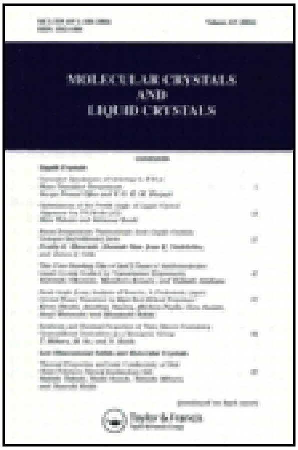

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On the Molecular Polarizability of Nematic Liquid Crystals

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On the Molecular Polarizability of Nematic Liquid Crystals†

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The refractive indices and the densities of CB-7, PCH-7 and CCH-7 are measured. An equation that relates the optical frequency permittivity tensor to the molecular polarizability tensor for nematic liquid crystals is obtained. The derived equation gives consistent results not only for the nematic phase, but also for both the solid and isotropic liquid states.

INTRODUCTION

For nematic liquid crystals, it is complicated to express the refractive indices in terms of the molecular polarizability tensor. For the electric response, it is necessary to take local field corrections into account. There have been many attempts[1-8] to evaluate local field corrections, but, as we know, there is no rigorous justification for any of them.

Because the order of the molecules in the nematic phase is not complete, the physical properties will in general depend on the average orientation. Let us consider the relation between the macroscopic coordinate system (x, y, z) and the molecular coordinate system (ξ, η, ζ) which is described by the Euler angles (α, β, γ). In a uniaxial nematic liquid the angles α and γ are isotropically distributed, so averages over them can be carried out explicitly. Then the orientational order parameter S is described by the angle between the director (along the z-axis) and the long molecular axis (along ζ-axis) as[9]

$$S = 1 - \tfrac{3}{2}\langle \sin^2 \beta \rangle.$$

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In the present work we extend the model of Kuznetsov *et al.*[7] to the case of a spheroidal cavity in the optical frequency range, where the permanent dipoles of the molecules are out of role. This leads to relations for the refractive indices as a function of the molecular polarizabilities and the order parameter that may be numerically important.

THE MODEL

Here we consider a molecule in the centre of a prolate spheroidal cavity with semi-axes equal to a and $b = c$; $a > b$. The molecule is characterized by a prolate spheroid with a polarizability tensor $\boldsymbol{\alpha}$. It is assumed that $\boldsymbol{\alpha}$ is an axially symmetric tensor relative to the long axis of the molecule with principal components α_l and α_t; α_l is along the long molecular axis. The rest of the liquid crystal molecules surrounding the cavity are approximated by a continuous medium with a permittivity tensor $\boldsymbol{\varepsilon}$. The tensor $\boldsymbol{\varepsilon}$ is assumed to be axially symmetric relative to the average director. The components of $\boldsymbol{\varepsilon}$ in directions parallel and perpendicular to the average director are $\varepsilon_{\|}$ and $\varepsilon_{\perp}$.

The local field $\hat{E}_L$, which is acting on the isolated molecule, is written as the sum of the cavity field $\hat{E}_C$ and the reaction field $\hat{E}_R$ of the induced dipole:[10]

$$\hat{E}_L = \hat{E}_C + \hat{E}_R. \tag{1}$$

Moving along the lines followed in Ref. 11, we get for the cavity field:

$$\hat{E}_C = \mathbf{g} \cdot \hat{E}, \tag{2}$$

where $\hat{E}$ is the external field and $\mathbf{g}$ is a diagonal tensor in the (x, y, z) system whose principal axes coincide with the principal axes of $\boldsymbol{\varepsilon}$. To calculate the principal components of $\mathbf{g}$ we reduce the problem of determining the field within such a spheroid located in a medium with dielectric constant $\boldsymbol{\varepsilon}$ to the problem of determining the field in a uniformly polarized spheroid, whose semi-axes are $a/(\varepsilon_{\|})^{1/2}$ and $b/(\varepsilon_{\perp})^{1/2}$, with dielectric constants $1/\varepsilon_{\|}$ and $1/\varepsilon_{\perp}$ located in a vacuum. Therefore we have:

$$g_{\|} = \frac{\varepsilon_{\|}}{\varepsilon_{\|} - \Omega_{\|}(\varepsilon_{\|} - 1)}; \qquad g_{\perp} = \frac{\varepsilon_{\perp}}{\varepsilon_{\perp} - \Omega_{\perp}(\varepsilon_{\perp} - 1)}. \tag{3}$$

