Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Stegemeyer, H. , Meister, R. , Hoffmann, U. and Kuczynski, W.(1991) 'Induced smectic C* phases', Liquid Crystals, 10: 3, 295 — 310
To link to this Article: DOI: 10.1080/02678299108026277
URL: http://dx.doi.org/10.1080/02678299108026277

LIQUID CRYSTALS, 1991, VOL. 10, NO. 3, 295–310

Induced smectic C* phases

Concentration dependence of the ferroelectric properties and the effect of a local field

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(*Received 2 January 1991; accepted 16 March 1991*)

Induced ferroelectric S_C^* phases are formed by non-chiral S_C host phases doped with chiral dipolar guest molecules. In those mixtures the spontaneous polarization P_S and the tilt angle Θ has been investigated as a function of the mole fraction x_G of the chiral dopant. In most cases the reduced polarization $P_0=P_S/\sin\Theta$ has been found to depend linearly on x_G. The polarization power which is defined by $\delta_P=(\partial P_0/\partial x_G)_{\Delta T}$ is discussed in terms of the molecular structure of the chiral dopants. There are systems in which $P_0(x_G)$ deviates positively from linearity. This behaviour can be understood by considering a local field correction to P_0. By assuming a local field of Lorentz type a theoretical relation for $P_0(x_G)$ has been derived which explains the experimental results. The effect of a local field is considerable if the transverse dipole moment and the polarizability of the chiral dopant are large.

1. Introduction

Induced smectic C* phases are formed by the addition of chiral dopants (mesogenic or not) to achiral smectic C host phases. If the chiral guest molecules have permanent dipoles transverse to their long axes the induced S_C^* phases show ferroelectricity [1–3]. It has been found that the tilt angle Θ as well as the spontaneous polarization P_S depend strongly on the mole fraction x_G of the chiral dipolar guest molecules [2, 3]. In their extended thermodynamic model Zeks *et al.* [4] take into account a coupling between Θ and P_S. Because of this relation, which has been verified experimentally we introduce a reduced polarization P_0 which also depends on the concentration of the chiral dopant,

$$P_0(x_G)=\frac{P_S(x_G)}{\sin\Theta(x_G)}. \tag{1}$$

Whereas the concentration dependence of $P_S(x_G)$ and $\Theta(x_G)$ was found to be non-linear, in a number of systems $P_0(x_G)$ is linear and does not depend on the nature of the achiral smectic C host phase [2, 3, 5]. Thus, we define a material constant, the polarization power δ_P

$$\delta_P=\left(\frac{\partial P_0(x_G)}{\partial x_G}\right)_{x_G\to 0} \tag{2}$$

at a constant temperature difference below the transition S_C^*–S_A or S_C^*–cholesteric. δ_P describes the ability of a given chiral dipolar dopant to induce a spontaneous

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polarization in a smectic C host phase [3]. It should be mentioned that in all systems investigated hitherto δ_P is independent of the nature of the host phase. Recently, a positive deviation from the linear relation of $P_0(x_G)$ has been reported for chiral dopants with strong transverse dipole moments [6, 7].

At a molecular level the spontaneous polarization originates from the average transverse dipole moments of all chiral guest molecules in the tilted host phase. Therefore, to a first approximation we expect a linear increase of P_0 with the number density of guest molecules. To explain the deviation from linearity of $P_0(x_G)$ we introduce a local field correction and derive a relationship between P_0 and x_G which explains the experimental results sufficiently.

2. Experimental

The structure and phase sequence of the host and guest substances are listed in table 1. The host substance 8007 was synthesized using the method described by Schubert and Weissflog [8], the substances IS 1662, IS 2612, NCB 808, NCB 84 and ZLI 4420 were made available by courtesy of E. Merck (Darmstadt). The guest substance A9 was provided by Professor Heppke, Th*06 by Dr Tschierske, RO-41-6152 and RO-41-5447 were made available by courtesy of Hoffmann-La Roche. All other substances have already been reported in previous articles [2, 3].

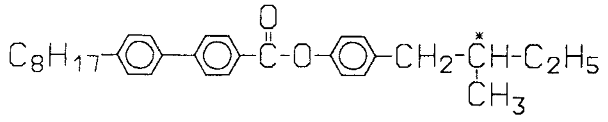
The phase diagrams of the mixtures were determined by polarizing microscopy and differential scanning calorimetry. The temperature of the sample was controlled by an improved version of a Mettler FP 5/52 hot stage with a relative accuracy of 10^{-2} K. Both the spontaneous polarization and the tilt angle have been measured on the same sample of dimensions 0·7 cm × 0·7 cm × 16 μm. Planar alignment of the S_C^* phase was achieved by cooling slowly from the cholesteric phase in the presence of an applied low frequency voltage. By this procedure we obtained the bookshelf geometry and avoided chevron structures. The spontaneous polarization was measured by a Diamant bridge [9] and the tilt angle was derived from the optical switching angle of the sample.

3. Results

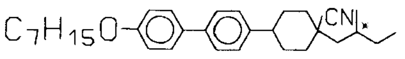
3.1. *Phase diagrams*

In order to prove the effect of the achiral host phase on P_0 the chiral guest compound ZLI 4420 was dissolved in the different host phases 8008, NCB 808 and RO-41-5447. The phase diagrams of the first two mixed systems have already been published [3], that of the mixture ZLI 4420/RO-41-5447 is given in figure 1. In all three systems the S_C^* phase extends over the whole concentration range $0 < x_G \leqslant 1$. Although RO-41-5447, as well as ZLI 4420, exhibit an S_A phase in their pure state this phase vanishes at intermediate concentrations of ZLI 4420 (see figure 1).

