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Ferroelectricity of induced S_C^* phases with novel chiral dopants

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Induced S_C^* phases can be obtained by dissolving chiral dopants in achiral S_C host phases. If the chiral guest molecules bear a transverse dipole, ferroelectricity will occur. The novel dopants under discussion are characterized by chiral centres and the transverse dipole situated not in the alkyl end groups of the mesogenic molecules, but directly in their rigid cores. As a rigid core, analogues of decalin were used. In those dopants, rotation around the molecular long axis is sterically restricted. According to the microscopic model of Zeks, this leads to enhanced values of the spontaneous polarization P_s. The magnitude as well as the sign of the spontaneous polarization P_s of the S_C^* phases induced by the novel dopants in different host phases has been investigated. It has been found for the first time that for a given dopant, the polarization as well as the sign of P_s depends on the structure of the host phase. The results are discussed in terms of two microscopic models. They can be understood taking into account the situation that the potential of the restricted long axial rotation is determined by the hard core interactions of the molecules involved or that an orientation of the host dipoles by a guest/host interaction takes place.

1. Introduction

Induced chiral smectic C phases (S_C^* phases) are formed by dissolving chiral guest molecules bearing one or more dipolar groups transverse to the molecular long axis in an achiral smectic C host phase. The chiral dopant molecules may be mesomorphic by themselves or not. It has been shown [1, 2] that the induced S_C^* phases are ferroelectric with a spontaneous polarization, P_s, which depends on the molecular structure of the dopant and its mol fraction x_G [3]. The advantage of these mixed S_C^* phases is that other properties important for applications can be adjusted through the nature and composition of the host phase (for example phase transition temperature, rotational viscosity, birefringence).

Normally, the molecules building ferroelectric S_C^* phases, as well as those formerly used as dopants carry the transverse dipole $\mu_\perp$ and the chiral centre (asymmetric carbon atom *) in an alkyl end chain attached to a rigid core (for example benzene or biphenyl rings) [4] as sketched in formula I*a*. An extreme increase in P_s was obtained by linking the transverse dipole directly to the chiral centre [4, 5] (*cf.* formula I*b*). However, in all molecules of type **I**, the transverse dipolar group can more or less rotate with respect to the plane of the rigid core. Considering the microscopic model of Zeks *et al.*, such a rotation would decrease the resulting value of P_s in the same manner as rotation of the whole molecule around its long axis [6, 7]. Consequently, in dopant molecules of the general formula **II** these rotational processes (rotation angle ψ) are expected to be restricted.

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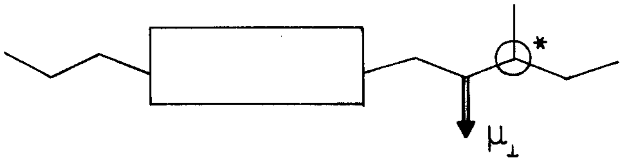
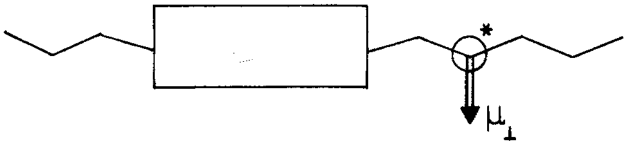
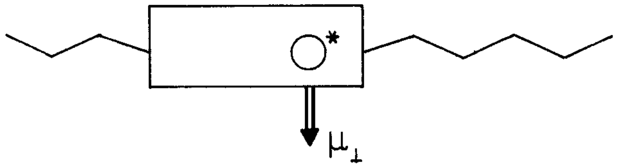


I*a*

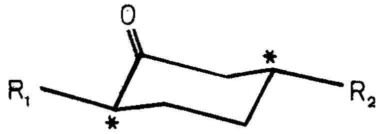


I*b*



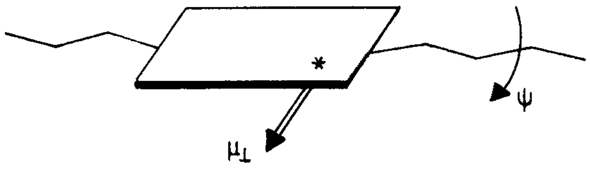
II

In type **II** molecules the chiral centre, as well as the transverse dipole, is introduced directly into the rigid core. Some attempts of this kind have been reported in the literature [8, 9], and induced S_C^* phases formed with type **II** dopants have been published by us recently [10]. The common core structure of all dopants reported in [10] was the cyclohexanone ring **III**:

