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Complex Dielectric Permittivity of Di-propyloxyazoxybenzene (3.OAOB) and Racemic Methylbutyl-phenyl-hexyloxybenzoate (CE6) on the Basis of the Nordio-Rigatti-Segre Theory

W. Otowski [a b], W. Demol [a c] & W. Van Dael [a]

[a] Department of Physics, Catholic University of Leuven, Celestijnenlaan 200 D, B-3001, Leuven, Belgium

[b] "Laboratorium voor Akoestiek en Warmtegeleiding." Institute of Physics, Technical University of Cracow, Podchorażych 1, 30-929, Kraków, Poland

[c] Laboratorium voor Moleculefysica

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Complex Dielectric Permittivity of Di-propyloxyazoxybenzene (3.OAOB) and Racemic Methylbutyl-phenyl-hexyloxybenzoate (CE6) on the Basis of the Nordio-Rigatti-Segre Theory

W. OTOWSKI,† W. DEMOL‡ and W. VAN DAEL§

Department of Physics, Catholic University of Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium

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Results of dielectric relaxation studies of two thermotropic liquid crystal substances, 3.OAOB and racemic CE6, are discussed on the basis of the Nordio-Rigatti-Segre theory.

Due to the anisotropy of the molecular structure, different contributions of the longitudinal and transversal components of the permanent dipole moment to the dielectric spectra can be observed.

Theoretical values for the dielectric increment of the four basic relaxation modes are calculated in two different ways and compared with the experimental results.

Keywords: dielectric properties, liquid crystals, dipole moments

INTRODUCTION

A variety of experimental methods has been used to study the molecular dynamics of liquid crystals. The method of dielectric relaxation spectroscopy is of interest due to its wide frequency range and its ability to follow the reorientational motions of dipolar groups or whole molecules. Due to anisotropic properties of both the molecular and medium structures, several reorientational processes can be observed in a nematic liquid crystal.

The understanding of any relaxation process requires the knowledge of the correlation function of the time-dependent variables associated with the process.

In the Nordio-Rigatti-Segre (NRS)[1] theory, the effect of molecular ordering on

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†Temporarily at the "Laboratorium voor Akoestiek en Warmtegeleiding." Permanent address: Institute of Physics, Technical University of Cracow, Podchorążych 1, 30-929 Kraków, Poland.

‡Laboratorium voor Moleculefysica.

§Author for correspondence.

the microscopic dipole correlation function is considered. By solving the diffusion Smoluchowski's equation they arrive at four different relaxation modes

$$\langle \mu_{\parallel}(0)\mu_{\parallel}(t)\rangle = \underbrace{\Phi^1_{00}\mu_l^2}_{A} + \underbrace{\Phi^1_{01}\mu_t}_{B}$$

$$\langle \mu_{\perp}(0)\mu_{\perp}(t)\rangle = \underbrace{\Phi^1_{10}\mu_l^2}_{C} + \underbrace{\Phi^1_{11}\mu_t}_{D}$$

which can be connected to reorientations around the long and short molecular axes. The term A is related to the reorientation around the short molecular axis. The B term is connected with pure reorientational movements about the long axis of the deflected molecule. The term C is related to a stochastic precessional movement of the long molecular axis about the director and the last term D originates from the rotation about the long axis of the precessing molecule. It will be shown below that both terms C and D overlap and give a broadened relaxation region for the perpendicular direction.

In this paper we present the theoretical calculation of the dielectric increments of the relaxation modes of two substances CE6 and 3.OAOB, based on the NRS theory. The theoretical values are compared with our experimental results.[2,3]

THEORY

Using Kubo's linear theory, it has been shown[4] that the relation between the dielectric spectrum and the motions of the molecular dipoles can be written as

$$\frac{(\hat{\varepsilon}_\lambda(\omega) - \varepsilon_{\infty\lambda})}{(\varepsilon_\lambda - \varepsilon_{\infty\lambda})} \cdot \frac{\{\hat{\varepsilon}_\lambda(\omega) - \Omega^\varepsilon_\lambda(\omega)[\hat{\varepsilon}_\lambda(\omega) - \varepsilon_{\infty\lambda}]\}\cdot \varepsilon_\lambda}{\{\varepsilon_\lambda - \Omega^\varepsilon_\lambda[\varepsilon_\lambda - \varepsilon_{\infty\lambda}]\}\cdot \hat{\varepsilon}_\lambda(\omega)}$$