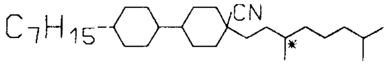
The phase diagrams of the other mixtures under investigation are shown in figures 2 (*a*)–2 (*d*). As the S_C^* phase in the pure guest compound A9 is only monotropic in the mixtures with 8007 (see figure 2 (*a*) and NCB 808 (see figure 2 (*b*)) the existence of the S_C^* phase is restricted to mole fractions $x_G \leqslant 0{\cdot}8$. These mixtures could be supercooled with respect to the crystalline phase. In the system A9/NCB 808 which shows higher ordered smectic phases crystallization could not be obtained at all. In this system a wide two phase region S_A/I was observed above $x_G \geqslant 0{\cdot}1$. By extrapolation of the phase transition temperature T_S^{C/S_A} to $x_G = 1$ (cf. figure 2 (*b*)) we obtained a value of 68°C for pure A9 which has also been reported in [10]. As the S_I^* phase vanishes with increasing mole



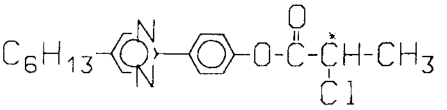
CE8 C 48 S_G 63·3 S_J^* 64·7 S_F^* 66·7 S_I^* 69 S_C^* 85 S_A 135 Ch 141 I



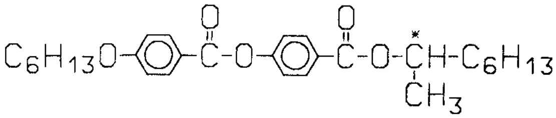
ZLI 4420 C 69 S_C^* 110 S_A 111 Ch 132 I



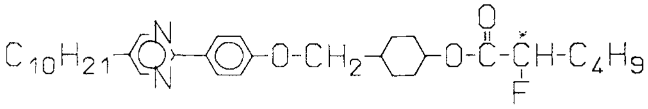
C7D C 45 (S_B 42) I



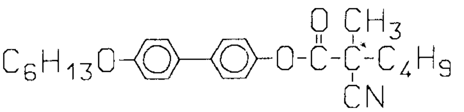
IS 1662 C 83·4 I



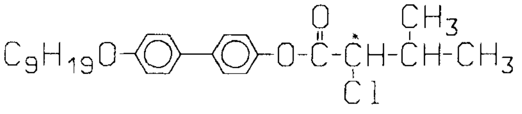
S 811 C 48·5 I



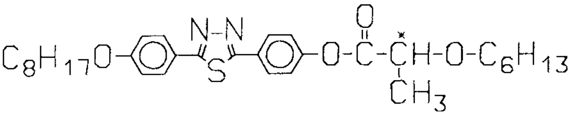
RO-41-6152 C 87·2 (S_X^* 84·3) S_I^* 108·4 S_C^* 129·9 S_A 137·2 I



IS 2612 C 50·2 I

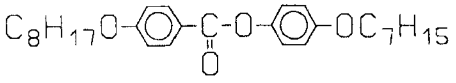


A9 C 80·8 (S_X^* 62·5 S_C^* 68·0) S_A 81·8 I

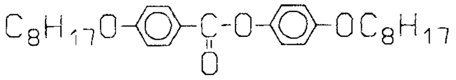


Th*06 C 87·0 S_C^* 139·2 I

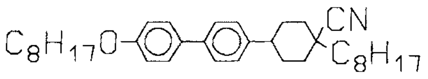
Table 1. (*a*) Molecular structures and transition temperatures (*T*/°C) of the chiral dipolar guest molecules.



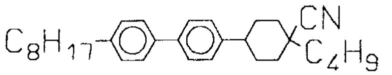
8007 C 62·9 S_C 69·1 N 86·6 I



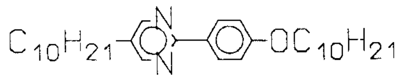
8008 C 62 S_C 73 N 90 I



NCB 808 C 78·2 (S_F 40·0 S_I 50·4) S_C 117·3 S_A 147·4 N 149·1 I



NCB 84 C 42·0 S_G 49·4 S_C 72·1 S_A 88·0 N 118·1 I



RO-41-5447 C 41 S_C 74 S_A 77 I

Table 1. (*b*) Molecular structure transition temperatures (*T*/°C) of the achiral smectic C host phases.

