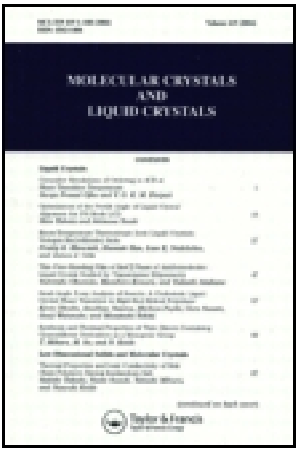

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Relations Between Structure and Material Properties in Ferroelectric Smectic C* Phases

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RELATIONS BETWEEN STRUCTURE AND MATERIAL PROPERTIES IN FERROELECTRIC SMECTIC C* PHASES

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Abstract The ferroelectric properties of induced smectic C* phases with novel chiral dopants were investigated which are characterized by a rigid molecular core directly bearing chiral centres and a transverse dipole. A strong influence of the achiral host phase on the magnitude and the sign of the spontaneous polarization was observed. The host effect is discussed in terms of an extended microscopic model considering hard-core interactions of the dopant molecules with their surrounding host phases.

INTRODUCTION

By solving mesogenic or non-mesogenic chiral dopants possessing a transverse dipole $\mu_\perp$ ferroelectricity can be induced in achiral smectic C phases.[1,2] In these so-called induced smectic C* phases the spontaneous polarization P_S and the tilt angle θ are dependent on the nature and the mole fraction x_d of the chiral dopant. Introduction of the reduced polarization P_0 defined by eq. 1

$$P_0 = P_S / \sin\theta \qquad (1)$$

allows a comparison of the dopant`s behaviour in different host phases.

P_0 has been found to be independent on the host phase if the transverse dipole $\mu_\perp$ and the chiral centres are part of the side chains of the dopant molecules (model A).[2,3] If these units are part of the central rigid core of the molecule (model B), however, the magnitude and even sometimes the sign of the polarization depends on the nature of the host phase. This has been shown for the first time in the case of dopants with decaline derivatives as central cores.[4]

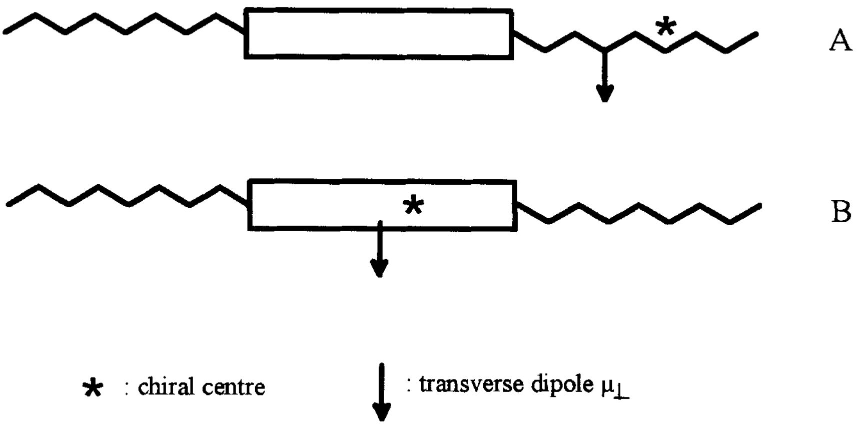
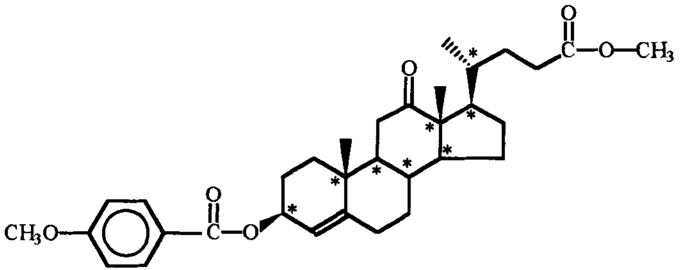


