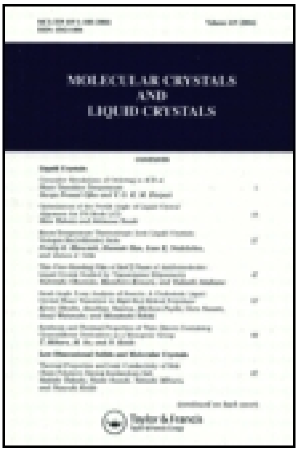

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Determination of the Hindered Rotation Degree of Chiral Molecules Around Their Long Molecular Axes in the Sc* Phase of 4-(2′-Methylbutyl)-4′-n-Octylbiphenyl-4-Carboxylate

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DETERMINATION OF THE HINDERED ROTATION DEGREE OF CHIRAL MOLECULES AROUND THEIR LONG MOLECULAR AXES IN THE S_C* PHASE OF 4-(2'-METHYLBUTYL)-4'-n-OCTYLBIPHENYL-4-CARBOXYLATE

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Abstract Chiral 4-(2''-methylbutyl)-phenyl-4'-octylbiphenyl-4-carboxylate (CE8) has been studied by dielectric, densytometric, refractic and X-ray measurements. On the basis of these measurements the effective value of the molecular dipole moment (μ), the angle between the vector of the molecular dipole moment and the long axis of molecule (γ) as well as the transverse (α_t) and longitudinal (α_l) molecular polarizabilities have been calculated[8]. In addition the sign and the magnitude of spontaneous polarization (P_s), the tilt angle (θ) and the helical pitch (λ) have been measured for the same liquid crystal CE8. Knowing the molecular parameters μ, γ, α_t, α_l and θ from the experiment and the molecular structure from computer investigation, the spontaneous polarization P_s has been calculated as the vector sum of the components of molecular dipole moments μ perpendicular to the tilt direction. To do it the rotational potential given by B.Zeks[2] has been used. According to this approximation the measured spontaneous polarization P_s is induced by hindered rotation of the molecules around their long axes and is expressed by molecular parameters μ, γ, α_t, α_l, tilt angle θ and the hindered rotation parameter η. The hindered rotation parameter for CE8 shows that dipolar ordering in this smectic C* phase is rather weak in the comparison with the strong orientational order of long molecular axes of the same phase.

INTRODUCTION

Introduction of the chirality into some or all molecules of the smectic C phase induces a ferroelectric S_C* phase with a spontaneous polarization $\mathbf{P}_s$. In this case the average long axis orientation, given by the molecular direction **n**, is tilted from the layer normal **z** through an average angle $\theta(T)$. The tilt direction of the molecules in the layer processes around the normal z. As one goes from one layer to another, result of a helicoidal structure with a pitch $\lambda(T)$ is obtained. From molecular point of view the spontaneous polarization $\mathbf{P}_s$ represents the vector sum of the components of the molecular dipole moments μ perpendicular to the tilt plane. Since the discovery of ferroelectricity in chiral smectic S_c^* phase by Meyer et al.[1], a variety of theoretical and experimental investigations has been performed in order to understand the origin, as well the magnitude and the sign of the spontaneous polarization.

The microscopic origin of the spontaneous polarization P_s arises from chirality - induced broken symmetry of the potential $U(\psi)$ for molecular rotation about the long axis. If the molecule forming ferroelectric S_C^* phase carries the effective permanent dipole moment μ_e and mean molecular polarizability $\bar{\alpha}$, the P_s can be expressed as[3]:

$$P_s = N\mu_e\langle\cos\delta\rangle + N\bar{\alpha}E_l \qquad (1)$$

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 $< \cos\delta >$ is carried out by standard statistical methods over the whole sample. Equation (1) shows that the spontaneous polarization is described by a kind and a structure of the molecules which build the S_C^* phase and appropriate to these molecules single particle potential $U(\psi)$[2-6]. 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 CE8.

