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H. Stegemeyer[a]; R. Meister[a]; K. -H. Ellermann[a]; H. -J. Altenbach[a]; W. Sucrow[a]
[a] Department of Chemistry, University of Paderborn, Paderborn, Germany

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Ferroelectric properties of liquid-crystalline S_C^* phases induced by optically active cyanocyclohexylcyclohexanone derivatives

by H. STEGEMEYER*, R. MEISTER, K.-H. ELLERMANN,
H.-J. ALTENBACH and W. SUCROW†
Department of Chemistry, University of Paderborn,
D-4790 Paderborn, Germany

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Derivatives of optically active cyanocyclohexylcyclohexanone have been synthesized and used as dipolar chiral dopants to induce ferroelectric S_C^* phases in an achiral host phase. The dopant molecules are the first examples in which the chiral centres are incorporated into a rigid core with transverse dipoles directly attached. The spontaneous polarization P_s and the tilt angle θ of the induced S_C^* phases have been measured. P_s is strongly influenced by the relatively small changes of the molecular structure of the cyclohexanones, for example a change of the sign of P_s or a vanishing value of P_s. These effects are discussed in terms of a sterically hindered rotation of the dopant molecules around their long axes and explained by the assumption that the transverse dipole must not be necessarily parallel to P_s in the equilibrium state of rotation.

1. Introduction

By adding chiral guest molecules to an achiral smectic C host phase its C_{2h} symmetry will be broken and changed to C_2 [1]. We call those phases induced smectic C* phases [2]. If the chiral guest molecules bear a transverse dipole moment the resulting S_C^* phases are ferroelectric [3]. We have shown that the tilt angle θ between the local director and the smectic layer normal, as well as the spontaneous polarization P_s, depend in different ways on the mole fraction x_G of the dipolar chiral guest compound [4, 5]. As a strong coupling between θ and P_s has been demonstrated by Zeks *et al.* [6] we introduce a reduced polarization P_0 defined by

$$P_0(x_G) = P_s(x_G)/\sin\theta(x_G). \tag{1}$$

In an induced S_C^* phase with moderate transverse dipole moments $P_0(x_G)$ depends linearly on x_G and is independent of the nature of the S_C host phase [4, 5]. In the case of strong transverse dipoles $P_0(x_G)$ deviates from linearity which we have explained recently by a local field correction [5].

Within one layer of the S_C^* phase the transverse dipoles of the chiral guest molecules will be forced on average into the same direction by a steric strain caused by the tilt. If we consider a rotational motion of the guest molecules around their long axes it becomes obvious that the macroscopic dipole moment of the layer averages out if there is a statistical distribution of the transverse dipoles $\mu_\perp$ with respect to the long axes. This

* Author for correspondence.
† Deceased.

has been taken into account by Zeks *et al.* in their microscopic model [6] by a hindered rotation of the molecules around their long axes which can be described by the rotational potential

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

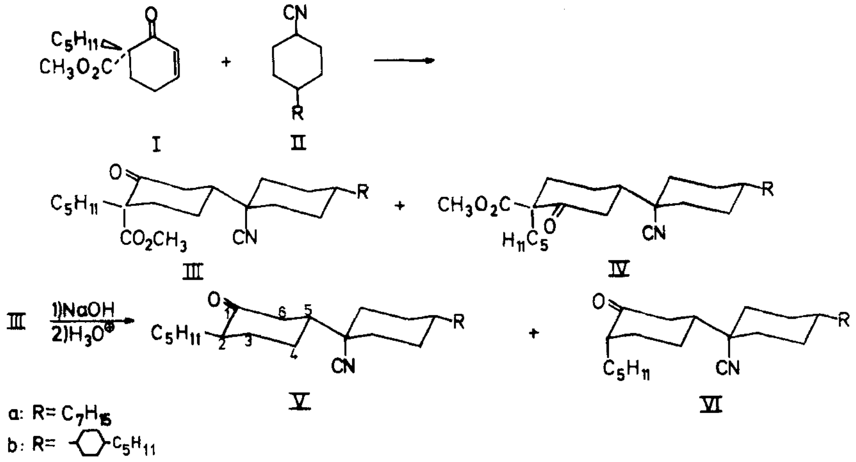
The angle ψ gives the position of $\mu_\perp$ with respect to the direction of P_s. The first term is of chiral character whereas the second one is non-chiral and a_1 and a_2 are constants describing the magnitude of both parts of the rotational potential. As the outer shape of the chiral dipolar guest molecule is not ellipsoidal in general $U(\psi)$ is not influenced only by the interaction of $\mu_\perp$ with its surroundings but also by a microscopic friction caused by steric interaction of the rotating molecule. In this paper we demonstrate induced S_C^* phases in which steric effects of the chiral guest molecules have to be considered to explain the experimental results.

