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Liquid Crystals

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Viscoelastic behaviour of ferro- and antiferroelectric phases

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Viscoelastic behaviour of ferro- and antiferroelectric phases

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We have investigated the viscoelastic behaviour exhibited by chiral smectic C* phases in homeotropic orientation. For an appropriate scattering geometry and using the light scattering technique, the orientational diffusivities $\frac{k_3}{\eta}$ (SmC*) and $\frac{k_3}{\eta}$ ($\mathrm{SmC_A}$*) associated with the Goldsone mode in ferro- and antiferroelectric phases of C_{11}thiobenzoate and C_8tolane compounds have been measured. $\frac{k_3}{\eta}$ ($\mathrm{SmC_A}$*) is about 100 times weaker than $\frac{k_3}{\eta}$ (SmC*). This divergence may be largely attributed to the mode of the molecular arrangement in ferro- and antiferroelectric phases, in spite of the same helical structure observed in the two phases.

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1. Introduction

It is well known that many liquid crystals are organic compounds which exihibit intermediate phases during the transition from the solid to isotropic liquid states. These phases possess simultaneously solid and isotropic liquid properties [1]. Indeed, in liquid crystal phases there is a long range orientational order (as in a solid) in at least one direction, and isotropic liquid order (as in a normal liquid) in other directions. The orientational order undergoes thermal fluctuations about an equilibrium direction, the fluctuation amplitude being controlled by liquid crystal elasticity. Information about the elastic properties can be therefore deduced from amplitude measurement, using the light scattering technique to measure the intensity and spectrum of light scattered by angular fluctuations of the director **n** [2–11]. From these measurements in nematic phases can be deduced the orientational diffusivities: D_{splay}, D_{twist} and D_{bend} associated, respectively, with splay, twist and bend deformations.

Since the discovery of disk-like (discotic) liquid crystals, several experimental and theoretical investigations have been performed in order to understand the viscoelastic behaviour of the observed phases. Our contribution in this field was to use the light scattering technique which leads generally to information about the dynamic behaviour of the collective excitations in nematic phases [5–7, 11]. The most important result deduced from this study is that discotic and rod-like nematic phases present the same viscoelastic behaviour, in spite of the difference between molecular shapes. One may conclude that the viscoelastic behaviour of the liquid crystal phases is essentially governed by the mode of the molecular arrangement, and not by the molecular shape.

Recently, chiral ferro- and antiferroelectric smectic C phases (SmC* and $\mathrm{SmC_A}$*) have been observed [12]. Information about the molecular arrangement in these phases was obtained by various experimental methods including X-ray diffraction analysis [13, 14], calorimetric investigation [15], electro-optic response studies, optical measurements [16–18] and light scattering experiments [8–10]. The most important results deduced from these studies show that the $\mathrm{SmC_A}$* phase is characterized by an alteration of the tilt direction of the average molecular orientation and the direction of the in-plane spontaneous polarization by nearly ±180° between adjacent smectic layers. Due to the chirality, the directions of the spontaneous tilt and the in-plane polarization precess slowly around the layer normal on moving along the direction perpendicular to the smectic layer. This induces the formation of a modulated helicoidal structure. In contrast to the SmC*, where the basic structural unit is a smectic layer, the helicoidal structure in $\mathrm{SmC_A}$* can be obtained by a slow rotation of two neighbouring layers. In fact, this structure is a double-twisted helicoidal structure, formed by two identical SmC* helixes gearing into each other. Because

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of the difference between the molecular arrangement modes in SmC* and SmC_A* phases, one may expect different viscoelastic behaviour in these phases.

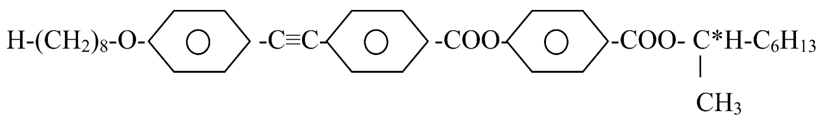
In order to test these predictions, we investigate two chiral liquid crystal compounds, the C_{11}thiobenzoate and C_8tolane, belonging to the thiobenzoate and tolane series, respectively [17, 18]. The experimental technique used here is the light scattering technique, similar to that used by the Slovenia group. We measured the photocurrent correlation function and deduced the orientational diffusivities associated with thermal fluctuations of the orientational order.