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 of this object are rigidly attached to the local Ox'y'z' system of Cartesian coordinates as shown in Figure 1. The molecule has a polarizability α_l along the long axis n and polarizabilities α_t along both l and m axes located in the 0 point. The mean polarizability $\bar{\alpha}$ is:

$$\bar{\alpha} = \frac{\alpha_l + 2\alpha_t}{3} \qquad (2)$$

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

$$\mu' = \left[\mu'_x, \mu'_y, \mu'_z\right] = \left[\mu \sin\gamma \cos\varphi_0, \mu \sin\gamma \sin\varphi_0, \mu \cos\gamma\right] \qquad (3)$$

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

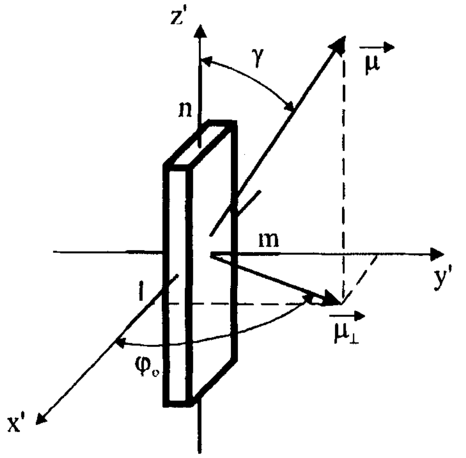

FIGURE 1 The structure of a brick-like molecule of the S_C* phase.

Let us choose the laboratory Oxyz system of coordinates with the origin 0 common for 0x'y'z' and 0xyz ones. Let the molecule rotates about the point 0. The position of the moving system (0x'y'z') with respect to the fixed one (0xyz) is described by three Euler's angles θ, φ and ψ defined in Figure 2.

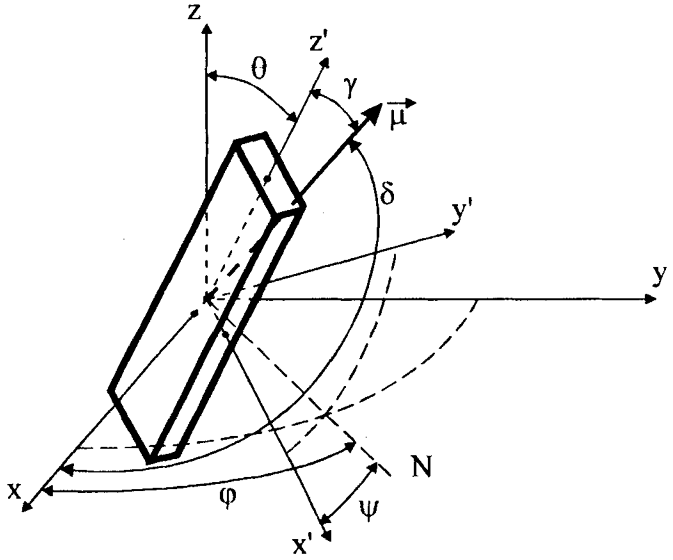

FIGURE 2 The Euler's angles, the line of intersection of the planes x0y and x'0'y' is the line of nodes and it is denoted by 0N.

Using the Euler's angles the molecular dipole moment μ in the laboratory 0xyz system is given by expression (4):

$$\begin{bmatrix}\mu_x\\ \mu_y\\ \mu_z\end{bmatrix}=\begin{bmatrix}\cos\varphi\cos\psi-\sin\varphi\cos\theta\sin\psi & -\cos\varphi\sin\psi-\sin\varphi\cos\theta\cos\psi & \sin\varphi\sin\theta\\ \sin\varphi\cos\psi+\cos\varphi\cos\theta\sin\psi & -\sin\varphi\sin\psi+\cos\varphi\cos\theta\cos\psi & -\cos\varphi\sin\theta\\ \sin\theta\sin\psi & \sin\theta\cos\psi & \cos\theta\end{bmatrix}\begin{bmatrix}\mu'_x\\ \mu'_y\\ \mu'_z\end{bmatrix} \tag{4}$$

The tilt plane is determined by the normal to the smectic layer z (0z) and molecular direction **n** (0z'). If the long axes of molecules n are assumed to be parallel to the y0z plane, then the spontaneous polarization P_s is induced perpendicularly to the tilt plane, i.e. direction of $\mathbf{P}_s$ coincides with 0x one. In this case, the line of ON nodes coincides with 0x axis and it means that in "our laboratory" 0xyz system $\varphi = 0$ and we obtain:

$$\mu_x = \mu\cos\delta \tag{5}$$

where $$\cos\delta = (\cos\psi\cos\varphi_0\sin\gamma - \sin\psi\sin\varphi_0\sin\gamma) \tag{6}$$

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

$$\langle\cos\delta\rangle = \sin\gamma(\cos\varphi_0\langle\cos\psi\rangle - \sin\varphi_0\langle\sin\psi\rangle) \tag{7}$$

where the angle ψ describes the orientation of the molecular axis l (0x' axis) with respect to the $\mathbf{P}_s$ direction (0x axis) as we see in Figure 3.

