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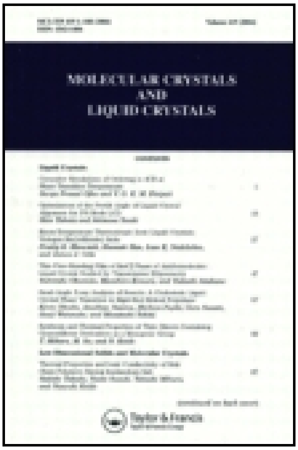

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Molecular Association and Electro-Optical Properties of Liquid-Crystalline 3-(4-Ethoxyphenyl)-7-Nonyloxycumarine

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MOLECULAR ASSOCIATION AND ELECTRO-OPTICAL PROPERTIES OF LIQUID-CRYSTALLINE 3-(4-ETHOXYPHENYL)-7-NONYLOXYCUMARINE

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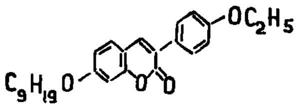
Abstract Electro-optical and dielectric properties of mesogenic 3-(4-eth oxyphenyl)-7-nonyloxycumarine in solution, in the isotropic and liquid-crystalline phases have been investigated. It was established that the molecular-dipolar and macroscopic dielectric properties of the sample investigated differ greatly.

At present, there are no data in the literature on the experimental investigations of the structural organization of dialkoxyphenyl cumarines in the liquid-crystalline and isotropical liquid states. However, it has been suggested[1] that contact pairs play an important role in the formation of the mesomorphic state in this class of compounds.

In the present paper, the investigations of 3-(4-ethoxyphenyl)-7-nonyloxycumarine (EPNOC) are described.



K 106,6°C S_A 111,2°C N 118,5°C I

With the aim of analysis of the dipolar structure of EPNOC molecules, the molar Kerr constants K_M and dipole moments in solutions and the anisotropy of the optical polarisability of molecules Δb were measured. The procedure of measuring K_M, and Δb have already been described[2].

Table 1 gives the experimental values of electric characteristics of EPNOC molecules which may be used for the determination of another important parameter, the angle β formed by the direction of the permanent dipole moment of the molecule and the axis of its greatist polarizability (longitudinal axis of the molecule):

$$K_M = \frac{\Delta n}{E^2}\frac{M}{\rho} = P^2 Q\left(\frac{n^2+2}{3}\right)^2 \frac{2\pi N_A}{15nkT}\Delta b\left[\Delta b + Q\frac{\mu_0^2}{2kT}(3\cos^2\beta-1)\right] \qquad (1)$$

where N_A and k are Avogadre's number and Boltsmann's constant, n is the birefringence of the substance being investigated in an electric field of strength E, M and ρ are its molecular weight and density, P and Q are the factors of the internal field (Onsager).

TABLE I Optical anisotropy Δb $[cm^3]$, Kerr constant K_M $[cm^5(300V)^{-2}mol^{-1}]$, dipole moment μ[D] and angle β[°] of EPNOC

	in solution			in the isotropic melt		
$b, 10^{-23}$	$K_M, 10^{-8}$	μ_0	β	$K_M, 10^{-8}$	μ	β
2,5	1,6	4,1	53	-5,7	4,3	90

The use of experimental data given in Table I and eq.(1) yield the value of β=53° for the EPNOC molecules.

The experimentally found value and direction of the dipole moment in the EPNOC molecule have suggested that for the sample being investigated a slight positive value of dielectric anisotropy $\Delta\varepsilon$ may be expected in the liquid-crystalline state:

$$\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp = \frac{4\pi\rho}{M} N_A PQ\left[\Delta b + Q\frac{\mu_0^2}{2kT}(3\cos^2\beta-1)\right]S = +0,6. \qquad (2)$$

However, direct mesurements of the main values of dielectric permittivities in the directions parallel, $\varepsilon_\parallel$, and perpendicular, $\varepsilon_\perp$ to the director (optical axis) of EPNOC homogeneously oriented by the magnetic field in the nematic and smectic phases showed that this liquid crystal is characterized by a high negative dielectric anisotropy. The temperature dependences of $\varepsilon_\parallel$, $\varepsilon_\perp$, $\Delta\varepsilon$ and the dielectric per-

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mittivity of EPNOC in the isotropic phase ε_{is} are shown in Fig.1.

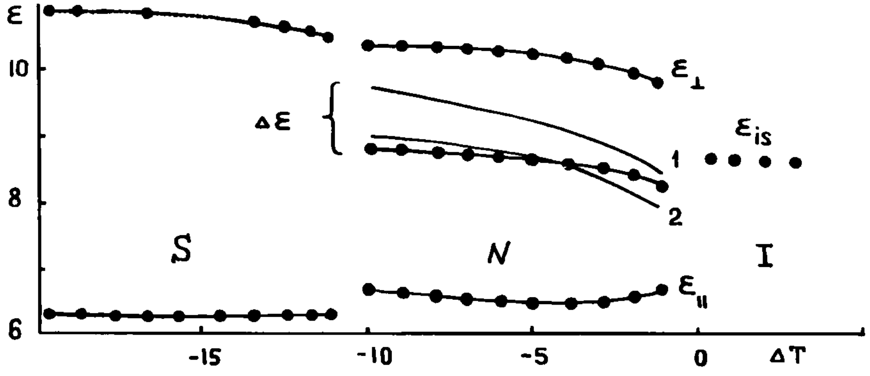

FIGURE 1 Dielectric permittivities $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, ε_{is} and dielectric anisotropy $\Delta\varepsilon$ of EPNOC vs relative temperature $T = T - T_{is}$. Curves 1 and 2 were calculated from eq.2 at ß equal 90° and 77°, respectively.