$$= 1 - i\omega F[C_\lambda(t)], \qquad \lambda \equiv \perp \text{ or } \parallel \quad (1)$$

where $\hat{\varepsilon}_\lambda(\omega)$ is the frequency dependent value, ε_λ the static value and $\varepsilon_{\infty\lambda}$ the value at infinite frequency of the dielectric permittivity. $\Omega^\varepsilon_\lambda(\omega)$ and $\Omega^\varepsilon_\lambda$ are shape factors depending on both the dielectric anisotropy and the molecular shape. F indicates a one-sided Fourier transform and the dipole moment time-correlation functions are given by

$$C_\lambda(t) = \frac{\langle (\mu_d)_{i\lambda}(0)\ \Sigma_j\ (\mu_d)_{j\lambda}(t)\rangle}{\langle (\mu_d)_{i\lambda}\ \Sigma_j\ (\mu_d)_{j\lambda}\rangle}. \quad (2)$$

For the molecular dipole moment, we use Bordewijk's internal field factor[5]

$$\mu_{d\gamma} = \mu_\gamma \cdot \left(1 - \frac{1}{\varepsilon_0} N\alpha_\gamma \Omega^{sh}_\gamma\right)^{-1}, \qquad \gamma \equiv l, t \quad (3)$$

where Ω_γ^{sh} are shape factors depending on the molecular shape only, N is the number density, ε_0 is the dielectric permittivity of vacuum and α_γ are the polarizabilities parallel and perpendicular to the long molecular axis.

The left-hand side of Equation (1) can often be approximated by $(\hat{\varepsilon}_\lambda(\omega) - \varepsilon_{\infty\lambda})/(\varepsilon_\lambda - \varepsilon_{\infty\lambda})$, and in a first approximation the cross correlation terms in the right-hand side can be ignored. One obtains

$$\frac{(\hat{\varepsilon}_\lambda(\omega) - \varepsilon_{\infty\lambda})}{(\varepsilon_\lambda - \varepsilon_{\infty\lambda})} = 1 - i\omega F\left[\frac{\langle(\mu_d)_\lambda(0)(\mu_d)_\lambda(t)\rangle}{\langle(\mu_d)_\lambda^2\rangle}\right] = 1 - i\omega F[C'_\lambda(t)]. \tag{4}$$

Araki *et al.*[6] deduced a formula for the correlation functions in a nematic potential, independent of any assumed model for reorientation:

$$C'_\parallel(t) = \frac{1}{3\langle(\mu_d)_\parallel^2\rangle}[(\mu_d)_l^2(1 + 2S)\Phi_{00}(t) + (\mu_d)_t^2(1 - S)\Phi_{01}(t)] \tag{5a}$$

$$C'_\perp(t) = \frac{1}{3\langle(\mu_d)_\perp^2\rangle}\left[(\mu_d)_l^2(1 - S)\Phi_{10}(t) + (\mu_d)_t^2\left(1 + \frac{S}{2}\right)\Phi_{11}(t)\right]. \tag{5b}$$

$\Phi_{ij}(t)$ are functions expressing the four relaxation modes involving the motion of the molecular axes in Euler space.

For the model of small-step rotational diffusion, Nordio *et al.*[1] have shown by solving the Smoluchowski diffusion equation that

$$\Phi_{ij}(t) = \sum_p a_{ij}^p \exp\left(-\frac{t}{\tau_{ij}^p}\right) \tag{6}$$

where τ_{ij}^p are functions of the rotational diffusion tensor and the nematic potential. Since expression (6) is largely dominated by the first term,[7] we can write:

$$\Phi_{ij}(t) = a_{ij}^1 \exp\left(-\frac{t}{\tau_{ij}}\right), \qquad a_{ij}^1 \approx 1. \tag{7}$$

By taking the one-sided Fourier transform of the dipole correlation functions, we obtain

$$(\hat{\varepsilon}_\parallel(\omega) - \varepsilon_{\infty\parallel}) = \frac{G_{00}}{1 + \omega\tau_{00}} + \frac{G_{01}}{1 + \omega\tau_{01}} \tag{8a}$$

$$(\hat{\varepsilon}_\perp(\omega) - \varepsilon_{\infty\perp}) = \frac{G_{10}}{1 + \omega\tau_{10}} + \frac{G_{11}}{1 + \omega\tau_{11}}. \tag{8b}$$

