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THE INFLUENCE OF ALIPHATIC SPACERS' POSITION ON THE POLARITY AND DIELECTRIC PROPERTIES OF LIQUID CRYSTALLINE MOLECULES

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Abstract For liquid crystals with the polar CN-end-group and variation of aliphatic spacer position, the dipole moments and Kerr effect in solutions as well as the dielectric permittivity in melts had been studied. It was shown that a strong change of their physical properties took place when the spacer separated CN-group from the main molecular chain.

INTRODUCTION

It is known that a high polarity of thermotropic mesogenes can be achived by leading so polar group as CN-group into their chemical structure. Incidentally, liquid crystals (LC) with essentially different polar characteristics can be synthesized by varing the position of the most polar group in molecular structure[1]. By another way the change in LC polar properties is possible to get with the introduce of different length aliphatic chains (spacers) into their molecules. The flexible aliphatic spacer may be included between the mesogeneous core of the molecule and its polar CN-group or directly into its mesogeneous core. The spacer disturbs a "rigid" LC molecule's structure due to the partial or even fully free rotation possibility of its polar groups, and influences on the one's mesomorphous properties[2]. The spacer presence in LC molecules is also the reason of their electrical characteristics essential change, which reflects in the change of macroscopic

dielectrical and electrooptical properties of mesophases[3].

EXPERIMENTAL

At the present work we have studied the influence of the length and position of aliphatic spacers on electrooptical and dipole characteristics of LC molecules with the CN-end-group: the connection between molecular parameters and macroscopic dielectric properties of mesophases also has been studied.

As the objects under investigation there were used a number of cyanobiphenyl esters of carboxilic acids series with the different length spacers in the central part of ester's molecule; also there were used some similar chemical structure LCs with or without spacers in their molecular chains. Chemical formulas, types of mesophases and corresponding transition temperatures of all the samples are situated in the Table 1.

TABLE 1 Chemical structures and transition temperatures of the investigated LC samples.

N	Structural formula	Phase transition temperatures (C°)
1	C_6H_{13}-Ph-COO-Ph-Ph-CN	C 65°N 218°I
2	C_6H_{13}-Ph-CH_2-COO-Ph-Ph-CN	C 80°I
3	C_7H_{15}-Ph-$(CH_2)_4$-COO-Ph-Ph-CN	C 67°S_A105°I
4	C_4H_9-Cy-COO-Ph-Ph-CN	C 80°N 242°I
5	C_4H_9-Cy-$(CH_2)_2$-COO-Ph-Ph-CN	C 71° S_A124°N 174°I
6	C_4H_9-Cy-$(CH_2)_5$-COO-Ph-Ph-CN	C 80°S_A109°I
7	C_4H_9-Cy-$(CH_2)_6$-COO-Ph-Ph-CN	C 71°S_A136,5°I
8	C_7H_{15}-Ph-COO-Ph-CN	C 43,5°N 55°I
9	C_7H_{15}-Ph-COO-Ph-O-$(CH_2)_4$-CN	C 61°N 68°I
10	$C_7H_{15}O$-Ph-N=N-Ph-CN	C 94°N 112°I
11	C_7H_{15}-Ph-N=N-Ph-O-$(CH_2)_4$-CN	C 68°N 83°I
12	$C_6H_{13}O$-Ph-CH=CH-COO-Ph-CN	C 76,5°N 141°I
13	C_4H_9O-Ph-CH=CH-COO-Ph-$(CH_2)_2$-CN	C 91° N 118°I

Molecular dipole moments μ and molar Kerr constant values K_M of the samples were obtained by means of the methods of dipolar polarization's study and investigation of electrical birefringence (Kerr effect) in diluted solutions of the samples in benzene (N1-7) and in tetramethylchloride (N8-13). The installation with the visual birefringence registration technique was used to measure Kerr effect in LC solutions[4]. AC electric field at 40 kHz freguency with the amplitude up to 2 kV was applied to glass cell 2 cm in length along the optical light path. The Kerr cell had a form of glass tube with welded plane-parallel titanium electrodes, and with the gap between the latter equal to 0,05 cm. A thin mica elliptical compensator with the intrinsic optical phase difference of 0,01 2π was used for the registration of electrical birefringence.