The concept of the synthesis of the chiral guest molecules under discussion was the following. Normally, the chiral centre of a guest molecule as well as its transverse dipole is located in the alkyl chain attached to the rigid molecular core. Because of the chain flexibility the dipole can rotate with respect to the molecular long axis which reduces P_s. Therefore, it seems to be more effective to introduce the chiral centres as well as the transverse dipole groups directly into the rigid core of the molecule. Because of this concept the chiral cyclohexanone derivatives have been synthesized and used as guest molecules.

2. Experimental

2.1. *Preparation of the chiral dopants*

The optically active cyanocyclohexylcyclohexanone derivatives used as chiral dopants were prepared by starting with (+)-(*S*)-6-methoxycarbonyl-6-pentyl-2-cyclohexenone (**I**) which has been obtained from the racemate by enzymatic resolution with pig liver esterase (enantiomeric excess: >99 per cent). Michael reaction of **I** with lithiated cyanocyclohexane derivatives **II** resulted in a mixture of diastereomers **III** and **IV**, which could easily be separated by chromatography. Hydrolysis and decarboxylation of **III** or **IV**, respectively, gave a *cis/trans* isomeric mixture of **V** and **VI** in one or the other enantiomeric form, from which the thermodynamically more stable compounds **V** could be obtained enantiomerically pure by crystallization. The reaction scheme is



Details of the synthetic methods were taken from [7] and will be published separately.

The resulting compounds **IIIa**, **IIIb**, **Va** and **Vb** are liquid-crystalline but do not exhibit a S_C^* phase by themselves. They form S_A and/or S_B phases. The phase sequences and phase transition temperatures are

IIIa C 54·4°C S_A 58·7°C I,

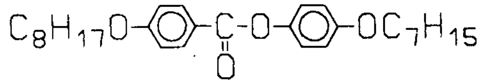
IIIb C 84·4°C (S_B 51·7°C) S_A 153·9°C I,

Va C 64·1°C (S_B 58·9°C) S_A 92·0°C I,

Vb C 81·2°C S_B 178·1°C I.

2.2. *Host phase*

As a host substance the compound 4*n*-octyloxybenzoate(4-*n*-heptyloxyphenylester) (8007) has been used which was synthesized according to a method given by Schubert and Weissflog [8]. 8007 exhibits only S_C and nematic liquid-crystalline phases whose transition temperatures are



8007

C 62·9°C S_C 69·1°C N 86·1°C I.

2.3. *Measuring procedures*

The phase diagrams of the mixed systems were obtained by polarizing microscopy and differential scanning calorimetry (Perkin–Elmer DSC2). The spontaneous polarization and the tilt angle have been measured on the same sample which was placed between two polyimid coated conducting glass plates (cell dimensions 0·7 cm × 0·7 cm × 15 μm). The sample temperature was controlled by means of an improved version of a Mettler hot stage FP 5/52 (relative accuracy 10^{-2} K). To obtain a bookshelf geometry and to avoid chevron structures the sample was cooled slowly from the cholesteric phase in the presence of an applied low frequency electric field. The spontaneous polarization was measured by a Diamant bridge [9] 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.

3. Results

As the liquid-crystalline guest compounds **IIIa**, **IIIb**, **Va**, and **Vb** do not exhibit a S_C^* phase they have been used as chiral dipolar dopants in the achiral host compound 8007. Because of the orthogonal smectic phases (S_A and/or S_B) of the guest compounds the temperature range of the S_C^* phase of the mixtures in 8007 decreases so strongly with x_G that we could only obtain S_C^* phases up to x_G of 0·1. As a typical example the phase diagram of the system **Va**/8007 is shown in figure 1; the phase diagrams of the other mixtures are quite similar.

