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Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

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M. A. Osipov^{ab}; R. Meister^c; H. Stegemeyer^c

^a Institute of Theoretical Physics, Technical University Berlin, Berlin, Germany ^b Institute of Crystallography, Russian Academy of Science, Moscow, Russia ^c Institute of Physical Chemistry, University Paderborn, Paderborn, Germany

To cite this Article Osipov, M. A. , Meister, R. and Stegemeyer, H.(1994) 'A microscopic model considering the effect of molecular biaxiality on ferroelectric ordering of liquid crystalline smectic C* phases', *Liquid Crystals*, 16: 2, 173 – 183

To link to this Article: DOI: 10.1080/02678299408029145

URL: <http://dx.doi.org/10.1080/02678299408029145>

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A microscopic model considering the effect of molecular biaxiality on ferroelectric ordering of liquid crystalline smectic C* phases

by M. A. OSIPOV†

Institute of Theoretical Physics, Technical University Berlin,
D-10623 Berlin, Germany

and R. MEISTER and H. STEGEMEYER*

Institute of Physical Chemistry, University Paderborn,
D-33095 Paderborn, Germany

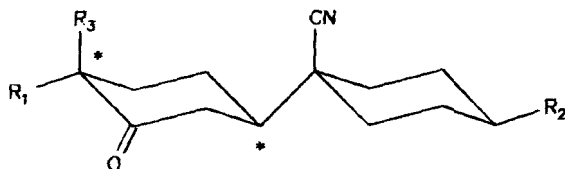
(Received 26 April 1993; accepted 19 August 1993)

On the basis of a mean-field approach, a microscopic model is presented to explain some ferroelectric properties of induced smectic C* phases of chiral dipolar guest molecules in an achiral smectic C host phase. The molecular biaxiality of the chiral dopants has been taken into account, resulting in a polar and quadrupolar ordering of the molecular short axes in the rotational distribution function of the guest molecules. This model explains the dependence of the magnitude and sign of the spontaneous polarization on the molecular structure of a series of cyclohexanone derivatives used as chiral dopants, as well as the effect of a local field at higher dopant concentrations.

1. Introduction

Induced smectic C* phases are obtained by mixing chiral guest substances with achiral host substances that show a smectic C phase. The measured spontaneous polarization P_s , as well as the tilt angle θ depend on both compounds and show a non-linear dependence on the mol fraction x_G of the guest substance. In most cases the reduced polarization $P_0 = P_s/\sin\theta$ depends only on the guest substance and shows a linear dependence $P_0(x_G)$. With substances that show the above behaviour the polarization power $\delta_p = \partial P_0/\partial x_G$ characterizes the possibility of a given chiral dopant to induce a spontaneous polarization.

In a previous article [1], four cyclohexanone derivatives as dopants were investigated. In these substances, both the chiral centres and the transverse dipoles were placed in the central core, in contradiction to most other substances where the dipole and chiral centre are located in an alkyl side chain. The molecular structure of the central core is given as follows:



* Author for correspondence.

† Alexander von Humboldt Fellow. Permanent address: Institute of Crystallography, Russian Academy of Science, Leninsky pr. 59, Moscow 117333, Russia.

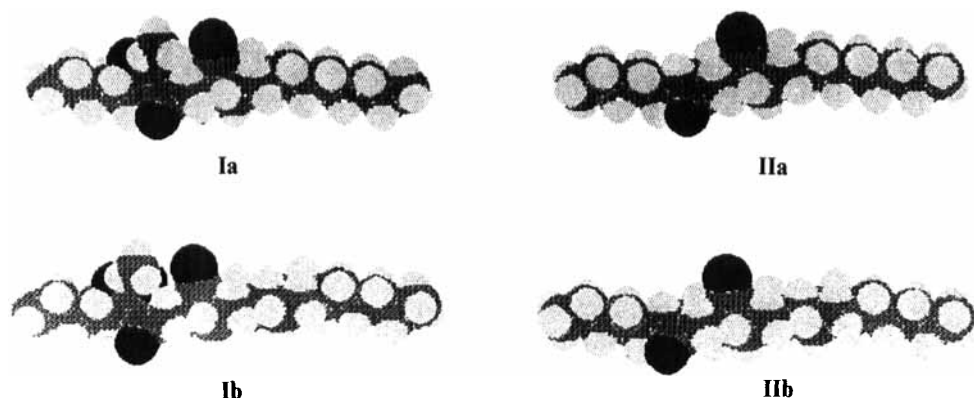


Figure 1. Space filling models (computer program Alchemy II) of the cyclohexanone derivatives used as chiral dopants.