In this paper some theoretical predictions are first given, concerning director thermal fluctuations in a chiral smectic liquid crystal. We next describe the experimental method: materials, technique and scattering geometry. Finally, the experimental results and the discussion are presented.

The collective fluctuations in the SmC* phase can be divided into one branch associated with fluctuations of the amplitude of the tilt angle (amplitude mode), and a branch associated with fluctuations of the phase of the tilt angle (phase mode) which is well known as the Goldstone mode. Due to the helicoidal structure, light scattered by the fluctuations of the orientational order is centred at $q_0=2\pi/p$ and $2q_0$, where p is the helix period.

For the SmC_A* phase, four dispersion branches can be observed: two at high frequency represent helically modulated tilt excitations which depend strongly on the temperature and are observable very close to the phase transition temperature (SmA↔SmC_A*); the other two, low frequency dispersion branches, are the acoustic-like and optic-like phason branches. The acoustic-like mode that was observed for the first time by Musevic *et al.* [9] has a minimum relaxation rate at $2q_0$, whereas the optic-like mode that is a direct consequence of a doubling of the smectic unit cell is centred at q_0 [8]. These two modes can be distinguished by the molecular

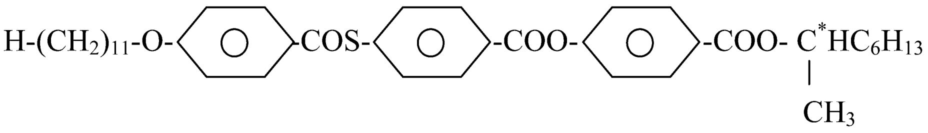
C_8tolane



Cr	SmJ*	SmI^*_A	SmC^*_A	SmC^*_{FI1}	SmC^*_{FI2}	SmC*	SmC^*_α	SmA	I
67.6°C	(65°C)	71.6°C	95.1°C	96°C	97°C	104°C	105.5°C	135.3°C	

(*a*)

C_{11}thiobenzoate



Cr	SmC^*_A	SmC^*_{FI1}	SmC^*_{FI2}	SmC*	SmC^*_α	SmA	I
95.5°C	101°C	104.5°C	111°C	127°C	128°C	149°C	

(*b*)

Figure 1. Chemical formulae and phase sequences corresponding to (*a*) C_8tolane and (*b*) C_{11}thiobenzoate.

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fluctuation modes: for the acoustic-like mode (the antiferroelectric mode), the molecules of neighbouring layers fluctuate spontaneously in the same direction, whereas for the optic-like mode (a ferroelectric mode), molecular fluctuations alternate. Nevertheless, in the light scattering experiment, one can detect separately the acoustic-like and the optic-like branches in an appropriate scattering geometry. We note that the optic-like phason mode could be detected more easily than the acoustic-like mode because of the difference between the scattering cross-sections: the scattered intensity associated with the acoustic-like mode is proportional to the fourth power of the tilt angle, whereas that of the optic-like mode is quadratic in the tilt angle.

Because of the experimental constraints, in this paper the analysis of the light scattered by phason mode at $\mathbf{q}_s = 2\mathbf{q}_0$ is presented, where $\mathbf{q}_s$ is the scattering wave vector and is linked to the incident and scattered wave vectors $\mathbf{K}_i$ and $\mathbf{K}_s$ by the following expression:

$$\mathbf{q}_s = \mathbf{K}_s - \mathbf{K}_i.$$

When $\mathbf{q}_s$ is parallel to the helix axis, the relaxation rate corresponding to the Goldstone mode is given by [8]:

$$\tau^{-1} = \frac{k_3}{\eta}(q_s \pm 2q_0)^2$$

where k_3 is the twist orientational elastic constant and η is the effective rotational viscosity. It is be noted that from the τ^{-1} expression, the acoustic-like phason mode (or Goldstone mode) is expected to be a gapless mode with zero frequency at $\mathbf{q}_s = 2\mathbf{q}_0$.