Using[4]

$$\langle(\mu_d)_{\|}^2\rangle = \frac{1}{3}\left[(\mu_d)_l^2(1 + 2S) + (\mu_d)_t^2(1 - S)\right] \tag{9a}$$

$$\langle(\mu_d)_{\perp}^2\rangle = \frac{1}{3}\left[(\mu_d)_l^2(1 - S) + (\mu_d)_t^2\left(1 + \frac{S}{2}\right)\right] \tag{9b}$$

the amplitudes of the four relaxation modes can be calculated as

$$G_{00} = \frac{(\mu_d)_l^2(1 + 2S)(\varepsilon_{\|} - \varepsilon_{\|\infty})}{(\mu_d)_l^2(1 + 2S) + (\mu_d)_t^2(1 - S)} \tag{10a}$$

$$G_{01} = \frac{(\mu_d)_t^2(1 - S)(\varepsilon_{\|} - \varepsilon_{\|\infty})}{(\mu_d)_l^2(1 + 2S) + (\mu_d)_t^2(1 - S)} \tag{10b}$$

$$G_{10} = \frac{(\mu_d)_l^2(1 - S)(\varepsilon_{\perp} - \varepsilon_{\perp\infty})}{(\mu_d)_l^2(1 - S) + (\mu_d)_t^2\left(1 + \frac{S}{2}\right)} \tag{10c}$$

$$G_{11} = \frac{(\mu_d)_t^2\left(1 + \frac{S}{2}\right)(\varepsilon_{\perp} - \varepsilon_{\perp\infty})}{(\mu_d)_l^2(1 - S) + (\mu_d)_t^2\left(1 + \frac{S}{2}\right)} \tag{10d}$$

The second way to estimate the amplitudes of the four relaxation modes is to apply the following procedure.

For two well separated relaxation regions one can write (compare to Equation (8)):

$$\hat{\varepsilon}_{\lambda}(\omega) - \varepsilon_{\infty\lambda} = \frac{\varepsilon_{0\lambda} - \varepsilon_{\infty 1\lambda}}{1 + i\omega\tau_{1(\lambda)}} + \frac{\varepsilon_{\infty 1\lambda} - \varepsilon_{\infty\lambda}}{1 + i\omega\tau_{2(\lambda)}} \tag{11}$$

where $\tau_{1\lambda}$ and $\tau_{2\lambda}$ are the correlation times for both processes.

Using the Bordewijk-de Jeu equation[5]

$$(\varepsilon_{\lambda} - \varepsilon_{\infty\lambda}) \cdot K_{\varepsilon\lambda} = \frac{N}{\varepsilon_0 k_B T} g_{\lambda}\langle(\mu_d)_{\lambda}^2\rangle \tag{12}$$

and Equation (9), one obtains:

$$((\varepsilon_{\parallel} - \varepsilon_{\infty 1\parallel}) + (\varepsilon_{\infty 1\parallel} - \varepsilon_{\infty\parallel}))K_{\varepsilon_{\parallel}} = \frac{N}{\varepsilon_0 k_B T} g_{\parallel} \frac{1}{3} [(\mu_d)_t^2(1 + 2S) + (\mu_d)_t^2(1 - S)] \quad (13a)$$

$$((\varepsilon_{\perp} - \varepsilon_{\infty 1\perp}) + (\varepsilon_{\infty 1\perp} - \varepsilon_{\infty\perp}))K_{\varepsilon_{\perp}} = \frac{N}{\varepsilon_0 k_B T} g_{\perp} \frac{1}{3} \left[(\mu_d)_t^2(1 - S) + (\mu_d)_t^2 \left(1 + \frac{S}{2}\right) \right] \quad (13b)$$

where g_λ is the Fröhlich-Kirkwood dipole correlation factor, k_B is the Boltzman constant and T is the temperature.

