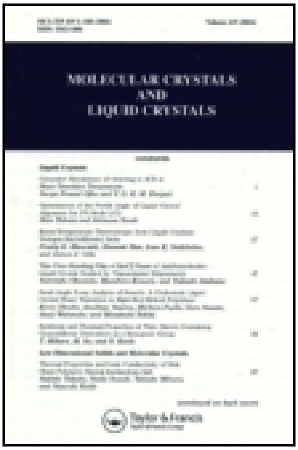

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Influence of Quadrupolar Ordering Factor on Supermolecular Structure in Ferroelectric Sm C*

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Influence of Quadrupolar Ordering Factor on Supermolecular Structure in Ferroelectric Sm C*

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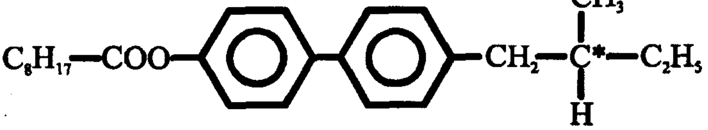
We have synthesized the compound: 2-methylbutyl-4-n-nonanoyloxybiphenyl-4'-carboxylate (MBOBC).



MBOBC shows the inversions in the sign of the spontaneous polarization, what was first reported by Goodby et al.[1] and Eidenschink et al.[2]. This ferroelectric liquid crystals has been studied by dielectric, densytometric, refractometric an X-ray measurements. After comparing the P_S taken from experiment and obtained from theoretical approximation[3,4,5], the contribution of the dipolar a_1 and quadrupolar a_2 terms in the rotational potential have been estimated.

Keywords: ferroelectric liquid crystal; rotational potential; quadrupolar ordering

INTRODUCTION

If liquid crystalline tilted smectic C* phase is formed by chiral molecules, the rotational distribution function $f(\psi)$ of the transverse short l molecular axis of inertia around the long n one will differ from cylindrical symmetry. The angle ψ describes the rotation of the transverse l molecular axis around the long n one. The microscopic origin of the spontaneous polarization P_S arises from broken symmetry of the potential $U(\psi)$[3] for molecular rotation around the long axis.

If the molecule forming ferroelectric Sm C* phase carries the effective permanent dipole moment μ_e and mean molecular polarizability $\bar{\alpha}$, the P_S can be expressed as[6]:

$$P_S = N\mu_e\langle\cos\delta\rangle + N\bar{\alpha}E_L, \qquad (1)$$

where: N is the molecular density number, E_L is the local electric field effected on the molecule in the $\mathbf{P_S}$ direction and δ is the angle between the effective dipole moment μ_e and the $\mathbf{P_S}$ vector.

The averaging in $\langle\cos\delta\rangle$ is carried out by standard statistical methods over the whole sample[3-11]. In the work reported in this paper, we intend to introduce our point of view on this subject and discuss it on the basis of our laboratory results for MBOBC where the sign of the spontaneous polarization P_S was found to invert with a change in temperature[1,2].

We can show that this inversion may be produced by the change between dipolar and quadrupolar coupling as the temperature fall down, what was suggested in[10,12] and was doubted by Goodby[11].

THEORY

Let us suppose that in our model a molecule looks like a rigid brick having chirality center and dipole moment μ built into its integral structure. The main molecular axes of inertia l, m, n and polar p, chiral d and quadrupolar b characteristic axes[10] of this object are rigidly attached to the local 0x'y'z' system of Cartesian coordinates as shown in Fig. 1. The mean polarizability is located in the 0 point.

In the 0x'y'z' system of coordinates the vector μ can be written as:

$$\mu' = [\mu'_X, \mu'_Y, \mu'_Z] = [\mu\sin\gamma\cos\varphi_0, \mu\sin\gamma\sin\varphi_0, \mu\cos\gamma] \qquad (2)$$

where: γ is the angle between the vector μ and the molecular director n (0z' axis), φ_0 is the angle between polar axis p ($\mu_\perp$ the projection of the μ on 0x'y' plane) and l molecular axis which coincides with 0x' one.

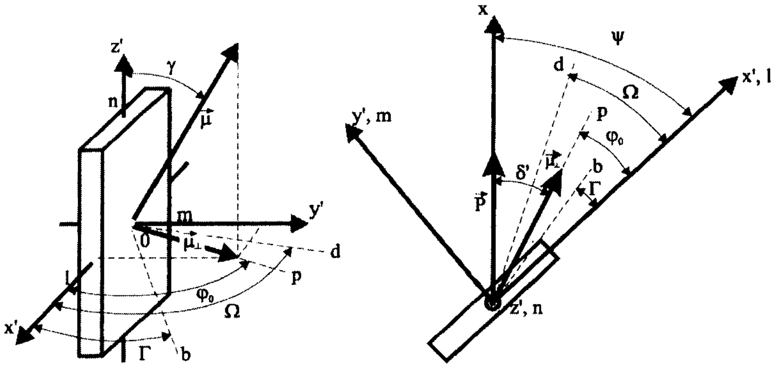


FIGURE 1. The structure of brick-like molecule of the Sm C* phase and view along long molecular axis.