Molar Kerr constants of the samples were calculated according to the following relationship:

$$K_M = \frac{\delta n_1}{(n_1^2+2)^2(\varepsilon_1+2)^2} \cdot \frac{M}{\rho_1} \cdot \frac{(K_{12}-K_1)}{W} \qquad (1)$$

where n_1, ε_1, ρ_1 are the refractive index, dielectric permittivity and density of the solvent; M is the molecular weight of the solute, and W is its weight fraction in the solution. $(K_{12}-K_1) = (\Delta n_{12} - \Delta n_1)/E^2$ is the surplus birefringence value of the solution regarding to the solvent, devided by the squared electric field strength, E^2. From now on subscripts 12 refer to the solution; 1 and 2 refer to the solvent and solute, respectively. The values of $(K_{12} - K_1)$ were determined from the slopes of the experimental dependences $\Delta n_{12}=f(E^2)$ for the samples solutions, excluding the solvent's effect $\Delta n_1 = f(E^2)$. All dependences of electric birefringence values Δn vs squared electric field strength, E^2, were linear in accodance with the Kerr law. The experimental dependences $(K_{12} - K_1)$ vs W for some samples in benzene are presented in Figure 1. Table 2 contains K_M values of the

investigated LC samples; the dipole moments μ of the same samples, measured by Guggenheim-Smith method[5], are presented here too.

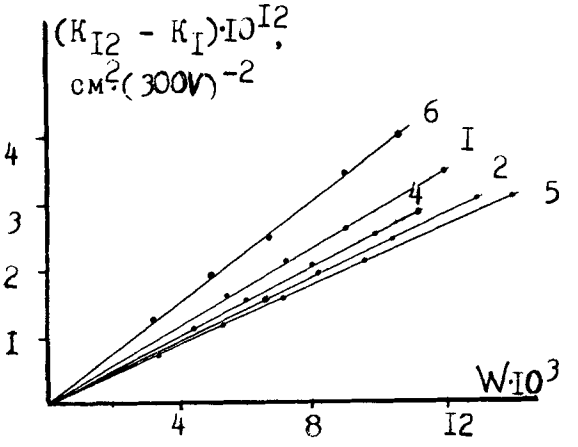


FIGURE 1 The dependences of Kerr constants $(K_{12}-K_1)$ vs W for the samples NN 1,2,4-6 in benzene.

According to [5], the dipole moment of the soluted substance may be determined from the concentrational dependences of its solution dielectric permittivity ε_{12} and refractive index n_{12}:

$$\mu^2 = \frac{27kT}{4\pi N_A} \cdot \frac{M}{\rho_1(\varepsilon_1+2)^2} \left(\frac{\varepsilon_{12}-\varepsilon_1}{W} - \frac{n_{12}^2-n_1^2}{W} \right) \quad (2)$$

Here k is Boltzmann constant, N_A is the Avogadro's number, T is absolute temperature.

The experimental dependences $(\varepsilon_{12}-\varepsilon_1)$ vs W and $(n_{12}^2-n_1^2)$ vs W of all the investigated LC solutions were linear functions in the concentration's range $W = (0,4 : 2,5)10^{-2}$. The dielectric permittivities of solutions, ε_{12}, were measured by means of zero beats technique at 700 kHz frequency of the standard capacity metter; a titanium cylindric capacitor with its own capacity ϕ2,86 pF was used. The refractive indices, n_{12}, were determined on refractometer IRF-23 using the line, corresponding to the wavelength λ = 5780 Å.

RESULTS AND DISCUSSION

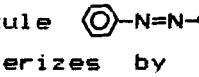
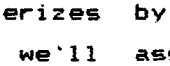
The comparison of the experimental μ values of investigated LCs permits to conclude that the presence of

TABLE 2 The electrooptical and dipole characteristics of the samples.

