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## Liquid Crystals

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## Dielectric, viscosity, and pitch measurements of a ferroelectric liquid crystal exhibiting the phase sequence smectic M-smectic C

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A chiral liquid crystal compound exhibiting the ferroelectric smectic C phase and the recently discovered ferroelectric smectic M phase has been studied by measurements of the Goldstone-mode relaxation frequency and dielectric strength, the spontaneous polarization, the tilt angle and the helical pitch. The data allow the determination of the Goldstone-mode rotational viscosity and the pitch controlling elastic constant. The results indicate that the smectic M phase is characterized by a larger molecular order within the smectic layers compared to the smectic C phase confirming the assumption of a tilted hexatic structure for the smectic M phase.

### 1. Introduction

Recently [1], a new type of smectic phase, smectic M, was observed in several chiral diphenylpyrimidine compounds where this phase occurs between the smectic C phase and higher ordered phases such as the smectic J. Although the detailed structure of the smectic M phase is still not clarified, there is evidence that the molecules are tilted and do not possess long range positional order within the smectic layers thus placing the smectic M phase presumably into the group of tilted hexatic phases such as smectic I and smectic F. In these phases a bond orientational order exists [2]: within the smectic layers, the molecules show a hexagonal-like positional order which is of the short range type; the orientation of these locally defined hexagons, however, exhibits a true long range ordering. (In principle, the bond orientational order is present in the smectic C phase also, because a non-zero tilt leads always to the appearance of a non-zero bond orientational order [2]; in the smectic C phase, however, this order parameter is very small.)

If the smectic M phase consists of chiral molecules it exhibits a helical superstructure and ferroelectric properties with the spontaneous polarization  $P_s$  being significantly larger than in the high temperature smectic C phase (diphenylpyrimidine esters of chiral  $\alpha$ -chlorocarboxylic acids show values between 300 and 600 nC cm<sup>-2</sup>) [3]. The large  $P_s$  values may be promising for electro-optical applications, however, the switching time is determined not only by the value of  $P_s$  but also by the magnitude of the Goldstone-mode rotational viscosity  $\gamma_\phi$  related to the motion of the molecules on the smectic cone made up by the tilt angle.

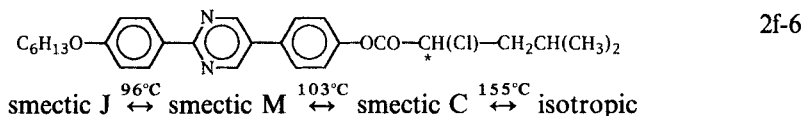
In this study, we present the first investigation of the dielectric properties, the viscosity, and the helical pitch of a compound showing the phase sequence smectic M-smectic C. In the smectic M phase, a slowing down of the Goldstone-mode relaxation frequency and a pronounced increase of the rotational viscosity and the

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helical pitch is observed. These results are in accord with the assumption that the smectic M phase differs from the smectic C phase by a considerable increased bond orientational order.

## 2. Experimental

The compound under investigation is *R*-4-hexyloxyphenyl-[4-(1-chloro-3-methylbutanoyloxy)-phenyl]-(2,5)-pyrimidine (abbreviated in the following as '2f-6') the molecular structure and phase sequence of which is given below:



The determination of the transition temperatures and the classification of the smectic phases on the basis of texture observations and X-ray and miscibility investigations are described in [1].