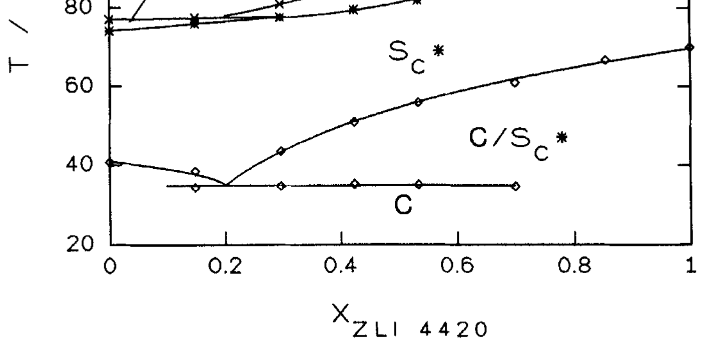
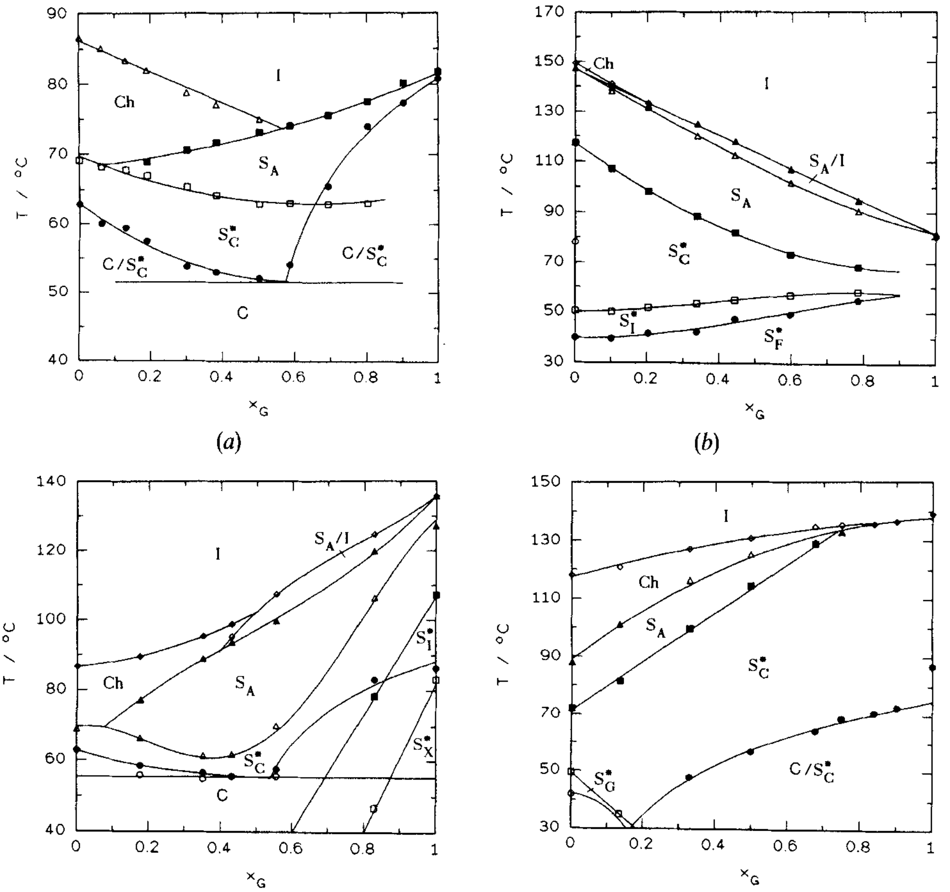


Figure 1. Phase diagram of the mixed system ZLI 4420/RO-41-5447.



(a) (b)

(c) (d)

Figure 2. Phase diagrams of the mixed systems (a) A9/8007; (b) A9/NCB 808, (c) RO-41-6152/8007; (d) Th*06/NCB 84.

fraction of A9 we conclude that the unknown low temperature phase of A9 mentioned in [10] is of type S_F^* (cf. figure 2(b)).

The phase diagram of the mixture RO-41-6152/8007 is rather complicated (see figure 2(c)) because of the highly ordered smectic phases of the guest substance. However, the S_C^* phase extends over the whole concentration range. But by insertion of the broad S_A phase, the S_C^* temperature span is rather small. At higher guest concentrations we found a rather broad two phase region S_A/I.

The phase diagram of the mixed systems Th*06/NCB 84 (see figure 2(d)) exhibits a broad S_C^* phase over the whole concentration range. The S_A phase vanishes at $x_G = 0\cdot7$ as well as the cholesteric one.

Further details of the phase behaviour of the mixed systems under discussion may be taken directly from figures 1 and 2.

3.2. *Tilt angle and spontaneous polarization*

The polarization and the tilt angle of each mixture were measured as a function of temperature. From this data we derived the concentration dependence of P_S and Θ at a constant temperature below the phase transition S_C^* to CH or S_A. The functions $P_S(x_G)$ and $\Theta(x_G)$ are given in figures 3–5.

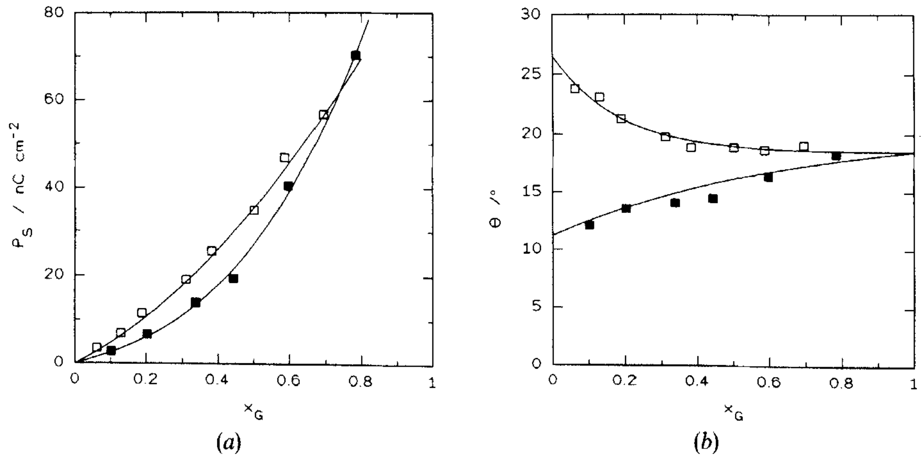
The concentration dependence P_S for A9 in the host phases 8007 and NCB 808 is rather similar in both cases and shows a negative deviation from linearity (see figure 3 (*a*)). We could not measure P_S at concentrations of $x_G > 0{\cdot}8$ for in the mixed system A9/8007 crystallization occurred (cf. Figure 2 (*a*)). In the mixed system A9/NCB 808 the temperature range of the S_C^* phase becomes too narrow for $x_G > 0{\cdot}8$. Extrapolation of the measured P_S values to $x_G = 1$ results in a rather higher value than that reported for pure A9 [11] for which the authors found $P_S = 40\,\mathrm{nC\,cm^{-2}}$ at $\Delta T$of 5 K. This low value may be caused by the fact that the S_C^* phase of A9 is only monotropic. In figure 3 (*b*) the concentration dependence of the tilt angle Θ of A9 shows a quite different behaviour for the two host phases 8007 and NCB 808. The sign of the slope of $\Theta(x_G)$ is opposite in both cases. An extrapolation of the curves for both systems to $x_G = 1$ leads to a tilt angle of 18° which is identical with the value measured by small angle X-ray scattering for pure A9 [11].