In figure 2 the absolute value of the spontaneous polarization $|P_s|$ is given as a function of the mole fraction of the chiral guest molecules **IIIa**, **Va** and **Vb** for a temperature 5 K below the phase transition S_C^* to cholesteric or S_C^* to S_A. In **Va** $|P_s|$

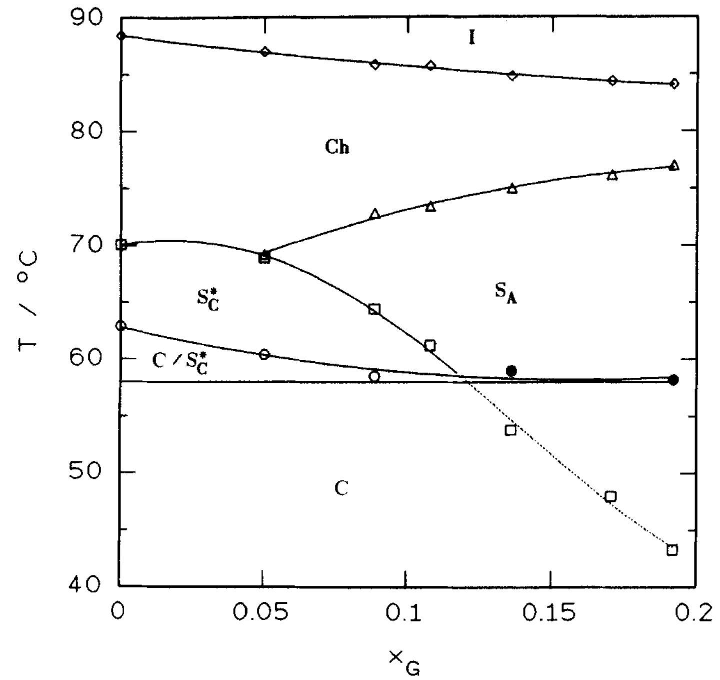


Figure 1. The phase diagram of the chiral dopant **Va** in the host compound 8007.

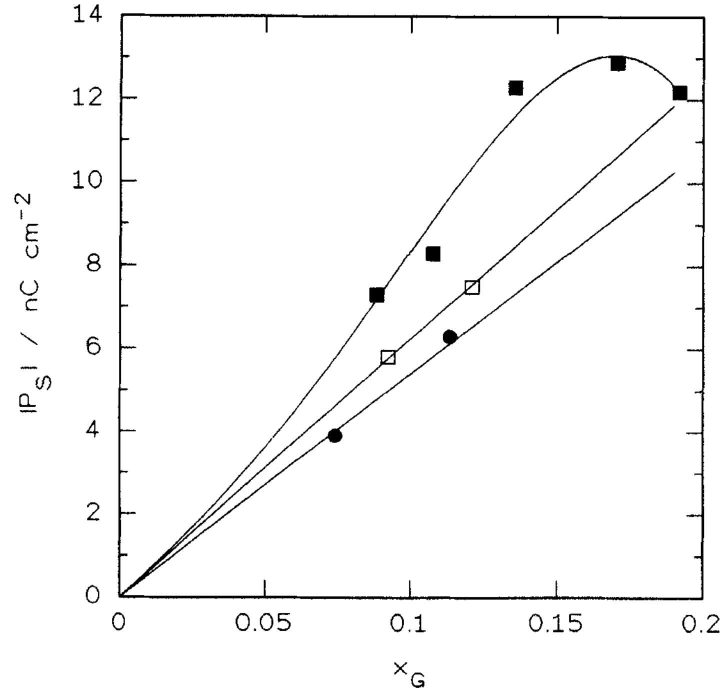


Figure 2. The absolute value of the spontaneous polarization $|P_s|$ plotted as a function of the mole fraction x_G of several chiral dopants in 8007. Temperature: 5 K below $T_{S_C^*Ch}$ or $T_{S_C^*S_A}$. □, **IIIa**; ■, **Va**; ●, **Vb**.

could be measured up to x_G of 0·2 in the supercooled state. For **IIIa** and **Vb** the amounts obtained by the synthesis were so small that only two mixtures could be investigated. In figure 3 the tilt angle θ is shown for the mixtures which is only slightly dependent on the guest substance. From P_s and θ we have obtained the reduced polarization according to equation (1) whose absolute value $|P_0|$ is plotted versus x_G in figure 4. As it has been found in other cases [4, 5] $P_0 = f(x_G)$ is linear.

