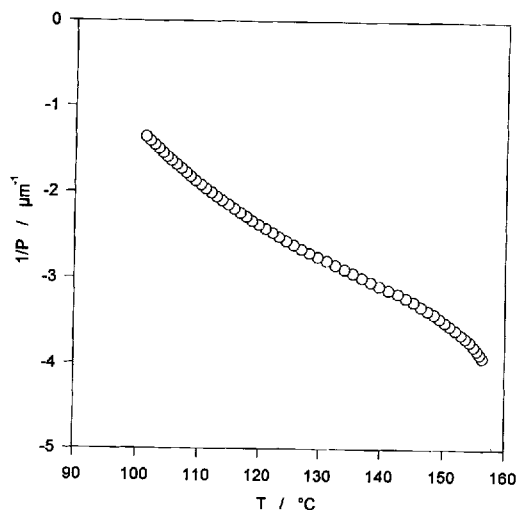


Figure 11. Temperature dependence of the twisting power $1/P$ for M96(L,D). Negative values indicate a left-handed helix.

teric pitch for M96(L,L) is depicted in figure 6. The filled symbols represent the values obtained by counting the observed discontinuous colour change steps in the $10\ \mu\text{m}$ cell with temperature variation as outlined in [4]. Difficulties have been encountered with the Cano-Grandjean method, since only the innermost ring could be observed as a homeotropically oriented region. Open triangles in figure 6 depict the data obtained by this method which yields values about equal to the cholesteric pitch. Figure 7 shows the twisting power $1/P$ for M96(L,L), with the twist inversion temperature $\vartheta_i = 114^\circ\text{C}$ at zero twisting power. At this point the structure changes from right handed at high temperatures ($\vartheta > \vartheta_i$) to left handed at lower temperatures ($\vartheta < \vartheta_i$).

The temperature dependence of the cholesteric pitch of the (L,D)-configured molecule (M96(L,D)) was obtained by temperature dependent spectral measurements. M96(L,D) displays iridescent colours over nearly the whole temperature range of the cholesteric phase, indicating that the wavelength of the selective reflection λ_0 lies in the visible range of the spectrum. Further proof can be found in figure 8, which depicts the N^* phase, photographed in reflection, directly displaying selective reflection colours for different temperatures. The appearance of a blue phase also suggests this behaviour, since blue phases are usually observed when the pitch of the succeeding cholesteric phase is smaller than about $1\ \mu\text{m}$.

Transmission spectra were recorded as a function of temperature and show a minimum in the transmitted light intensity for $\lambda = \lambda_0$ (see figure 9); this allows the determination of the pitch $P = \lambda_0/\bar{n}$. Superimposed maxima and minima in the spectrum are due to the cell gap interference. Evaluation of the interference maxima and

minima lead to a value of $\bar{n} = 1.5$ and the transmission spectra yield the temperature dependence of the cholesteric pitch for M96(L,D) as depicted in figure 10. Comparison of the number of colour changes, from λ_0 as a function of temperature and from texture observations in reflection, also show good agreement with a value $\bar{n} = 1.5$. Figure 11 depicts the corresponding dependence of the twisting power on temperature. The cholesteric structure is left handed, as determined for several wavelengths by the method introduced in [12].

3.2. The ferroelectric smectic C^* phase

The S_C^* phase can easily be identified by texture observations, using a polarizing microscope and samples

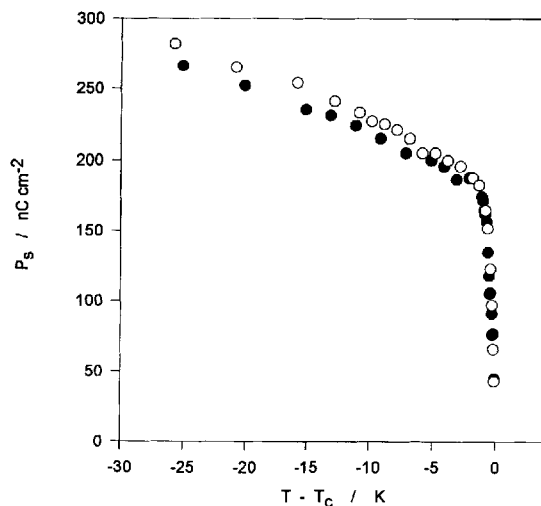


Figure 12. Temperature dependence of the spontaneous polarization P_s for M96(L,L) (●) and M96(L,D) (○).