For the chiral dopant RO-41-6152 in 8007 we found a monotonic increase of P_S with x_G (see figure 4 (*a*)). The function $\Theta(x_G)$ runs through a minimum (cf. figure 4 (*b*)). In the case Th*06 in NCB 84 both curves for P_S and Θ exhibit a non-linear increase with x_G (see figure 5).

Summarizing these results we can see that there is neither a linear dependence of P_S on the number density of the chiral dipolar guest molecules nor a systematic relation of Θ on the concentration of the different guest/host systems.

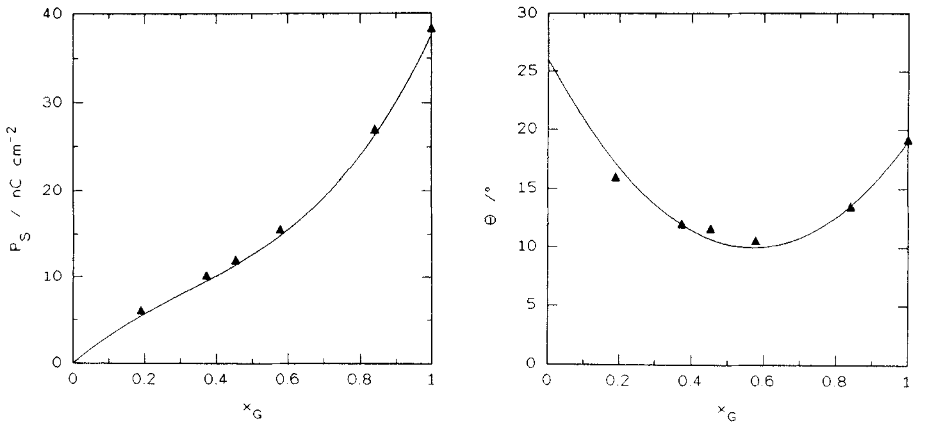
3.3. *Dependence of P_0 on concentration and on the nature of the host*

Because of the relation between the spontaneous polarization and the tilt angle mentioned in the Introduction we have investigated the dependence of the reduced polarization P_0 (cf. equation (1)) on the mole fraction of the chiral guest compound. The results for $P_0(x_G)$ are given in figures 6 to 9. In figure 6 the value of P_0 for ZLI 4420 is given as a function of x_G for three host phases which are quite different in their



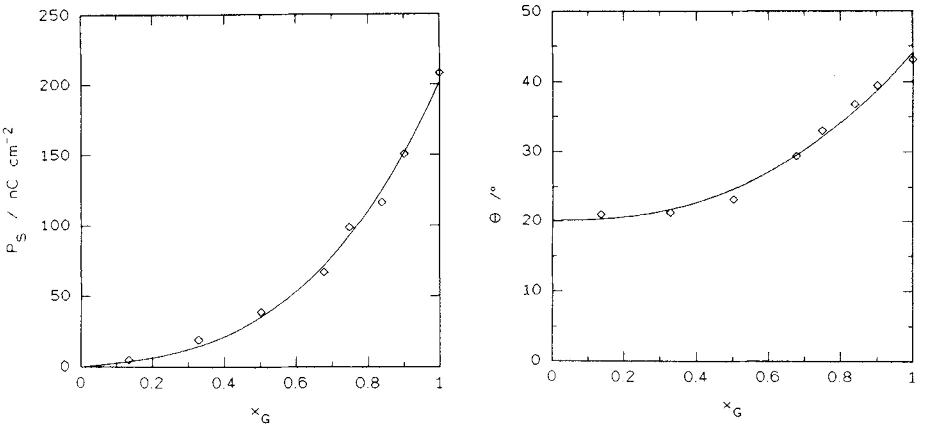
(*a*) (*b*)

Figure 3. (*a*) P_S as a function of the mole fraction x_G of the chiral guest compound A9 in 8007 (□) and NCB 808 (■) at a temperature 5 K below the transition S_C^* to Ch or S_A; (*b*) Θ as a function of x_G for A9/8007 (□) and A9/NCB 808 (■) at a temperature 5 K below the transition S_C^* to Ch or S_A.



(a) (b)

Figure 4. (a) P_S as a function of x_G for the system RO-41-6152 in 8007 at a temperature 5 K below the transition S_C^* to Ch or S_A. (b) Θ as a function of x_G for the system RO-41-6152 in 8007; conditions as in (a).



(a) (b)

Figure 5. (a) P_S as a function of x_G for the system Th*06 in NCB 84 at a temperature 20 K below the transition S_C^* to I or S_A. (b) Θ as a function of x_G for the system Th*06/NCB 84; conditions as in (a).

molecular structure and their phase behaviour. The relation $P_0(x_G)$ is linear and the data for the different hosts fit the same curve. Consequently, P_0 and also the polarization power δ_P (cf. equation (2)) of a given chiral guest compound are independent of the nature of the host phase as reported in [3]. The values of the polarization power of different chiral guests are summarized in table 2.

The question arises if $P_0(x_G)$ is generally a linear function of concentration. We have investigated the guest compound A9 in which the transverse C-Cl dipole is directly connected to the chiral centre. As shown in figure 7 the function $P_0(x_G)$ in this case shows a strong deviation from linearity. As the host compound we have used NCB 808 and 8007. The P_0 data obtained for these different hosts fit the same curve

Table 2. Polarization power δ_p of several chiral guest molecules (molecular structure cf. table 1).