Polarization power δ_p and sign of the spontaneous polarization of chiral dopants in the smectic C host phase 8007 [1].

Chiral dopant	Sign of P_0	$\delta_p/nC \text{ cm}^{-2}$
Ia	Positive	+240
Ib	(Negative)	≈ 0
IIa	Negative	-370
IIb	Negative	-235

For details we refer to [1]. Space fillings models of these dopants are shown in figure 1.

On examination of the ferroelectric properties, some unexpected results were obtained. A sign inversion of P_S appears, dependent on the structure of the achiral substituents of the guest. From the table, it can be seen that for **IIa** and **IIb** a negative sign P_S appears, while for **Ia** the sign is positive. With **Ib** as a dopant, no spontaneous polarization could be measured.

The results could be interpreted by taking some steric effects into account, but no molecular statistical equations for the observed phenomenological coefficients could be given. Also the effect of quadrupolar ordering was not taken into account.

In this article a molecular statistical theory of ferroelectric ordering in smectic C* phases will be developed which takes into account polar and quadrupolar ordering.

Starting from the mean field approximation of the free energy in the smectic C* phase, a formula for the spontaneous polarization is obtained where the coefficients are determined in terms of the intermolecular interaction potential. This general expression for P_S is used for a qualitative interpretation of the experimental results obtained in [1] and discussed above.

The main idea of this explanation is related to the fact that the minima of the polar and non-polar parts of the effective one-particle potential generally do not coincide. Then there is a competition between these two ordering mechanisms, which can be responsible for the change in absolute value and sign of P_S for substances with different molecular structures.

The molecular statistical theory also gives an expression for the local field correction which was used in [2] to explain a non-linear behaviour of $P_0(x_G)$.

2. Effect of molecular biaxiality on the spontaneous polarization

2.1. General results

In this section we consider in more detail the molecular statistical theory of ferroelectric ordering in a smectic C^* phase composed of biaxial molecules. It should be noted that the effect of biaxiality has not been taken into account in the existing theory of ferroelectric smectics [3, 4], except for the simple microscopic model proposed by Urbanc and Zeks [5]. We shall see, however, that the biaxial ordering of strongly asymmetric molecules in the smectic C phase appears to be an important phenomenon which enables one to explain the unusual variation of the absolute value and the sign of the spontaneous polarization induced by a change in the non-chiral part of the molecule [1].

In the molecular-field approximation, the free energy of a liquid crystal can be written in the form

$$F = \rho kT \int f(y) \ln f(y) dy + (1/2)\rho^2 \int \Omega(\zeta_{12} - r_{12}) V(y_1, y_2) f(y_1) f(y_2) dy_1 dy_2 - (1/2)\rho^2 kT \int (\Omega(\zeta_{12} - r_{12}) - 1) f(y_1) f(y_2) dy_1 dy_2, \tag{1}$$

where ρ is the number density and the variable y denotes both the position \mathbf{r} and the orientation ω of the biaxial molecule, $V(y_1, y_2)$ is the attractive interaction potential between the molecules '1' and '2', ζ_{12} is the distance of minimum approach for the two molecules and $\Omega(\zeta_{12} - r_{12})$ is the step-function; $\Omega(\zeta_{12} - r_{12}) = 0$ if the molecules penetrate each other (i.e. $\zeta_{12} < r_{12}$) and $\Omega(\zeta_{12} - r_{12}) = 1$ if they do not. Here, $r_{12} = |\mathbf{r}_{12}|$ is the intermolecular distance. Note that the function ζ_{12} is completely determined by the shape of a rigid molecule. Finally, $f(y) = f(\mathbf{r}, \omega)$ is the one-particle distribution function which depends both on the position and orientation.

The first term in equation (1) is the mixing entropy of the liquid crystal and the second one is the internal energy. The third term is the so-called packing entropy which is determined by the molecular geometry.

The distribution function $f(y)$ can be determined by minimization of the free energy (1)

$$f(\mathbf{r}, \omega_1) = Z^{-1} \exp \left(-(kT)^{-1} \int V_{\text{eff}}(\omega_1, \omega_2, \mathbf{r}_{12}) f(\mathbf{r}_2, \omega_2) d\mathbf{r}_2 d\omega_2 \right), \tag{2}$$

with

$$V_{\text{eff}}(1, 2) = V(1, 2)\Omega(\zeta_{12} - r_{12}) + kT(\Omega(\zeta_{12} - r_{12}) - 1) \tag{3}$$

and

$$Z = \int \exp(-V_{\text{eff}}(y)) dy. \tag{4}$$

Note that the effective potential $V_{\text{eff}}(1, 2)$ in equation (3) is a sum of two terms which represent (i) the contributions from the intermolecular attraction and (ii) the steric repulsion. In equation (3) we can specify the orientation of a biaxial molecule by two unit vectors \mathbf{a} and \mathbf{b} in the direction of the molecular long and short axes, respectively, cf. figure 2.