$\Omega_{\|}$ and $\Omega_{\perp}$ are the depolarizing factors of a prolate spheroid with eccentricity $e = [1 - (b^2\varepsilon_{\|}/a^2\varepsilon_{\perp})]^{1/2}$. Now we rotate $\mathbf{g}$ to the molecular coordinate system using the known formalism for rotation.[13] Thus we obtain

$$g_{\xi\xi} = g_{\perp} + (g_{\|} - g_{\perp})\cos^2\gamma\sin^2\beta; \tag{4.a}$$

$$g_{\eta\eta} = g_{\perp} + (g_{\|} - g_{\perp})\sin^2\gamma\sin^2\beta; \tag{4.b}$$

$$g_{\zeta\zeta} = g_{\|} - (g_{\|} - g_{\perp})\sin^2\beta. \tag{4.c}$$

We then define the components g_l and g_t in directions parallel and perpendicular to the long molecular axis as averages of g_{ii} for all molecules.

$$g_l = \langle g_{\zeta\zeta} \rangle = g_{\|} - (2/3)(1 - S)\Delta g \tag{5.a}$$

and

$$g_t = \tfrac{1}{2}(\langle g_{\xi\xi} \rangle + \langle g_{\eta\eta} \rangle) = g_{\perp} + (1/3)(1 - S)\Delta g, \tag{5.b}$$

where $\Delta g = g_{\|} - g_{\perp}$.

Following the treatment of the reaction field problem given in Ref. 7, we obtain:

$$\hat{E}_R = \mathbf{r} \cdot \boldsymbol{\alpha} \cdot \hat{E}_L, \tag{6}$$

where the tensor $\mathbf{r}$ is diagonal and its principal axes coincide with those of $\boldsymbol{\varepsilon}$. Assuming that $(4/3)\pi Nab^2 = 1$, the principal values of $\mathbf{r}$ are given by:

$$r_{\|} = \frac{4\pi N\Omega_{\|}(1 - \Omega_{\|})(\varepsilon_{\|} - 1)}{\varepsilon_{\|} - \Omega_{\|}(\varepsilon_{\|} - 1)}; \tag{7.a}$$

$$r_{\perp} = \frac{4\pi N\Omega_{\perp}(1 - \Omega_{\perp})(\varepsilon_{\perp} - 1)}{\varepsilon_{\perp} - \Omega_{\perp}(\varepsilon_{\perp} - 1)}. \tag{7.b}$$

Then, it follows that the components of $\mathbf{r}$ in directions relative to the long molecular axis are:

$$r_l = r_{\|} - (2/3)(1 - S)\Delta r \tag{8.a}$$

and

$$r_t = r_{\perp} + (1/3)(1 - S)\Delta r, \tag{8.b}$$

where $\Delta r = r_{\|} - r_{\perp}$.

Combining Eqs. (1), (2) and (6) yields:

$$\hat{E}_L = \mathbf{g} \cdot \hat{E} + \mathbf{r} \cdot \boldsymbol{\alpha} \cdot \hat{E}_L. \tag{9}$$

Hence

$$\hat{E}_L = \mathbf{g} \cdot \mathbf{f} \cdot \hat{E} \tag{10.a}$$

with

$$\mathbf{f} = (\mathbf{I} - \mathbf{r} \cdot \boldsymbol{\alpha})^{-1}. \tag{10.b}$$

Substituting Eq. (10.a) in the known equation[14] for the polarization,

$$\frac{\boldsymbol{\varepsilon} - \mathbf{I}}{4\pi} \hat{E} = N\langle \boldsymbol{\alpha} \cdot \hat{E}_L \rangle,$$

it follows that

$$\frac{\boldsymbol{\varepsilon} - \mathbf{I}}{4\pi} = N\langle \boldsymbol{\alpha}^* \rangle; \tag{11.a}$$

$$\boldsymbol{\alpha}^* = \mathbf{g} \cdot \mathbf{f} \cdot \boldsymbol{\alpha}. \tag{11.b}$$