Substance	δ_P/nC cm^{-2}
CE8	8
ZLI 4420	25
C7D	42
IS 1662	50
S 811	121
RO-41-6152	129
IS 2612	238

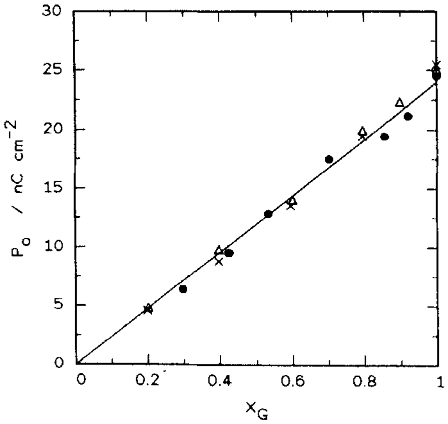


Figure 6. The reduced polarization P_0 as a function of the mole fraction x_G of the chiral guest compound ZLI 4420 at a temperature 5 K below the transition S_C^* to S_A or Ch. Different host phases: 8008 (×), NCB 808 (△) and RO-41-5447 (●).

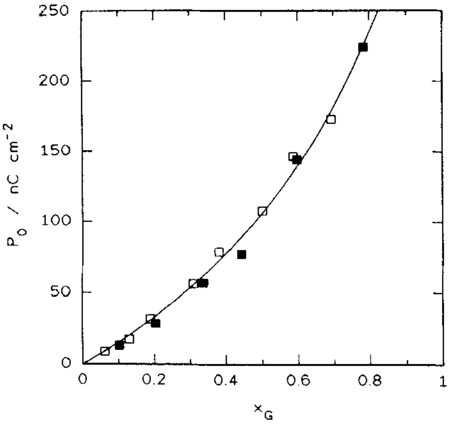


Figure 7. P_0 as a function of the mole fraction x_G of the chiral guest compound A9 in different host phases: 8007 (□) and NCB 808 (■) at a temperature 5 K below the transition S_C^* to S_A.

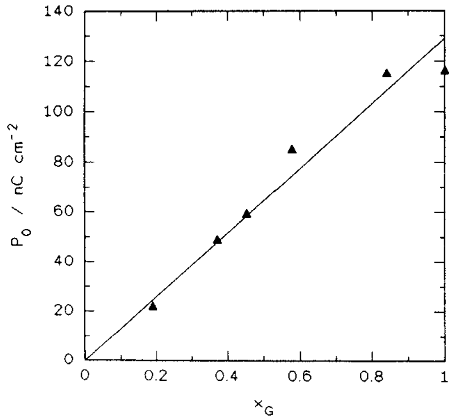


Figure 8. P_0 as a function of the mole fraction x_G of the chiral guest compound RO-41-6152 in 8007 as a host phase at a temperature 5 K below the transition S_C^* to S_A.

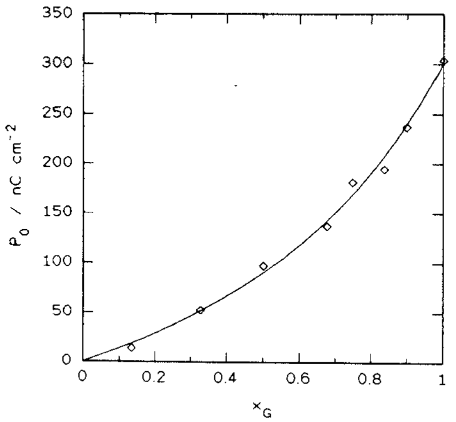


Figure 9. P_0 as a function of the mole fraction x_G of the chiral guest compound Th*06 in NCB 84 as a host phase at a temperature 5 K below the transition S_C^* to S_A or I.

(cf. figure 7) demonstrating the independence of P_0 on the host even when $P_0(x_G)$ is non-linear. The data for $P_0(_G)$ for another guest compound RO-41-6152 also bearing a strong C-F dipole at the chiral centre are given in figure 8. To our surprise in this case a linear relation results for $P_0(x_G)$. The chiral thiadiazole derivative Th*06 in the host compound NCB 84 exhibits a curve $P_0(x_G)$ which also deviates strongly from linearity (cf. figure 9).

The relation $P_0 = f(x_G)$ can be given by an empirical formula

$$P_0(x_G) = \frac{a x_G}{1 - b x_G}. \tag{3}$$

The constant a is identical with the polarization power δ_P (cf. equation (2)) where b governs the deviation from linearity. The empirical formula of equation (3) can also be applied to the linear function $P_0(x_G)$ with $b = 0$. The data concerning equation (3) for the systems under discussion are given in table 3. It should be mentioned that non-linear concentration functions P_S/Θ (which is very similar to P_0) have also been found in other

Table 3. Concentration dependence of P_0 for several chiral guest molecules in terms of the constants a and b according to equation (3).

Substance	$a=\delta_P/\text{nC cm}^{-2}$	b
RO-41-6152	129	0
A9	145	0·61
Th*06	129	0·57

guest host systems [6, 12]. It has to be explained why $P_0(x_G)$ is linear in most cases but non-linear in other systems. This will be done with a model developed in the following section.

4. Theory

We start from the microscope model given by Zeks *et al.* [4, 13] in which the ordering of the transverse dipoles $\mu_\perp$ is assumed to be induced by the tilt only and a hindered rotation of the molecules around their long axes is taken into account. If the angle ψ describes the orientation of $\mu_\perp$ around the molecular long axis the potential for the hindered rotation is given by

$$U(\psi)=-a_1\Theta\cos\psi-a_2\Theta^2\cos 2\psi. \qquad (4)$$

The first term is of chiral character whereas the second is non-chiral and exists in tilted systems. There are two positions of $\mu(\psi)$ with a minimum of $U(\psi)$ at $\psi=0$ and π with the deepest minimum of U at $\psi=0$. On the basis of this rotational model Buka *et al.* [14] gave an interpretation of the experimental temperature dependence of P_S/Θ by a two parameter fit procedure.This procedure was successful for systems with a linear concentration dependence of $P_0(x_G)$ [5, 14] but failed in those mixtures with a non-linear function of $P_0(x_G)$ as described in section 3.3 [15]. Therefore, it was suggested to introduce a correction for molecules with very strong transverse dipoles. For this correction we consider the effect of a local field E_l on the ferroelectric properties of an induced S_C^* phase. As sketched in figure 10 the transverse dipoles of the chiral guest molecules will be forced, on average, into the same direction by the steric strain in the tilted smectic layer. The transverse dipoles are shown by arrows with their negative ends in an up position which also gives the direction of P_S. We cut a spherical cavity around an arbitrary molecule which is affected by a local field of Lorentz type [16]