In the general case the averaging over positional and orientational degrees of freedom equation (2) appears to be a very complicated procedure. It can be simplified in

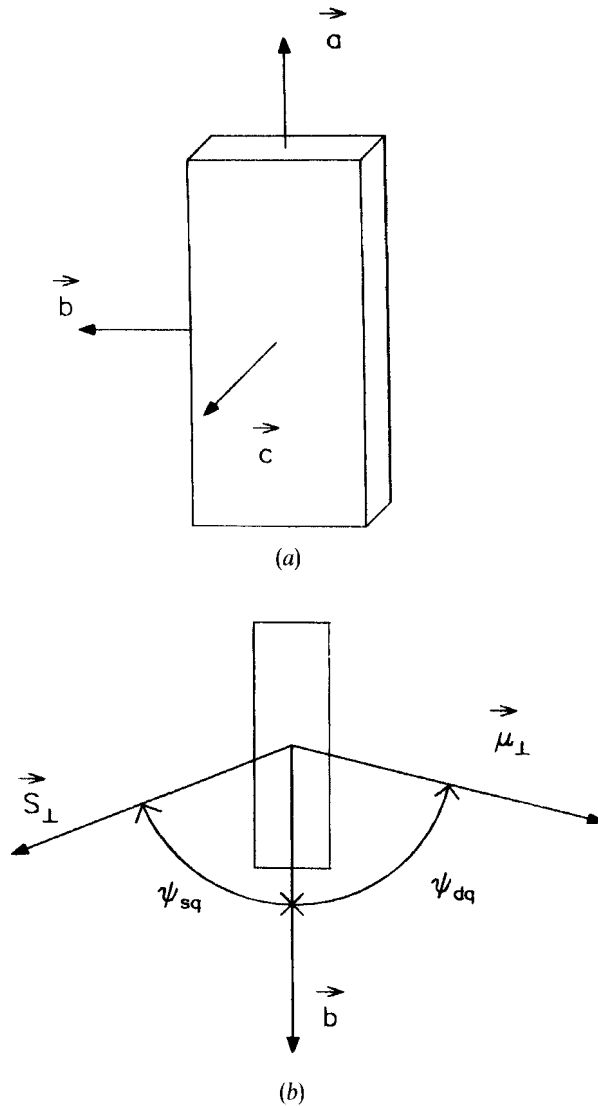


Figure 2. (a) Biaxial rigid dopant molecule whose orientation is specified by the unit vectors \mathbf{a} , \mathbf{b} and \mathbf{c} . (b) Cross-section of a biaxial dopant molecule showing the relative positions of its transverse dipole μ_\perp and its steric dipole \mathbf{S}_\perp with respect to the molecular plane.

the approximation of the perfect translational order of the molecular centres in the smectic C phase and perfect orientational order of the molecular long axes. This approximation seems to be reasonable for the smectic C phase, since both the orientational and translational order should be close to saturation far from the N-I and N-S_A transition points. In this approximation, the one-particle distribution function depends only on the orientation of the molecular short axis \mathbf{b} and equation (2) can be rewritten as

$$f(\mathbf{b}_1) = Z^{-1} \exp\left(- (kT)^{-1} \int V_{\text{eff}}(\mathbf{b}_1, \mathbf{b}_2) f(\mathbf{b}_2) d^2 \mathbf{b}_2\right) \quad (5)$$

where $V_{\text{eff}}(\mathbf{b}_1, \mathbf{b}_2)$ is the effective interaction potential averaged over the positional distribution of the molecular centres of mass in the smectic structure

$$V_{\text{eff}}(\mathbf{b}_1, \mathbf{b}_2) = \sigma \rho \int V_{\text{eff}}(\mathbf{n}, \mathbf{b}_1, \mathbf{b}_2, \mathbf{r}_{12}) r_{12}^2 \delta(\mathbf{u}_{12} \mathbf{k}) d\mathbf{r}_{12} d^2 \mathbf{u}_{12} + (1 - \sigma) \rho \int V_{\text{eff}}(\mathbf{n}, \mathbf{b}_1, \mathbf{b}_2, \mathbf{k} r_{12}) r_{12}^2 dr_{12}, \quad (6)$$

where \mathbf{n} is the director, \mathbf{k} is the unit vector normal to the smectic planes, $\mathbf{u}_{12} = \mathbf{r}_{12}/r_{12}$ is a unit vector in the direction of \mathbf{r}_{12} and σ is the fraction of the nearest neighbours (with respect to the total number of neighbouring molecules) which are in the same plane with the given molecule. $\delta(\mathbf{u}_{12} \mathbf{k})$ is the δ -function which is non-zero only when $\mathbf{u}_{12} \perp \mathbf{k}$. Note that the argument in round brackets means the scalar product.