The viscosity  $\gamma_\phi$  can be determined by different methods such as measurements of the electro-optical switching time or the polarization reversal current. Here, we use a method described recently [4–5] which is based on dielectric measurements of the Goldstone-mode dielectric strength  $\Delta\epsilon_G$  and its relaxation frequency  $f_G$ . In addition to the dielectric data, this method requires the knowledge of the spontaneous polarization  $P_s$  and the tilt angle  $\theta$ . Then, the viscosity  $\gamma_\phi$  can be calculated as [4–5]

$$\gamma_\phi = \frac{1}{4\pi\epsilon_0} \frac{P_s^2}{\Delta\epsilon_G f_G \theta^2} \quad (1)$$

For the polarization and dielectric measurements the sample was placed into a conductively coated glass cell (thickness  $4\ \mu\text{m}$  for  $P_s$  and  $10\ \mu\text{m}$  for  $\epsilon$  measurements, electrode area  $16\ \text{mm}^2$ ) which was placed into a Mettler FP82 hot stage. The spontaneous polarization  $P_s$  was determined using the field reversal method, i.e.  $P_s$  was obtained from the time-integral of the current peak resulting from the reversal of  $P_s$  caused by an applied triangular electric field. A Solartron-Schlumberger 1254 impedance analyser was used to determine the complex dielectric constant  $\epsilon = \epsilon' + i\epsilon''$  in the frequency range of  $10^0$ – $10^5$  Hz. Because Cole–Cole plots showed slight deviations from the ideal circular shape and the conductivity, especially at higher temperatures, was relatively large, we analysed our data using the Havriliak–Negami equation [6] in order to obtain the Goldstone-mode relaxation frequency  $f_G$  and dielectric strength  $\Delta\epsilon_G$ .

The values of the tilt angle  $\theta$  are based on X-ray measurements of the smectic layer spacing and were taken from an earlier study [7] of the 2f-6 compound.

## 3. Results

Because of the non-zero bond orientational order parameter of the smectic C phase, a second order transition between smectic C and a tilted hexatic phase cannot exist, i.e. there should be either a first order transition or a continuous evolution between smectic M and smectic C, provided that smectic M is a tilted hexatic phase [2]. Our results indicate that for the 2f-6 compound most of the physical properties show a distinct change of their temperature dependence at the transition but do not exhibit a discontinuity indicating the absence of a first order transition.

Figure 1 (a) shows the temperature dependence of the spontaneous polarization: at the transition temperature  $T_{\text{scI}}$  from the isotropic liquid to the smectic C phase ( $T = 155^\circ\text{C}$ )  $P_s$  jumps from zero to  $\approx 120 \text{ nC cm}^{-2}$  followed by a smooth increase with decreasing temperature. At a temperature  $\approx 52 \text{ K}$  below  $T_{\text{scI}}$  a sudden increase of  $P_s$  is observed indicating the continuous transition to the smectic M phase. Very similar behaviour is observed for the Goldstone-mode dielectric strength  $\Delta\epsilon_G$  (see figure 1 (b)). The relaxation frequency  $f_G$  of the Goldstone-mode decreases slightly in the smectic C phase with decreasing temperature but at the transition to smectic M a precipitous drop of  $f_G$  sets in which persists over the whole temperature range of the smectic M phase (see figure 1 (b)). Only the tilt angle  $\theta$  is apparently not affected by the smectic M–smectic C transition: the  $\theta$  values exhibit only a slight increase from  $33^\circ$  at the smectic C–isotropic clearing point to  $34.5^\circ$  at the smectic J–smectic M transition without showing any marked behaviour at the transition from smectic M–smectic C. Our data for  $P_s$ ,  $f_G$ ,  $\Delta\epsilon_G$ , and  $\theta$  are consistent with a continuous transition from the