Surprisingly, for the guest compound **IIIb** in 8007 no spontaneous polarization could be detected. Even at the highest concentration which could be obtained ($x_G = 0{\cdot}117$) $|P_s|$ certainly was less than 0·5 nC cm^{-2} which is within the limit of accuracy of our measurements.

Additionally, we measured the sign of polarization which is given by a convention shown in figure 5. For **Va** and **Vb** in 8007 we found a negative polarization. For the ester derivative **IIIa**, however, the polarization is positive. The mixture **IIIb**/8007 whose polarization is about zero could be switched by alternating the field direction. From this observation we could demonstrate that there is an extremely weak spontaneous polarization which is negative.

From the concentration dependence of P_0 we can obtain the polarization power δ_p which is defined by

$$\delta_p = (\partial P_0(x_G)/\partial x_G)_{\Delta T} \tag{3}$$

describing the ability of a given guest compound to induce a spontaneous polarization in a given host phase at a fixed temperature difference below the phase transition (here: $\Delta T = 5$ K). The values of δ_p are given in the table.

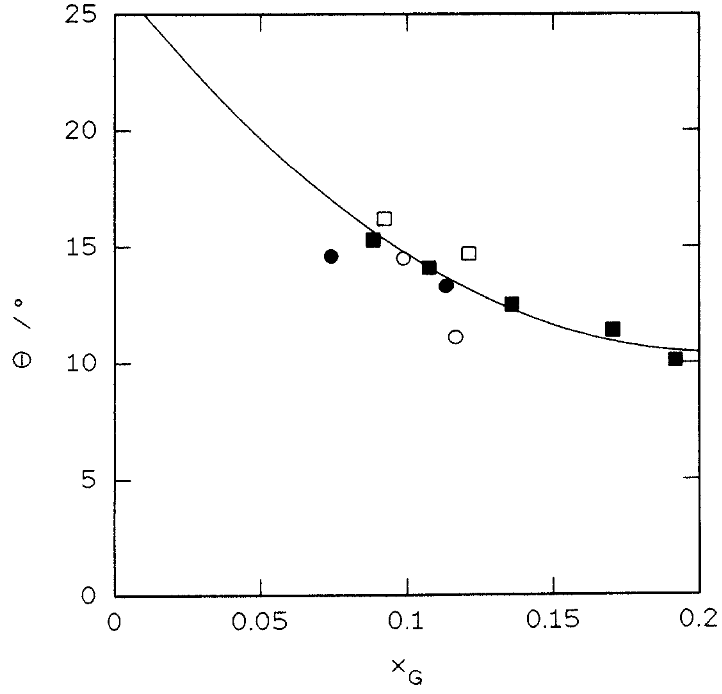


Figure 3. The tilt angle θ as a function of the mole fraction x_G of several chiral dopants in 8007. The full line is a guide for the eye. Temperature: 5 K below $T_{S_C^*\mathrm{Ch}}$ or $T_{S_C^*S_A}$. □, **IIIa**; ○, **IIIb**; ■, **Va**; ●, **Vb**.