2.2. Effective interaction potential in the smectic C^* phase

In the general case the orientation of any rigid biaxial molecule can be specified by two unit vectors \mathbf{a} and \mathbf{b} in the direction of the long and one ‘short’ axis, respectively. However, sometimes it is convenient to introduce also the second short axis $\mathbf{c} = [\mathbf{a}\mathbf{b}]$, see again figure 2. Note that the expression in square brackets means the vector product. In the approximation of perfect order in the smectic C phase orientation of the long axis \mathbf{a} is fixed ($a_\alpha a_\beta = n_\alpha n_\beta$) and the tensors $b_\alpha b_\beta$ and $c_\alpha c_\beta$ are related by the following equation:

$$b_\alpha b_\beta + c_\alpha c_\beta + n_\alpha n_\beta = \delta_{\alpha\beta}, \quad (7)$$

where $\delta_{\alpha\beta}$ is the unit tensor, $\alpha, \beta = x, y, z$. From symmetry reasons, the effective interaction potential in the smectic C^* phase depends not only on the direction of the molecular short axes $\mathbf{b}_1, \mathbf{b}_2$, but also on the vector order parameter $\xi = (\mathbf{n}\mathbf{k})[\mathbf{n}\mathbf{k}]$, where \mathbf{k} is the smectic plane normal and \mathbf{n} is the director. (Note that the equilibrium spontaneous polarization in the smectic C^* phase is along ξ and $|\xi| = \sin 2\theta$, where θ is the tilt angle.) Now the interaction potential can be expanded in powers of ξ

$$V_{\text{eff}}(1, 2) = V_0(\mathbf{b}_1, \mathbf{b}_2) + C_\alpha^{(d\theta)} \xi_\alpha + C_{\alpha\beta}^{(q\theta)} \xi_\alpha \xi_\beta, \quad (8)$$

where the interaction potential $V_0(\mathbf{b}_1, \mathbf{b}_2)$ does not depend on ξ and can be also approximately represented as a sum of polar (index dd) and non-polar (index qq) (in the lowest order) terms:

$$V_0(\mathbf{b}_1, \mathbf{b}_2) \approx V_{\text{dd}}(\mathbf{b}_1 \mathbf{b}_2) + V_{\text{qq}} P_2(\mathbf{b}_1 \mathbf{b}_2) \quad (9)$$

where $P_2(\mathbf{b}_1 \mathbf{b}_2)$ is the second Legendre polynomial.

Now let us discuss the physical meaning of the different terms in equations (8) and (9). The first term in equation (9) represents a contribution from the usual dipole–dipole interaction modulated by the asymmetric molecular shape. In the general case the second term is the anisotropic part of the non-polar potential which can be determined both by the van der Waals interaction between the transverse molecular polarizabilities, and by steric repulsion between flat molecules. In general, this term possesses a quadrupolar symmetry and can be interpreted qualitatively as an interaction between induced quadrupoles (which determine the molecular polarizability) and between the so-called ‘steric quadrupoles’ [6].

The second term in equation (8) is chiral by symmetry and the coupling constant $C^{(d\theta)}$ should come from the interaction between the dipole (electric or steric) and the average tilt. The coupling constant $C^{(d\theta)}$ is determined by the molecular chirality and

the corresponding chiral and polar intermolecular interactions (which are responsible for this contribution to the effective potential) are discussed in detail in [3,4]. By contrast, the last term in equation (8) is non-chiral and represents an interaction between molecular ‘quadrupole’ and the tilt.