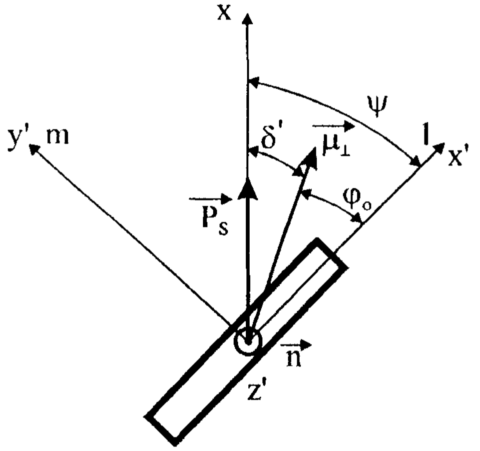

FIGURE 3 View along long molecular axis n. φ_0 is the angle between the transverse dipole moment $\mu_\perp$ and the molecular axis l. δ' is the angle between $\mu_\perp$ and $\mathbf{P}_s$.

The values of $<\cos\psi>$ and $<\sin\psi>$ can be calculated from the following equations:

$$\langle\cos\psi\rangle = \frac{\int_0^{2\pi}\exp\frac{-U(\psi)}{kT}\cos\psi d\psi}{\int_0^{2\pi}\exp\frac{-U(\psi)}{kT}d\psi} \qquad (8)$$

and

$$\langle\sin\psi\rangle = \frac{\int_0^{2\pi}\exp\frac{-U(\psi)}{kT}\sin\psi d\psi}{\int_0^{2\pi}\exp\frac{-U(\psi)}{kT}d\psi} \qquad (9)$$

where $-U(\psi)$ is the rotational potential of a molecule around its long axis given by Zeks et al.[2-6], k - Boltzmann constant.

Zeks has proposed a single particle potential in three terms form:

$$U(\psi') = U_1(\psi') + U_2(\psi') + U_3(\psi') \qquad (10)$$

where the angle ψ' describes the orientation of transverse dipole moment $\mu_\perp$with respect to $\mathbf{P_s}$ direction. In the case, the transverse component $\mu_\perp$ is perpendicular to l axis and $U(\psi')$ takes form[2] :

$$U(\psi') = -a_1\sin\theta\cos\psi' - a_2\sin^2\theta\cos 2\psi' - a_3 q\sin\theta\cos\psi' \qquad (11)$$

where $q = \frac{2\pi}{\lambda}$.

The first one tells us that for chiral molecule the tilt θ tends to induce the polar ordering of $\mu_\perp$ in the $\mathbf{P_s}$ direction. The second one has nonchiral character and leads to a bipolar, quadrupole ordering with the l axis perpendicular to the $\mathbf{P_s}$ vector. The third term results directly from the elastic forces associated with the unwound helix of the S_C* phase. It has its minimum when the molecular axis l is perpendicular to $\mathbf{P_s}$ direction.

The following form of the rotational potential is proposed when the $\mu_\perp$ forms the angle φ_o with the l axis:

$$U(\psi) = -a_1\sin\theta\cos(\psi - \varphi_o) - a_2\sin^2\theta\sin 2\psi - a_3 q\sin\theta\sin\psi \qquad (12)$$

where parameters a_1, a_2 and a_3 are different for various kind of a ferroelectric liquid crystal .

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

$$\exp\frac{-U(\psi)}{kT} = \sum_{n=1}^{\infty}\frac{1}{n!}\left[\frac{-U(\psi)}{kT}\right]^{n} \tag{13}$$

Considering only the first term of Eq.13 and integrating Eq.8 and Eq.9 a theoretical expression for < cosδ > can be obtained as:

$$\langle\cos\delta\rangle = \sin\gamma\,\frac{\sin\theta}{2kT}(a_1 + a_3 q\sin\varphi_o) \tag{14}$$