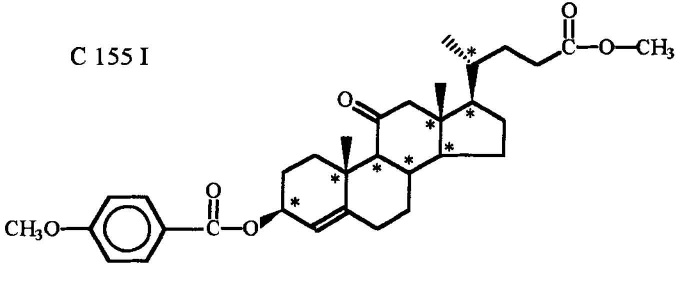
FIGURE 1 Model of dopant structure

In order to prove if the influence of the host phase is related to the general structure of the dopant, we investigated the behaviour of recently synthesized steroid derivatives as chiral dopants of type B in various achiral host phases. The structure of the **chiral dopants** is given below. They are not mesogenic; Their melting points (in °C) are added to the structures. The asterics denote the chiral centres.



AS157

C 155 I



AS161

C 140 I

The chiral centres and the main transverse dipoles of these novel dopants are part of the central rigid core of the molecules according to model B. The two dopants only differ in the position of the central carbonyl group (11- and 12-position). This does not effect the outer shape of the molecules which have been modeled by molecular mechanics. In figure 2 a superposition of the structures of the two dopants under discussion is given. It can be seen that the outer shape of the molecules remains approximately the same with the central carbonyl groups pointing in opposite directions with respect to the plane of the steroid skeleton. In AS157 the 12-CO dipole is situated below the molecular plane whereas in AS161 the 11-CO dipole is located above this plane.

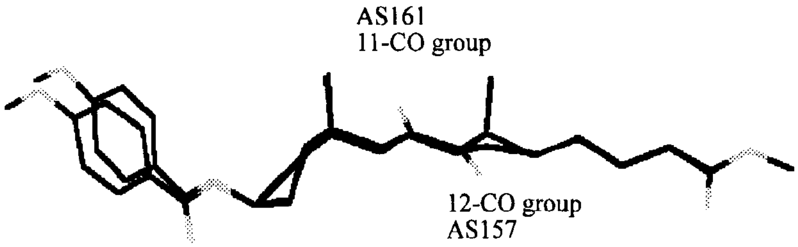
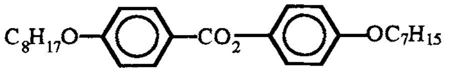


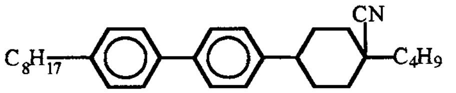
FIGURE 2 Superposition of the structures of the dopants AS157 and AS161 viewed along the plane of the steroid skeleton.

The following **host phases** have been used (phase transition temp. are given in °C).



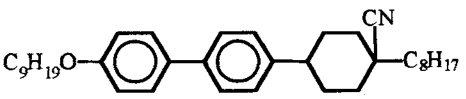
8OO7

C 63 S_C 70 N 88 I



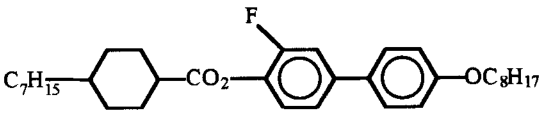
NCB 84

C 42 S_G 49 S_C 71 S_A 88 N 118 I



NCB 908

C 72 S_C 120 S_A 149 I



BDH-o-F

C 41 S_F 84 S_I 91 S_C 144 S_A 147 N 176 I

The host substance 8OO7 was synthesized using a method described by Schubert and Weissflog. The other three substances were made available by courtesy of E.Merck, Darmstadt.