For simplicity, we shall consider only the most simple contributions to the last two terms in equation (8) which correspond to the effective interaction between one molecule and the tilt. In this case

$$C_{\alpha}^{(d\theta)} = C_{\alpha}^{(d\theta)}(\mathbf{b}_1) + C_{\alpha}^{(d\theta)}(\mathbf{b}_2) \quad (10)$$

and

$$C_{\alpha\beta}^{(q\theta)} = C_{\alpha\beta}^{(q\theta)}(\mathbf{b}_1) + C_{\alpha\beta}^{(q\theta)}(\mathbf{b}_2) \quad (11)$$

where the vector $\mathbf{C}^{(d\theta)}$ and the tensor $C_{\alpha\beta}^{(q\theta)}$ are given by the following general expressions:

$$\mathbf{C}^{(d\theta)} = C_x^{(q\theta)}\mathbf{b} + C_y^{(q\theta)}\mathbf{c} \quad (12)$$

and

$$C_{\alpha\beta}^{(q\theta)} = C_{xx}^{(q\theta)}b_{\alpha}b_{\beta} + C_{xy}^{(q\theta)}(b_{\alpha}c_{\beta} + c_{\alpha}b_{\beta}) + C_{yy}^{(q\theta)}c_{\alpha}c_{\beta}. \quad (13)$$

The last two terms in equation (8) can be further simplified if one uses the specific definition of the molecular short axis \mathbf{b} . For example, it is possible to take \mathbf{b} along the vector $\mathbf{C}^{(d\theta)}$. In this case $C_y^{(q\theta)} = 0$ and $C_{\alpha}^{(d\theta)}\xi_{\alpha} = C^{(d\theta)}(\mathbf{b}\xi)$. This means that the vector \mathbf{b} has been taken along some real physical vector parameter of the molecule which is actually ordered along ξ in the smectic C* phase. It is known from the molecular theory of ferroelectric ordering [3,4] that this vector can be the transverse steric dipole. However, with this definition of the short axis \mathbf{b} , the tensor $C_{\alpha\beta}^{(q\theta)}$ is not necessarily diagonal. This can take place, for example, when the steric dipole is tilted with respect to the main axis of the transverse steric ‘quadrupole’ (see figure 2(b)).

When the molecular biaxiality is large (i.e. when the molecules are ‘flat’), the molecular ‘planes’ tend to align parallel to ξ and this effect can be stronger than the corresponding tendency for the steric dipole. In this case, it is more convenient to use another definition of the short axis \mathbf{b} which transforms the tensor $C_{\alpha\beta}^{(q\theta)}$ into the diagonal form

$$C_{\alpha\beta}^{(q\theta)} = C_x^{(q\theta)}b_{\alpha}b_{\beta} + C_y^{(q\theta)}c_{\alpha}c_{\beta}. \quad (14)$$

Note that in this case the vector $\mathbf{C}^{(d\theta)}$ is not parallel to \mathbf{b} and is given by the general equation (12).

Substituting now equations (12), (14) and (9) into (5) and (8), we obtain the following expressions for the one-particle distribution function and the effective mean-field potential as a function of the angle ψ between the molecular short axis \mathbf{b} and ξ . The angle ψ describes the rotation of the biaxial molecule around its long axis

$$f(\psi) = Z^{-1} \exp(-(kT)^{-1}U(\psi)), \quad (15)$$

with

$$U(\psi) = V_{\text{dd}}\langle \cos \psi \rangle \cos \psi + (3/2)V_{\text{qq}}\langle \cos 2\psi \rangle \cos 2\psi + \Delta V_{\text{d}\theta}\xi \cos(\psi - \psi_{\text{sq}}) + \Delta V_{\text{q}\theta}\xi^2 \cos 2\psi, \quad (16)$$

with

$$\Delta V_{\text{d}\theta} = \sqrt{[(C_x^{(d\theta)})^2 + (C_y^{(d\theta)})^2]}, \quad (17)$$

$$\cos \psi_{\text{sq}} = C_x^{(d\theta)}/\Delta V_{\text{d}\theta}, \quad (18)$$

and

$$\Delta V_{q\theta} = C_x^{(q\theta)} - C_y^{(q\theta)}. \quad (19)$$

Note that the angle ψ_{sq} is a parameter of the molecular structure. In the simple steric model, presented on figure 2 (b), ψ_{sq} is the angle between the transverse steric dipole and the principle axis of the transverse steric quadrupole (i.e. the tilt angle of the steric dipole with respect to the molecular ‘plane’). Note that the quantity $\Delta V_{q\theta}$ can be considered as a measure of molecular biaxiality.