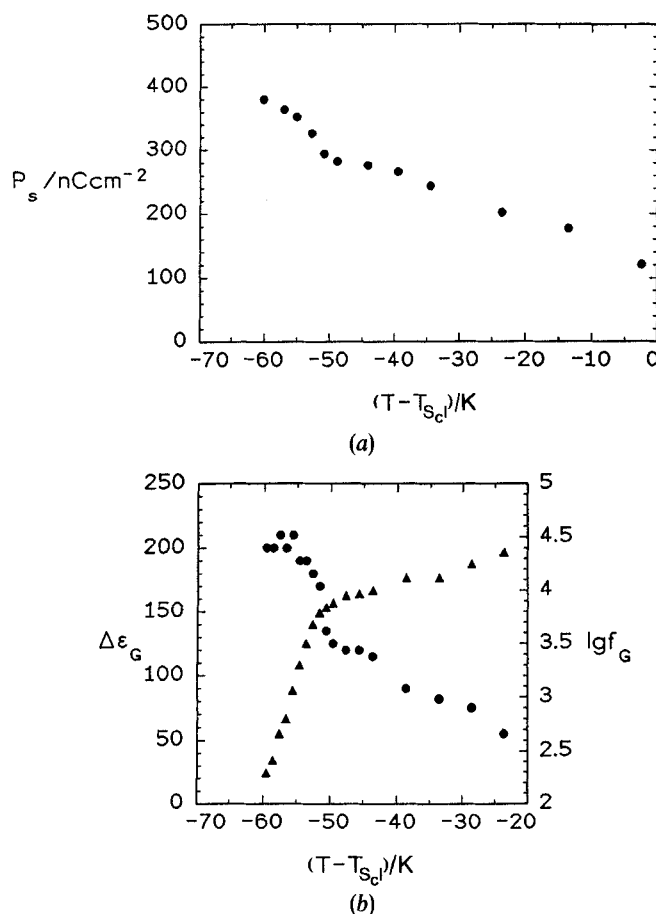


Figure 1. (a) Temperature dependence of the spontaneous polarization  $P_s$  in the smectic M and C phase of compound 2f-6.  $T_{\text{scI}}$  denotes the smectic C–isotropic transition temperature ( $155^\circ\text{C}$ ). (b) Temperature dependence of the Goldstone-mode relaxation frequency  $f_G$  (right scale,  $\blacktriangle$ ) and dielectric strength  $\Delta\epsilon_G$  (left scale,  $\bullet$ ) in the smectic M and C phase of compound 2f-6.

liquid smectic C phase to a tilted hexactic phase where the growth of the bond orientational order does not affect the tilt angle but leads to an increase of the spontaneous polarization and a simultaneous slowing down of dynamic properties such as the relaxation frequency of the Goldstone-mode.

The values of the rotational viscosity  $\gamma_\phi$  calculated according to equation (1) are shown in figure 2 as a function of the reciprocal temperature. In the smectic C phase, an Arrhenius-like behaviour is observed the activation energy amounting to 0.5 eV which is similar to values found in other compounds [4, 5, 8]. In the smectic M phase, a pronounced increase of  $\gamma_\phi$  by two orders of magnitude takes place. The temperature dependence is still Arrhenius-like but the activation energy now amounts to 6.3 eV which is more than twelve times larger than in the smectic C phase. As the slowing down of the Goldstone-mode relaxation frequency, this result reflects the growth of the in-plane molecular ordering in the smectic M phase.

Only a few studies of the ferroelectric properties at other smectic C to hexatic (smectic I or F) phase transitions have been published. The increase of the spontaneous polarization  $P_s$  observed here at the transition to the smectic M phase is comparable to the behaviour of  $P_s$  at the smectic C to smectic I transition of the compounds HOBACP [9] and 8SI [10]. Also the constancy of the tilt angle at the transition to the smectic M phase is in accord with the behaviour found in 8SI and some similar compounds where the tilt angle stays nearly constant or decreases slightly at the transition to the smectic I phase [11]. In contrast to our results, the dielectric strength  $\Delta\epsilon_G$  of the Goldstone-mode was found to decrease at the smectic C to smectic I transition of 8SI [12] and a commercial mixture (Merck ZLI 4004) [13]. However, in [12] and [13] the  $\epsilon$  values of the smectic C and I phase are compared at the same frequency and the apparent decrease of  $\Delta\epsilon_G$  may be caused by the slowing down of the relaxation frequency  $f_G$ . To our knowledge, a temperature dependence of the viscosity  $\gamma_\phi$  across a smectic C to hexatic phase transition has not been reported in the literature.