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

$$\mu_e = \mu \text{ and } \quad E_l = \frac{P_s}{3\varepsilon_o} \tag{15}$$

where ε_o is electric permittivity of free space and then the required theoretical relation for the spontaneous polarization P_{sL} is :

$$P_{sL} = \frac{N\mu\sin\gamma\,\frac{\sin\theta}{2kT}(a_1 + a_3 q\sin\varphi_o)}{1-\frac{N}{3\varepsilon_o}\bar{\alpha}} \tag{16}$$

If we cut a spherical molecular Onsager cavity (with a radius characterized by r) around rotating molecule surrounded by a medium, described by the mean electric permittivity $\bar{\varepsilon}$, we have:

$$\mu_e = F\mu \text{ and } E_l = h\frac{\mu\langle\cos\delta\rangle}{\varepsilon_0 4\pi r^2} \tag{17}$$

where h and F Onsager's factors can be written:

$$h = \frac{3\bar{\varepsilon}}{2\bar{\varepsilon}+1} \tag{18}$$

$$F = \left[1 - \underline{\alpha}\,\frac{2\bar{\varepsilon}-2}{(2\bar{\varepsilon}+1)\varepsilon_o 4\pi r^2}\right]^{-1} \tag{19}$$

For the Onsager local field approximation we obtain:

$$P_{sO} = N\mu\sin\gamma\,\frac{\sin\theta}{2kT}(a_1 + a_3 q\sin\varphi_0)\left(F + \frac{h\bar{\alpha}}{\varepsilon_0 4\pi r^2}\right) \tag{20}$$

Generally from both (16) and (20) formulas it results:

- -the greater dipole moment μ for a given molecule $\Rightarrow P_s$ will be greater ,
- -the greater transverse dipole moment $\mu_\perp = \mu \sin\gamma \Rightarrow P_s$ will be greater,
- -the sign of P_s depends on the sign of A factor:

$$A = (a_1 + a_3 q \sin\varphi_0)\sin\gamma \qquad (21)$$

Factor A describes a mutual relation between the steric effects (a_1), elasticity (a_3) molecule structure (φ_0, γ) and medium structure (q).

As we can see the Equation (20) demonstrates a linear form with respect to concentration N of chiral molecules, as the Equation (16) seems to have a nonlinear character.

EXPERIMENTAL, RESULTS AND DISCUSSION

In order to test and develop this theory the 4-(2'-methylbutyl)-4'-n-octylbiphenyl-4-carboxylate (CE8) with the phase sequence:

$$71S_C^*81S_A137.2N^*138.7BP140Iso$$

has been studied by dielectric, dipolometric, densytometric, refractometric and X-ray measurements[7,8]. In [7] on the basis of the above measurements we have calculated for CE8 the following molecular parameters:

$\mu = 7.1 * 10^{-30}$ Cm
$\gamma = 64°$
$\varphi_0 = 23°$
$\alpha_l = 8.0 * 10^{-39} C^2m^2J^{-1}$
$\alpha_t = 5.9 * 10^{-39} C^2m^2J^{-1}$
$\bar{\alpha} = 6.6 * 10^{-39} C^2m^2J^{-1}$

On the other hand the temperature dependence of the spontaneous polarization $P_s(T)$, the helical pitch $\lambda(T)$ and the tilt angle $\theta(T)$ in the Sc* phase for the same liquid crystal have been measured · The results of our measurements are presented in figures 4,5 and 6 respectively.

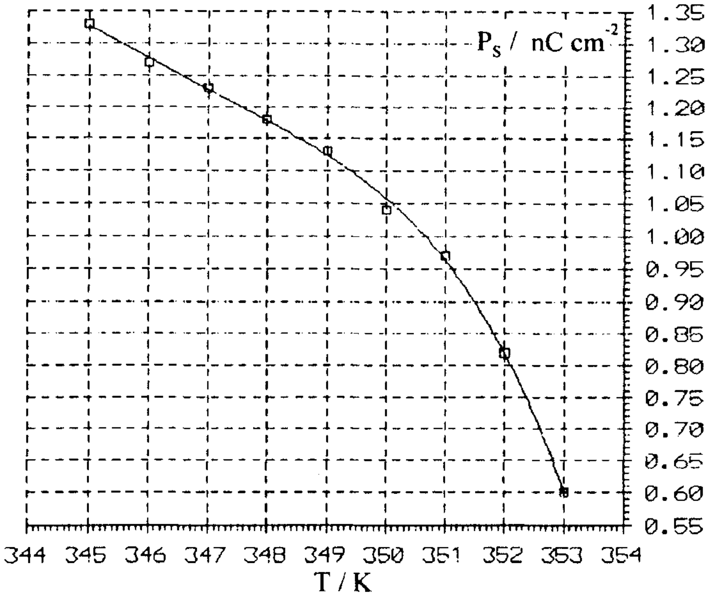

FIGURE 4 Temperature dependence of the spontaneous polarization $P_s(T)$ for CE8.