N	$K_M \cdot 10^9$ $cm^5/(300V)^2$	μ D	$\Delta b \cdot 10^{25}$ cm^3	β^o	$\Delta\varepsilon$ at $\Delta T=-5^oC$
1	11,6	6,2	190	0	-
2	3,6	5,3	190	30	-
3	3,4	5,3	190	30	+8,5
4	4,3	5,5	150	20	+6,5
5	3,8	5,4	170	30	+6,0
6	3,5	5,3	170	30	+6,0
7	3,2	5,2	170	30	+6,5
8	7,0	6,1	135	10	+15
9	0,7	4,4	120	45	+4,5
10	11,0	5,8	230	0	+8,0
11	0,1	3,7	210	56	-0,2
12	6,9	7,1	170	10	+16
13	3,9	5,4	180	30	+8,5

aliphatic spacer always decreases the dipole moment of LC substances. The dipole moment's change is more significant when spacer separates the polar CN-group from the mesogeneous core of molecules (N 8-13), than when it divides the molecules in high- and weak-polar parts(N 1 - 7). At the last case it can be mentioned the conversion of structure N1 to NN 2,3, and the influence of the benzene cycle change to cyclohexane one in the sample N4. Apparently, the alteration of LC molecules polarity after the including of normal aliphatic spacers, mentioned above, may be connected with the rotation degree increase of one molecular part relatively its other part, which

leads to change of mutual arrangement of the polar bonds in molecule, and, as a result, change off its total dipole moment.

In the case, when the spacer separates CN-group from the main chain of the molecule, it is possible to estimate the free orientation degree of this polar group. It is known that azobenzene molecule  does not have a dipole moment and characterizes by a "trans"-position relatively N=N bond[6]. If we'll assume that the same conformation is corresponded to the mesogeneous core of LC N 11, it will be possible to present the dipole moment of this substance as a sum of two group's dipole moments:  (μ = 1,28 D) and CH_3-CN (μ = 3,4 D)[6], combining with each other by a chain of four CH_2-groups. Assuming the rotation around the valent bonds in methylenous chain as fully free, we can calculate the mean value of LC N11 dipole moment $\bar{\mu}$ with the Eyring's formula[7]:

$$\bar{\mu}^2 = \sum_{i=1}^{n} \mu_i^2 + 2 \sum_{i=1}^{n} \sum_{s<i} \prod_{k=i}^{s+1} \cos \Theta_k \, \mu_i \, \mu_k \qquad (3)$$

where μ_i is the group's dipole moment values; $\cos \Theta_k \mu_i \mu_k$ is the couple product of these dipole moment values and the cosines of all angles Θ_k, on which the valent bonds, connecting the given pair of dipoles, change their directions along the molecular chain.

Using Eq.(3), mentioned above the group dipole moment values, and $\Theta_k = 109^{\circ}28'$[7], we have calculated $\bar{\mu}$ = 3,7 D for the sample N11, which is equal to its experimental value. This coincidence means that the methylenous chain of four CH_2- groups can ensure a practically fully free rotation of CN-end- group in the sample N11. The latter fact is completaly in accordance with the properties of freely joined polymer chains with the remained angles between the valent bonds[7].

By the similar way it may be estimated $\bar{\mu}$ values for the samples N9, 13, using the evaluations of their mesogeneous core dipole moments from the data for the

samples without spacers in molecular chains (N8,12). For the sample N9 $\bar{\mu}$ = 4,5 D is near the experimental μ value. For the sample N13 $\bar{\mu}$ = 4,4 D is noticeably smaller than the corresponding experimental μ value (5,4 D).Thus, it is possible to say about the existance of correlation between polar CN-group and the main molecular chain for this LC.

The data of the Table 2 also show that the decrease of the intermolecular orientational correlations of the polar groups in LCs under investigation leads to more significant molar Kerr constants' change in comparison with their dipole moments' change. So, when μ values alterate on one and half with the appearence of the spacer (see N8 and N9, N10 and N11), the molar Kerr constant of these samples change by an order. The dramatical change of this electrooptical characteristic is connected with the fact that K_M depends not only on the dipole moment μ values, but also on the angle β , which the dipole moment forms with the molecular axis of the greatest polarizability. According to Langevin-Born theory for axiallysymmetric molecules it is just right[4]:

$$K_M = \frac{2\pi N_A}{9} \cdot \frac{\Delta b}{45kT} \cdot \left[2\Delta a + \frac{\mu^2}{kT}(3\cos^2\beta - 1) \right] \qquad (4)$$

where Δa and Δb are the anisotropies of electrical and optical polarizabilities.