2. Experimental

The materials used here have been recently synthesized [17, 18] and are denoted by C_8tolane and C_{11}thiobenzoate; their chemical formulae and phase transition sequences are shown in figures 1 (*a*) and 1 (*b*), respectively. The sample (powder at ambient temperature) was placed between two treated glass plates, and the sample thickness fixed at 100 µm by a mica spacer. Using an electric oven, the sample was heated until it reached its isotropic phase; it was then cooled slowly (0.01°C min^{-1}) from the isotropic phase to the SmC* or SmC$_A$* phase. To observe the orientational state of the bulk liquid crystal, the oven was placed between a crossed polarizer and analyser. A good homegenous homeotropic alignment could thus be reached, in which the helix axis is perpendicular to glass plates.

The scattering geometry in which the scattering wave vector $\mathbf{q}_s$ must be parallel to the helix axis is illustrated in figure 2. More experimental details have been described elsewhere [6, 7].

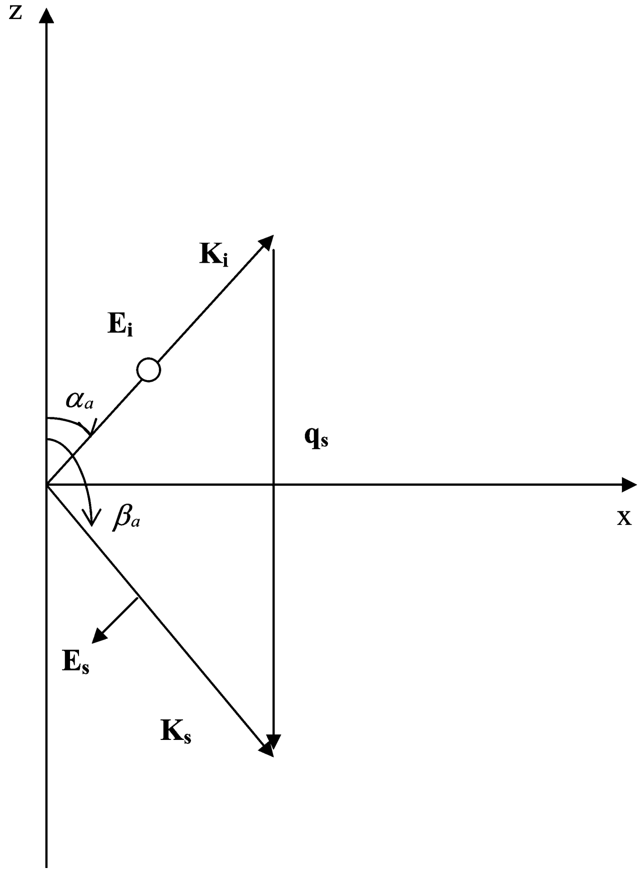
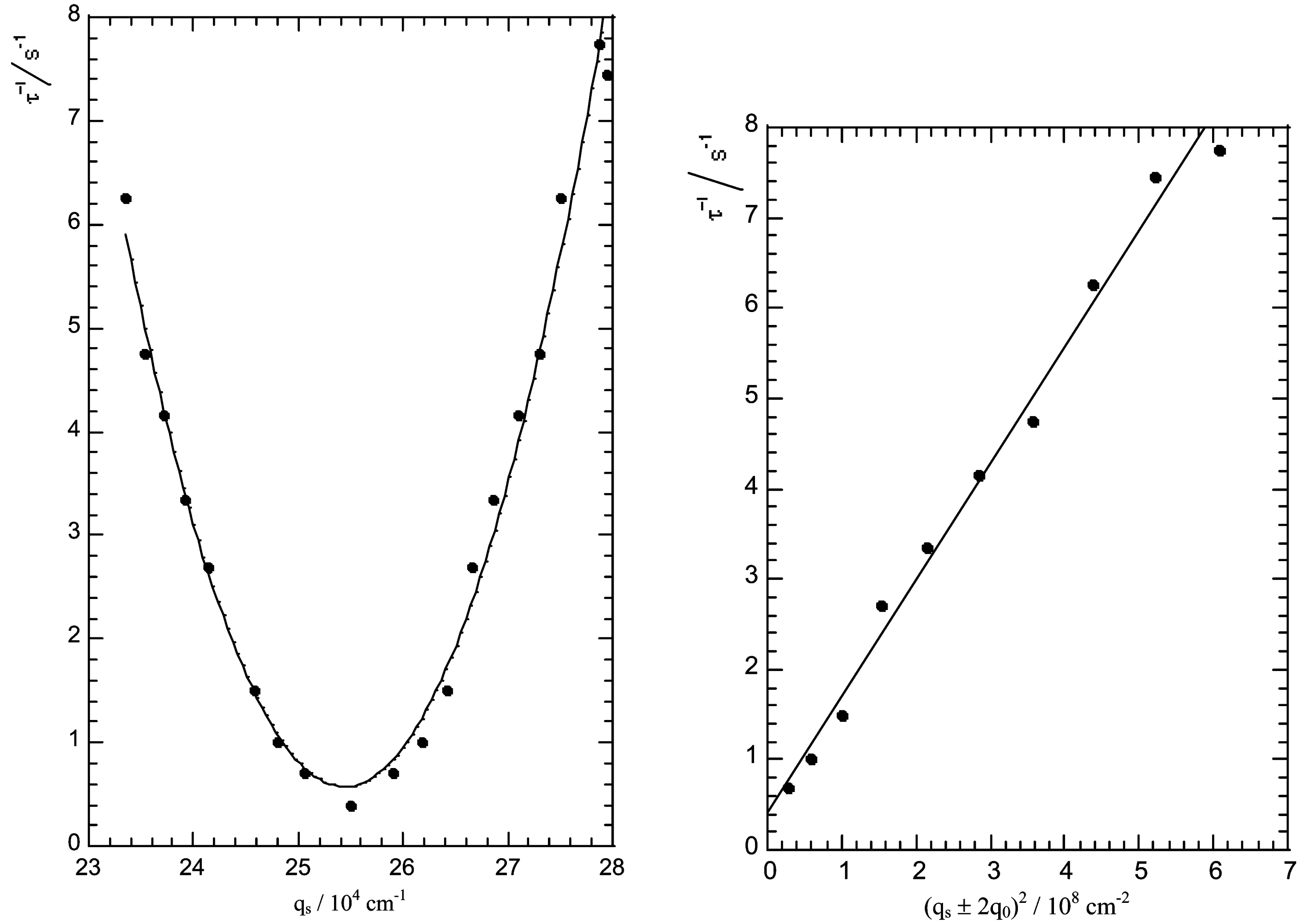