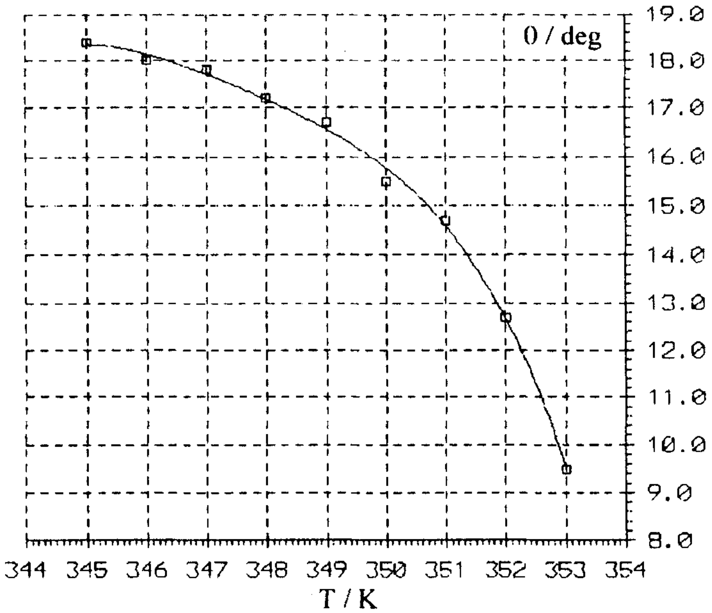

FIGURE 5 Temperature dependence of the tilt angle θ for CE8.

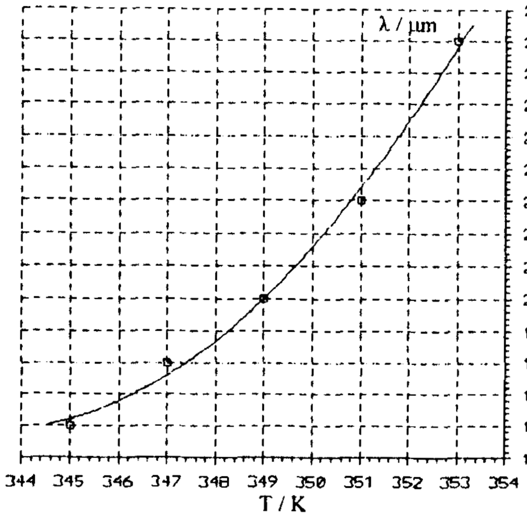

FIGURE 6 Temperature dependence of the pitch λ for CE8.

Knowning the temperature dependence of the spontaneous polarization $P_s(T)$, thermal dielectric and densytometric characteristics as well as μ, γ and $\bar{\alpha}$ we can calculate:

$$\langle\cos\delta'\rangle_L = \frac{P_s(T)\left(1 - \frac{N(T)}{3\varepsilon_0}\bar{\alpha}\right)}{N(T)\mu\sin\gamma} \tag{22}$$

and

$$\langle\cos\delta'\rangle_O = \frac{P_s(T)}{N(T)\mu\sin\gamma\left(F + \frac{h\bar{\alpha}}{\varepsilon_0 4\pi r^2}\right)} \tag{23}$$

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

$$\langle\cos\delta'\rangle = \frac{\langle\cos\delta\rangle}{\sin\gamma} = \frac{\sin\theta(T)}{2kT}\left(a_1 + a_3\sin\varphi_0\frac{2\pi}{\lambda(T)}\right) \tag{24}$$

On the basis of (24), (23), (22), the following functions $F_L(T)$ and $F_O(T)$ can be defined:

$$F_L(T) = \frac{\langle\cos\delta'\rangle_L 2kT}{\sin\theta(T)} = a_1 + a_3\sin\varphi_0\frac{2\pi}{\lambda(T)} \tag{25}$$

and

$$F_O(T) = \frac{\langle\cos\delta'\rangle_O 2kT}{\sin\theta(T)} = a_1 + a_3\sin\varphi_0\frac{2\pi}{\lambda(T)} \tag{26}$$

The results of calculations are given in Table 1

TABLE 1 The P_S, θ and λ measurements and results of some calculations.