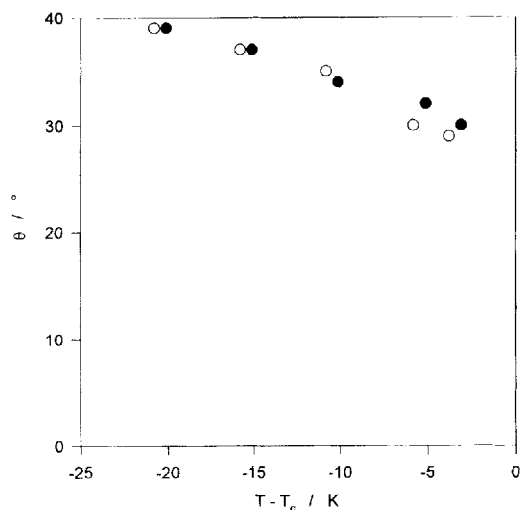


Figure 13. Temperature dependence of the tilt angle of the S_C^* phase for M96(L,L) (●) and M96(L,D) (○).

prepared between two untreated glass slides. Typical fan-shaped textures are observed when cooling below the $N^*-S_C^*$ transition, and the intrinsic equidistant stripes of the disclination lines due to the helical director configuration are exhibited. The temperature dependence of the spontaneous polarization for M96(L,L) and M96(L,D) is depicted in figure 12. A two-phase region of about 0.5°C in the vicinity of the $N^*-S_C^*$ transition is clearly detectable. After the two-phase region has been passed, the spontaneous polarization only displays a small temperature dependence. A similar behaviour is also observed for the temperature dependence of the tilt angle, depicted in figure 13.

4. Discussion

The nature of the cholesteric twist inversion in pure compounds is not yet known and two possible explanations, the conformer hypothesis [3, 5] and the additive partial twisting power hypothesis [1, 4], have been proposed. The conformer hypothesis can neither be proven nor disproven at present, since the conformers cannot be detected experimentally.

A new compound has now been synthesized which exhibits a temperature induced cholesteric twist inversion. In contrast to all other compounds that exhibit this phenomenon, this material allows an independent chemical variation of the configuration of each chiral centre, adding a further piece of information.

The additive partial twisting power hypothesis can now at least be checked qualitatively, as it implies that the temperature dependences of the twisting powers of the synthesized (L,L)- and the (L,D)-configured diastereomers can be explained by a combination of the twisting powers of each individual chiral centre. The assumption

of additive partial twisting powers leads to the following predictions: (i) if the cholesteric phase of the (L,L)-configured molecule exhibits a twist inversion with temperature, then the (L,D)-configured system should *not* show a temperature induced inversion and (ii) if the partial twisting powers of the individual chiral centres have different signs, producing a twist inversion as in M96(L,L), the change in the configuration of one of the chiral centres should lead to a greater macroscopically observable twisting power and a smaller cholesteric pitch. These qualitative predictions are indeed fulfilled in the case reported and so provide first experimental evidence for the partial twisting power hypothesis. From the measurements, the following signs for the twisting powers are found: '1' = L left, '2' = L right and '2' = D left.

It should be stressed that we do *not* deny the existence of different conformers, but rather propose, based on the measurements presented, that the influence of the conformers on the temperature dependence of the cholesteric pitch is small compared to the influences of chirality.

5. Conclusions

The synthesis and characterization are reported of a new diastereomeric compound in two different configurations. The (L,L)-configured system exhibits a temperature induced inversion of the handedness of the cholesteric structure, which was verified by different methods. Measurements of the temperature dependence of the cholesteric pitch for both compounds provide first qualitative evidence for the hypothesis that the twist inversion in pure compounds is mainly governed by the influence of individual chiral centres, each with its unique temperature dependence of the twisting power.

Investigations aimed at obtaining quantitative evidence for this hypothesis, such as the synthesis of the partially racemic systems (L,DL), (DL,L) and (DL,D) as well as measurements on mixtures of the (L,L)- and (L,D)-configured systems, are being undertaken at present and will be reported in due course [19].

This work was supported by a grant from the Deutsche Forschungsgemeinschaft.

Appendix

General procedure for the synthesis of
(S)-4-[4-n-alkyloxybenzoyloxy]-

4'-[2-chloro-3-methylbutyroyloxy]biphenyl

0.005 mol of 4-n-alkyloxybenzoyloxy-4'-hydroxybiphenyl [17] and 0.66 g (0.0065 mol) of *N*-methylmorpholine were dissolved in 30 ml of absolute toluene. 0.77 g (0.005 mol) of (*S*)-2-chloro-3-methylbutyroyl

chloride [18] was added in drops while constantly stirring the solution. The mixture was left untouched for one day at room temperature and was then heated for one hour at 80°C. The resulting solid was filtered off and the solvent evaporated. The product was recrystallized several times from ethanol until the clearing point remained constant. Yield: 65–70 per cent. M96(L,L): Elemental analysis: calculated for $C_{29}H_{31}O_5Cl$ (495.01): C 70.37, H 6.31, Cl 7.16; found: C 70.28, H 6.19, Cl 7.07 per cent. M96(L,D): Elemental analysis: calculated for $C_{29}H_{31}O_5Cl$ (495.01): Cl 7.16; found: Cl 6.97 per cent.

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