$K_{\varepsilon\lambda}$ is an internal field tensor given by

$$K_{\varepsilon\lambda} = \frac{\varepsilon_\lambda + (\varepsilon_{\infty\lambda} - \varepsilon_\lambda)\Omega_\lambda^\varepsilon}{\varepsilon_\lambda}.$$

If one assumes that $\tau_{m(\lambda)}$ and τ_{ij} (Equation (8)) can be identified one deduces according to[8]:

$$\tau_{1(\parallel)} = \tau_{00}; \quad (\varepsilon_{\parallel} - \varepsilon_{\infty 1\parallel}) = \frac{N}{\varepsilon_0 k_B T} \frac{g_{\parallel}}{3K_{\varepsilon\parallel}} (1 + 2S)(\mu_d)_t^2 \quad (14a)$$

$$\tau_{2(\parallel)} = \tau_{01}; \quad (\varepsilon_{\infty 1\parallel} - \varepsilon_{\infty\parallel}) = \frac{N}{\varepsilon_0 k_B T} \frac{g_{\parallel}}{3K_{\varepsilon\parallel}} (1 - S)(\mu_d)_t^2 \quad (14b)$$

$$\tau_{1(\perp)} = \tau_{10}; \quad (\varepsilon_{\perp} - \varepsilon_{\infty 1\perp}) = \frac{N}{\varepsilon_0 k_B T} \frac{g_{\perp}}{3K_{\varepsilon\perp}} (1 - S)(\mu_d)_t^2 \quad (14c)$$

$$\tau_{2(\perp)} = \tau_{11}; \quad (\varepsilon_{\infty 1\perp} - \varepsilon_{\infty\perp}) = \frac{N}{\varepsilon_0 k_B T} \frac{g_{\perp}}{3K_{\varepsilon\perp}} \left(1 + \frac{S}{2}\right) (\mu_d)_t^2 \quad (14d)$$

Using the Vuks internal field factor, Equations (12) and (14a–d) can be modified as follows[16]:

$$(\varepsilon_\lambda - \varepsilon_{\infty\lambda}) \cdot K_{\varepsilon\lambda} \cdot \frac{1}{(\bar{\varepsilon}_\infty + 2)^2} = \frac{N}{9\varepsilon_0 k_B T} g_{\lambda \mathrm{Vuks}} \langle \mu_\lambda^2 \rangle \quad (15)$$

$$\tau_{1(\parallel)} = \tau_{00}; \quad (\varepsilon_{\parallel} - \varepsilon_{\infty 1\parallel}) = \frac{N}{27\varepsilon_0 k_B T} \frac{g_{\parallel \mathrm{Vuks}}}{K_{\varepsilon\parallel}} (1 + 2S)(\overline{\varepsilon_\infty} + 2)^2 \mu_t^2 \quad (16a)$$

$$\tau_{2(\parallel)} = \tau_{01}; \qquad (\varepsilon_{\infty 1\parallel} - \varepsilon_{\infty\parallel}) = \frac{N}{27\varepsilon_0 k_B T} \frac{g_{\parallel Vuks}}{K_{\varepsilon\parallel}} (1 - S)(\overline{\varepsilon_\infty} + 2)^2 \mu_l^2 \quad (16b)$$

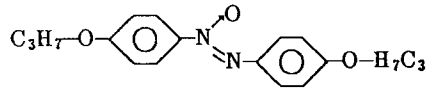
$$\tau_{1(\perp)} = \tau_{10}; \qquad (\varepsilon_\perp - \varepsilon_{\infty 1\perp}) = \frac{N}{27\varepsilon_0 k_B T} \frac{g_{\perp Vuks}}{K_{\varepsilon\perp}} (1 - S)(\overline{\varepsilon_\infty} + 2)^2 \mu_l^2 \quad (16c)$$

$$\tau_{2(\perp)} = \tau_{11}; \qquad (\varepsilon_{\infty 1\perp} - \varepsilon_{\infty\perp}) = \frac{N}{27\varepsilon_0 k_B T} \frac{g_{\perp Vuks}}{K_{\varepsilon\perp}} \left(1 + \frac{S}{2}\right) (\overline{\varepsilon_\infty} + 2)^2 \mu_l^2. \quad (16d)$$

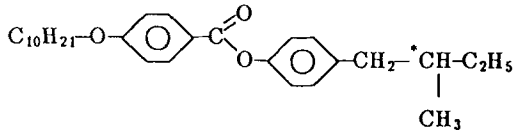
In the isotropic phase, Equation (15) reduces to the Kirkwood-Fröhlich equation.