The angular brackets in Eq. (11.a) denote an average over the orientations of all molecules in relation to the laboratory system. Eq. (11.a) yields

$$\varepsilon_{\parallel} = 1 + 4\pi N\langle \alpha_{\parallel}^* \rangle \tag{12.a}$$

and

$$\varepsilon_{\perp} = 1 + 4\pi N\langle \alpha_{\perp}^* \rangle. \tag{12.b}$$

The averages at the right-hand side of Eqs. (12) give:

$$\langle \alpha_{\parallel}^* \rangle = \bar{\alpha}^* + (2/3)S\Delta\alpha^*; \tag{13.a}$$

$$\langle \alpha_{\perp}^* \rangle = \bar{\alpha}^* - (1/3)S\Delta\alpha^*, \tag{13.b}$$

where

$$\bar{\alpha}^* = \frac{(g_l f_l \alpha_l + 2g_t f_t \alpha_t)}{3} \tag{13.c}$$

and

$$\Delta\alpha^* = g_l f_l \alpha_l - g_t f_t \alpha_t. \tag{13.d}$$

Consequently the refractive indices ($\varepsilon \equiv n^2$) of the nematic phase can be expressed in molecular properties and the order parameter as:

$$n_{\parallel}^2 = 1 + \tfrac{4}{3}\pi N\left[\frac{g_l\alpha_l(1 + 2S)}{1 - r_l\alpha_l} + \frac{g_t\alpha_t(2 - 2S)}{1 - r_t\alpha_t}\right] \tag{14.a}$$

and

$$n_{\perp}^2 = 1 + \tfrac{4}{3}\pi N\left[\frac{g_l\alpha_l(1 - 2S)}{1 - r_l\alpha_l} + \frac{g_t\alpha_t(2 + 2S)}{1 - r_t\alpha_t}\right]. \tag{14.b}$$

Eqs. (14) show that, if the density and the order parameter are known, it is possible to infer the polarizability α_l and α_t from the experimental values of $n_{\parallel}$ and $n_{\perp}$. For the calculations, we have to estimate a value for the ratio b/a. This ratio will be assumed to be equal to the corresponding ratio for the molecule. In the following treatment, we will adopt the procedure of de Jeu and Bordewijk[8] to estimate the ratio b/a.

For the isotropic liquid $n_{\parallel} = n_{\perp} = n_i$ and $S = 0$, therefore we have

$$n_i^2 = 1 + \tfrac{4}{3}\pi N\left[\frac{\bar{g}\alpha_l}{1 - \bar{r}\alpha_l} + \frac{2\bar{g}\alpha_t}{1 - \bar{r}\alpha_t}\right], \tag{15}$$

where

$$\bar{g} = \frac{(g_{\parallel} + 2g_{\perp})}{3} \qquad (16.\text{a})$$

and

$$\bar{r} = \frac{(r_{\parallel} + 2r_{\perp})}{3}. \qquad (16.\text{b})$$

EXPERIMENTAL RESULTS

The refractive indices $n_{\parallel}$, $n_{\perp}$ and n_i for CB–7, PCH–7 and CCH–7, in the nematic and isotropic phases, were measured as functions of temperature with a Leitz-Jelley microrefractometer. Further experimental details have been reported elsewhere.[15]

The densities ρ were determined as functions of temperature with a digital density meter DMA60 + DMA602 HT P (Heraeus/Paar). Table I presents the experimental data relating to the refractive indices and densities for the compounds studied. Our data for CB–7 are in good agreement with literature data.[16,17]

ORDER PARAMETERS

As known, the problem of the local field in the optical case is not yet fully understood. On the other hand, the local field correction for the magnetic response is negligible. Therefore the definition of the order parameter through the diamagnetic susceptibility anisotropy is preferable.

Here we did not make magnetic measurements and we will use the reported mass susceptibilities for CB–7[18] and for PCH–7.[19] For CCH–7 we will use the volume susceptibility data of Schad *et al.*[20] and our density data.

In order to calculate the order parameter from magnetic susceptibility data we have to estimate values for the molecular diamagnetic anisotropy $\Delta\chi^M (= \chi_l^M - \chi_t^M)$. These were evaluated by an additive scheme. In this scheme, the molar susceptibility element was viewed as the sum of the corresponding susceptibility terms of the different groups of atoms or bonds. We proposed *a priori* to base the conformations of the molecules on the standard values for the bond lengths and angles of the various constituent groups. As shown in Figure 1, we consider the molecular axes to be along the lines joining the outer *para*-carbon atoms of the benzene-benzene rings, and benzene-cyclohexane rings, assuming the molecule to be rigid. The sum of the susceptibility contributions of all the various bonds and groups parallel