					ONSAGER				LORENTZ	
T	P_S	θ	λ	N 10^{-27}	h	F	$\langle\cos\delta'\rangle_O$	F_O 10^{23}	$\langle\cos\delta'\rangle_L$	F_L 10^{23}
K	nC/cm^2	deg	µm	m^{-3}				J/K		J/K
345	1.33	18.4	1.6	1.339	1.311	1.874	0.00055	1.642	0.00104	3.133
346	1.27	18.0	1.7	1.338	1.311	1.873	0.00051	1.610	0.00099	3.065
347	1.23	17.8	1.8	1.337	1.311	1.872	0.00050	1.577	0.00096	3.000
348	1.18	17.2	1.9	1.336	1.311	1.871	0.00048	1.567	0.00092	2.983
349	1.13	16.7	2.0	1.335	1.311	1.869	0.00047	1.562	0.00089	2.981
350	1.04	15.5	2.1	1.334	1.311	1.868	0.00043	1.548	0.00081	2.942
351	0.97	14.7	2.3	1.333	1.311	1.867	0.00040	1.532	0.00076	2.910
352	0.82	12.7	2.5	1.332	1.311	1.866	0.00034	1.488	0.00064	2.830
353	0.60	9.5	2.8	1.331	1.311	1.865	0.00025	1.476	0.00047	2.775

Supposing that for the S_C* phase the factors a_1 and a_3 do not depend on temperature and then plotting the left hand sides of the Equations (26) and (27) versus $\lambda(T)^{-1}$ one may expect to obtain a straight line. In Fig. 7 the relations $F_L(T) = f(\lambda(T)^{-1})$ and $F_O(T) = f(\lambda(T)^{-1})$ are plotted. This figure shows that experimental data fit the straight line very well but a_1 and a_3 determined with Onsager local field approximation differ from those determined with Lorentz one (see Table 2)

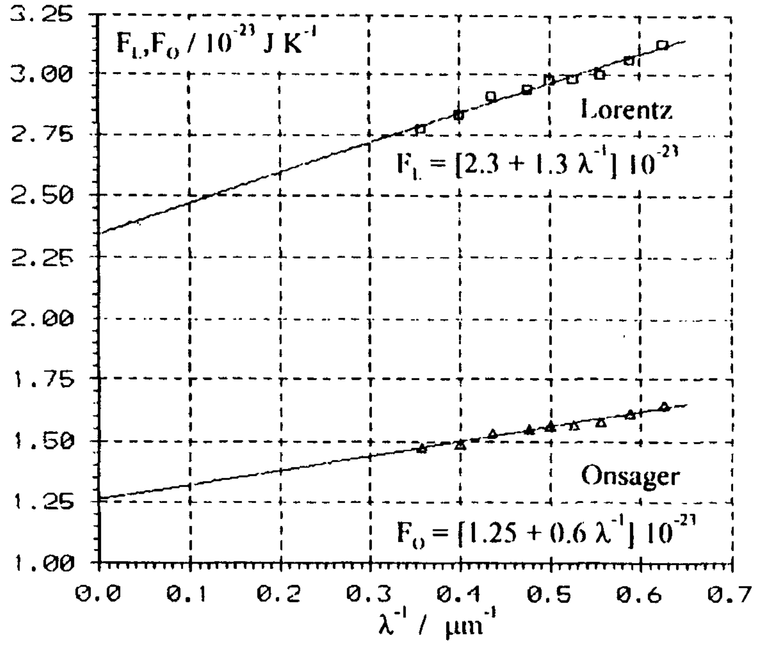

FIGURE 7 The relations $F_L(T) = f(\lambda(T)^{-1})$ and $F_O(T) = f(\lambda(T)^{-1})$.