Figure 2. Scattering geometry in homeotropic orientation. The wave vectors $\mathbf{K}_i$ and $\mathbf{K}_s$, symmetric with respect to the helix axis, are in ordinary and extraordinary polarizations, respectively.

3. Results and discussion

With the C_8tolane compound, the temperature was fixed at 88.6°C by means of an electronic regulator. Experiments were then performed in the antiferroelectric phase (SmC$_A$*). We analysed light scattered by thermal fluctuations corresponding to the acoustic-like mode (or Goldstone mode). For each selected incident angle, and keeping $\mathbf{q}_s$ parallel to the helix axis, we measured the damping time τ in the ordinary–extraordinary geometry. In figure 3 (*a*), the plotted curve shows the change of the relaxation rate τ^{-1} versus $\mathbf{q}_s$. In the selected range scattering angles, the data are well fitted by a parabolic function where a minimum is obtained at $\mathbf{q}_s = 25 \times 10^4$ cm^{-1}. This value allows us to deduce the helix period, $p = 0.5$ µm, which is in good agreement with selective reflexion measurement [19].

On the other hand, the Goldstone mode is expected to be a gapless branch with zero relaxation rate τ^{-1}. Here, within the limits of experimental errors we deduce a minima frequency of 0.6 Hz, which is close to zero. This small deviation can be attributed to the



(*a*) (*b*)

Figure 3. (*a*) Variation of relaxation rate versus q_s; (*b*) variation of relaxation rate versus $(q_s \pm 2q_0)^2$, corresponding to the SmC$_A$* phase of C$_8$tolane.