TABLE I

Densities and refractive indices for the compounds studied at Na_D-line

CB–7				PCH–7				CCH–7			
T[K]	ρ[g cm^{-3}]	$n_\perp$	$n_\parallel$	T[K]	ρ[g cm^{-3}]	$n_\perp$	$n_\parallel$	T[K]	ρ[g cm^{-3}]	$n_\perp$	$n_\parallel$
302.0	1.0012	1.521	1.702	303.0	0.9520	1.484	1.593	343.0	0.8932	1.456	1.502
303.5	0.9998	1.521	1.698	306.0	0.9497	1.484	1.589	345.6	0.8908	1.455	1.498
305.0	0.9985	1.521	1.695	309.0	0.9472	1.483	1.586	347.6	0.8889	1.455	1.494
306.5	0.9970	1.521	1.692	312.0	0.9445	1.483	1.581	349.7	0.8870	1.454	1.491
308.0	0.9956	1.522	1.688	315.0	0.9419	1.482	1.578	351.7	0.8851	1.454	1.486
309.0	0.9946	1.523	1.683	318.0	0.9391	1.482	1.575	353.6	0.8831	1.454	1.484
310.0	0.9935	1.523	1.680	321.0	0.9362	1.482	1.569	354.5	0.8815	1.454	1.481
312.0	0.9912	1.525	1.672	324.0	0.9333	1.483	1.563	355.5	0.8803	1.454	1.477
314.0	0.9886	1.527	1.660	326.0	0.9312	1.483	1.559	356.5 NI	0.8760	1.462	1.462
314.5	0.9878	1.531	1.655	328.0	0.9289	1.484	1.551	359.0	0.8741	1.461	1.461
315.4 NI	0.9840	1.573	1.573	329.0	0.9275	1.485	1.547	362.0	0.8718	1.460	1.460
318.0	0.9815	1.571	1.571	330.0 NI	0.9230	1.506	1.506	367.0	0.8681	1.457	1.457
321.0	0.9787	1.570	1.570	332.0	0.9212	1.505	1.505				
326.0	0.9746	1.567	1.567	335.0	0.9188	1.503	1.503				
				340.0	0.9150	1.501	1.501				

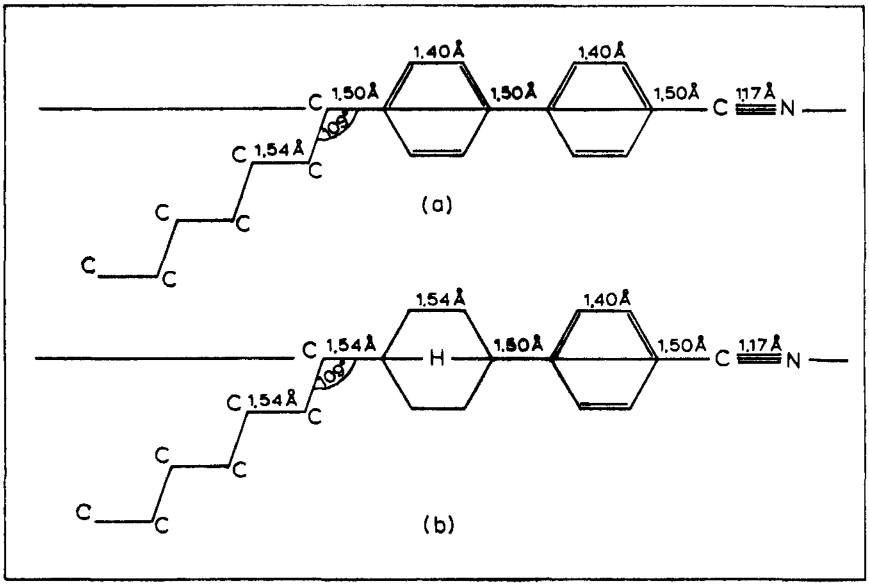

FIGURE 1 Molecular models: (a) CB–7 and (b) PCH–7.

and normal to the molecular axis gives χ_l^M and χ_t^M, respectively.

The magnetic anisotropies of the various groups and of the compounds studied are summarized in Table II. In our calculations, the contribution of the —C_6H_4 group is considered to be as that of the benzene ring; for the benzene molecule[21] $\Delta\chi^M = 29.85 \times 10^{-6}$ cm^3 mol^{-1}. In addition, we have assumed that the contribution of the alkyl group and that of the —C_6H_{10} group is effectively isotropic. Moreover, we have chosen for the C≡N and C—C bonds the data of Flygare[22] and of Davies,[23] respectively.

Figure 2 shows the calculated order parameters for the compounds studied as functions of a reduced temperature τ; $\tau = (T - T_{NI})/T_{NI}$. We may conclude that the replacement of a phenyl ring by a cyclohexyl ring decreases the order parameter markedly. The coincidence of the S-curves for PCH–7 and CCH–7 may be attributed to our assumption that the contribution of the —C_6H_{10} group to the magnetic anisotropy is effectively isotropic.