$$E_l=\frac{1}{3\varepsilon_0}P_S. \qquad (5)$$

Actually, the Lorentz field concerns a cubic phase structure, but as the transverse dipoles are distributed statistically within a smectic C layer, to a first approximation, we neglect the symmetry of the phase. The single molecule is polarized by the dipoles outside the cavity with positive charge carriers at the surface of the upper half sphere and negative ones at the lower. By this polarization the single molecule will be affected in two ways: (i) its dipole will be turned into the direction of P_S, and (ii) the molecule will be polarized resulting in an additional induced dipole moment μ_i which also points in the direction of P_S. Thus is follows

$$P_S=N_1(\mu_{or}+\mu_i), \qquad (6)$$

where N_1 is the number density of the dipoles and μ_{or} and μ_{i} are given by

$$\mu_{\mathrm{i}} = \alpha_{\mathrm{v}} E_{\mathrm{l}} \tag{7}$$

and

$$\mu_{\mathrm{or}} = \langle \mu \rangle = \mu_{\perp} \langle \cos \psi \rangle. \tag{8}$$

α_{v} is the polarizability of the molecule in the neighbourhood of the transverse dipole. The expectation value of $\cos\psi$ can be calculated by standard statistical methods

$$\langle \cos\psi \rangle = \frac{\int_0^{2\pi} \exp(-U/kT) \cos\psi \, d\psi}{\int_0^{2\pi} \exp(-U/kT) \, d\psi}. \tag{9}$$

Considering the local field correction we must extend the rotational potential $U(\psi)$ of equation (4) given by Zeks *et al.* [4, 13] by a third term

$$U(\psi) = -a_1 \Theta \cos\psi - a_2 \Theta^2 \cos 2\psi - E_{\mathrm{l}} \mu_{\perp} \cos\psi. \tag{10}$$

The integrals in equation (9) cannot be calculated in a closed form. Thus, we expand the exponential in a series

$$\exp(x) = \sum_n \frac{1}{n!} x^n, \tag{11}$$

with $x = -U/kT$. Considering terms up to the nth order we obtain after integration:

$$\langle \cos\psi \rangle_1 = \frac{a_1\Theta + E_{\mathrm{l}}\mu_{\perp}}{2kT}, \tag{12a}$$

$$\langle \cos\psi \rangle_2 = \frac{(a_1\Theta + E_{\mathrm{l}}\mu_{\perp})(2kT + a_2\Theta^2)}{4(kT)^2 + (a_1\Theta + E_{\mathrm{l}}\mu_{\perp})^2 + (a_2\Theta^2)^2}, \tag{12b}$$

$$\langle \cos\psi \rangle_3 = \frac{(a_1\Theta + E_{\mathrm{l}}\mu_{\perp})[8(kT)^2 + 4kTa_2\Theta^2 + 2(a_2\Theta^2)^2 + (a_1\Theta + E_{\mathrm{l}}\mu_{\perp})^2]}{16(kT)^3 + 4kT(a_1\Theta + E_{\mathrm{l}}\mu_{\perp})^2 + 4kT(a_2\Theta^2)^2 + 2(a_1\Theta + E_{\mathrm{l}}\mu_{\perp})^2 a_2\Theta^2}. \tag{12c}$$

To a first approximation we use $\langle \cos\psi \rangle_1$ from equation (12 *a*) which only contains the term $a_1\Theta$ of the chiral part of $U(\psi)$ according to equation (10) besides the expression for the local field. From equations (6), (7), (8) and (12 *a*) we obtain

$$P_{\mathrm{S}} = N_1 \left[\frac{\mu_{\perp} a_1 \Theta}{2kT} + \left(\frac{\mu_{\perp}^2}{2kT} + \alpha_{\mathrm{v}} \right) E_{\mathrm{l}} \right]. \tag{13}$$

E_{l} can be eliminated by means of equation (5) to give

$$P_{\mathrm{S}} = \frac{N_1 \left(\dfrac{\mu_{\perp} a_1 \Theta}{2kT} \right)}{1 - \dfrac{N_1}{3\varepsilon_0} \left(\dfrac{\mu_{\perp}^2}{2kT} + \alpha_{\mathrm{v}} \right)}. \tag{14}$$

The relation between the number density N_1 of the chiral dipolar guest molecules and their mole fraction x_{G} is given by

$$N_1 = N_0 x_{\mathrm{G}}, \tag{15}$$

where N_0 is the total number density. Considering equation (15) and dividing by Θ we obtain

$$P_0=\frac{P_S}{\Theta}=\frac{N_0\left(\dfrac{\mu_\perp a_1}{2kT}\right)x_G}{1-\dfrac{N_0}{3\varepsilon_0}\left(\dfrac{\mu_\perp^2}{2kT}+\alpha_v\right)x_G}. \tag{16}$$

This expression for $P_0(x_G)$ is similar to the experimental function given in section 3.3 by equation (3). A positive deviation of $P_0(x_G)$ can be expected for large transverse dipole moments $\mu_\perp$ and if the polarizability α_v of the molecular neighbourhood of the dipole is large.