For the understanding of this very great discrepancy between the molecular-dipolar characteristics found in dilute EPNOC solutions in bensene and macroscopic dielectric properties of the same sample in the liquid-crystalline state, the results of measurements of dipole moments and the investigations of electric birefringence in the isotropic melt of EPNOC are given below.

The value of μ (Table) was found by using the experimental values of refractive index (n_{is} = 1.576) and dielectric permittivity (ε_{is} = 8.6 at T = 124°C) and the equation

$$\mu^2 = \frac{9(\varepsilon-n^2)(2\varepsilon+n^2)}{\varepsilon(n^2+2)^2} kT \frac{M}{4\pi N_A \rho} \qquad (3)$$

The value of dipole moment obtained in the isotropic phase was found to differ only slightly from that determined in EPNOC solutions in bensene. However, the Kerr effect measured in the isotropic phase of EPNOC differs from that of the same sample in solutions not only in absolute value but also in sign (Table I).

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The use of K_M values obtained at a relatively high temperature $\Delta T=T-T_{is}= 100°C$ and those of μ and Δb (Table I) and the application of eq. (I) lead to the value of angle $\beta\approx 90°$. The electric characteristics of EPNOC obtained in the isotropic melt qualitatively agree with the results of dielectric investigations of this liquid crystal in the mesomorphic state.

In Fig.1 curve 1 determines the value of dielectric anisotropy calculated by using the experimental values of μ , Δb and $\beta=90°$ obtained in the isotropic phase of EPNOC and by applying eq. (2). For the quantitative correspondence between the experimental values of $\Delta\varepsilon$ and those calculated from eq. (2), the value of angle β should be taken equal to 77° (Fig.1,curve 2). Hence, in order to correlate the molecular-dipolar characteristics of EPNOC with the value and sign of its macroscopic dielectric anisotropy, it is necessary to take into account a considerable decrease in the contribution of the longitudinal component of the dipole moment to orientational polarization ($\beta=77°$) and the corresponding marked increase in the significance of its normal component when of the substance passes from a dilute solution into the isotropic phase and subsequentes into the liquid-crystalline state. The estimation of the value of β from the results of the investigation of dispertion of the main dielectric permittivities of EPNOC in the liquid-crystalline state leads to a similar result. Fig.2 shows the dependence of $\varepsilon_{\parallel}$ on the frequency of the electric field f.

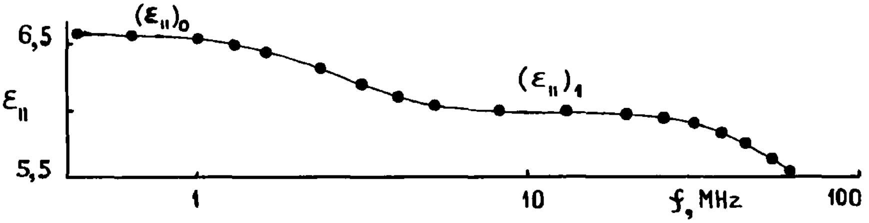

FIGURE 2 Dependence of $\varepsilon_{\parallel}$ on the frequency at 114°C.

This frequency dependence is characterized by two dispersion regions related to the exclusion from the dipolar polarization of

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the liquid crystal of rotation mechanisms of polar molecules about the transverse and the longitudinal ones, respectively. The data shown in Fig.2 indicate that in the frequency range used here the orientational mechanism of rotation of molecules about the transverse axis due to the existance of a certain longitudinal component of dipole moment differing from zero, $\mu\cos\beta$, is completely ruled out. The corresponding low-frequency change in dielectric permittivity, $(\varepsilon_{\parallel})_0 - (\varepsilon_{\parallel})_1$ may be used for the determination β .

$$(\varepsilon_{\parallel})_0 - (\varepsilon_{\parallel})_1 = PQ^2 \frac{4\pi\rho N_A}{M} \frac{\mu^2\cos^2\beta}{3kT}(1+2S) \tag{4}$$

The experimental value of $(\varepsilon_{\parallel})_0 - (\varepsilon_{\parallel})_1 = 0.6$ and eq. 4 give the value of $\beta = 77°$.

Hence, the reason for this considerable difference between the electro-optical properties of EPNOC in a dilute solution and in bulk is an appreciable change in dipolar characteristics upon the transition of the substance being analyzed from solution into the isotropical liquid phase and, further, into the liquid-crystalline state A drastic decrease in the longitudinal component of the dipole moment may probably be related to the formation of contact pairs as early as in the isotropic phase of EPNOC. This molecular association may be accompanied by partial compensation for longitudinal components of the dipole moment with the retention of the considerable value of its normal component. These molecular associates are evidently structural elements for passing into the liquid-crystalline state because as has been shown above, the dipolar characteristics found in the isotropic phase describe the dielectric properties of EPNOC in the liquid-crystalline state.

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