The characteristic molecular axes p, d and b are placed in the 0x'y' plane and form with the short l molecular axis of inertia angles: φ_0, Ω and Γ respectively. As molecules are treated as rigid brick, so three molecular axes p, d and b are assumed to be fixed in such a way, that angles φ_0, Ω and Γ remain unchanged when a molecule rotates around the long n axis. In the laboratory 0xyz system of coordinates where P_S coincides with 0x axis[4,5]:

$$\mu_X = \mu \cos\delta, \tag{3}$$

where:

$$\cos\delta = (\cos\psi \cos\varphi_0 \sin\gamma + \sin\psi \sin\varphi_0 \sin\gamma). \tag{4}$$

Since φ_0 and γ are constant for a given kind of molecule, the average of $\cos\delta$ for a whole sample takes form:

$$\langle\cos\delta\rangle = \sin\gamma(\langle\cos\psi\rangle\cos\varphi_0 + \langle\sin\psi\rangle\sin\varphi_0) = \sin\gamma\cos\delta', \tag{4'}$$

where the angle ψ describes the orientation of the molecular axis l (0x' axis) with respect to the P_S direction (0x axis) as we see in Fig. 1.

The values of $\langle \cos\psi \rangle$ and $\langle \sin\psi \rangle$ can be calculated by standard statistical methods[4,5,6].

Where characteristic molecular axes d and b form the angles Ω and Γ with the l axis of inertia, we define a single particle potential $U(\psi)$ in the following form:

$$U(\psi) = -a_1 \sin\theta \cos(\psi - \Omega) + a_2 \sin^2\theta \cos 2(\psi - \Gamma) - a_3 \sin\theta\, q \sin\psi\,, \qquad (5)$$

where $q = 2\pi/\lambda$ and parameters a_1, a_2, a_3 (different for various kind of a FLC) are assumed to be positive.

In this form of $U(\psi)$ the first polar term with a_1 coefficient forces to orient the chiral axis d parallel to P_S, while the second quadrupolar one with a_2 and the third flexoelectric with a_3 try to turn b and l axes perpendicular to P_S direction. This form of potential is in good agreement with [3-11] because the angle Ω can assume any value between $-\pi$ and π and Γ any one between $-\pi/2$ and $\pi/2$.

Using this potential, we can expand the exponential in a power series:

$$\exp\left(\frac{-U(\psi)}{kT}\right) = \sum_{n=1}^{\infty} \frac{1}{n!}\left[\frac{-U(\psi)}{kT}\right]^n . \qquad (6)$$

Considering only the first two terms of Eq. (6), a theoretical expression for $\langle \cos\delta \rangle_2$ can be obtained as:

$$\begin{aligned}\langle \cos\delta \rangle_2 &= \sin\gamma \frac{\sin\theta}{2kT}\left[a_1 A + a_3 q \sin\varphi_0 + \frac{a_2 \sin^2\theta}{2kT}\left(a_1 D - a_3 q C\right)\right] = \\ &= \sin\gamma \langle \cos\delta' \rangle_2 \,, \end{aligned} \qquad (7)$$

where:

$$A = \cos\Omega \cos\varphi_0 + \sin\Omega \cos\varphi_0\,, \qquad (8)$$

$$D = \sin\Omega \cos\varphi_0 \sin 2\Gamma + \cos\Omega \cos\varphi_0 \cos 2\Gamma - \sin\Omega \sin\varphi_0 \cos 2\Gamma\,, \qquad (9)$$

$$C = \sin\varphi_0 \cos 2\Gamma + \cos\varphi_0 \sin 2\Gamma\,. \qquad (10)$$

In the Lorentz field approximation, we should put into (1) the following quantity:

$$\mu_e = \mu, \text{ and } E_L = \frac{P_S}{3\varepsilon_0}, \tag{11}$$

where: ε_0 is electric permittivity of free space and then the required theoretical relation for the spontaneous polarization P_S is:

$$P_S \frac{N\mu}{1 - \frac{N}{3\varepsilon_0}\overline{\alpha}} \sin\gamma \frac{\sin\theta}{2kT}\left[a_1A + a_3q\sin\varphi_0 - \frac{a_2\sin^2\theta}{2kT}(a_1D - a_3qC)\right]. \tag{12}$$

As we can see in (12) the sign and the character of spontaneous polarization P_S is described by mutual relation between coupling forces (a_1, a_2, a_3), their relations to molecular structure (Ω, Γ, φ_0, γ) and medium structure (λ, θ).