2.3. Mean-field potential for the chiral guest molecule

Equation (16) for the one-particle mean-field potential can be readily generalized to the case of a chiral dopant in a non-chiral smectic C matrix. In this case equation (16) should be rewritten as

$$\begin{aligned} U_G(\psi_G) = & (V_{dd}^{(11)}x_G\langle\cos\psi_G\rangle + V_{dd}^{(12)}(1-x_G)\langle\cos\psi_H\rangle)\cos\psi_G \\ & + (V_{qq}^{(11)}x_G\langle\cos 2\psi_G\rangle + V_{qq}^{(12)}(1-x_G)\langle\cos 2\psi_H\rangle)\cos 2\psi_G \\ & + \Delta V_{d\theta}^{(12)}\xi\cos(\psi_G - \psi_{sq}) + \Delta V_{q\theta}^{(12)}\xi^2\cos 2\psi_G, \end{aligned} \quad (20)$$

where x_G is the molar fraction of the chiral guest molecules and the coupling constants $V^{(11)}$ and $V^{(12)}$ represent the interaction between two guest molecules and the interaction between a guest and a host molecule, respectively. The angles ψ_G and ψ_H are the angles between the vector ξ and the short axis \mathbf{b}_G and \mathbf{b}_H of the guest and host molecules, respectively.

Note that the order parameters $\langle\cos\psi_G\rangle$, $\langle\cos 2\psi_G\rangle$ and $\langle\cos\psi_H\rangle$, $\langle\cos 2\psi_H\rangle$ are generally not only equal, but also can differ substantially if the structure of the guest and host molecules is essentially different.

2.4. Influence of the molecular biaxiality on the value and sign of the spontaneous polarization

In the general case, the spontaneous polarization of the smectic C* liquid crystal can be written as

$$\mathbf{P}_S = \rho\langle\boldsymbol{\mu}_\perp\rangle = \rho(\mu_x\langle\mathbf{b}\rangle + \mu_y\langle\mathbf{c}\rangle), \quad (21)$$

where $\boldsymbol{\mu}_\perp$ is the transverse molecular dipole and the averaging is performed with the one-particle distribution function equation (15).

Note that both $\langle\mathbf{b}\rangle$ and $\langle\mathbf{c}\rangle$ are parallel to ξ and thus the spontaneous polarization \mathbf{P}_S can also be expressed as

$$\mathbf{P}_S = \rho\mu_\perp\langle\cos(\psi - \psi_{dq})\rangle\xi, \quad (22)$$

where ψ_{dq} is the angle between the transverse dipole $\boldsymbol{\mu}_\perp$ and the molecular short axis \mathbf{b} defined above (see figure 2 (b)).

The majority of ferroelectric liquid crystals do not possess a very large spontaneous polarization and thus the order parameter $\langle\cos\psi\rangle$ is usually small. This corresponds also to induced smectic C* phases (mixtures of chiral dopants and smectic C host phases). For example, $\langle\cos\psi\rangle \approx 10^{-2}$ for the liquid crystal material DOBAMBC according to the results of NMR measurements and also theoretical estimates [3]. This means that the coupling constant $(V_{dd}\langle\cos\psi\rangle + \Delta V_{d\theta}\xi)$ is also small and one can

expand the expression for the distribution function in powers of this parameter, taking into account the first two terms. (It should be noted, however, that this procedure is invalid for ferroelectric crystals with extremely large spontaneous polarizations of the order of 10^3 nC cm² (see, for example, [7, 8]). In such systems, the order parameter $\langle \cos \psi \rangle$ is expected to be close to unity.) Finally one obtains the following expression for the spontaneous polarization

$$P_S = (1/2)\rho\chi\mu_{\perp}(\Delta V_{d\theta}/kT) \sin 2\theta \langle \cos(\psi - \psi_{dq}) \cos(\psi - \psi_{sq}) \rangle_0, \quad (23)$$

$$= (1/4)\rho\chi\mu_{\perp}(\Delta V_{d\theta}/kT) \sin 2\theta (\cos \psi_+ \langle \cos 2\psi \rangle + \cos \psi_0), \quad (24)$$

with

$$\psi_+ = \psi_{dq} + \psi_{sq}, \quad (25)$$

$$\psi_0 = \psi_{dq} - \psi_{sq}, \quad (26)$$

where ψ_0 is the angle between the electric and steric dipole and χ is the dielectric susceptibility

$$\chi = [1 - (2\rho)^{-1}(V_{dd}/kT)(\cos \psi_+ \langle \cos 2\psi \rangle + \cos \psi_0)]^{-1} \quad (27)$$

and the quadrupolar order parameter $\langle \cos 2\psi \rangle$ is determined by the following self-consistent equation

$$\langle \cos 2\psi \rangle = Z_0^{-1} \int \cos 2\psi \exp(-V_0(\psi)/kT) d\psi, \quad (28)$$

with

$$V_0(\psi) = ((3/2)V_{dd} \langle \cos 2\psi \rangle + (1/2)V_{q\theta} \sin 2\theta) \cos 2\psi \quad (29)$$

and

$$Z_0 = \int \exp(-V_0(\psi)/kT) d\psi. \quad (30)$$

Note that in this approximation, the quadrupolar order parameter has the same value as in the corresponding non-chiral smectic C phase, since it is indeed determined mainly by non-chiral intermolecular interactions.