EXPERIMENTAL

The di-propyloxyazoxybenzene



has been synthesized in the Institute of Chemistry of the Siedlce Agricultural and Pedagogical College and the racemic methylbutyl-phenyl-hexyloxybenzoate



placed at our disposal by BDH Chemicals (Great Britain).

The complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$ of 3.OAOB was measured using a coaxial line setup, rectangular waveguides[12] and a multidecameter.[8] In the nematic phase the samples were oriented by means of a magnetic field. In the case of the coaxial line $B = 0.25\ T$ was used (only the homeotropic alignment was obtained). For rectangular waveguides, both homeotropic and planar alignment were obtained using a magnetic field ($B = 0.5\ T$). The sample holders were filled with the substance at a temperature of about 10 K above the clearing point. The measurements were carried out, both on cooling and heating (stability better than 0.5 K).

The measurements for CE6 were performed with a HP4284 (30 Hz–1 MHz) and a HP4192A (10 kHz–13 MHz) capacitance bridge under computer control. The sample was placed between the plates of a plane capacitor (stainless steel, electrode spacing 0.5 mm). This cell was heated by means of a two-step temperature control (stability better than 0.01 K). Homeotropic and planar alignment was obtained using a magnetic field ($B = 0.75\ T$) parallel or perpendicular to the capacitor plates.

RESULTS AND DISCUSSION

The amplitudes of the four relaxation modes are calculated according to Equations (10a–d) (or 14a–d) and Equations (16a–d) and compared with experimental data (Figures 1 and 2) for one temperature in the isotropic phase and one in the nematic phase. The results are summarized in Table I. Experimental constraints made that, for CE6, only the Φ^1_{00} mode (kHz or MHz region) could be measured (Figure 1), whereas for 3.OAOB in the nematic phase, two modes (Φ^1_{00} and Φ^1_{01}) were observed separately for parallel orientation and one broadened relaxation region (Φ^1_{10} + Φ^1_{11}) for the perpendicular direction (Figure 2).

The length and the width of the CE6 molecule, necessary to calculate the shape factors, were estimated (from the bond lengths and the density) to be 28.3 Å and 6.9 Å respectively. The clearing temperature was equal to 43.75°C. The calculations were performed for T = 41.44°C in the nematic phase and T = 49.87°C in the isotropic phase. The refractive index data were provided by R. Hellemans.[10] The values for $\varepsilon_{\infty\lambda}$ were obtained by multiplying n^2_λ by 1.05 and from these values the polarizabilities were determined using[4]

$$\alpha_l = \frac{\varepsilon_0}{N}\left[\Omega_l + \frac{1}{(\varepsilon_{\infty\perp} - 1) + \frac{1}{3}(\varepsilon_{\infty\parallel} - \varepsilon_{\infty\perp})\left(1 + \frac{2}{S}\right)}\right]^{-1} = 9.51 \times 10^{-39}\ \mathrm{Fm}^2$$

$$\alpha_t = \frac{\varepsilon_0}{N}\left[\Omega_t + \frac{1}{(\varepsilon_{\infty\perp} - 1) + \frac{1}{3}(\varepsilon_{\infty\parallel} - \varepsilon_{\infty\perp})\left(1 - \frac{1}{S}\right)}\right]^{-1} = 4.89 \times 10^{-39}\ \mathrm{Fm}^2.$$

The value of the order parameter S was estimated from the Maier-Saupe mean field theory. A vector model calculation[11] predicts a molecular dipole moment of 7.6×10^{-30} Cm and an angle between the dipole and the long molecular axis

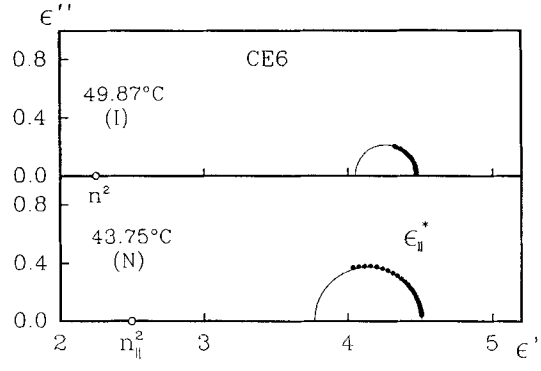


FIGURE 1 The Cole-Cole diagrams obtained for CE6 for the isotropic phase and for parallel orientation in the nematic phase.