The 2f-6 compound exhibits [14] selective reflection of visible light in both the smectic C and smectic M phase thus enabling an easy determination of the pitch of the helical superstructure in these phases. Figure 3 shows the wavelength  $\lambda_{\max}$  of maximum reflected light intensity determined from homeotropically aligned samples using a

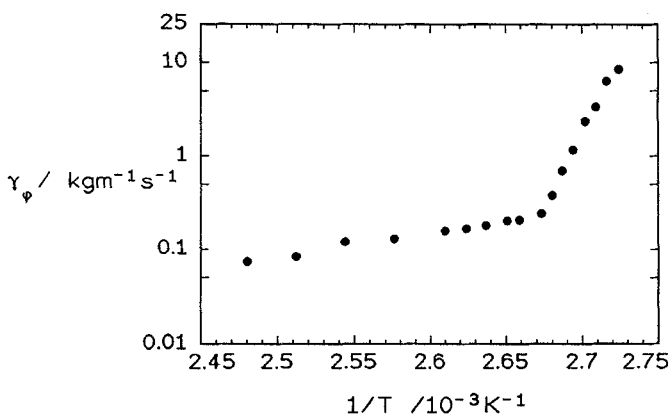


Figure 2. Temperature dependence of the rotational viscosity  $\gamma_\phi$  in the smectic M and C phase of compound 2f-6.

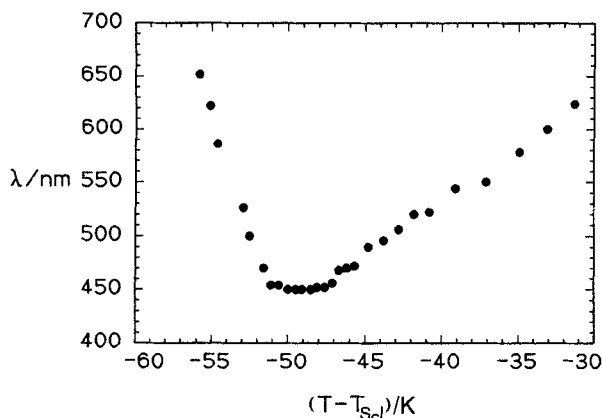


Figure 3. Temperature dependence of the wavelength  $\lambda_{\max}$  of maximum selective reflection in the smectic M and C phase of compound 2f-6.

diode array spectrometer with a wavelength range from 350 nm to 750 nm. The values of the helical pitch  $p$  are related to the values of  $\lambda_{\max}$  as  $\lambda_{\max} = \bar{n}p$ , where  $\bar{n}$  is an effective refractive index. In the smectic C phase,  $p$  shows the usual decrease with decreasing temperature whereas in the smectic M phase a steep increase is observed. Together with our dielectric data, the values of the pitch controlling elastic constant  $K_{\phi} = K_3 \cos^2 \theta + K_2 \sin^2 \theta$ , which is a combination of bend and splay elastic constants ( $K_3$  and  $K_2$ , respectively), can be calculated according to [4–5]

$$K_{\phi} = \frac{1}{2\epsilon_0 \Delta\epsilon_G q^2} \frac{P_s^2}{\theta^2} \quad (2)$$

Here,  $q = 2\pi/p$  is the wavevector of the helical pitch which we have calculated from the selective reflection wavelength  $\lambda_{\max}$  assuming an effective refractive index  $\bar{n} = 1.6$ . The values of the elastic constant  $K_{\phi}$  (see figure 4) show the same behaviour as the values of the helical pitch as is to be expected if the pitch is not influenced by external fields or by variation of the chirality (enantiomeric excess).