Experimental

Because of the non-mesogenity of the dopants mixtures could only be investigated up to mole fractions $x_d \approx 0.2$. Phase transition temperatures were obtained by polarizing microscopy. P_S and θ were measured on the same samples using commercially available testing cells (E.H.C.) with switching areas of 1 and 0.25 cm² and sample-thickness between 6 and 10 µm. The spontaneous polarization was measured by the field-reversal method, while the tilt angle θ and the sign of P_S were derived from the switching behaviour of the optical director.

RESULTS

In figure 3 and 4 the spontaneous polarization P_S and the tilt angle θ of the investigated systems are given as a function of the mole fraction of the dopant. All values are related to temperatures 5 K below the phase transition $S_C{}^*/S_A$ or $S_C{}^*$/Chol, respectively.

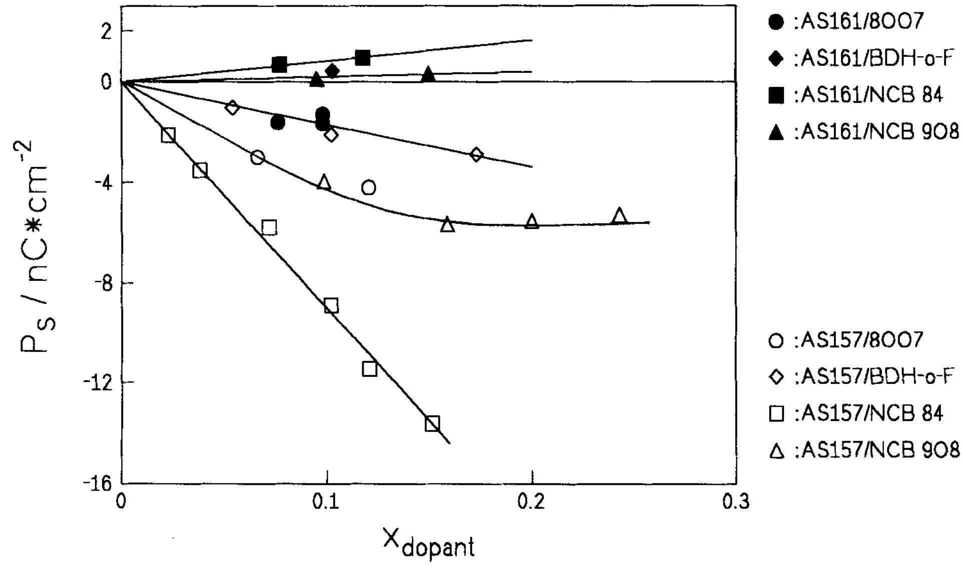


FIGURE 3 $P_S(x_d)$ of the dopants AS157 and AS161

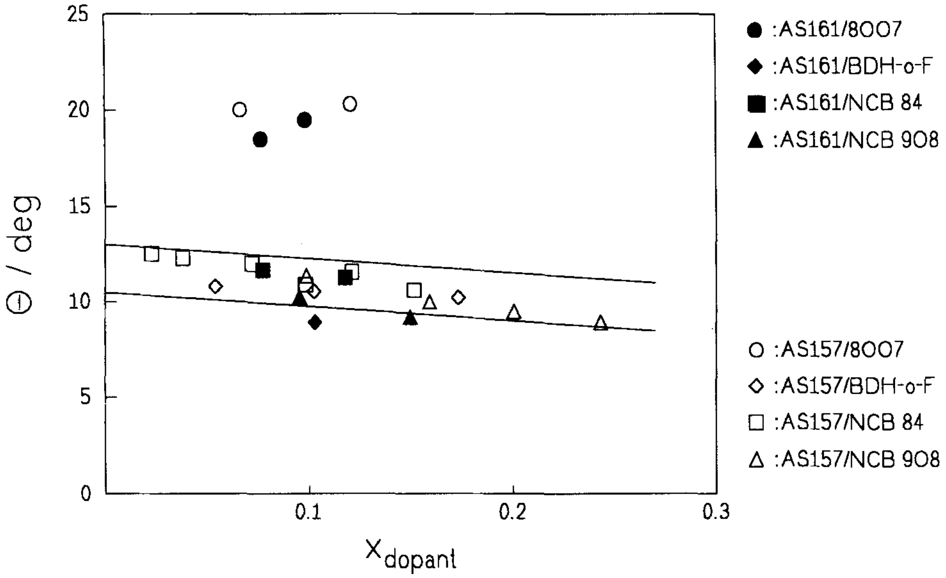


FIGURE 4 $\theta(x_d)$ of the dopants AS157 and AS161

The reduced polarization P_0 is given in figure 5. For most of the systems the polarization linearly depends on the mole fraction x_d. As it can be seen the polarization strongly depends on the nature of the achiral host phase. For example, by changing the host phase in the case of the dopant AS157 an enhancement of the polarization by a factor 5 results. For AS161, this host phase dependence additional leads to a sign inversion of P_0.