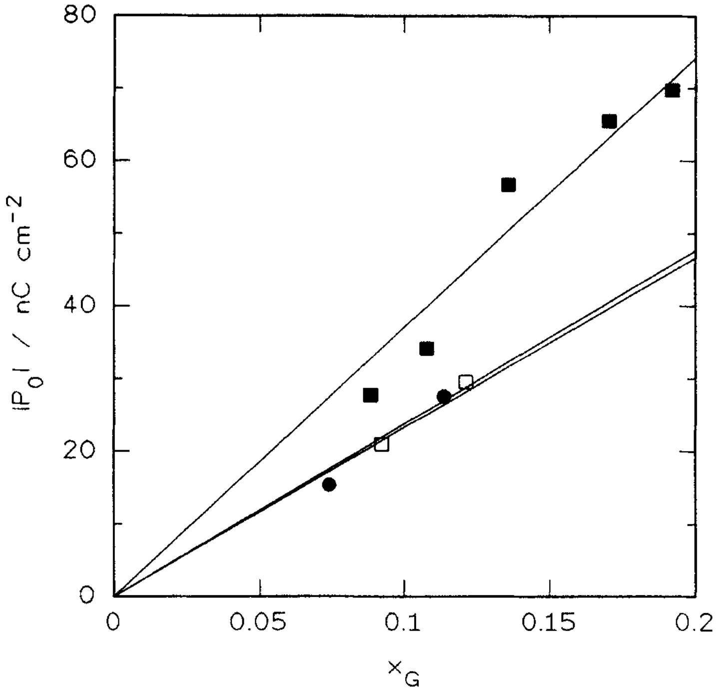


Figure 4. The absolute value of the reduced polarization $|P_0|$ as a function of the mole fraction x_G of several chiral dopants in 8007. Temperature 5 K below $T_{S_C^*Ch}$ or $T_{S_C^*S_A}$. □, **IIIa**; ■, **Va**; ●, **Vb**.

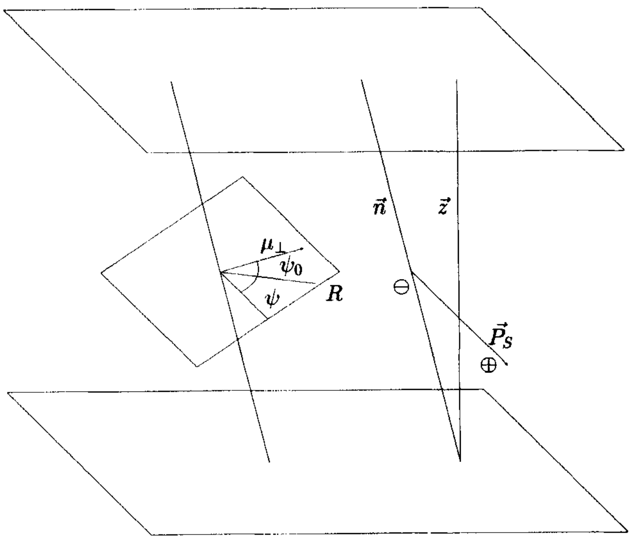


Figure 5. Left-hand-side: The molecular frame showing the orientation of a guest molecule in the S_C^* host phase. R: reference axis. Right-hand-side: Sign convention for the spontaneous polarization. The sign of P_s in this configuration is positive.

Table Polarization power δ_p and sign of the spontaneous polarization of chiral dopants in the S_C^* host phase of 8007.

Chiral dopant	Sign of P_0	δ_p/nC cm^{-2}
IIIa	Positive	+240
IIIb	(Negative)	≈0
Va	Negative	−370
Vb	Negative	−235

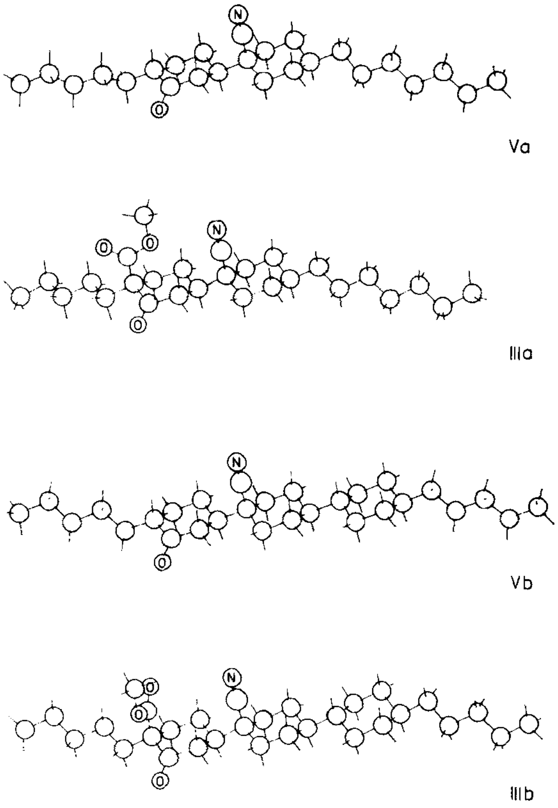


Figure 6. Calculated molecular conformations of the chiral dopants.

Comparing the molecule structures in figure 6 we recognize that the molecular skeleton of the cyclohexanone ring with its two chiral centres and the adjacent cyano group is identical in all guest compounds. Introducing a third cyclohexane ring in **Va** to give the resulting compound **Vb** the value of δ_p is somewhat decreased but P_0 remains negative. Addition of an ester group to the cyclohexanone ring in **IIIa** changes the sign of P_0 and the introduction of the third cyclohexane ring causes the loss of spontaneous polarization in **IIIb**. In the next section we try to understand these structural features by taking into account the restricted rotation of the guest molecules around their molecular long axes.

