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ELECTRO-OPTICAL PROPERTIES AND POLAR STRUCTURE OF LIQUID CRYSTALLINE PHENACYL ESTERS

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Abstract Kerr-constants and dipole moments in solutions of liquid crystalline phenacyl esters of different carboxylic acids were measured. On the base of experimental data the influence of the changes in esters chemical structure to ones properties are discussed.

INTRODUCTION

Polarity of liquid crystal (LC) substances' molecules is an important factor in forming of their macroscopic dielectric properties determining the possibility of their practical utilization. That is why establishing the dipolar structure of new mesogenous substances is an integral part of solving the problem posed by purpose-oriented synthesis of LC.

The aim of the present work was to determine magnatude and orientation of the constant dipole moment for a range of new thermotropic LC, as well as clarify the influence that changes in chemical structure of molecules have on their dipolar and electro-optic characteristics.

EXPERIMENTAL

Nine samples of phenacyl esters of various carboxylic acids with bridging $-CH_2-$ groups between acidic and ketone parts of molecules were studied (see Table, sample synthesis described[1]). Electric birefringence (Kerr effect) and dielectric permittivity have been measured in diluted solutions of the samples in benzene. Dipole moment μ of LC samples were determined by Guggenheim-Smith technique based on the analysis of concentration dependence of dielectric permittivity ε and refrective index n displayed by the solute:

$$\mu^2 = \frac{27kT}{4\pi N_A} \frac{1}{\rho_1(\varepsilon+2)^2} \left(\frac{\varepsilon_{12}-\varepsilon_1}{W} - \frac{n_{12}^2 - n_1^2}{W}\right) M_2 \qquad (1)$$

where N_A - Avogadro number, k - Boltzmann's constant, T - absolute temperature, ρ - density, M and W - molecular weight of the solute and its weight fraction in solution. From now on subscripts 12 refer to the solution, 1 and 2 - to solvent and solute, respectively. Solvent's characteristics at T= 21°C, where all measurements have been performed: ε_1= 2,2825; n_1= 1,5018; ρ_1= 0,879 g/cm^3.

TABLE 1 Dipolar and electro-optical characteristics of phenacyl esters.

N	Structural formula	$\Delta b 10^{25}$ cm^3	$K_M 10^{10}$ (CGSE)	μ D	μ_{th} D	β°
1	$H_{15}C_7$-Ph-COO-CH_2-C(=O)-Ph-C_6H_{13}	135	2,0	2,3	2,8	49
2	$H_{13}C_6$-Ph-COO-CH_2-C(=O)-Ph-OC_8H_{17}	175	-1,5	3,6	3,0	56
3	$H_{17}C_8O$-(F)Ph-COO-CH_2-C(=O)-Ph-C_6H_{13}	175	3,2	3,3	3,6	51
4	$H_{17}C_8O$-(F)Ph-COO-CH_2-C(=O)-Ph-O$C_{10}H_{21}$	215	-3,8	4,1	3,9	61
5	$H_{13}C_6$-Ph-COO-CH_2-C(=O)-(F)Ph-OC_8H_{17}	175	-1,3	3,6	2,8	59
6	H_9C_4-Ph-COO-CH_2-C(=O)-Ph-Br	110	-1,3	2,6	2,4	65
7	H_9C_4-Cy-COO-CH_2-C(=O)-Ph-Br	80	-1,3	2,5	2,4	67
8	H_7C_3-Cy-Ph-COO-CH_2-C(=O)-(F)Ph-OC_8H_{17}	200	-10,7	3,7	2,8	75
9	$H_{17}C_8O$-(F)Ph-COO-CH_2-C(=O)-Ph-Cy-C_3H_7	200	6,8	3,3	3,6	47

The experimental μ values were determined with error $\pm$ 0,1 D.