It should also be noted that equations (24)–(30) can be used in the case of non-chiral smectics C phases with chiral molecules, *if the transverse electric dipole of a host molecule is much smaller than that of the guest molecule*. In this simple case, one has only to substitute in equations (24) and (27) ρ for $\rho_0 x_G$ and V_{dd} for $V_{dd}^1 x_G^2$, where x_G is the molar fraction of chiral molecules. Then the coupling constants $\Delta V_{d\theta}$ and $\Delta V_{q\theta}$ must be also interpreted as contributions from the corresponding interactions between guest and host molecules. In such a system, the spontaneous polarization is determined only by the ordering of the guest dipoles. In the more general case, however, the dipoles of the host molecules can also give some contribution. This more complicated case will be considered elsewhere.

Now let us try to use equations (24)–(27) in the interpretation of the experimental data obtained by Stegemeyer *et al.* [1]. The systematic variation of the chiral guest structure has been performed and the spontaneous polarization has been measured for four different chiral dopants (see figure 1) in the same host smectic C phase. In this

paper, the so-called polarization power δ_P is introduced which relates to P_S at small x_G by the following equation:

$$\delta_P = \frac{P_S}{x_G \sin \theta}. \quad (31)$$

It should be noted that the difference in the four chiral dopants presented in figure 1 is determined by only two elements: the ester group which is added to the cyclohexanone ring in **Ia** and **Ib** and the third cyclohexane ring in **Ib** and **IIb**. Within the present approach we can assume qualitatively that the addition of the ester group is equivalent to the introduction of a large steric dipole and the addition of the third cyclohexane ring increases the effective molecular steric quadrupole, since the biaxial rigid core of the molecule is enlarged.

Let us consider first the two chiral dopants **Ia** and **IIa** which do not possess the third cyclohexane ring. It is reasonable to assume that for such molecules the biaxial ordering of the molecular hard cores (which are relatively small) is weak and one can neglect the first term (i.e. the quadrupolar order parameter $\langle \cos 2\psi \rangle$) in equation (24) for the spontaneous polarization. Then the difference between the values and signs of the spontaneous polarization for substances **Ia** and **IIa** should be determined, in the first approximation, only by the parameter $\cos \psi_0$, where ψ_0 is an angle between the transverse electric and steric dipole. Note that the absolute value and the direction of the electric dipole is about the same in both molecules.

According to [1], the transverse dipole of **IIa** is dominated by the cyano group and is inclined at an angle of 40° to the normal to the molecular plane. In the guest molecule **Ia**, the ester group also contributes to the dipole and the resulting transverse dipole moment is inclined at 15° to the normal to the molecular plane. At the same time, the main contribution to the transverse steric dipole of **Ia** comes from the ester group which is roughly parallel to the electric dipole. Therefore, the angle ψ_0 should be small and the parameter $\cos \psi_0$ must be positive and relatively large. The resulting spontaneous polarization must also be positive which agrees with experiment. By contrast, the spontaneous polarization of **IIa** is negative, which can be explained by the strong change in steric dipole. This is determined now, most probably, by the average bend of the molecule which points approximately in the opposite direction. Then the angle $\psi_0 > 90^\circ$ and the parameter $\cos \psi_0$ is negative, which also holds for δ_P (see table).

It should be noted, of course, that this interpretation is very qualitative and it does not explain, for example, why the absolute value of the spontaneous polarization is larger for **IIa**. However, we did not take into account several additional factors, and this difference can be determined, for example, by some 'basic' negative contribution which can come from the ordering of host molecules (which do possess some transverse dipoles in the present case, cf. [1]).

Now let us consider the structure of the remaining two guest molecules **Ib** and **IIb**. The third ring increases the molecular biaxiality and in this case one cannot neglect the effect of the biaxial ordering of the molecular short axes. Therefore, the spontaneous polarization is determined now by both terms in equation (24). What happens when one adds the third cyclohexane ring to the molecule **Ia**? We assume that the introduction of this ring increases mainly the quadrupolar order parameter $\langle \cos 2\psi \rangle$ in equation (24) and, as a result, the additional term $\sim \cos \psi_+ \langle \cos 2\psi \rangle$ is added to the spontaneous polarization. Note that this term is negative, since the angle $\psi_+ \approx 180^\circ$ when $\psi_0 \approx 0^\circ$, and the electric and steric dipoles point more or less in opposite directions. Thus the two terms in equation (24) for the spontaneous polarization,

induced by **Ib**, can compensate each other and the resulting polarization can be close to zero as has been observed experimentally (cf. table).