It is obvious, that under the condition of full or partially full rotation of polar groups in the molecule, the value of angle β has a sense of the "mean" or "effective" angle between the dipole moment direction and the molecular axis of the greatest polarizability. The values of the angles β, calculated according to Eq.(4), and the experimental magnitudes of K_M, Δb and μ of the investigated samples are presented in the Table 2. Situated here Δb values (Δa had been taken equal to Δb) were determined using the anisotropy of molar refraction values $\Delta R = [(n_e^2-1)/(n_e^2+2) - (n_o^2-1)/(n_o^2+2)]M/\rho$ in nematic LCs phase. The refractive indices of ordinary n_o and

extraordinary n_e rays were measured by means of the prism method[8].

As it was mentioned, the most considerable changes of K_M and β values take place for the samples N9 , 11 (in comparison with the samples without spacers in their structures), where CN- polar group orientates practically free relatively the main molecular chain. For the LC N13 with the partially correlated CN-group motion, the change of K_M and β values are smaller in comparison with LC N12. So, in the case when the spacer separates CN-group from the main molecular chain, the direct dependence of electrooptical and dipole characteristics on spacer's length takes place.

The range of cyanobiphenyl esters (LCs N1-7) did not displaces practically significant dependence of the characteristics under investigation on the spacer length.

The differences between the polar structures of the samples are strongly reflected in the dielectric properties of the mesomorphous substances. The measurements of macroscopic dielectric anisotropy $\Delta\varepsilon = \varepsilon_{//} - \varepsilon_{/}$ of uniformly oriented nematic samples by determining of the main values of dielectric permittivities $\varepsilon_{//}$ and $\varepsilon_{/}$ in 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 the investigated LCs directly depend on μ and β (Table 2), in accordance with the theory of dielectric anisotropy of nematics[9]:

$$\Delta\varepsilon = 2\pi N_A (\rho/M) F \cdot G \cdot [2\Delta a + G(\mu^2/kT)(3\cos^2\beta - 1)]S \quad (5)$$

where F and G are the internal field factors in Onsager's theory, ρ is the density, and S is the order degree of mesophase.

According to Eq.(5), the positive $\Delta\varepsilon$ will decrease with the μ decreasing and β increasing, and changes its sign to negative one when the value of the angle β is $> 55^o$. The

same character takes place for the relative experimental data in the Table 2.

It must also be mentioned that the presence of aliphatic spacer in LC molecules influences on the dielectric relaxation of LCs. The Figure 2 shows the frequency dependences of the dielectric permittivity $\varepsilon_{//}$ and Cole-Cole diagrams for two LC samples (as an example). The similar dispersion curves were received for all the samples.

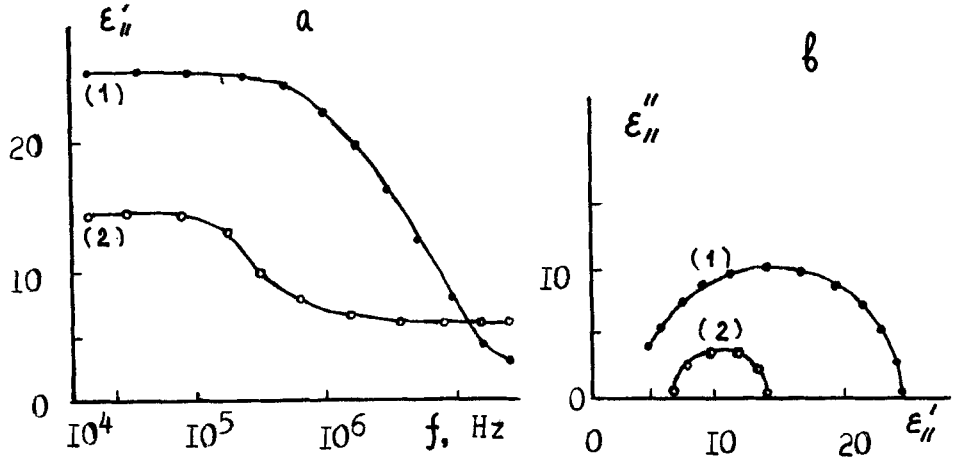


FIGURE 2 a- The frequency dependences of the main dielectric permittivities $\varepsilon'_{//}$ for LC N8 (1) and N9 (2) at $\Delta T = -5^{\circ}C$; b- the Cole-Cole diagrams for the same samples at the $\Delta T = -5^{\circ}$.