The pronounced increase of the helical pitch  $p$  and the elastic constant  $K_{\phi}$  in the smectic M phase can be interpreted as a result of the growing bond orientational order. This order in the smectic I and F phases, and probably in the smectic M phase, is a true long range three dimensional order, i.e. the orientation of the hexatic order is the same not only within a given smectic layer but also in the adjacent layers. Since a coupling between bond orientational order and tilt exists, this order tends to align the tilt direction homogeneously throughout the whole sample thereby competing with the chiral interactions causing the helical distribution of the tilt orientation. Because the bond orientational order parameter of hexatic phases grows continuously with decreasing temperature starting from the order parameter value of the smectic C phase [2], we expect that the tilt aligning interactions of the bond orientational order overcome more and more the chiral interactions, i.e., the helical pitch in the smectic M phase should grow continuously with decreasing temperature as is indeed observed experimentally. Unfortunately, our experimental set-up does not allow us to observe selective reflection in the infrared range and we cannot decide whether the pitch of the smectic M phase becomes infinite or stays finite at temperatures far below the smectic M–smectic C transition. Only one further example for a pitch measurement in a chiral

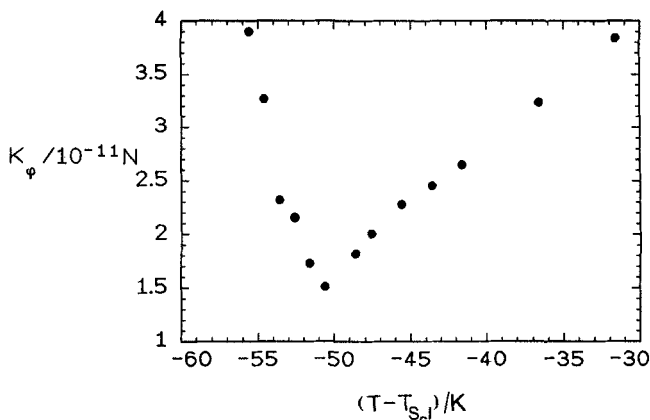


Figure 4. Temperature dependence of the pitch controlling the elastic constant  $K_\phi$  in the smectic M and C phase of compound 2f-6.

hexatic phase has been reported [15]: in the smectic I phase of 8SI a similar increase of the helical pitch  $p$ , as we report here for the smectic M phase of 2f-6, was observed. Certainly, further studies of other chiral hexatic compounds are needed in order to check whether the pronounced increase of the pitch is a general feature of chiral hexatic phases.

In conclusion, we have presented the first dielectric, viscosity, and pitch measurements of a compound showing the recently discovered smectic M phase; to our knowledge, this is also the first study of the rotational viscosity and the pitch controlling elastic constant in a more ordered ferroelectric smectic phase than smectic C. The slowing down of the Goldstone-mode relaxation frequency as well as the pronounced increase of the rotational viscosity and the helical pitch indicate a distinct increase of the molecular order within the smectic layers at the transition from the smectic C to the smectic M phase. Since X-ray measurements [1] have shown the absence of long range positional order, our results confirm the assumption of bond orientational order within the smectic layers, i.e. smectic M is presumably a tilted hexatic phase. According to theory, four types of tilted hexatic phases are predicted [16] which differ in the tilt direction with respect to the orientation of the bond orientational order; two of them are experimentally observed in thermotropic liquid crystals: smectic I (tilt parallel to a local bond) and smectic F (tilt halfway between two local bonds,  $30^\circ$  from each). In lyotropic liquid crystals, a third hexatic phase, smectic L, is observed showing a tilt direction locked at an arbitrary value between  $0^\circ$  (smectic I) and  $30^\circ$  (smectic F) [17]. The fourth phase with an unlocked tilt direction has still not been observed experimentally. Concerning the smectic M phase, miscibility studies have clearly shown that this phase is neither smectic I nor smectic F [1]. Whether smectic M corresponds to one of the two remaining hexatic phases cannot be decided on the basis of the results presented here. Thus, X-ray studies of monodomain samples are needed to obtain a definite conclusion about the structure of the smectic M phase.

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