5. Discussion

5.1. *Polarization power and molecular structure*

There are at least two important molecular quantities which influence the polarization power δ_P. The first is the size and direction of the molecular dipole, and the second the potential energy of a molecule for the rotation around its long axis. This can be seen by equation (16) in which the two quantities $\mu_\perp$ and a_1 are involved in the numerator. Let us consider first the relationship between the molecular structure and the dipole moments. Generally, it can be said that the greater the dipole moment for a given molecular structure the greater will be δ_P. There is one more molecular property which opens a quantitative statement. The angle ξ between the dipole and the molecular long axis scales the transverse dipole as $\mu_\perp=\mu\sin\xi$ (cf. figure 11). Dipoles staying perpendicular to the long molecular axis cause a large value of δ_P. Another

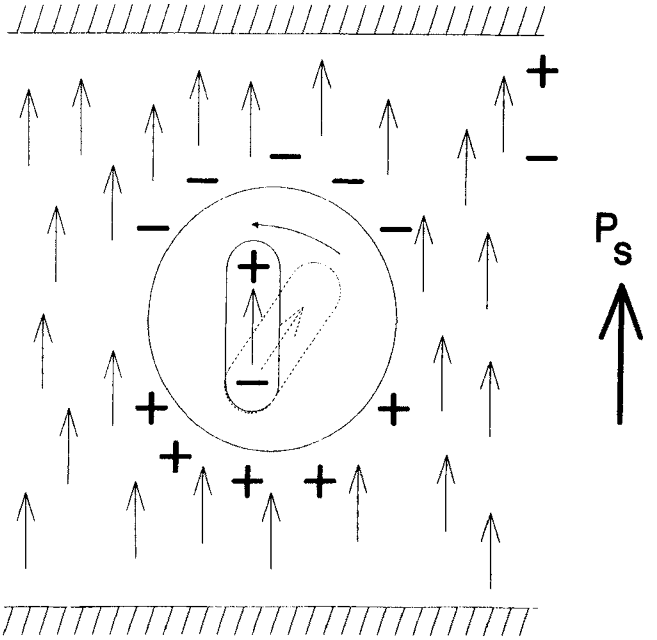


Figure 10. Model of an ensemble of transverse dipoles of chiral guest molecules in a layer of a smectic C host phase demonstrating the effect of a local field on a single dipole.

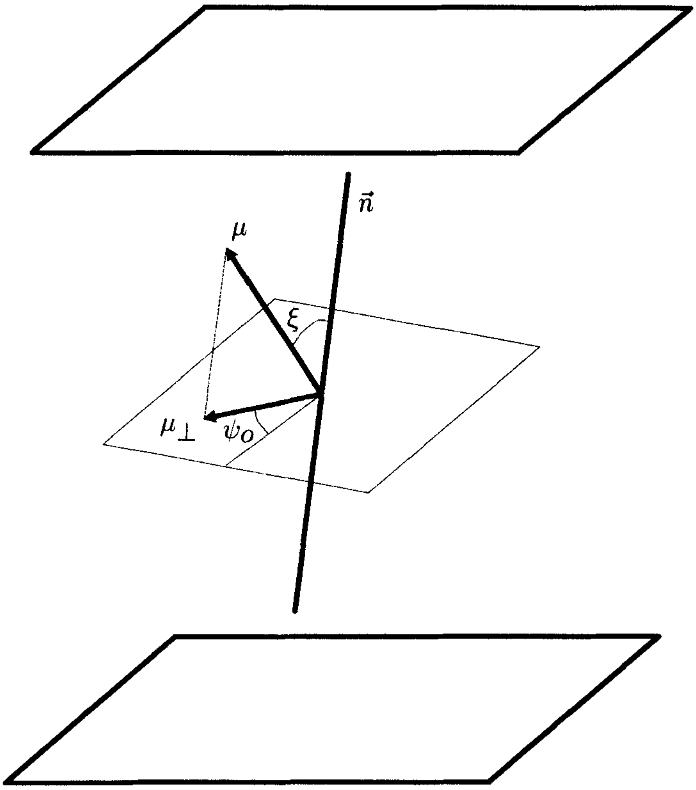


Figure 11. Model of a molecule lying in a smectic C layer. The molecule possesses its minimal potential energy.

influence is the distance between the dipole and chiral centre. The further they are apart the more internal rotations are possible. The result is that the average dipole decreases very quickly with the distance to the chiral centre. Therefore, it is important for high values of δ_P that the dipole is placed near the chiral centre, at best directly connected to it.

The potential energy for the rotation of a molecule around its long axis is given by the model of Zeks (cf. equation (4)). Now let us consider the influence of the molecular structure on the potential parameters a_1 and a_2. Some steric effects should increase the values of the a_i. This steric effect could be due to a branch in the alkyl chain or to a rigid molecular structure. As for a high δ_P we need a large value of a_1. The group of the molecule that causes the steric effects should be near the chiral centre in order to affect a_1. If the groups that cause the steric effects have a great distance to the chiral centre they merely affect a_2 but not a_1 because the possibility of internal rotations of the molecule diminishes the chiral effects very sharply. So, as a result it can be said that the chiral centre of a molecule should be placed near a branch in the alkyl chain and/or near the rigid part of the molecule to maximise the influence of steric effects on a_1.

Still another angle comes into play on considering the relation between the molecular dipole $\mu_\perp$ and the potential energy $U(\psi)$ for rotation around the long molecular axis. Assume that the molecule lies in the position of minimal potential energy. Let ψ_0 be the angle between the transverse dipole $\mu_\perp$ and the $\psi = 0$ direction (cf.

figure 11). Then the chiral term a_1 is scaled by $a'_1 = a_1 \cos\psi_0$. Consider the situation, when $\psi_0 = 90°$. Then there will be no spontaneous polarization though $\mu_\perp$ may exhibit very large values.