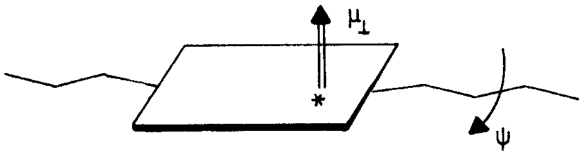


III

We have shown that a molecular reference axis must not necessarily coincide with the direction of the transverse dipole. For instance the transverse dipole can be directed perpendicular to the core plane or be in plane of it (formula IV*a* and *b*). As the potential of the molecular rotation around the long axis is mainly caused by hard core interactions, these different dipole conformations can lead to P_s values of different signs depending on the substituents in the core **III** [10]. Also, an example of $P_s = 0$ has been observed in a derivative with a type **III** core, and this is explained by a dipole direction just within the tilt plane. Details of the restricted molecular rotation of the dopant molecules in terms of the microscopic model [6, 7] will be given in the discussion (§ 4).



IV*a*



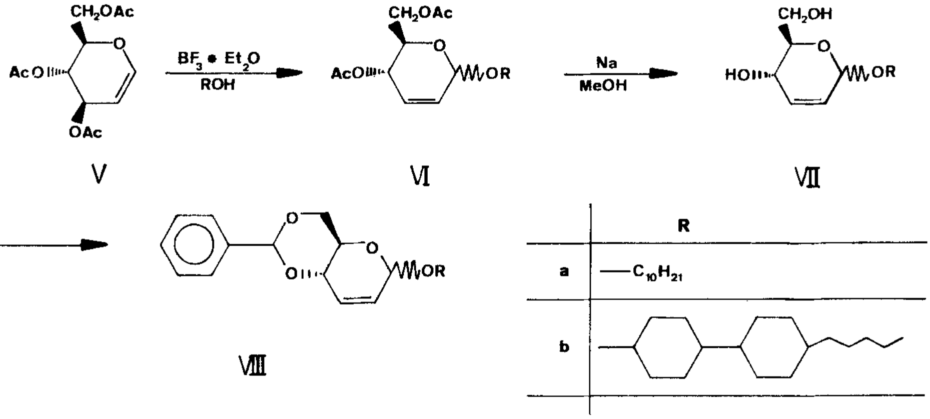
IV*b*

In this paper we present results on induced ferroelectric S_C^* phases formed by new chiral dopants with a chiral decalin-analogous skeleton as the rigid core, see table 1. For these dopants it has been found for the first time that the sign and magnitude of P_s depends on the nature of the host phase.

2. Experimental

2.1. *Chiral dopants* (*see table 1*)

The preparation of the chiral dopants is illustrated by the following reaction scheme:



The optically active compounds **VIII***a* and **VIII***b* used as chiral dopants were prepared from the chiral pool of carbohydrates by starting with the known 3,4,6-tri-*O*-acetylglucal **V** [11]. By employing the Ferrier-reaction [12] on **V** with decanol or 4-(4′-pentylcyclohexyl)cyclohexanol, respectively a mixture of diastereoisomers **VI** was formed with the α-anomer dominating. The compounds **VI** were separated by chromatography on silica gel using CH_2Cl_2/ethyl acetate 80:20. After deprotection, acetalization with benzaldehyde could be carried out on **VI** by using the Noyori-method [13], i.e. reaction of the trimethylsilylether derivatives of **VII** with benzaldehyde catalysed by trimethylsilyl triflate (TMSOFfl). After crystallization from ethanol the pure anomeric compounds **VIII***a* and **VIII***b* could be obtained. Details of the synthetic procedure will be published elsewhere [14].

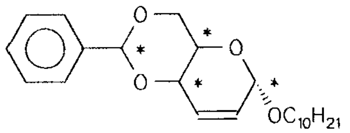
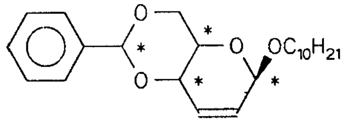
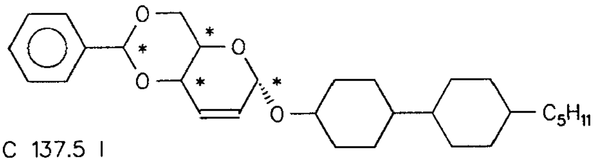
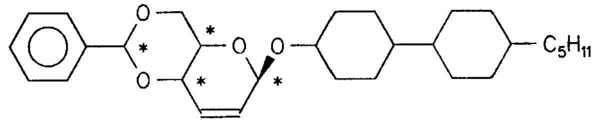
2.2. *Host substances*

The structures and phase sequences of the host substances are listed in table 2. The host substance 8007 was synthesized using the method described by Schubert and Weissflog [15]. HOAB was bought from Kodak and purified by recrystallization and column chromatography. The substance NCB 808 and NCB 84 were made available by courtesy of E. Merck, Darmstadt. Hoffman-La Roche provided the substance RO-41-5447 and Merck Ltd, UK the substance BDH-o-F.