4. Restricted rotation around the molecular long axis

Let us consider the rotation of the chiral guest molecule around its long axis. In order to describe this rotation we have to choose a transverse reference axis within the molecule. In general, this axis can be chosen quite arbitrarily. But to obtain an easy expression for the potential energy $U(\psi)$ associated with the rotation we choose the axis in the way that $U(\psi)$ is given by the Zeks model [6]

$$U(\psi)=U_1+U_2=-a_1\theta\cos\psi-a_2\theta^2\cos 2\psi. \tag{2a}$$

In equation (2*a*) ψ is the rotation angle between the direction parallel to P_s and the molecular reference axis. The chiral potential U_1 is antisymmetric with respect to $\psi=90°$ and is non-zero only for chiral molecules. The achiral potential U_2 is symmetric with respect to $\psi=90°$ and exists for both chiral and achiral molecules. The rotational potential energies U_1 and U_2 are firstly caused by steric interactions between the rotating molecule and its surroundings. They depend only at second order on the direction of the transverse dipole $\mu_\perp$ because the S_C^* phases are improper ferroelectrics. This becomes obvious if we consider a flat molecule, for example a cyclohexane derivative, in which $\mu_\perp$ can be directed either perpendicular to the molecular plane or parallel to it. So the direction of $\mu_\perp$ does not coincide with the reference axis but is rotated to it by an angle ψ_0 (see figure 5). By this procedure U_1 and U_2 remain antisymmetric or symmetric to $\psi=90°$, respectively. But $\mu_\perp$ has no longer to be parallel to P_s if the molecule is in its minimum rotational potential energy.

To calculate P_s standard methods of statistical mechanics must be used

$$P_s=N_1\langle\mu_\perp\rangle=N_1\mu_\perp\langle\cos(\psi+\psi_0)\rangle, \tag{4}$$

where N_1 is the number density of the chiral guest molecules. This equation can be transformed into

$$P_s=N_1\mu_\perp(\langle\cos\psi\rangle\cos\psi_0-\langle\sin\psi\rangle\sin\psi_0), \tag{5}$$

with

$$\langle\cos\psi\rangle=\frac{\int_0^{2\pi}\cos\psi\exp[-U(\psi)/kT]\,d\psi}{\int_0^{2\pi}\exp[-U(\psi)/kT]\,d\psi} \tag{6}$$

and

$$\langle\sin\psi\rangle=\frac{\int_0^{2\pi}\sin\psi\exp[-U(\psi)/kT]\,d\psi}{\int_0^{2\pi}\exp[-U(\psi)/kT]\,d\psi}. \tag{7}$$

By symmetry, it follows that $\langle\sin\psi\rangle=0$ for the Zeks potential (cf. equation (2*a*)).

The integrals in equation (6) cannot be solved in a closed form. By expanding the exponential in a series we recently have derived [5] that to a first approximation the expectation value of $\cos\psi$ is

$$\langle\cos\psi\rangle=\frac{a_1\theta}{2kT}. \tag{8}$$

In this equation the local field correction considered in [5] is omitted as it does not play any role at the low guest molecule concentrations used in the present case. Inserting equation (8) into (5) we obtain

$$P_s = N_1 \mu_\perp \frac{a_1 \theta}{2kT} \cos \psi_0 . \tag{9}$$

Compared with the calculations carried out without considering ψ_0 [5], P_s is scaled by an additional factor of $\cos \psi_0$. From equation (9) it becomes obvious that there might be a situation in which $P_s = 0$ although $\mu_\perp$ is large and a_1 non-zero but $\psi_0 = 90°$ and $270°$.

Dividing equation (9) by θ and inserting the mole fraction x_G which is related to N_1 by

$$N_1 = N_0 x_G \tag{10}$$

(N_0 total number density) we obtain

$$P_0 = \frac{P_s}{\theta} = N_0 x_G \mu_\perp \frac{a_1}{2kT} \cos \psi_0 . \tag{11}$$

Here, the quantity P_0 is slightly different to that given in equation (1) but the deviation is small because of the small values of θ.