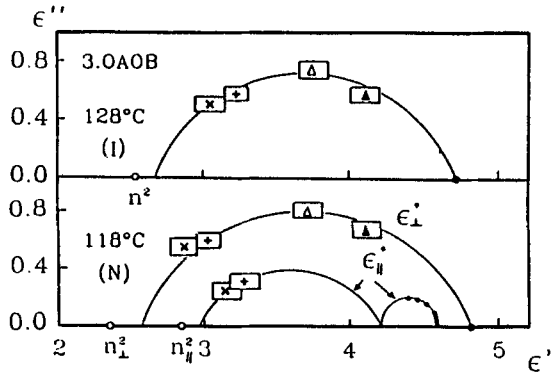


FIGURE 2 The Cole-Cole diagrams obtained for 3.OAOB for the isotropic phase and for two orientations in the nematic phase.

(corrected for a mesomerism effect) of 57°. We preferred however, to use a dipole moment value which was obtained from measurements in a diluted solution with CCl_4 as a solvent

$$\mu = 8.6 \times 10^{-30} \text{ Cm}.$$

The dimensions of 3.OAOB molecule were taken from Reference 12. The length and the width were estimated to be 22.2 Å and 6.5 Å, respectively. The clearing temperature was equal to 123.64°C. The calculations were performed for T = 118°C in the nematic phase and T = 128°C in the isotropic phase. The refractive index values were taken from Reference 5. The values for $\varepsilon_{\infty\lambda}$ were obtained from experiment (see Reference 2). The polarizabilities were determined using Reference 4

$$\alpha_{\parallel} = 8.92 \times 10^{-39} \text{ Fm}^2$$

$$\alpha_{\perp} = 3.28 \times 10^{-39} \text{ Fm}^2.$$

The value of the order parameter S was taken from Reference 13. A vector model calculation[14] predicts a molecular dipole moment of 8.0×10^{-30} Cm and an angle β between the total dipole moment and the long molecular axis of molecule of 76°.

Column (1) in Table I contains values which have been calculated according to Equations (10a–d). As one can see the same values can be obtained from Equations (14a–d) using the Bordewijk-de Jeu Equation (12). If one assumes however, that the Vuks internal field is a better approximation one can estimate the amplitudes of the four relaxation modes using Equations (16a–d). Column (2) in Table I contains values which have been calculated according to this model. The same results can be obtained by replacing $\mu_{\lambda d}$ in Equations (10a–d) by μ_{λ}.

For both substances, the best agreement between the experimental and theoretical results is found using the Bordewijk-de Jeu internal field factor (column 1).

From experimental data (Figures 1 and 2) as well as from calculated quantities (Table I) one can deduce the following conclusions:

TABLE I

Theoretical (Equations (10a–d) (1) and Equations (16a–d) (2)) and experimental values of the dielectric relaxation amplitudes

		CE6			3.OAOB		
		THEORY		EXP	THEORY		EXP
		(1)	(2)		(1)	(2)	
NEMATIC	$\varepsilon_{\parallel} - \varepsilon_{\infty 1\parallel}$	0.95	1.18	0.77	0.30	0.39	0.32
	$\varepsilon_{\infty 1\parallel} - \varepsilon_{\infty\parallel}$	0.99	0.77	—	1.28	1.18	1.36
	$\varepsilon_{\parallel} - \varepsilon_{\infty\parallel}$	1.94	1.95	—	1.58	1.57	1.68
	$\varepsilon_{\perp} - \varepsilon_{\infty 1\perp}$	0.22	0.34	—	0.03	0.05	—
	$\varepsilon_{\infty 1\perp} - \varepsilon_{\infty\perp}$	1.95	1.84	—	2.18	2.14	—
	$\varepsilon_{\perp} - \varepsilon_{\infty\perp}$	2.17	2.18	—	2.21	2.19	2.20
ISOTROPIC	$\varepsilon - \varepsilon_{1\infty}$	0.45	0.64	0.42	0.08	0.15	—
	$\varepsilon_{1\infty} - \varepsilon_{\infty}$	1.71	1.52	—	1.93	1.85	—
	$\varepsilon - \varepsilon_{\infty}$	2.16	2.16	—	2.01	2.00	2.00