2.3. *Measuring procedures*

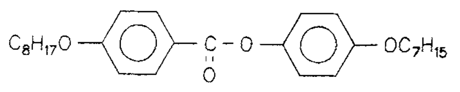
The phase diagrams of the mixed systems were obtained by polarizing microscopy and differential scanning calorimetry (Perkin–Elmer DSC 2). The temperature was controlled with an improved Mettler FP 5/52 hot stage. The spontaneous polarization and the tilt angle were measured on the same samples. These were made using

Table 1. Structural formulae of the dopants **VIII** and the sign of polarization P_s induced by them in the host phases 8007 and NCB 808.

		Sign P_S	
		8007	NCB 808
 C 74.0 I	αVIIIa	< 0	< 0
 C 70.0 I	βVIIIa	< 0	< 0
 C 137.5 I	αVIIIb	> 0	< 0
 C 125.0 I	βVIIIb	> 0	< 0

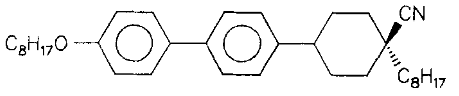
commercially available EHC-cells or cells made of two polymide coated glass plates with a switching area of 0·5 cm². To obtain a book-shelf geometry and to avoid chevron structures the samples were cooled slowly from the cholesteric phase in the presence of a low frequency electric ac field. The spontaneous polarization was measured by a Diamant bridge [16] and with the polarization current reversal method [17], while the tilt angle was derived from the switching angle of the optical director measured in the cell. The sign of the polarization was determined from the relative configuration of the electric field and the switching position of the sample during observation under the polarizing microscope.

Table 2. Structural formulae and phase transition temperatures (in °C) for the different smectic C host phases.