Changing the position of the central carbonyl group from the 11- to the 12-position also significantly influences the values of the spontaneous polarization. The two dopants are characterized by opposite signs of P_S in a given host phase The dopant AS157 induces a negative polarization whereas in most mixed systems with AS161 a positive polarization was measured. Without exception the polarization induced by the dopant AS157 in a given host phase is larger than the polarization induced by AS161.

Note that the host phase dependence of these new chiral dopants is not a consequence of the definiton of P_0 (cf. eq. 1) but is also confirmed by the measured values of P_S. In principle, the magnitude of the spontaneous polarization is related to the value of the tilt angle θ. In the case of these steroid derivatives the tilt angles of the systems, measured at 5 K below the phase transition, are approximately equal and differ only up to 2-3 degrees. Considering a proportionality between P_S and θ this only can stand for differences in P_S up to 30 %.

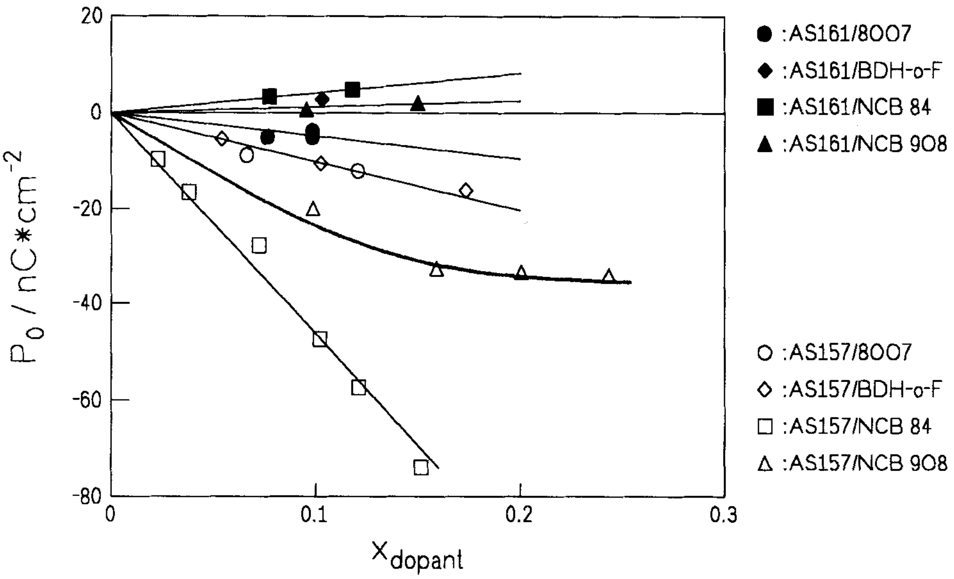


FIGURE 5 $P_0(x_d)$ of the dopants AS157 and AS161

From the concentration dependence of P_0 we obtain the polarization power δ_P given by [2]

$$\delta_P = (\partial P_0(x_d) / \partial x_d)_{\Delta T} \qquad (2)$$

describing the ability of a guest molecule to induce a spontaneous polarization in a given host phase at a fixed temperature below the phase transition. The values are given in table 1.

