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Kerr-effect in solutions and molecular polarity of liquid crystalline fluorenes

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As part of a broader study of liquid crystal polymers with side groups containing fluorene moieties, more information was required about the properties of fluorene derivatives. With this aim in mind, the solution Kerr-effects for five fluorene-based mesogens have been measured and used in conjunction with other results to determine the polarizability anisotropies and dipole moments.

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1. Introduction

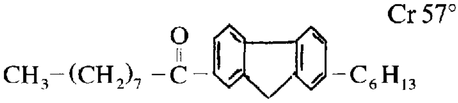
Examination of correlations between molecular structure and macroscopic physical properties of mesomorphic phases is one of the main problems of the physics of liquid crystals (LC). Because of this, the determination of the molecular characteristics of a LC material is an important step in the process of reaching a general understanding of the LC behaviour of new types of LC substances (including LC polymers) and, as usual, this determination is carried out using solutions of LC materials in organic solvents. Our work is dedicated to an on-going study of LC materials based on fluorene derivatives which have previously not been studied in detail [1–4].

Electro-optical properties of thermotropic liquid crystals are defined by their electrical conductivity, macroscopic dielectric anisotropy and elastic-viscosity. The electrical conductivity of a mesomorphic substance mainly depends on the ion impurity content, so it may be easily regulated by doping or purification of the LC sample. The dielectric anisotropy is closely connected with the value and direction of the molecular permanent dipole moment of the LC substance. That is why the determination of dipolar characteristics is very important in connection with the possibility of successful synthesis of new LC substances having particular, required electro-optical properties.

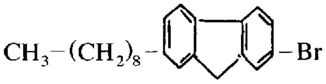
In the present work, the results of electro-optical investigations of five fluorene derivatives with different polar substituents are reported. These substances produce smectic phases of different modifications (S_A, E), between the crystalline (Cr) and isotropic (I) states. The molecular structures of the samples under investigation and their phase transition temperatures are presented below:

(1) 2-Nonyl-7-propionylfluorene Cr 80°C S_A 105°C I

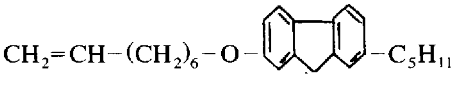
(2) 2-(4-Methylpentyl)-7-nonanoylfluorene Cr 57°C S_A 98°C I



(3) 2-Brom-7-nonylfluorene Cr 31°C S_A 80°C I



(4) 2-Pentyl-7-(7-octenyloxy)fluorene Cr 71°C E 86°C S_A 92°C I



(5) 2-Pentyl-7-(8-decenoyloxy)fluorene Cr 73°C S_A 79°C I

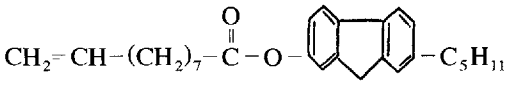


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Table 1. Optical, electro-optical and dipole characteristics of LC fluorenes.

	$\Delta b \times 10^{36}$ /F m^2	$\frac{\varepsilon_{12}-\varepsilon_1}{W}$	$\frac{n_{12}^2-n_1^2}{W}$	$\frac{(K_{12}-K_1)\times 10^{20}}{W}$	$K_M \times 10^{25}$ /m^5 V^{-2}	$\mu \times 10^{30}$ /C m	β/°	μ/β (calculated)
1	180	3·68	0·213	14·5	15·6	11·7	32	—
2	180	3·69	0·190	12·0	14·5	12·3	36	—
3	220	1·49	0·230	11·1	12·8	8·0	24	8·7/21
4	145	0·812	0·180	0·5	0·5	4·7	60	—
5	145	0·920	0·138	0·2	0·3	5·7	60	6·0/60

The synthesis and some other properties of the LCs investigated were reported earlier [1–4].