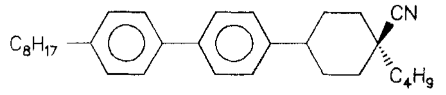
8007

C 62.9 S_C 70.0 N 88.3 I



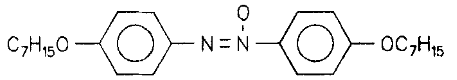
NCB 808

C 78.2 (S_F 40.0 S_I 50.4) S_C 117.3 S_A 147.4 N 149.1 I



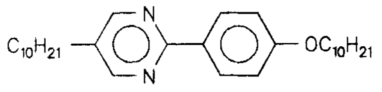
NCB 84

C 42.0 S_G 49.0 S_C 71.0 S_A 88.0 N 117.5 I



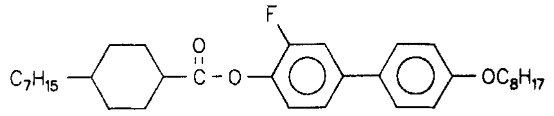
HOAB

C 74.5 S_C 94.5 N 123.7 I



RO–41–5447

C 40.0 S_C 74.0 S_A 76.5 I

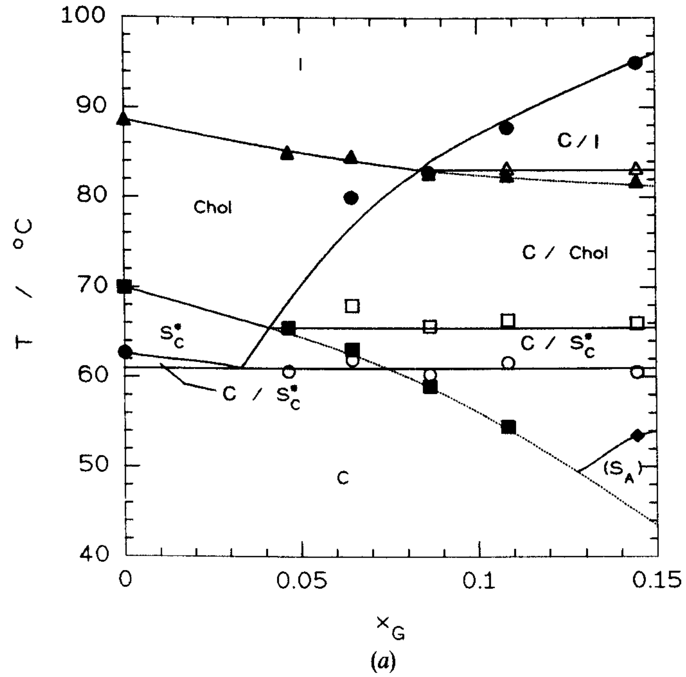


BDH–o–F

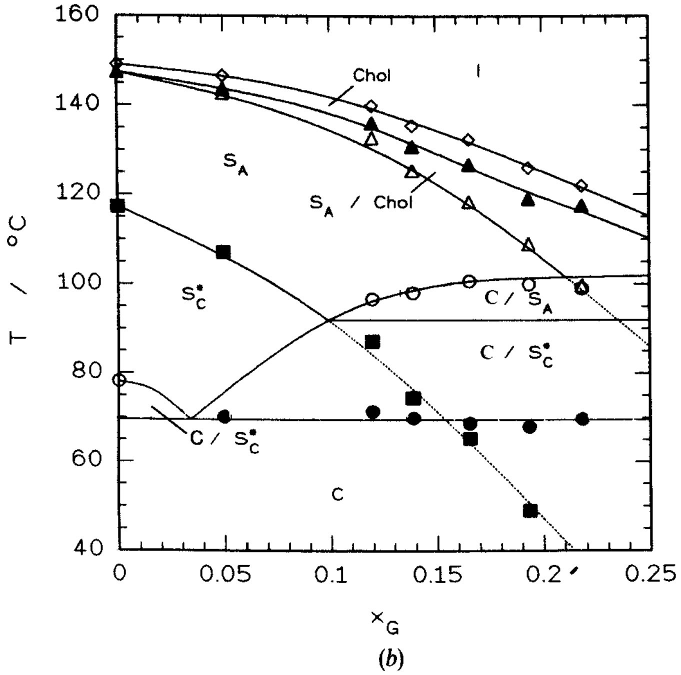
C 41.3 S_X 83.8 S_I 90.9 S_C 143.8 S_A 146.9 N 176.0 I

3. Results

As the glucose derivatives of general formula **VIII** (cf. table 1) do not exhibit liquid-crystalline phases they can only be used as chiral dipolar dopants in different achiral smectic C host phases. However, in all cases the temperature range of the induced S_C^* phases decreases so strongly with the mol fraction x_G of the non-mesogenic dopants that we could obtain S_C^* phases only up to about $x_G = 0{\cdot}1$. In some cases we observed a supercooling of the S_C^* phases with respect to the solid state and therefore could investigate mixtures up to $x_G = 0{\cdot}2$. As typical examples, the phase diagrams of the dopant α-**VIII***b* in the hosts 8007 and NCB 808 are shown in figure 1.



(*a*)



(*b*)

Figure 1. (*a*) The phase diagram for the chiral dopant α-VIII*b* in the host compound 8007. (*b*) The phase diagram for the chiral dopant α-VIII*b* in the host compound NCB 808.

We measured the spontaneous polarization P_s, the tilt angle θ and the sign of P_s of the glucose derivatives **VIII** in the different host phases listed in table 2.

The absolute values of P_s for the compounds α-**VIII***a* and β-**VIII***a* with the decyloxy-chain are rather small and do not exceed 0·5 nC cm^{-2} at the highest possible dopant concentrations. In the equatorial bicyclohexyloxy derivative β-**VIII***b* we measured P_s values up to 1 nC cm^{-2}. However, despite these small P_s values, the sign of P_s in different host phases could be determined and is given in table 1. The sign of P_s is given by a convention shown in figure 5 of [10] which has been commonly accepted. The axial derivative α-**VIII***b* indeed induces S_C^* phases with higher P_s values. The temperature dependence of P_s in the host 8007 is given in figure 2(*a*) exhibiting a normal behaviour. However, in the host NCB 808, an anomalous temperature function of P_s has been found with $|P_s|$ running to a maximum at intermediate temperatures (see figure 2 (*b*)). In figure 3 the P_s data are given as a function of x_G for different host phases. Solutions of a α-**VIII***b* in the host NCB 84 exhibit extremely small values of P_s which could not be measured quantitatively. However, the S_C^* phases of these mixtures are switchable in an electric field, and therefore a negative sign of P_s could be determined. Figure 4 shows the tilt angle θ as a function of x_G for α-**VIII***b* in different host phases. The most remarkable result is that the sign of P_s for the dopants **VIII***b*, but not for **VIII***a*, depends on the nature of the host phase (see table 1 and figure 3).