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contribution of the transverse component q_x of the scattering wave vector $\mathbf{q}_s$ to the dispersion relation, which is expressed as:

$$\tau^{-1} = \frac{k_3}{\eta}(q_s \pm 2q_0)^2 + \frac{k_+}{\eta}q_x^2$$

where $k_+ = \frac{1}{2}(k_s + k_B)$ is the effective transverse elastic constant [9], k_s and k_B are splay and bend elastic constants, respectively, and η is the corresponding viscosity. This contribution exists because in a back scattering geometry we avoid positioning the detector in the reflected beam direction. Then, there is a small mismatch of $\mathbf{q}_s$ and $2\mathbf{q}_0$. The transverse component q_x could be estimated as $q_x = q_s \times 10^{-2}$, corresponding to a weak misalignment of $\mathbf{q}_s$ with respect to the helix axis of about one degree; we then deduce $k_+/\eta \approx 10^{-7}\,m^2\,s^{-1}$. This value is ten times larger than that measured by Sun *et al.* in the SmC$_A$* phase of (*R*)-MHPOBC liquid crystal [20]. The difference is probably due to the viscosity coefficient, which seems to be larger in the (*R*)-MHPOBC phase than in the C$_8$tolane phase.

In figure 3 (*b*) we plot the relaxation rate versus $(q_s \pm 2q_0)^2$. The experimental data are well fitted by a straight line whose slope gives the orientational diffusivity associated with the Goldstone mode: $k_3/\eta = 1.3 \times 10^{-12}\,m^2\,s^{-1}$. We should note that this value is one-tenth of that measured by Musevic *et al.* in the antiferroelectric phase of EHPOCBC [8], and one-hundredth of the k_3/η determined by Sun *et al.* in the SmC$_A$* phase of (*R*)-MHPOBC [20]. The differences may be an effect of the compound nature (molecular length and rigidity), which can significantly affect the viscosity coefficient and elastic constant.

The antiferroelectric and ferroelectric phases of the C$_{11}$thiobenzoate compound were investgated separately. More precisely, we analysed the scattered light associated with the Goldstone mode in back scattering geometry, with the scattering wave vector closely