Dielectric permittivity of solutions, ε_{12}, was measured by means of zero beats technique at 700 kHz frequency of a standard capacity meter. Titan cylindric capacitor with intrinsic capasity of 92,87 pF served as the measuring cell. Refractive indices were determined on refractometer IRF-23 using the line corresponding to the wavelength λ= 5780 Å Hg.

Apparatus with visual birefringence registration was

used to measure Kerr effect in LC solutions.[2] Measurements were performed in a sine-like electric field at 40 kHz frequency with the strength of AC field, E, up to $5 \cdot 10^5$ V/cm in the cell 2 cm in length along the optical ray path. The cell had the form of a glass tube with welded plane-parallel titan electrodes, with the gap between the latter equal to 0,05 cm. Butt ends of the tube were close off by the thin quartz glass wafers without tension. A thin mica elliptical compensator with intrinsic optical phase difference of 0,01 2π was used to register Kerr effect.

Molar Kerr constants of substances under investigation, K_M, were determined by means of the following relationship:

$$K_M = \frac{6n_1}{(n_1^2 + 2)^2(\varepsilon_1 + 2)^2} \frac{M_2}{\rho_1} \frac{(K_{12} - K_1)}{W} \qquad (2)$$

where $(K_{12}-K_1)/W$ - slope of the dependance of birefringence, Δn, divided by squared electric field strength, E^2, $(\Delta n_{12}/E^2 - \Delta n_1/E^2) = K_{12} - K_1$, on the weight fraction of the solute, W, with the solvent influence substracted. Experimental dependences $(K_{12}-K_1) = f(W)$ for some of the samples are presented in Fig.1.

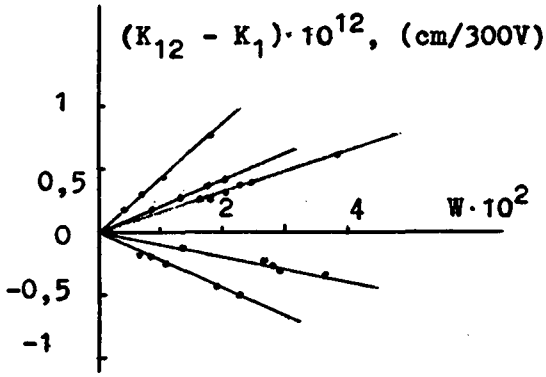


FIGURE 1 Experimental dependences $(K_{12}-K_1) = f(W)$ for the samples N 1,2,3,5,9.

According to Langevin-Born theory, following equation links the molar Kerr constant to parameters of polar anisotropic axially-symmetric molecules:

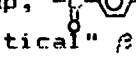
$$K_M = \frac{2\pi N_A}{9} \frac{\Delta b}{45kT} \left[2\Delta b + \frac{\mu^2}{kT} (3\cos^2\beta - 1) \right] \quad (3)$$

where Δb - magnitude of molecule's optical polarizability anisotropy, β - angle between orientation of the constant dipole moment, μ, and the axis of the molecule's greatest polarizability[3]. Values Δb were determined basing on molar refractions' anisotropy of samples in nematic phase. Refractive indices of ordinary and extraordinary rays were measured by means of prism method[4]. Experimentally determined Δb and values β calculated according to (3) are are presented in the table.

DISCUSSION

Data presented in the table show that within a relatively small variation range of dipole moments magnitude, μ = (2,3 - 4,1)D, besides molar Kerr constants' magnitude varying dramatically (several fold), it changes its sign as well. Such a change in molecular chemical structure as substitution of the end group $-C_nH_{2n+1}$ for $-OC_nH_{2n+1}$ in the ketone part of esters increases their dipole moment (compare samples N1 and N2, as well as N3 and N4), and significantly affects angle β, a circumatance resulting in sign reversal of molar Kerr constants when one goes from N1 to N2, and, respectively, from N3 to N4, since β passes through its "critical" value (54,7°) and the second term of eq.(3) turns negative. Introducing fluoride atoms as side substitutes into the chains of studied esters has a considerably lower impact on their dipole characteristics than substitution of the end groups (compare N2 and N5). Comparison between data obtained for samples N1 and N6 makes it possible to conclude that while substituting brome atom for alkyl group will only slightly increase dipole moment of the ester, such a change will alter its orientation angle with respect to the greatest polarizability axis (from 49°to 65°), and cause the sign of molar Kerr constant to tern from positive to negative. Exchanging benzene ring for cyclohexane one in the course of going from sample N6 to N7 vertually does not