Previously, we have found that the tilt angle reduced polarization

$$P_0 = \frac{P_s}{\sin\theta} \tag{1}$$

in induced S_C^* phases with dopants of the general formula **I***a* or **I***b*: (i) is a linear function of x_G (at small values of x_G), and (ii) the function $P_0(x_G)$ does not depend on the nature of the smectic C host phase [2, 3, 18]. In figure 5 the P_0 values of α-**VIII***b* in 5 different host phases are given. It can be seen that in these cases, $P_0(x_G)$: (i) is non-linear even at small x_G values and (ii) depends on the nature of the host phase. Even the sign of P_0 (and also of P_s) is changed in different host phases. In the hosts NCB 84 and NCB 808, $P_s < 0$ has been found, whereas in the other hosts $P_s > 0$. It should be emphasized that the anomalous temperature dependence of P_s has been observed in mixtures with NCB 808 (cf. figure 2(*b*)) which also exhibit negative P_s values. In this mixed system, $|P_s|$ as a function of x_G runs through a maximum and tends to zero at about $x_G = 0{\cdot}2$. One might expect a sign reversal of P_s in this curve, but at higher mol fractions an S_C^* phase no longer exists.

4. Discussion

Let us first compare the behaviour of the four different dopants with the common molecular structure **VIII** of the rigid core (cf. table 1). All four dopants under discussion possess the same decalin-analogous core with a transverse dipole moment resulting from the two oxygen atoms in the ether bonds within the unsaturated ring and attached to it. Why does α-**VIII***b* exhibit rather large P_s values, but not the others? These effects can be understood in terms of a non-uniform rotational distribution around the molecular long axis, as given by the microscopic model of Zeks *et al.* [6, 7]. The rotational potential is given by

$$U(\psi) = -a_1\theta\cos\psi - a_2\theta^2\cos 2\psi, \tag{2}$$

where the rotation angle ψ gives the orientation of the transverse dipole $\mu_\perp$ with respect to the direction of P_s. The first term is of a chiral character and the second one is non-chiral; a_1 and a_2 are the amplitudes of both parts of the rotational potential. In general,