From equation (11) we can derive the polarization power δ_p

$$\delta_p = \left(\frac{\partial P_0}{\partial x_G}\right)_{\Delta T} = N_0 \mu_\perp \frac{a_1}{2kT} \cos \psi_0 . \tag{12}$$

From this equation it follows that δ_p is mainly determined by the values of $\mu_\perp$ and the constant a_1 which describes the magnitude of the chiral part of the rotational potential (cf. equation (2 *a*)). The sign of δ_p will be governed by the angle ψ_0.

5. Discussion

In the present induced S_C^* phases the chiral dopants to our knowledge are the first examples in which chiral centres as well as transverse dipoles are incorporated into a rigid core and not situated in an alkyl side chain as usual hitherto. Therefore, there is still a lack of knowledge regarding the relation between the molecular structure and the ferroelectric properties. As shown in the experimental part the new cyclohexanone derivatives do not exhibit S_C^* phases. They only form orthogonal smectic phases of type S_A and S_B. This can be compared with derivatives of cholesterol in which the chiral centres are also incorporated into a rigid skeleton and which only exhibit smectic phases of type A.

The conformations of the cyclohexanone derivatives have been calculated by a computer program (Alchemy) using standard bond lengths, bond angles and torsion angles. In our considerations we assume to a good approximation that the cyclohexane rings are coplanar to each other. The resulting conformations are given in figure 6. The chiral cyclohexanone skeleton in **Va** and **Vb** exhibits a C=O dipole in position 1 which is transverse to the molecular long axis. The α-cyano group of the adjacent cyclohexane ring is also a transverse dipolar group but perpendicular to the molecular plane. The C=O and the C≡N dipoles which are both neighbours to a chiral centre enclose an angle of 115°. As the bond dipole moment of C≡N is 3·5 D whereas C=O has only 2·3 D [10] the value of the resulting transverse moment $\mu_\perp$ in **Va** and **Vb** is dominated by the cyano group and results in a dipole of about 3 D. The direction of the resulting $\mu_\perp$ is perpendicular to the long axis and inclined by an angle of 40° against the normal to the molecular plane. In **IIIa** and **IIIb** the cyclohexanone skeleton additionally bears an ester group at the chiral carbon atom 2 with a partial dipole pointing along the same perpendicular direction as the $C \equiv N$ dipole. The resulting transverse dipole moment is now $\mu_{\perp} \approx 3{\cdot}5\,D$ with a direction inclined by 15° to the normal to the molecular plane. This angle depends somewhat on the rotational position of the ester group.

The influence of the changes in the molecular structure on the ferroelectric properties can be discussed as follows.

(i) Addition of the third cyclohexane ring (**IIIa**→**IIIb**, **Va**→**Vb**) decreases the absolute value of δ_p (see the table). Addition of the achiral third ring seems to reduced the constant a_1 of the chiral part of the rotational potential (cf. equation (12)).

(ii) The addition of the bulky ester group (**Va**→**IIIa**) leads to a reversal of the sign of P_0 and δ_p. As the direction of the resulting dipole $\mu_{\perp}$ does not change significantly we must discuss the position of the rotating molecule in its state of minimum potential energy which is characterized by the angle ψ_0 between $\mu_{\perp}$ and a molecular reference axis. This means that the direction of $\mu_{\perp}$ deviates from that of P_s because of steric effects between the guest molecule and its surroundings. From equation (11) it follows that P_0 is positive if $-90° < \psi_0 < 90°$ and negative when $90° < \psi_0 < 270°$.

(iii) Though all dipolar groups are preserved in **IIIb** in the same positions and directions as in **IIIa** the reduced polarization P_0 is zero. From equation (11) it can be derived that this is only the case if $\cos \psi_0 = 0$. Consequently, in **IIIb** the molecule must be in such an equilibrium state of rotation that $\mu_{\perp}$ is situated within the tilt plane and the angle between $\mu_{\perp}$ and P_s, ψ_0, is 90°.

Summarizing we can conclude that the equilibrium position of the rotating chiral guest molecule with respect to the tilt plane is governed by steric interactions with the surrounding host phase. Thus, the directions of P_s and $\mu_{\perp}$ do not necessarily coincide but can deviate by an angle ψ_0 which determines additionally the magnitude and the sign of the spontaneous polarization. By this concept we can explain qualitatively the ferroelectric properties of the S_C^* phases induced by the new cyclohexanone derivatives.

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