The molecular rotation is stopped for the nonexcited state. The molecule energy takes minimum value for the ψ_M angle in this state. If we know a_1,a_2 and a_3 factors in eq. 12, we would find the ψ_M angle from:

$$\frac{dU(\psi)}{d\psi} = 0 \qquad (27)$$

Since we know only a_1 and a_3 factors, but the quadrupolar term a_2 which can be important[9] is still unknown we may only estimate the ψ_M angle. If we neglect the quadrupolar term a_2, the ψ_M angle can be easly calculated from:

$$\psi_M = \arctan\left[\frac{a_3 q + a_1 \sin\varphi_o}{a_1 \cos\varphi_o}\right] \tag{28}$$

The above results of calculations of $\delta_M = \psi_M - \varphi_o$ we can see in Table 2. If the term a_2 is taken into considerations the ψ_M values will be higher but δ_M should not be higher than 57° when a_1 and a_3 are neglected.

For the range of temperatures T, when the $S_c{}^*$ phase exists, the following relation:

$$U(\psi) < \frac{kT}{2} \tag{29}$$

is satisfied for any angle ψ due to very weak rotational potential $U(\psi)$. It means that in the $S_c{}^*$ phase molecular rotations are hindered a bit - almost free. The rotational orientation of the given molecule in this state is described by $< \cos\delta' >$.

In the first approximation we can image that the N hindered rotational states characterized by $<\cos\delta'>$ consist of M molecules with stopped rotation with univocally defined by $\cos\delta_M$ orientation and (N-M) particles with free rotation ($<\cos\delta'> = 0$). Taking into account the above we have:

$$N\langle\cos\delta'\rangle = M\cos\delta_M \tag{30}$$

The hindered rotational parameter η is the following:

$$\eta = \frac{M}{N} = \frac{\langle\cos\delta'\rangle}{\cos\delta_M} \tag{31}$$

The results of calculations are gathered in Table 2.

TABLE 2 The results of δ_M and η calculations.

	ONSAGER				LORENTZ			
T	$a_1\ 10^{23}$	$a_3\ q10^{23}$	ψ_M	$\eta_O\ 10^4$	$a_1\ 10^{23}$	$a_3 q10^{23}$	ψ_M	$\eta_L\ 10^4$
K	J/K	Jμm/K	deg		J/K	Jμm/K	deg	
345	1.25	1.06	52.11	6.3	2.30	2.30	55.36	12.3
346	1.25	0.99	50.92	5.8	2.30	2.17	54.15	11.6
347	1.25	0.94	49.24	5.6	2.30	2.09	53.45	11.1
348	1.25	0.89	48.78	5.3	2.30	1.93	51.96	10.5
349	1.25	0.85	47.82	5.2	2.30	1.84	50.97	10.1
350	1.25	0.81	46.91	4.7	2.30	1.75	50.02	9.1
351	1.25	0.74	45.22	4.3	2.30	1.59	48.26	8.4
352	1.25	0.24	43.78	3.6	2.30	1.47	46.73	6.9
353	1.25	0.21	41.86	2.6	2.30	1.31	44.67	5.1

As we see in Table 2, the molecular rotations around the long axes in the S_C* phase are almost free. To illustrate this process we may say that, in general, for this examined ferroelectric liquid crystal, in each moment, only one molecule of any set of 1000 molecules stops, while the remaining ones rotate freely about their long axes, exactly as it is the case of S_A, N and Iso phases.

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REFERENCES

1. R.B.Meyer, L.Liebert, L.Strzelecki, P.Keller, J.Phys.(Paris) Lett., 36, L69 (1975).
2. B.Zeks, T.Carlson, C.Filipic, B.Urban, Ferroelectrics, 84, 3 (1988).
3. H.Stegemeyer, R.Meister, U.Hoffman, W.Kuczyński, Liq.Cryst., 10, 295 (1991).
4. A.Buka, A.Siemensmeyer, H.Stegemeyer, Liq.Cryst., 6, 701 (1989).
5. H.Stegemeyer, R.Meister, H.J.Altenbach, Liq.Cryst., 14, 1007 1993).
6. D.Dunmur, M.Grayson,Roy, Liq.Cryst., 16, (95 (1994).
7. Z.Raszewski, J.Rutkowska, J.Kędzierski, J.Zieliński, P.Perkowski, W.Piecek, J.Żmija, R.Dąbrowski, will be published at Ferroelectrics.
8. W.Kuczyński, H.Stegemeyer, Liq.Cryst.,5, 553 (1989).
9. T.Carlsson, B.Zeks, A.Levstik, C.Filipic, I.Levstik, R.Blinc ,Phys.Rev.A, 36, 1484 (1987).