TABLE 1 Values of the polarization power δ_P for the investigated systems $\Delta T = 5$ K

Dopant	Host phase	δ_P / nC* cm^{-2}
AS157 (12-CO)	8OO7	-102.1
	BDH-o-F	- 94.4
	NCB 84	-482.6
	NCB 9O8	- 47.7
AS161 (11-CO)	8OO7	- 49.0
	BDH-o-F	+ 27.6
	NCB 84	+ 41.5
	NCB 9O8	+ 12.9

DISCUSSION

In general, two qualitative explanations for the observed host effect can be imagined.[4] The first model considers a contribution of the transverse dipoles of the host molecules to the value of the spontaneous polarization. In this case, the polarization consists of two parts, the first originating from the dopant molecules and the second from the achiral host molecules. A change of the host phase would lead to different values of P_S due to the different contributions of the hosts. In the present case, this model seems not to be consistent with the observed behaviour of the investigated systems. For both dopants, the highest values of the spontaneous polarization were measured in the same host phase NCB 84 (cf. table 1) but with opposite signs (with exception of the systems with 8OO7 as host phase). This can only be understood if the contribution of the host dipoles significantly changes its direction as a result of only small changes of the dopant structure (position of the central carbonyl group).

In the second model, the host molecules cause an orientational effect on the transverse dipoles of the dopant molecules. Within this model, the polarization is only given by the dopant dipoles but with an influence of the host molecules on their rotational distribution function around their long axes. This model seems more reasonable and compatible with the observed results and will be explained in the following.

According to the model of Zeks [5] the spontaneous polarization originates in a non-statistical rotational distribution of the molecules around their long axes, mainly influenced by hard-core interactions between the dopant molecules and their surrounding. The potential $U(\psi)$ of this molecular rotation is given by

$$U(\psi) = - a_1 \theta \cos \psi - a_2 \theta^2 \cos 2 \psi \quad (3)$$

where the rotation angle ψ describes the orientation of a molecular reference axis with respect to the direction of P_S. As mentioned in [6], in contradiction to the original model of Zeks[5], the molecular reference axis must not necessarily coincide with the direction of the transverse dipole $\mu_\perp$. A second angle ψ_0 is introduced, describing the shift between the direction of the molecular reference axis and the direction of $\mu_\perp$. In this case, the spontaneous polarization is given by the following equation [6]

$$P_S = \rho \mu_\perp \langle \cos (\psi + \psi_0) \rangle \quad (4)$$

ρ = number density of the dopant molecules.