EXPERIMENTAL

In our continuos efforts to test and develop the microscopic origin of spontaneous polarization P_S, particularly trying to estimate the Žeks' a_1, a_2 and a_3 coefficients, the FLC methylbutyl 4-n-nonanoyloxy-biphenyl-4'-carboxylate (MBOBC) with the phase sequence:

C 312.0 K (39°C) Sm C* 314.5 K (41.5°C) Sm A* 332.5 K (59.5°C) I,

has been studied by dielectric, densitometric, refractometric, electrooptic and X-ray measurements. Our results for P_S, θ, λ where in good agreement with data presented in [1,2].

RESULTS AND DISCUSSION

On the basis of dielectric, refractometric, and densitometric measurments and some computer calculations we have got molecular parameters of the MBOBC molecule:

$\mu = 13.35\ 10^{-30}$ [Cm], $\gamma = 72°$, $\varphi_0 = -43°$, $\overline{\alpha} = 5.8\ 10^{-39}$ [$C^2m^2J^{-1}$].

Knowing the temperature dependence of the spontaneous polarization $P_S(T)$ and thermal densitometric characteristic $\rho(T)$ as well as μ, γ, φ_0 and $\overline{\alpha}$ we can calculate (from (1), (4) and (11)):

$$\langle\cos\delta'\rangle = \frac{P_S(T)\left(1-\frac{N(T)}{3\varepsilon_0}\overline{\alpha}\right)}{N(T)\mu\sin\gamma}. \tag{13}$$

On the other hand our theoretical investigations (7) lead us to the expression:

$$\langle\cos\delta'\rangle_2 = \frac{\sin\theta}{2kT}\left[a_1A + a_3q\sin\varphi_0 - \frac{a_2\sin^2\theta}{2kT}(a_1D - a_3qC)\right]. \tag{14}$$

The equation (13) (taken from the experiment) and the equation (14) (taken from the theory) can be compared and on its base the following function $F(T)$ can be defined:

$$F(T) = \frac{\langle\cos\delta'\rangle 2kT}{\sin\theta(T)} = a_1A + a_3q(T)\sin\varphi_0 - \frac{a_2\sin^2\theta(T)}{2kT}\left[a_1D - a_3q(T)C\right]. \tag{15}$$

In Fig. 2 the relation $F = f(q)$ is plotted. Supposing that for SmC* phase the factors a_1, a_2 do not depend on temperature and then plotting the left side of the Eq. (15) versus q one may notice, that for the small values of q (for which $\sin^2\theta \ll 1$ $F(T)$ can be described by a straight line:

$$F(q) = a_1A + a_3q\sin\varphi_0. \tag{16}$$

If we know: $a_1A = 5.49\cdot 10^{-23}$ $[\mathrm{J}]$ and $a_3\sin\varphi_0 = -4.27\cdot 10^{-29}$ $[\mathrm{Jm}]$ from the above linear approximation, the function $L(T)$ on the base of equation (15) can be written:

$$L(T,\Gamma,\Omega) = \frac{\left[F(T) - a_1A(\Omega) - a_3q(T)\sin\varphi_0\right]2kT}{a_3q(T)C(\Gamma) - a_1D(\Gamma,\Omega)} = a_2\sin^2\theta(T). \tag{17}$$

Using the least square method, we can chose the proper (for given molecule) unknown angles Ω and Γ for which the points $\left(L(T,\Gamma,\Omega), \sin^2\theta(T)\right)$ will lie along a straight line as good as possible.

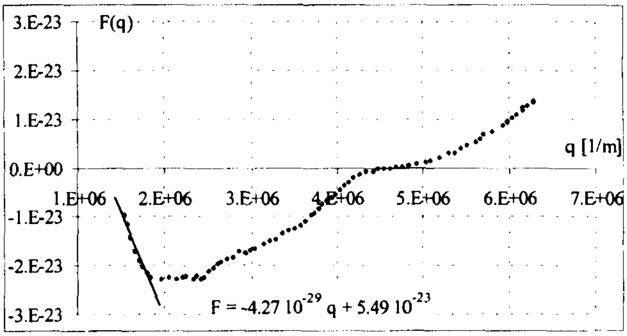


FIGURE 2. The relation $F = f(q)$.

Fig. 3 shows that the date L calculated from (17) fit the straight-line very well when Ω = -45° and Γ = 50°. The estimated in this way quadrupolar ordering factor $a_2 = 4.0 \cdot 10^{-20}$ J is in good agreement with[11]. In this case the quadrupolar part of the rotational potential (5): $a_2 \sin^2 \theta = 1.5\,kT$ (at T = 280 K (7°C), θ = 20.7°) is comparable to the thermal energy kT, whole the polar one: $a_1 \sin\theta = 0.005\,kT$ seems to be about 300 times weaker.

