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EFFECT OF ALIPHATIC SPACERS ON ELECTRO-OPTICAL AND DIELECTRIC PROPERTIES OF STRONGLY POLAR LIQUID CRYSTALS

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Abstract The molecular mechanism of dipolar polarisation in liquid crystals containing a nitrile group "not rigidly" bonded to the mesogenic fragment of molecules with different chemical structures was considered.

Recently liquid crystalline substances the molecules of which contain strongly polar -C≡N groups in aliphatic side chains have been synthesized. These side chains are actually flexible chain parts between a rigid mesogenic ring of the molecule and its nitrile group. The present paper studies the effect of these flexible parts (spacers) on the dielectric properties of strongly polar liquid crystals.

The structural formulae of molecules of these liquid crystals and the temperature ranges of their mesomorphic state are given in Table I.

The table also lists the values of molar Kerr constants as well as molecular dipole moments measured in solutions of these samples in tetrachloromethane. The experimental data given in the table show that in all cases considered here the insertion of methylene groups between the main part of molecules of liquid crystals and the nitrile -C≡N groups leads to a certain decrease in the permanent dipole moment but affects the value of K_M to a much greater extent. The molar Kerr constant decreases almost twice when two methylene groups are present in the spacer and by one order of magnitude when the spacer containes four methylene groups. The latter result is evidently due to the decrease of correlation between the dipole direction of the -C≡N group and the longitudinal axis of the molecule.

TABLE I Kerr constants K_M [$cm^5(300V)^{-2}mol^{-1}$], dipole moment μ[D] and its direction in molecules ß, dielectric and optical characteristics of liquid crystals at relative temperature $\Delta T=T-T_{is}=-5°C$; and energy of activation U[kJ/mol]

N	Liquid crystal	$K_M 10^{-9}$	μ	ß°	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$(\varepsilon_{\parallel})_1$	n^2_e	U
1.	$C_6H_{13}O$-⟨⟩-CH=CH-COO-⟨⟩-CN K 76.8°C N 141°C I	6.9	7.1	10	23.5	7.5	4.2	3.1	73
2.	C_4H_9O-⟨⟩-CH=CH-COO-⟨⟩-$(CH_2)_2$CN K 91°C N 118°C I	3.9	5.4	30	16.0	7.5	7.4	3.0	97
3.	C_7H_{15}-⟨⟩-COO-⟨⟩-CN K 43.5°C N 55°C I	7.0	6.1	15	25.0	9.5	4.0	2.6	84
4.	C_7H_{15}-⟨⟩-COO-⟨⟩-O-$(CH_2)_4$CN K (62.2°C) N 47.5°C I	0.7	4.4	45	14.5	10.0	6.2	2.6	155
5.	$C_7H_{15}O$-⟨⟩-N=N-⟨⟩-CN K 94°C N 112°C I	11.0	5.8	0	15.5	7.5	3.1	3.1	67
6.	C_7H_{15}-⟨⟩-N=N-⟨⟩-O-$(CH_2)_4$CN K 68°C N 83°C I	0.1	3.7	56	6.8	7.0	5.7	3.1	210

This decrease in orientational correlation may be tentatively characterized by a change in the "effective" value of the angle ß formed by the direction of the dipole moment and the optical axis of the molecule. The value of ß was found by the equation

$$K_M = \frac{2}{9}\pi N_A \frac{\Delta b}{45kT}\left[2\Delta\alpha + \frac{\mu^2}{kT}(3\cos^2\beta - 1)\right] \quad (1)$$

from the experimental values of K_M, and the anisotropies of electric $\Delta\alpha$ and optical Δb polarisabilities of molecules (Table I). Here N_A is Avogadro's number and k is Boltzmann's constant and T is the temperature. The values of ß determined by this method are given in TableI.

The differences between the polar structures of the molecules of the samples under investigation are directly reflected in the dielectric properties of mesomorphic liquids. Indeed, the measurements of macroscopic dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, of uniformly oriented nematic sample by determining the main values of dielectric permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ in the directions parallel and perpendicular to the axis of the nematic order have shown that the value and even the sign of $\Delta\varepsilon$ for all investigated liquid crystals directly depend on and ß (Table I) in accordance with the theory of dielectric anisotropy of nematics[1]:

$$\Delta\varepsilon = 4\pi N PQ\left[\Delta\alpha + Q\frac{\mu^2}{2kT}(3\cos^2\beta - 1)\right]S, \quad (2)$$

where N is the number of molecules in unit volume, P and Q are the factors of the internal field and S is the degree of ordering of the mesophase. Hence, the value and sign of $\Delta\varepsilon$ of these liquid-crystalline samples both with and without aliphatic spacers are determined by the value and direction of their molecular dipole moment.