2. Experimental

Electric birefringence (Kerr-effect), dielectric permittivity and refractive indices were measured using dilute solutions of the samples in benzene (density $\rho = 0{\cdot}879 \times 10^3$kg m^{-3}, refractive index $n = 1{\cdot}5008$, relative dielectric permittivity $\varepsilon = 2{\cdot}2786$ at 22°C). All the measurements were made in the concentration range $10^{-4} < W < 2{\cdot}1 \times 10^{-2}$ (W = weight-fraction of the solute).

The dielectric permittivity (ε_{12}) of the solution was measured, with the frequency of the capacitance set at 700 kHz, using a zero beat (resonance) technique. A cylindrical titanium capacitor with intrinsic capacity 98·9 pF served as the measuring cell. Refractive indices of LC solutions (n_{12}) were determined with an IRF-23 refractometer using the mercury green line.

Molecular dipole moments μ were calculated according to the Guggenheim–Smith method [5]:

$$\mu = \frac{27kT}{45\pi N_A} \frac{M_2}{\rho_1(\varepsilon_1+2)^2} \left(\frac{\varepsilon_{12}-\varepsilon_1}{W} - \frac{n_{12}^2-n_1^2}{W} \right) \qquad (1)$$

where N_A = Avogadro's number, k = Boltzmann's constant, T = absolute temperature, and M_2 = the sample molecular weight. Experimentally determined from the slopes of the linear dependences $(\varepsilon_{12}-\varepsilon_1) = f(W)$ and $(n_{12}^2 - n_1^2) = \phi(W)$, the dielectric $(\varepsilon_{12}-\varepsilon_1)/W$ and optical increment $(n_{12}^2-n_1^2)/W$ values are presented in the table 1. Molecular dipole moments μ of the investigated samples are also presented here.

A visual technique for registering the optical birefringence was used to measure the Kerr-effect for the LC solutions [6]. The measurements were performed in the cell (2×10^{-2}m in length along the optical light path) using an a.c. electric field of 40 kHz frequency. The cell had the form of a glass tube with welded plane-parallel titanium electrodes, with a gap between the latter of $0{\cdot}01 \times 10^{-2}$m. A thin mica elliptical compensator with an intrinsic optical phase difference of $0{\cdot}01 \times 2\pi$ was used.

Molar Kerr constants (K_M) of the substances under investigation were determined by means of the following expression [7]:

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

where $(K_{12}-K_1)$—independent of the solvent's electrical birefringence Δn is related to the square of the electrical field strength, E^2; K_{12} and K_1 were determined from the slopes of the experimental dependences $\Delta n = f(E^2)$. These had a linear character in accordance with Kerr's law. The a.c. field strength, E, was varied up to 3×10^6V m^{-1}. Values of $(K_{12}-K_1)/W$ and K_M for all the fluorenes are presented in table 1.

The anisotropy of the molecular deformational polarizability was determined by measuring the refractive index, n_{is}, of the LC material in the isotropic phase and the refractive index of the ordinary ray n_o in the smectic phase. For this purpose, the prism method was used [8]. The values of n_{is} and n_o (for $\lambda = 5460$ nm) at different temperatures are presented in table 2.

Using these data, molar refractions, R_{is} and ΔR, anisotropies of refraction, were calculated by means of

Table 2. The refractive indices of LC fluorenes in their LC and isotropic phases at different temperatures $\Delta T = T_C - T$ (T_C = transition temperature from LC to isotropic phase).

	1	2	3	4	5
ΔT			n_o		
−1	1·496	1·491	1·503	1·495	1·489
−5	1·497	1·492	1·495	1·496	1·490
−10	1·498	1·494	1·494	1·500	—
−15	1·499	1·495	1·494	1·501	—
−25	—	—	1·497	—	—
			n_{is}		
0	1·556	1·544	1·571	1·544	1·567
10	1·552	1·540	1·567	1·540	1·528

the relationships:

$$R_{\mathrm{is}}=\frac{n_{\mathrm{is}}^2-1}{n_{\mathrm{is}}^2+2}\frac{M}{\rho}=\frac{1}{3}(R_{\mathrm{e}}+R_{\mathrm{o}}) \qquad (3)$$

$$\Delta R=R_{\mathrm{e}}-R_{\mathrm{o}}=3(R_{\mathrm{is}}-R_{\mathrm{o}})=\left(\frac{n_{\mathrm{is}}^2-1}{n_{\mathrm{is}}^2+2}-\frac{n_{\mathrm{o}}^2-1}{n_{\mathrm{o}}^2+2}\right)\frac{M}{\rho} \qquad (4)$$

where R_{o} and R_{e} = molar refractions of the ordinary and extraordinary rays, M = molecular weight, and ρ = density of the LC substance.