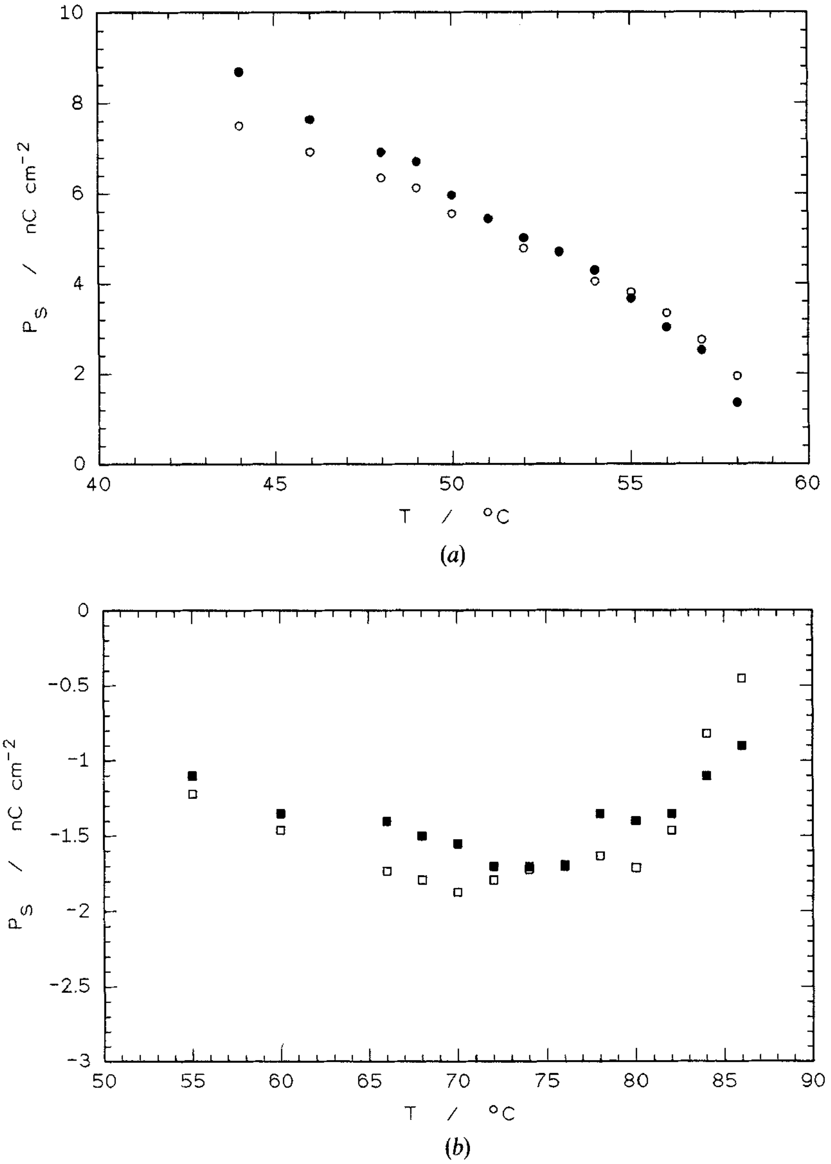


Figure 2. (*a*) Temperature dependence of the spontaneous polarization P_s of the dopant α-**VIII***b* in the host 8007 with $x_G = 0{\cdot}0864$. Measuring procedure: ●, Sawyer-Tower; ○, polarization reversal. (*b*) Temperature dependence of P_s for α-**VIII***b* in NCB 808 with $x_G = 0{\cdot}1200$. Measuring procedure: ■, Sawyer-Tower; □, polarization reversal.

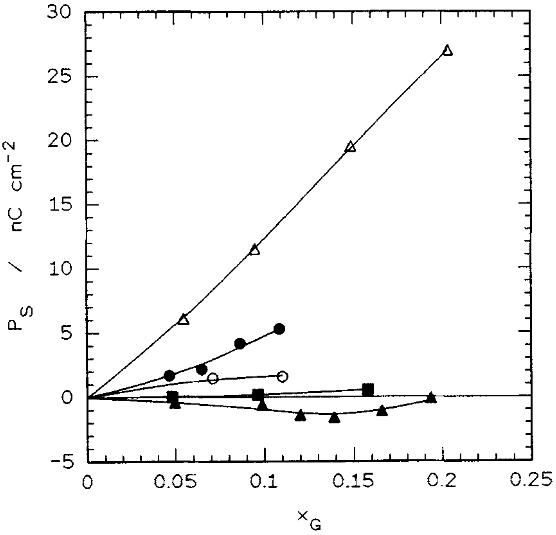


Figure 3. Spontaneous polarization P_s in different host phases as a function of the mol fraction x_G of the dopant α-VIII*b*. Temperature: 5 K below the transition S_C^*–chol or S_C^*–S_A. Host compounds: ●, 8007; ○, RO-41-5447; ■, BDH-o-F; ▲, NCB 808; △, HOAB.

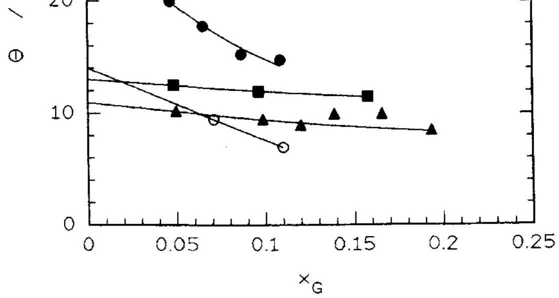


Figure 4. Tilt angles θ of the induced S_C^* phases as a function of x_G of the dopant α-VIII*b*. Temperature and symbols of the host compounds: cf. figure 3.

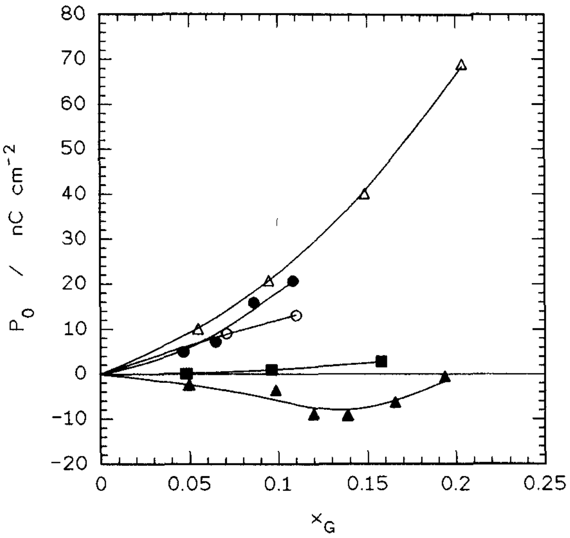


Figure 5. Reduced polarization P_0 as a function of the mol fraction x_G of the dopant α-VIII*b* in different host phases. Temperature and symbols of the host compounds: cf. figure 3.

the outer shape of a dopant molecule is not ellipsoidal. Consequently, $U(\psi)$ is not given only by the interaction of the transverse dipole with the surrounding host, but also by a microscopic friction originating from a hard-core interaction of the rotating dopant molecule.