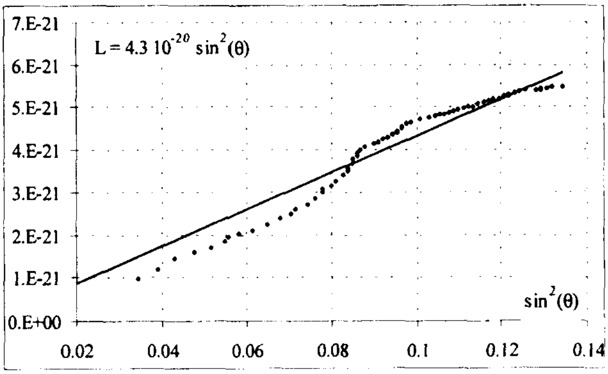


FIGURE 3. The relation $L = f(\sin^2\theta)$ for angles $\Gamma = 50°$ and $\Omega = -43°$.

As one can notice during the process of Ω and Γ fitting, a_2 (in the nature) is not the same for all temperatures range where SmC* phase exist.

CONCLUSIONS

The behavior of sign reversal in P_S versus temperature T observed in MBOBC can be explained in terms of the rotational potential (5).

If we suppose that the MBOBC molecule looks like a rigid brick characterized by molecular parameters:

$\mu = 13.35 \cdot 10^{-30}\,\mathrm{Cm}$, $\overline{\alpha} = 5.8 \cdot 10^{-39}\,\mathrm{C^2 m^2 J^{-1}}$, $\gamma = 72°$, $\varphi_0 = -43°$, $\Omega = -45°$ and $\Gamma = 50°$, the character of formation P_S may be described by $\langle \cos\delta' \rangle$ (7) which depends on $U(\psi)$ ($U(\psi)$ is specified by factors: $a_1 = 5.6\,10^{-23}\,\mathrm{J}$, $a_3 = 6.3 \cdot 10^{-29}\,\mathrm{Jm}$ and $a_2(T)$ given in Fig. 3).

1. In high temperature, e.g. for $T = 313$ K (40°C) > T_{N-P} (for this temperature the values of potential's factors: $a_1 \sin\theta = 0.77 \cdot 10^{-23}$ J, $a_2 \sin^2\theta \cong 0.0$ J, $a_3 q \sin\theta = 1.03 \cdot 10^{-23}$ Jm) the dipolar and flexoelectric coupling are dominated. In this situation: $\langle \sin\psi \rangle = 0.564$, $\langle \cos\psi \rangle = 0.525$ and then $\langle \cos\delta' \rangle = -3.3 \cdot 10^{-4}$, what implicate $P_S = -0.91\,\mathrm{nC/cm^2}$.

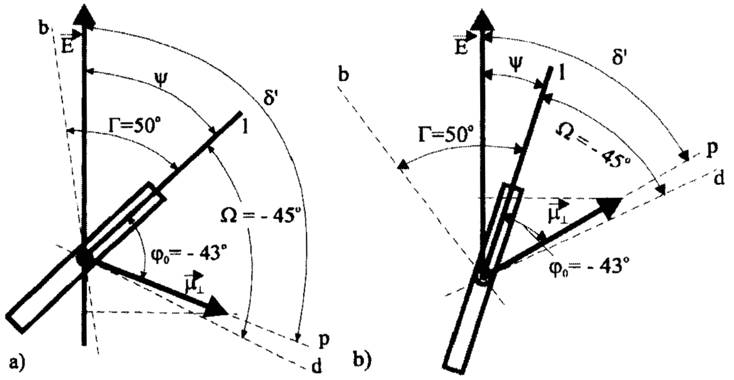


FIGURE 4. Geometrical relations between δ', ψ, φ_0, Γ and Ω for: a) $P_S < 0$, b) $P_S > 0$ (it is not in the scale).

2. In low temperature, e.g. for $T = 280\text{ K }(7°\text{C}) < T_{N-P}$ (for this temperature the values of potential's factors: $a_1 \sin\theta = 1.94 \cdot 10^{-23}$ J, $a_2 \sin^2\theta \cong 495.0 \cdot 10^{-23}$ J, $a_3 q \sin\theta = 3.91 \cdot 10^{-23}$ J) the quadrupolar coupling is dominating. In this case $\langle \sin\psi \rangle = 0.560$, $\langle \cos\psi \rangle = 0.530$ and then $\langle \cos\delta' \rangle = 5.5 \cdot 10^{-4}$, what implicate $P_S = 1.59\text{ nC/cm}^2$.

The geometrical relations between δ', ψ, φ_0, Γ and Ω for these two terminal temperatures T = 313 K (40°C) and T = 280 K (7°C) are presented in Fig. 4.

Acknowledgements

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