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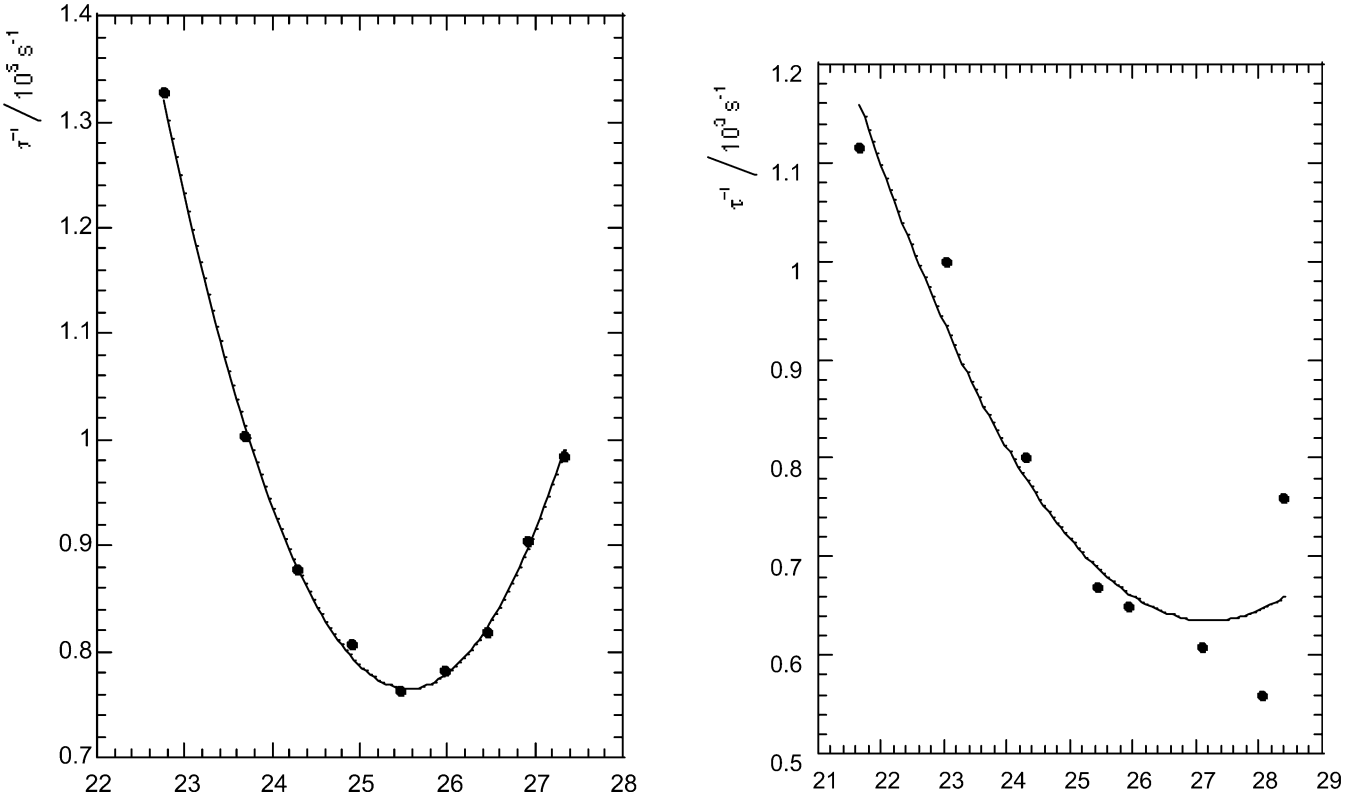
parallel to the helix axis. Temperatures were fixed at 100°C and 114°C, respectively. Figure 4 (*a*) shows the variation of relaxation rate versus $\mathbf{q}_s$ corresponding to the SmC$_A$* phase. The experimental data are fitted by a parabolic function where the relaxation rate minimum is obtained at $\mathbf{q}_s = 27 \times 10^4\,\mathrm{cm}^{-1}$. From the $\mathbf{q}_s$ value, the helical pitch p is deduced; its value is of the order 0.47 µm, a result in agreement with values deduced from selective reflexion measurements [19]. In addition to experimental errors, we should indicate that the contribution of the transverse component q_x induces experimental value fluctuations, because q_x depends on the scattering angle. Furthermore, the Goldstone mode is expected to be gapless; the non-zero frequency observed here could be attributed to a q_x contribution. Thus, the estimation of q_x at $q_x = q_z \times 10^{-2}$ leads to $k_+/\eta \approx 10^{-8}\,\mathrm{m^2\,s^{-1}}$ which is of the same order of magnitude as that found by Sun *et al.* [20].

On the one hand, and within the limits of experimental error, we can say that the orientational diffusivities k_3/η measured in the SmC$_A$* phases of C$_8$tolane and C$_{11}$thiobenzoate are of the same order of magnitude; on the other hand, they are one tenth the k_3/η measured by Musevic in the SmC$_A$* phase of MHPOBC and corresponding to the acoustic-like mode. Furthermore, they are about one-hundredth the values measured by Sun *et al.* To explain the causes of these divergences observed between k_+/η values on the one hand and between k_3/η values on the other, one can perform light scattering experiments at several temperatures, because helical pitch depends on temperature. Thus, supplementary information on the behaviour of orientational diffusivities can be deduced. We report in the table the values of orientational diffusivities deduced from our experiments and from experiments performed earlier by other authors.