To understand the different behaviour of the four dopants **VIII** we must consider their molecular structure. They differ from each other by the structure and position of the substituent *R*. In the dopants **VIII***a*, a decyloxy chain is attached to the rigid core. This chain is flexible and of rather small cross section. Therefore, one can expect that the potential of the rotation around the long axis (see equation (2)) will not exhibit such steep minima as in the case of the dopants **VIII***b* with their flat and less flexible bicyclohexane substituents. Thus, the rotational distribution around the long axis is different in both derivatives. Additionally, the position of *R* must be considered in the **VIII***b* dopants: in β-**VIII***b* the bicyclohexyloxy group is substituted in an equatorial position in the central core, leading to an extended molecular shape. In α-**VIII***b*, however, the substituent *R* is axially positioned in the core, resulting in a bent structure. The conformation of a α-**VIII***b* has been calculated by the computer program Alchemy II and is given in figure 6 as a space filling model. From figure 6 it can easily be derived that rotation around the long axis of the bent structure α-**VIII***b* is sterically hindered, leading to deeper minima in the rotational potential (see equation (2)). These cause larger values of P_s.

The most important question to be discussed in this paper is the dependence of the sign and magnitude of P_s for the dopant α-**VIII***b* on the nature on the host phase which has never been found previously in dopants of type **I***a* or **I***b*. We consider two models which take into account, in principle, the host effect and are sketched in figure 7.

Model 1 considers only a hard-core interaction of the rotating dopant molecule with its surrounding host molecules. As already discussed by us [10], because of the steric guest–host interaction, the direction of the transverse dipole $\mu_\perp$ must not necessarily coincide with a given reference axis of the dopant molecule, but can be rotated with respect to it by an angle ψ_0. Through this, $\mu_\perp$ will be no longer parallel to the direction

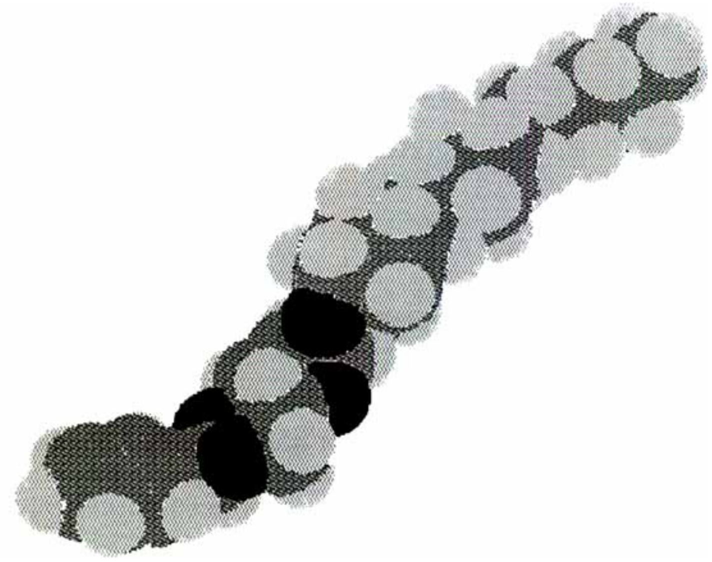


Figure 6. Computer calculated space filling molecular model of the chiral dopant α-VIII*b* (Alchemy II).