1. In the direction parallel to the nematic director of 3.OAOB and CE6 a low frequency (l.f.) relaxation process which is connected with the reorientation of the molecules around the short axis, does not exhibit any significant distribution of relaxation times.
2. In the direction parallel to the nematic director of 3.OAOB the high frequency (h.f.) relaxation process which is connected with the fast molecular motion of the deflected molecule about its long axis is characterized by a distribution of the relaxation times. Assuming an ellipsoidal shape of the 3.OAOB molecule one can write the following expression for the complex dielectric permittivity

$$\hat{\varepsilon}_{\parallel}(\omega) - \varepsilon_{\infty\parallel} = \frac{\Delta\varepsilon_{1\parallel}}{1 + \omega\tau_{1\parallel}} + \frac{\Delta\varepsilon_{2\parallel}}{1 + \omega\tau_{2\parallel}} + \frac{\Delta\varepsilon_{3\parallel}}{1 + \omega\tau_{\text{intra}}}$$

which is the main result of the Budo theory.[15] It is suggested[2] that the third term originates from fluctuations of the long molecular axis, most probably due to some intramolecular conformation changes. But as one can see, according to the N-R-S model prediction this effect is rather small:

$$\frac{\Delta\varepsilon_{3\parallel}}{1 + \omega\tau_{\text{intra}}} = (\varepsilon_{\infty 1\parallel} - \varepsilon_{\infty\parallel})_{\text{exp}} - (\varepsilon_{\infty 1\parallel} - \varepsilon_{\infty\parallel})_{\text{tho}} = 0.1.$$

TABLE II

The dipole correlation factors for the isotropic and nematic phases of 3.OAOB and CE6

Substance	g_{is}	$g_{\perp}$	$g_{\parallel}$
3.OAOB	0.80•	0.70•	1.08•
	0.71*	0.67+	0.95+
CE6	1.03•	0.91•	1.10•
	0.99*	0.91+	0.90+

*Fröhlich-Kirkwood dipole correlation factors.
+Vuks dipole correlation factors.
•Bordewijk-de Jeu dipole correlation factors.

3. From Figure 2 as well as from Table I one can suppose that the h.f. dielectric response observed in the perpendicular orientation is mainly connected with the reorientation of the molecule as a whole around its long axis. The second process observed for this orientation (the rotation about the long axis of precessing molecule) is much weaker than the first one. The ratio of amplitudes related to these processes is equal to 0.1 for CE6 and 0.01 for 3.OAOB, respectively.
4. From comparing the dielectric spectra of CE6 observed for the isotropic phase as well as from Table I, one can conclude that the non-oriented sample shows two well separated relaxation regions. However, for 3.OAOB in the isotropic phase one broadened relaxation region was observed. But as it follows from the N-R-S model the amplitude of the l.f. relaxation process is at least 12 times smaller than the h.f. one.
5. Equations (14a–d) and (16a–d) show that any theory of molecular dynamics of liquid crystals should include dipole-dipole interaction. From the content of this paper in conjunction with literature date, one can infer that taking into account the g-factor one can improve numerical analysis of dielectric spectra. Therefore we calculated the g_{λ}-factors for both substances under study. The results are given in Table II.

As one can see the $g_{\perp}$ values are less than unity, especially for 3.OAOB, which means that in both nematic phases the perpendicular components of the dipole moments show a tendency to anti-parallel correlations. The $g_{\parallel}$ values are almost equal to 1, consistent with little parallel dipole-dipole correlation. Closer to the nematic-smetic A transition however, the parallel component of the dipole moment of CE6 shows a strong tendency to anti-parallel correlation, whereas the perpendicular component shows a tendency towards parallel correlation.

CONCLUSIONS

As one can see the Nordio-Rigatti-Segre model seems to be a useful theory which can be used for qualitative and quantitative analysis of the dielectric spectra for

many liquid crystals. This model suggests a clear physical interpretation of the four relaxation modes which are active in a dielectric relaxation experiment. It should be pointed out however that more experimental evidence is needed. Furthermore, the results depend very critically on the angle between the dipole moment and the long molecular axis, a parameter which is very difficult to estimate accurately.

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