These results have shown that the relaxation curves are the Debye curves:

$$\varepsilon_{//} = (\varepsilon_{//})_1 + \frac{(\varepsilon_{//})_0 - (\varepsilon_{//})_1}{1 + (2\pi f\tau)^2} \qquad (6)$$

Here $(\varepsilon_{//})_0$ and $(\varepsilon_{//})_1$ are the low- and high-frequency limits of the dielectric permittivity $\varepsilon_{//}$, f is the electric field frequency. Each of these curves corresponds to one time of the dipolar relaxation τ at the used frequency range. The latter fact implies that for all the investigated LCs there is only one mechanism of dipolar

relaxation, related to the rotation of polar molecule around its short axis.

The temperature dependences of relaxation times τ, determined by the Eq.(6), are shown in the Figure 3.

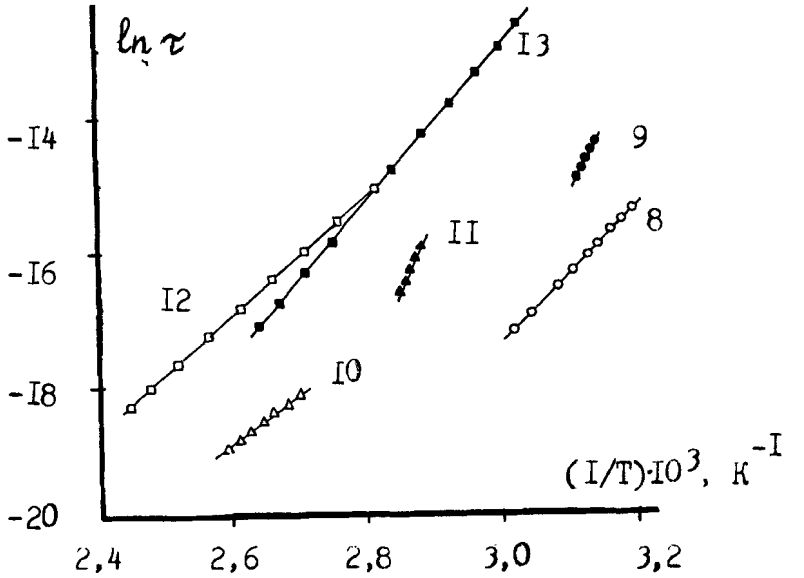


FIGURE 3 The temperature dependences of relaxation times τ for the samples N8-13.

The distinction of relaxation times, in the first turn, may be explained by the distinction of the samples' viscosity. In connection with this the translation viscosity η of the samples in mesomorphous state were measured. The viscous characteristics of the sample N12 (without spacer) and N13 (with two CH_2- groups-spacer-length) differ practically the same manner as their relaxation times. But for the samples N11 (with four CH_2-groups in the chain, η = 105 cP at $\Delta T = T-T_C=-2^oC$, where T_C is the transition temperature) and N10 (without spacer, η = 21 cP at the same ΔT) the viscosity values differ only on five fold when their τ distinguish on an order. That means that the relaxation time difference for the samples N10 and N11 can not be explain only the viscosity change. As well as the rotation of polar molecules around the

short axis is connected with the passing of the potential barrier, which is responsible for the long distance orientational order in LC substance, it is possible to associate the difference of relaxation times with the difference of order degree in the samples under investigation[3]. The latest is testified by the activation energy data too. So, the activation energy of molecular rotation around the short axis, U, for the sample N10 U = 37 kcal/mol, and U = 20 kcal/mol for the sample N11.

Thus, the experimental data of this work clear shows that the including of methylenous spacers into LCs may significantly influence on the polar structure of LC molecules, as well as on the value and sign of dielectric permittivity, and also strongly change the dispersion regions of macroscopic dielectric anisotropy.

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