Concerning the ferroelectric SmC* phase of C$_{11}$thiobenzoate, the variations of τ^{-1} versus $\mathbf{q}_s$ and $(\mathbf{q}_s \pm 2\mathbf{q}_0)^2$ is plotted in figures 5 (*a*) and 5(*b*), respectively. From the parabolic fit, we deduce the helix pitch, $p = 0.49$ µm, which is similar to that measured in the SmC$_A$* phase. This equivalence is not surprising because the helical structure of the SmC$_A$* phase is in fact a double-twisted helicoidal structure, formed by two identical SmC*



(*a*) (*b*)

Figure 4. (*a*) Variation of relaxation rate versus q_s; (*b*) variation of relaxation rate versus $(q_s \pm 2q_0)^2$, corresponding to the SmC$_A$* phase of C$_{11}$thiobenzoate.

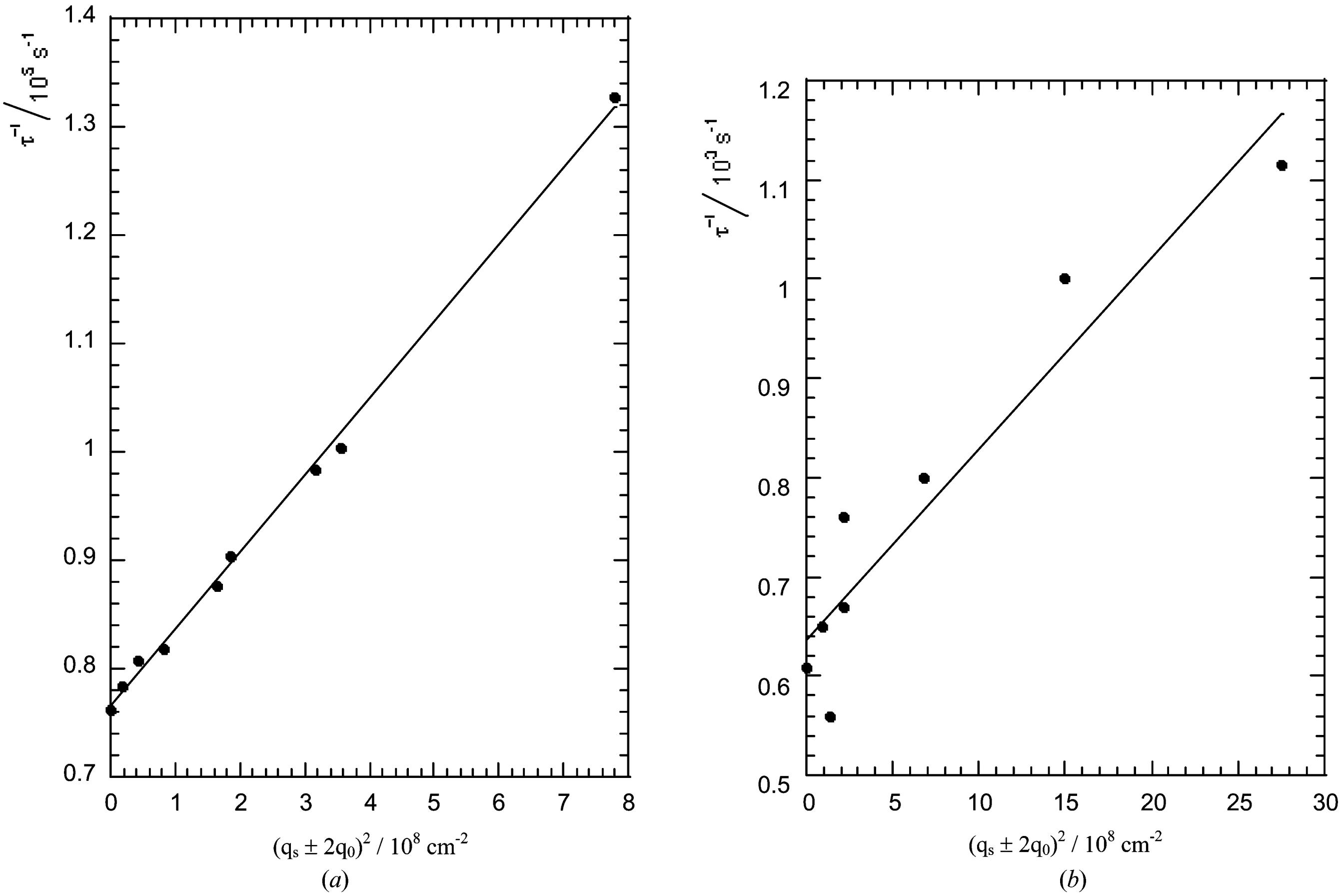
Table. Orientational diffusivities k_3/η and k_+/η associated with the Goldstone mode.