affect the dipole characteristics of the molecules. Adding the additional cyclohexane rings into the chains of phenacyl esters has practically no influence on values of μ (compare N8 and N5, N9 and N3), while significantly raising the magnitude of K_M, which is primarily linked to change in angles β of those molecules.

Changes in polar characteristics of phenacyl esters, indicated above, are caused, evidently, by specifics of their dipolar structure. First of all, one should mention the fact that that angle θ, the one between dipole moment of the most polar among the molecules making the benzacyl group,  , and para-axis of benzene ring, is close to "critical" β value ($\theta = \pi - 132^\circ$)[5]. That is why the angle between the total dipole moment of ester molecule, to which this group moment makes the greatest contribution, and the axis of the molecule's greatest elongation can, depending on the environment, easily swing either way in respect to the critical value of 54.7°, thus causing molar Kerr constant of the substances to change its sing.

In order to draw comparison between data obtained and the actual struture of investigated samples, a theoretical of dipole moments' magnitude has been performed for the studied samples. Calculation used the vector additive scheme basing on the known dipole moments of groups constituting their molecules. Two -dimentional case was considered, following general formula was used

$$\mu = [(\sum_{i=1}^{n} m_{xi})^2 + (\sum_{i=1}^{n} m_{yi})^2]^{1/2} \qquad (4)$$

where m_{xi} and m_{yi} - projections of dipole moments of polar groups on chosen axes, n- the number of polar groups in the molecule. The following group dipole moment values and its angles θ with the para- benzene rings axis had been used: C_6H_5-$COOCH_3$ μ = 1,83D ; $\theta = 110^\circ$; C_6H_5-$COCH_3$ μ =2,96D; $\theta = 132^\circ$; C_6H_5-F μ = 1,47D; $\theta = 0^\circ$; C_6H_5-Br μ =1,57D; $\theta = 0^\circ$; C_6H_5-CH_3 μ =0,37D; $\theta = 0^\circ$; C_6H_5-OCH_3 μ= 1,28D; $\theta = 72^\circ$.[5] All conformations of mesogenous nuclei of ester molecules, realized under assumption of free rotation around para-axes

of benzene rings and bridging $-CH_2-$ groups, were considered of equal probabilities. Thus, μ_i were calculated for each specific molecular conformation according to formula (4), and then averaged over the number possible conformations. Values μ_{theor} calculated under the described assumptions for all of the investigated LC are presented in the table.

Comparison with respective experimental characteristics enables to conclude that they agree sufficiently well for samples N3,4,6,7,9, with the difference growing for samples N1,2,5 and 8, though still confirming the overall pattern of variations induced in dipole moments of esters by changes in their chemical structure. The fact that $\mu_{theor} > \mu_{exp}$ for samples N2,5,8 may indicate that some conformation types are preferred for these molecules.

Performes analysis of phenacyl ester's polar structure demonstrates that inserting the fluoride atoms into various parts of ester molecule affects the rotational freedom of molecular chains in different manner. Thus the presence of fluoride atom in acidic part of ester molecules virtually does not hinder the total freedom of rotation around para-axes of benzene rings and $-CH_2-$ groups (samples N3,4,9). On the contrary, quantitative agreement between experimental and theoretical values of dipole moment can be achieved only when allowances are made for significant retardation of rotation in molecular chains (N5 and 8).

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