The same qualitative explanation can also be used in the case of the guest compound **IIb**. In this case, the ‘initial’ polarization, induced by the molecule **IIa**, is negative and the angle $90^\circ < \psi_0 < 180^\circ$. Then the introduction of the third ring is again equivalent to the appearance of the large ‘quadrupolar’ term in equation (24) which is positive (since the angle ψ_+ is now about 0°) and is subtracted from the ‘initial’ negative term. As a result the absolute value of the spontaneous polarization is decreased in accordance with experiment.

2.5. Concentration dependence of the spontaneous polarization and the local field effect

Let us consider now the dependence of spontaneous polarization on the concentration of chiral guest molecules in induced smectic C* phases. According to equations (24)–(27) and the discussion presented in §2.4, the polarization induced by a chiral guest in the smectic C phase is given by

$$P_S = \frac{1}{4} x_G \rho \chi(x_G) \mu_\perp \frac{\Delta V_{d0}}{kT} \kappa \sin 2\theta; \quad (32)$$

with

$$\chi(x_G) = \left[1 - x_G \frac{V_{dd}}{2kT} \kappa \right]^{-1} \quad (33)$$

and

$$\kappa = \cos \psi_+ \langle \cos 2\psi \rangle + \cos \psi_0. \quad (34)$$

Note that the mol fraction x_G of chiral molecules enters the expression for the spontaneous polarization in two different ways. Firstly, the spontaneous polarization is simply proportional to x_G at small $x_G \ll 1$. This is a well-known result which represents the fact that the spontaneous polarization appears only in the presence of chiral molecules and is determined mainly by an interaction between guest and host.

At the same time, the dielectric susceptibility χ also depends on x_G according to equation (33). This dependence comes from the interaction between the permanent dipoles of the guest molecules. The corresponding coupling constant V_{dd} in equation (33) can, in principle, be determined from the general equations (3), (6) and (9), substituting the dipole–dipole interaction potential. The resulting expression can be given as

$$V_{dd} = \mu_\perp^2 \Lambda, \quad (35)$$

where the parameter Λ depends on the molecular shape and on the tilt angle θ . The calculation of the parameter Λ represents a separate complicated problem which we shall not discuss here. In this paper we shall not need any specific information about Λ .

Now we can write the spontaneous polarization in the following simple form:

$$P_S = \frac{x_G a \sin 2\theta}{1 - x_G \mu_\perp^2 \Lambda \kappa / 2kT}, \quad (36)$$

with

$$a = \frac{1}{4} \rho \mu_\perp \frac{\Delta V_{d0}}{kT} \kappa, \quad (37)$$

Note that this expression is equivalent to the one obtained in [2], taking into account the local electric field corrections to the spontaneous polarization (if one neglects the molecular polarizability, which we did not take into account in the present theory).

Thus we see that the local field effects, discussed in [2], can be accounted for within the present approach, taking into consideration the dipole–dipole interaction modulated by the asymmetric molecular shape. It should be noted that the value of the parameter Λ can differ from the value $1/3\epsilon_0$ for a Lorentzian type field which has been assumed in [2] as a first approximation.

Note that there is an additional ‘geometrical’ factor κ in equation (36) which depends on the quadrupolar order parameter $\langle \cos 2\psi \rangle$. This difference, however, does not change the qualitative considerations of [2].

3. Conclusions

On the basis of the mean field theory of the molecular interaction in ferroelectric smectic C^* phases, a microscopic model has been developed which explains some effects of molecular structure on the sign and magnitude of the spontaneous polarization. This model considers the biaxiality of the molecules leading to a polar and quadrupolar ordering of the molecular short axes within the smectic planes. Both order parameters are sensitive to the molecular biaxiality and to the relative orientation of the electric and steric dipoles in a different way. Thus, in the case of a given dipolar chiral core, the resulting spontaneous polarization depends on the structure of the attached non-chiral substituents determining the molecular biaxiality. By this model, the experimental results formerly obtained [1] can be understood. Further, the effect of a local field explaining the non-linear behaviour of the function $P_o(x_c)$ [2] obviously follows from the theoretical model. As the polar and quadrupolar ordering depend on temperature in a different way according to the model given above, the sign reversal of P_s with temperature [9, 10, 11] can be explained; this will be discussed in another paper [12].

This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. M. A. Osipov is indebted to the Alexander von Humboldt-Stiftung for a fellowship and is grateful to Professor S. Hess for stimulating discussions.

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