Sample	Phase	$\frac{k_3}{\eta}/\mathrm{m^2\,s^{-1}}$	$\frac{k_+}{\eta}/\mathrm{m^2\,s^{-1}}$
C_8tolane	SmC_A*[a]	1.3×10^{-12}	$\approx10^{-7}$
C_{11}thiobenzoate	SmC_A*[a]	2×10^{-11}	$\approx10^{-8}$
	SmC*[a]	7×10^{-9}	—
(*R*)-MHPOBC	SmC_A*[b]	$\approx7\times10^{-9}$	4×10^{-8}
EHPOCBC	SmC_A*[c]	10^{-11}	6×10^{-10}

[a] Measurements this paper.
[b] From reference [20].
[c] From reference [8].

helixes gearing into each other. From figure 5(*b*), we deduce $k_3/\eta=7\times10^{-9}\,\mathrm{m^2\,s^{-1}}$, which is about 10 times greater than that measured in SmC_A* phases of the C_{11}thiobenzoate. The factor 10 can be attributed to the nature of the fluctuation mode of the molecules belonging to two adjacent layers: in the SmC_A* phase, the phason mode observed at $\mathbf{q}_s=2\mathbf{q}_0$ is an antiferroelectric mode, whereas in the SmC* phase the phason mode is ferroelectric. We should note that this interpretation agrees with Musevic measurements of $k_3/\eta\approx2\times10^{-11}\,\mathrm{m^2\,s^{-1}}$ for the acoustic-like phason mode (antiferroelectric mode) and $k_3/\eta=2\times10^{-10}\,\mathrm{m^2\,s^{-1}}$ for the optic-like phason mode (a ferroelectric mode) [8].

Among the values reported in the table, we remark that k_3/η measured in the SmC* phase of C_{11}thiobenzoate is 100 times larger than those measured in the SmC_A* phase of C_8tolane. This difference can be attributed to (a) the nature of the fluctuation mode (ferro- or antiferroelectric mode), and (b) the structural difference between two compounds that belong to different chemical series (thiobenzoate and tolane). This difference can be manifested in the viscosity coefficient corresponding to liquid crystal phases. So, one may conclude that the arrangement of molecules in liquid crystal phases contributes in great part to the viscoelastic behaviour of the phases. This conclusion is in agreement with that deduced previously from investigations performed on discotic and rod-like nematic phases, where we concluded that liquid crystal



(*a*) (*b*)

Figure 5. (*a*) Variation of relaxation rate versus q_s; (*b*) variation of relaxation rate versus $(q_s\pm2q_0)^2$, corresponding to the SmC* phase of C_{11}thiobenzote.

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behaviour is governed by molecular arrangement, not by molecule shape.

4. Conclusion

In this paper we have described an experimental study performed on the ferro- and antiferroelectric phases exhibited by C_{11}thiobenzoate and C_8tolane. Using the light scattering technique, we measured in these phases the orientational diffusivities $\frac{k_3}{\eta}(\mathrm{SmC_A}^*)$ and $\frac{k_3}{\eta}(\mathrm{SmC}^*)$ associated with the Goldstone mode observed at $\mathbf{q}_s = 2\mathbf{q}_0$. For both compounds, $\frac{k_3}{\eta}(\mathrm{SmC_A}^*)$ is about one-hundredth the value of $\frac{k_3}{\eta}(\mathrm{SmC}^*)$. This divergence is probably due to the arrangement of molecules in the phases. This result is in a good agreement with that deduced from previous investigations performed on discotic and rod-like nematic phases, where we concluded that viscoelastic behaviour corresponding in a liquid crystal phase is governed in a great part by molecular arrangement not by molecular shape. To support this result, a study of the effect of temperature and the use of other compounds of the same series are planned.

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