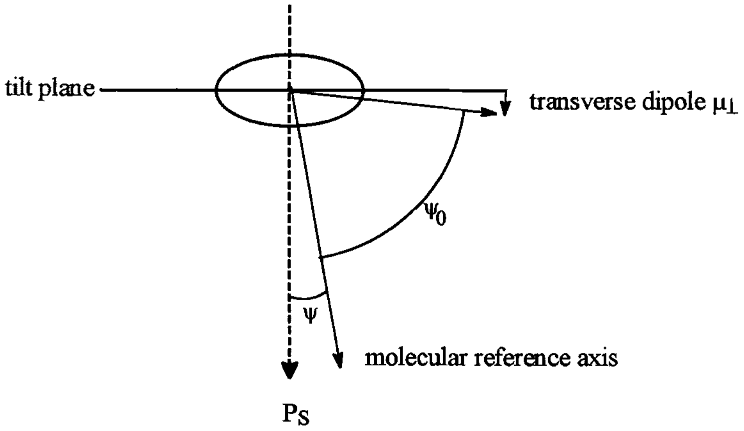


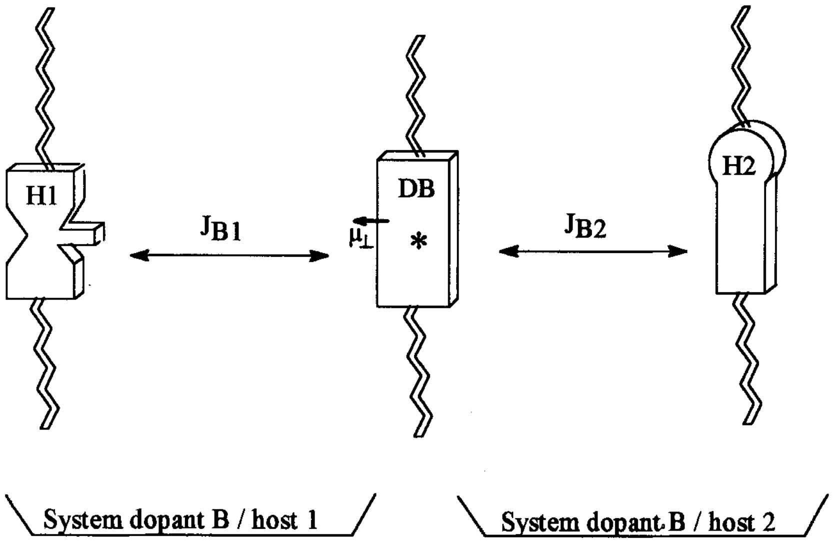
FIGURE 6 Schematic drawing of the conditions mentioned above. Viewing direction is along the molecular long axis.

If due to the expectation value $\langle \cos (\psi + \psi_0) \rangle$ $\mu_\perp$is located near the tilt plane its component in the direction of P_S is only small as it can be seen in figure 6. Thus, small values of P_S result even in the case of large transverse dipoles.[4,7] Furthermore, small changes in the orientation of the transverse dipole will considerably change the magnitude of the spontaneous polarization. If $\mu_\perp$ is rotated through the tilt plane, ($\langle \cos (\psi + \psi_0) \rangle < 0$), a sign inversion of P_S will take place.

We assume the observed host phase dependence to be related with such different orientations of $\mu_\perp$. This orientation and consequently the contribution of $\mu_\perp$ to P_S is determined by the rotational distribution function of the molecules according to the model of Zeks. As already mentioned, this rotational distribution will mainly be influenced by the hard-core interactions between the dopant molecules and the surrounding host molecules. An alteration of the host phase leads to different steric interactions between the guest molecules and the mean field built up by the host. This will primarily effect the orientation of the central rigid cores (model B) but only slightly the more or less flexible side chains of the molecules (model A).

For dopants of type B (as given by the steroid derivatives AS157 and AS161), the orientation of the transverse CO-dipole with respect to the the central core is fixed. In this case, a change in the orientation of the central core due to different steric effects between the dopant molecules and the host mean field directly influences the contribution of $\mu_\perp$ to P_S. In the case of the dopant AS161 this alteration of interaction in different hosts causes a rotation of $\mu_\perp$ through the tilt plane resulting in the observed sign inversion. For dopants of type A the steric interactions will be influenced in the same way when changing the host phase. But in this case, the orientation of $\mu_\perp$ is decoupled from the central core. Thus, the host phase effect on the orientation of the transverse dipole will be smoothed out due to a greater rotational freedom if $\mu_\perp$ is located in the flexible side chains of the molecules and no host dependence will be observed. This different behaviour of the dopant molecules of type A and B is sketched in figs. 7 and 8. In the case of molecules of structure A there is indeed also a steric interaction between the cores of the guest and host molecules (see fig. 8). But as the transverse dipole in the flexible side chains is more or less decoupled from the core it does not "feel" the difference in the mean fields of different host phases as it is the case in the strongly coupled dipoles of structure B dopants (cf. fig. 7).