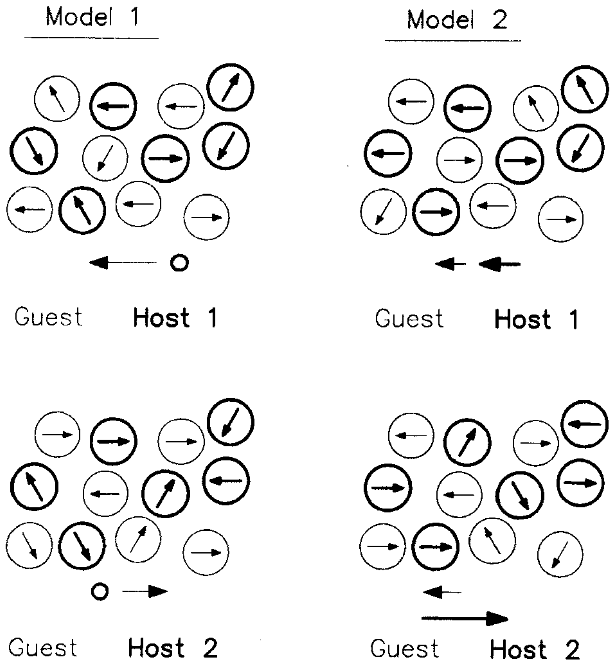


Figure 7. Two models demonstrating the spatial distribution of the transverse dipoles of the dopant in the host phases. The thick circles represent the cross sections of the host molecules with their transverse dipoles as arrows, and the thin circles refer to the dopant molecules.

of P_s if the dopant molecule is in its minimum rotational potential energy. For P_s it follows that:

$$P_s = N_1 \mu_\perp \langle \cos(\psi + \psi_0) \rangle, \tag{3}$$

with N_1 equalling the number density of the dopant molecules. By standard methods of statistical mechanisms we obtain [10]

$$P_s = N_1 \mu_\perp \frac{a_1 \theta}{2kT} \cos \psi_0. \tag{4}$$

From equation (4) it follows that P_s is not only given by the values of $\mu_\perp$ and a_1, but also that the minimum angle ψ_0 determines additionally the magnitude, as well as the sign of P_s. If $\mu_\perp$ is positioned within the tilt plane ($\psi_0 = 90°$), P_s will become zero, though $\mu_\perp$ possesses a finite value.

In the present case it seems to be possible that the minimum in the $U(\psi)$ curve for a given guest molecule will be governed by the nature of the host. This means that the minimum angle ψ_0 will be different for different hosts leading to different values as well as to different signs of P_s (cf. equation (4)). It should be emphasized that the NCB hosts (cf. table 2) with a strong out-of-plane cyano-dipole lead to induced S_C^* phases with negative P_s values. An argument for model 1 is the fact that P_s for all dopants **VIII** is rather small. This would mean that $\mu_\perp$ in all cases are positioned nearby the tilt plane. Small deviations from this position lead to a sign reversal of P_s according to equation (4).

Model 2 considers a strong intermolecular interaction between the guest and host molecules, for example, by dispersion forces. The existence of such an interaction is obvious from the fact that the chiral guest molecules induce a twist in the non-chiral smectic C host phase. As in chiral nematics, this twist is caused by an interaction of induced dipole–dipole and dipole–quadrupole transition moments [19]. The question arises whether through this guest–host interaction the dipole moments of the host molecules will be orientated with respect to $\mu_\perp$ of the guest molecule. Considering the steepness of the rotational potential, the ordering of the host substances may be weaker than for the guest substance, but as some host substances have rather large transverse dipoles, their contribution to P_s may be as great as the contribution of the guest substance. Given this case, two different situations are possible as shown in figure 7. First the dipole moments of the host molecules point in the same direction as $\mu_\perp$ of the dopant molecule; then all moments add up, leading to positive values of P_s. In the second possibility, the host moments are oppositely oriented to $\mu_\perp$. Therefore their contribution to the polarization must be subtracted from that of the dopants, leading to reduced and finally to negative P_s values.

It can be derived from figures 3 and 5 that the tendency of the dopant α-**VIII***b* is to give positive P_s values (extrapolation $x_G \rightarrow 1$). From table 2, it is seen that all the host compounds have transverse dipoles, the moment of which is only small in the host RO-41-5447 (ether group). An indication in favour of model 2 may be seen in the result that only the NCB hosts with their strong out-of-plane cyano-dipoles lead to a sign reversal of P_s. In the host HOAB, with its strong in-plane NO dipole, however, the largest positive P_s values were induced by a α-**VIII***b*.

In the present state of experimental information, we cannot clearly decide which of the two models works. Obviously, another possible way to explain the influence of the host on the magnitude and sign of P_s does not exist. It cannot be excluded that both effects, the hard-core interaction of the host with the rotating guest molecule and the orientation of the host dipoles, play a role in the resulting guest–host interaction. There is some support for model 1, because the dopants **VIII***a* with their less voluminous alkyloxy substituents do not show a sign reversal of P_s, although they possess the same central core as **VIII***b*. Further, an effect of the host phases on the sign of P_s has never been observed in the case of dopants of type **I**.

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