Now we turn to a discussion about the relationship of our experimental results for δ_P of some substances and the previous mentioned parameters of molecular structure (cf. table 2). Let us start with CE 8. The only dipole is the C = O group. Although there is a branch at the chiral centre, the distance between the dipole and the chiral centre is too large so that the polarization power becomes small and is 8 nC cm^{-2}. Next we considered ZLI 4420 with its strong CN dipole. But as for CE 8, the distance between the chiral centre and the dipole is too large. So the polarization power δ_P is only 25 nC cm^{-2}. The same argument can be used for C7D with a polarization power of 42 nC cm^{-2}. The molecular structure of IS 1662 shows two dipoles connected directly to the chiral centre. But in spite of that δ_P remains moderate ($\delta_P = 50$ nC cm^{-2}). There are several possible explanations: (i) the two dipoles subtract from each other; (ii) a large value for ψ_0; (iii) a_1 is small due to little steric hindrance. S 811 shows a larger value for δ_P of 121 nC cm^{-2}. Here only one dipole is connected directly to the chiral centre, but there is another carboxyl group, located further from the chiral centre. The increase of δ_P compared with IS 1662 may be attributed to: (i) the steric effect of the branch; (ii) there is no subtraction of two dipoles. Next we turn to RO-41-6152. This substance shows a similar location of dipoles around the chiral centre as IS 1662, but δ_P of 129 nC cm^{-2} is greater. The reason for this increase might be caused by: (i) a smaller value of ψ_0 than in IS 1662; (ii) addition of the C-F and the C = O dipole. Finally let us consider IS 2612, with δ_P of 238 nC cm^{-2}. This value, compared with IS 1662 and RO-41-5162 is attributed to: (i) the large CN dipole; (ii) steric hindrance by the methyl substituent.

Generally it can be summarized that the relation between the molecular structure of the chiral dopants and the polarization power deserves further experimental investigation.

5.2. *Non-linearity of $P_0(x_G)$*

The model given in section 4 in which the effect of a local field on the ferroelectric properties has been considered enables us to explain why there is a deviation from linearity of the function $P_0(x_G)$ in some cases (with $b > 0$ in equation (3)). A first attempt to take into acount the dielectric properties of the surrounding of the transverse dipoles was given by Walba *et al.* [17] by considering the effect of the permittivity ε on P_S (formula (3) in [17]). Beresnev *et al.* [18] and recently, Geelhaar *et al.* [19] found a considerable dependence of P_S in induced S_C^* phases on the permittivity of the achiral host. The factor a in equation (16) is identical to the polarization power δ_P. An estimate of a with $\mu = 5 \times 10^{-30}$ Cm and $a_1 = 1{\cdot}4 \times 10^{-22}$ J [14] gives about 12 nC cm^{-2} which is of the right order of magnitude. It must be considered that the estimated value of a is related directly to the phase transition S_C^* to Ch or S_A because of the definition of a_1 [14] where the experimental values in table 2 and 3 were obtained 5 or 20 K below the phase transition and therefore are somewhat larger. Because of the local field correction introduced in section 4 the factor b of the empirical formula (3) which governs the deviation from linearity of $P_0(x_G)$ results in

$$b = \frac{N_0}{3\varepsilon_0}\left(\frac{\mu_\perp^2}{2kT} + \alpha_v\right), \qquad (17)$$

which follows from equation (16). In equation (17) $\mu_\perp$ is the component of the molecular dipole moment transverse to the molecular long axis and α_v is the component of the polarizability tensor in the same direction. Consequently, non-linearity in $P_0(x_G)$ will be caused by those chiral dopants which have large transverse dipoles and which exhibit large values of α_v.

The result of a rough estimation of b in equation (17) with $\mu_\perp = 5 \times 10^{-30}$ Cm is about 0·2 which is in the order of magnitude of the experiment values (cf. table 3). It should be mentioned that α_v for only the C–Cl bond is two orders of magnitude smaller than the first term $\mu_\perp/2kT$ in equation (17). But the polarizability of other parts of the molecule, especially the neighbourhood of the transverse dipole of probably the whole molecule must be taken into account. This would cause an enhancement of α_v with respect to $\mu_\perp/2kT$. However, it is still an open question as to which part of the chiral molecule the transverse tensor component α_v is to be related. In systems with a linear function $P_0(x_G)$ which we have described earlier [3, 5] and also given in this paper obviously the resulting transverse dipole compounds are rather small often caused by an internal rotation of the dipole bearing groups. For the chiral guest molecule A9 with a strong C–Cl dipole directly connected to the chiral centre a strong deviation of b from zero can be expected (cf. equation (17)). On the other hand the linearity of $P_0(x_G)$ with $b \approx 0$ for the dopant RO-41-6152 with a C–F dipole at the chiral centre cannot be understood if we consider only the value of μ. For the bond moments C–Cl and C–F are nearly equal (1·87 and 1·85 Debye, respectively [20]). But according to equation (17) we also have to take into account the polarizability α_v. This quantity is different by a factor of 4 in the case of Cl and F. The values of the static average electric dipole polarizabilities are $0{\cdot}557 \times 10^{-24}$ cm^3 for F and $2{\cdot}18 \times 10^{-24}$ cm^3 for Cl [21]. Additionally, the neighbouring cyclohexane ring in RO-41-6152 is less polarizable than the benzene ring at an analogous position in the compound A9. A larger value of α_v for the chloro compound A9 with respect to the fluoro compound seems to be responsible for $b > 0$ in equation (17).

The non-linear behaviour of the chiral guest compound Th*06 seems to be obvious because of the properties of the thiadiazole ring. Firstly, a strong transverse dipole is located in this ring. Secondly, the transverse tensor component of the polarizability α_v of this ring is rather large. The bond refraction (for the Na D line) is 12·50 cm^3 for the S–C–S group compared with the much smaller value of 3·42 cm^3 for the C=O group [22].

It should be emphasized that the effect of a local field discussed in the paper is also present in neat ferroelectric S_C^* phases with high values of P_S but it is hidden there and cannot be detected separately. The local field effect only becomes obvious on dilution in the host of the induced S_C^* phases.

This work has been supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Heinz Nixdorf Institut (ZIT), Paderborn.

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