For discussing molecular mechanisms of dipolar polarization, it is necessary to use the results of experimental investigation of the dispersion of the main values of dielectric permittivities. In the frequency range $f=10^3-3\cdot10^7$Hz, the most complete data were obtained for the dispersion of $\varepsilon_{\parallel}$. According[1,2] the dipole part of molar di-

electric susceptibility $\sigma_{\parallel}$ contains the orientational mechanisms of dipolar polarization of the mesophase: the rotation of the polar molecule about the transverse $(\sigma_{\parallel})_{\parallel}$ and longitudinal axis $(\sigma_{\parallel})_{\perp}$:

$$\sigma_{\parallel}^{dip} = \frac{\varepsilon_{\parallel} - n_e^2}{4\pi} \frac{M}{\rho} = (\sigma_{\parallel})_{\parallel} + (\sigma_{\parallel})_{\perp} = \rho Q^2 N_A \left[\frac{\mu^2 \cos^2\beta}{3kT}(1+2S) + \frac{\mu^2 \sin^2\beta}{3kT}(1-S)\right], \quad (3)$$

where $n_e^2 = \varepsilon_{\infty}$ is extraordinary refractive index, M is the molecular weight and ρ is the density.

Fig.1 shows as an example the frequency dependences of dielectric permittivity $\varepsilon_{\parallel}$ for two liquid-crystalline samples (3 and 4).

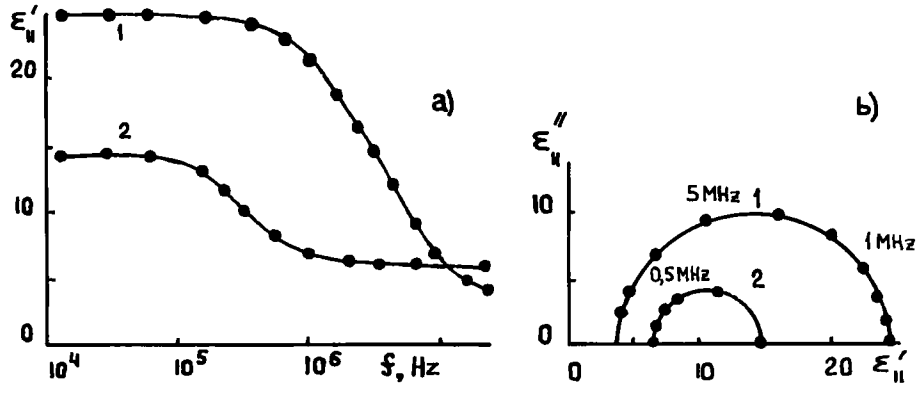

FIGURE 1 a)dielectric permittivities $\varepsilon_{\parallel}$ for samples 3 (1) and 4 (2) vs frequency at $\Delta T = T - T_{is} = -5°C$, b) Cole-Cole diagrams for samples 3 (1) and 4 (2).

It also shows the corresponding Cole-Cole diagrams. These results show that regardless of the presence or absence of aliphatic spacers in the molecules, the relaxation curves are Debye curves

$$\varepsilon_{\parallel} = (\varepsilon_{\parallel})_1 + \frac{(\varepsilon_{\parallel})_0 - (\varepsilon_{\parallel})_1}{1 + (2\pi f \tau)^2}. \quad (4)$$

Each of these curves corresponds to one time of dipole relaxation τ. This fact implies that for all liquid crystals investigated in the frequency range f, the only mechanism of dipolar relaxation related to the rotation of the polar molecule about the short axis $(\sigma_{\parallel})_{\parallel}$ is responsible for dispersion $\varepsilon_{\parallel}$. However, the values of high-frequency

limits of dispersion curves $(\varepsilon_{\parallel})_1$ found for different samples from the corresponding Cole-Cole diagrams (Fig.1, Table I) greatly differ from the value of n^2_e for the same substances. Sample 5 is an exception. For this sample $(\varepsilon_{\parallel})_1 - n^2_e = 0$, because the normal component of the dipole moment is absent in its molecule ($\beta = 0$). Hence, the mechanism of rotation of molecules about the longitudinal axis represented in eq. 3 by the term $(\varepsilon_{\parallel})_{\perp}$ is responsible for the experimental values of $(\varepsilon_{\parallel})_1 - n^2_e$.

Note that the introduction of the aliphatic spacers into the molecules of liquid crystals considerably displaces the dispersion of $\varepsilon'_{\parallel}$ towards lower frequencies (Fig.1) and greatly increases the activation energy U (Table I) of molecular rotation in the mesophase about the short axis. The values of U were found by using the temperature dependences. Hence, the aliphatic spacers in the molecules of strongly polar nematics can profoundly affect their dipolar structure and as a result can lead to changes in their equilibrium and dynamic dielectric properties.

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