DISCUSSION

From the refractive indices in the solid state, α_l and α_t can be determined using Eqs. (14) with $S = 1$. The density[24] and the refractive indices,[25] for Na_D-line, in the solid state for *p*-azoxyanisole (PAA) have been reported. Provided the PAA crystal can be treated as an approximately uniaxial

TABLE II

Calculated susceptibility anisotropies for the groups and compounds studies

Group or Compound	$\Delta\chi^{M}[10^{-6}\ \mathrm{cm}^3\ \mathrm{mol}^{-1}]$
$—C_6H_4$	+29.85
$—C_6H_{10}$	0 (assumed)
—R	−4.0
—C≡N	−8.8
CB-7	+46.9
PCH-7	+17.1
CCH-7	−16.8

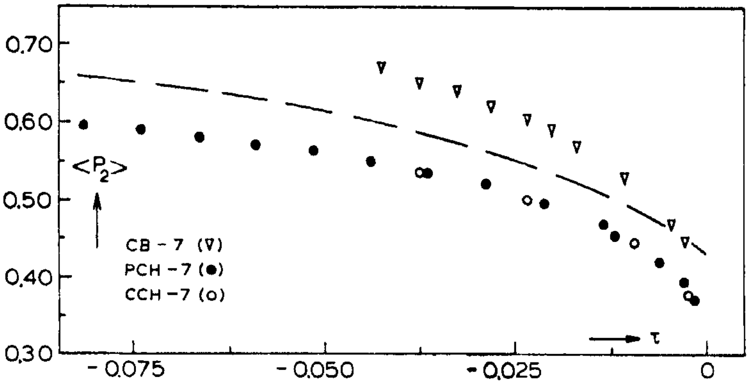

FIGURE 2 Order parameters *vs.* a reduced temperature (see text). The broken line is from the Maier–Saupe theory.

system, the values of α_l, α_t and $\Delta\alpha\,(=\alpha_l-\alpha_t)$ are calculated. These values are presented in Table III, (a) with the b/a value[8] obtained from the crystallographic data and (b) with the b/a value[8] obtained from the nematic phase data. The values in row (c) are obtained from the density,[26] the refractive indices[27] (for $\mathrm{Na_D}$ line), the order parameters[28] (from the NMR measurements), and the value b/a for the nematic phase of PAA together with Eqs. (14).

Comparing the values in the rows (a), (b) and (c) of Table III, taking account of the uncertainties in the various quantities, we conclude that Eqs. (14) give consistent results for both the nematic phase and the solid state.

Using the values of α_l and α_t for methyl chloride[29] (CH_3Cl), which are known from measurements of the Kerr constants in the gaseous state, with $b/a = 0.5$, one obtains from Eq. (15): $n_D = 1.339$ at 293 K. The experimental result is $n_D = 1.3389$.[30] It follows that Eq. (15) also gives consistent results for the isotropic liquid state.

TABLE III

Polarizabilities of PAA for Na_D-line (see text)

	$\alpha_l[\text{Å}^3]$	$\alpha_t[\text{Å}^3]$	$\Delta\alpha[\text{Å}^3]$
(a)	54	23	31
(b)	58	23	35
(c)	54	24	30

TABLE IV

Optical parameters for the compounds studied at Na_D-line

Compound	CB-7	PCH-7	CCH-7
$a/\text{Å}$	17.39	17.53	17.67
$b/\text{Å}$	7.16	7.44	7.75
$^a\alpha_l/\text{Å}^3$	54(59)	48(53)	43(47)
$^a\alpha_t/\text{Å}^3$	30(29)	31(30)	33(32)
$^a\Delta\alpha/\text{Å}^3$	24(30)	17(23)	10(15)
$n_{\text{calc}}(T_{\text{NI}})$	1.609	1.519	1.468
$n_{\text{exp}}(T_{\text{NI}})$	1.573	1.506	1.462

[a] Values in brackets are calculated from the model of de Jeu and Bordewijk.[8]

Using the order parameters calculated from the magnetic data, together with the refractive index data, the density data and Eqs. (14), one can get α_l, α_t and then $\Delta\alpha$. These values for the compounds studied are reported in Table IV.

It is possible to calculate the refractive index at T_{NI}, $n_{\text{calc}}(T_{\text{NI}})$, if we substitute the values of α_l and α_t in Eq. (15). These values for the compounds studied are also given in Table IV. Taking account of the uncertainties in S and the ratio b/a, we conclude that the agreement with the experimental results, $n_{\text{exp}}(T_{\text{NI}})$, is satisfactory.

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