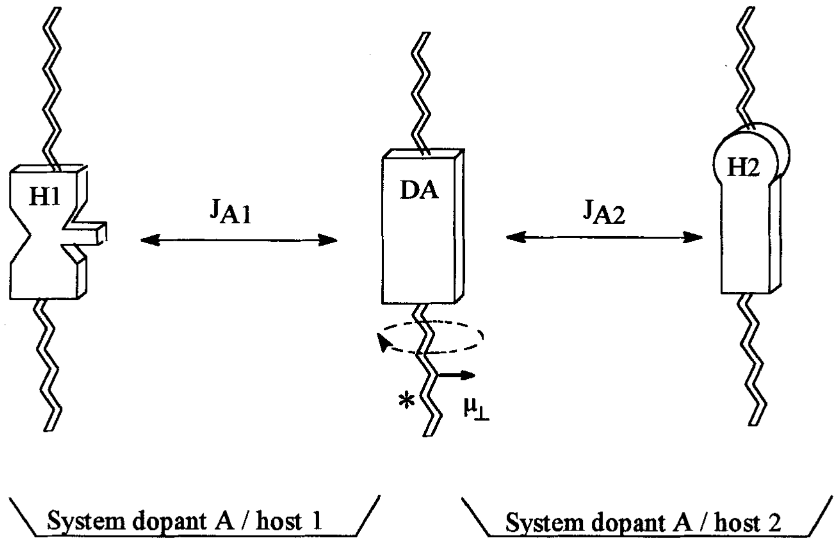
It is worth to mention that a sign inversion of P_S due to this considerations is not an independent effect but only a consequence resulting from the symmetry of the smectic C* phase.



- interaction J_{B1} (dopant-host 1) ≠ interaction J_{B2} (dopant-host 2)
- host molecules H1 and H2 differ in their steric dipoles[7]
- orientation of $\mu_\perp$ with respect to the central core is fixed

changing the host will lead to different values of P_0 and can cause sign conversion

FIGURE 7 Interaction of different host phases with dopants of type B



- interaction J_{A1} (dopant-host 1) ≠ interaction J_{A2} (dopant-host 2)
- host molecules H1 and H2 differ in their steric dipoles[7]
- transverse dipole $\mu_\perp$ is decoupled from the rigid core
  orientation of $\mu_\perp$ is not controlled by orientation of the core, effect of steric interaction will be smoothed out due to greater rotational freedom
  no measurable influence of the host phase on the value of P_0

FIGURE 8 Interaction of different host phases with dopants of type A

CONCLUSIONS

According to the behaviour of the steroid derivatives under discussion and to the results given in [4] for hetero analogues of decaline the host phase dependence of P_S and P_0 seems to be related to the general structure of the chiral dopants. The host effect can be expected, if the transverse dipole $\mu_\perp$ and the chiral centres are part of the central rigid core of the molecules. It can be understood by means of different orientational distributions of $\mu_\perp$ with respect to the direction of P_S generated by the steric effects between the guest molecules and the host mean field.

In order to find a measurable influence of the host phase two additional conditions have to be fullfilled:

The transverse dipole $\mu_\perp$ of the dopants has to be located nearly parallel to the tilt plane

($\langle \cos(\psi + \psi_0) \rangle \approx 0$) and the mole fraction x_d has to be moderate to obtain a significant change of the dopant`s surrounding when changing the host phase.

Meanwhile this concept of dopant structure has given proof in the case of another class of chiral dopants of the general structure B.[8] The results obtained with these novel dopants (epoxy derivatives [9], see general structure below) will be published elsewhere.

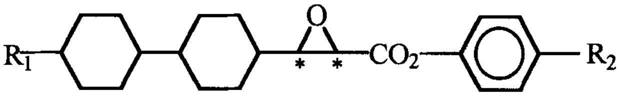


FIGURE 9 General structure of epoxy derivatives [9]

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