The anisotropy of molar refraction of the mesophase ΔR is related to the molecular anisotropy of the optical polarizability Δb and an order parameter, S, of the mesophase by the equation:

$$\Delta R=\frac{4}{3}\pi N_{\mathrm{A}}\Delta bS \qquad (5)$$

Taking into consideration equations (3)–(5) and using $S=0{\cdot}85$ (which is typical for smectic LCs [9]), Δb values have been estimated (see table 1).

The angles β between the dipole moment direction and the principal axis of the molecular polarizability were estimated from the Langevin–Born theory for axially-symmetric molecules using the equation

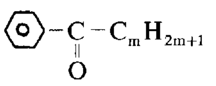
$$K_{\mathrm{M}}=\frac{2\pi N_{\mathrm{A}}}{9}\frac{\Delta b}{45kT}\left[2\Delta\alpha+\frac{\mu^2}{kT}(3\cos^2\beta-1)\right] \qquad (6)$$

The equality of the electrical ($\Delta\alpha$) and optical (Δb) anisotropy of polarizability has been assumed.

3. Discussion

Experimental data presented in table 1 show that the LC fluorenes investigated have essentially different polar characteristics. This is manifested in the dipole moment values, and also in the values of the molar Kerr constants. The latter characteristic for the first three samples varies by an order of magnitude from that for the last two.

For a correlation of the experimental results with the real molecular structures, molecular dipole moments and their directions have been calculated using well-known group dipole moments and applying the additivity principle. Under these conditions, LCs with acceptor- (N1-3) and donor- (N4,5) substituents in the fluorene ring system were examined separately: this helped us to estimate the conjunction effect on the total dipole moment of the LC. On the assumption that the experimental dipole moment value for samples N1,2 is the sum of the group dipole moments of compounds **I** and **II**



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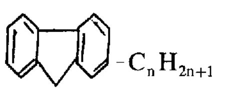

II

Knowing that $\mu=9{\cdot}87\times10^{-30}$C m for compound **I** ($m=1$) and the angle of its slope relative to the *para*-axis of the benzene ring is 132°, it is possible to evaluate the dipole moment of compound **II** [10] as $\mu\cong3{\cdot}33\times10^{-30}$C m and the angle ($\theta$) of its slope relative to the axis a, which is selected as the axis of molecular symmetry, $\theta\cong14°$ (figure 1). For the sample N3, μ and β values have been calculated in the same way, but using the group dipole moments of compound **II** and brombenzene ($\mu=5{\cdot}23\times10^{-30}$C m, the angle of the slope to the axis a, $\theta=24°$) [10, 11]. These results are given in the last column of table 1.

Analogous estimations of the conjunction effect for sample N4 with a polar donor substituent in the fluorene ring system had led to the following results for compound **II**: $\mu\cong1\times10^{-30}$ C m, $\theta\cong4°$. The group dipole moment of ⊙–OCH_3 is $\mu=4{\cdot}27\times10^{-30}$C m and the angle of its slope to the *para*-axis of the benzene ring was taken as 72° [10]. For sample N5, μ and β values were obtained using the evaluations of μ and β for compound **II** and the group dipole moment of ⊙–$COOCH_3$ ($\mu=5{\cdot}63\ 10^{-30}$ C m, the slope to the *para*-axis of the benzene ring is 66°) [10] (see table 1).

Sufficiently good agreement between the experimental and calculated μ and β values for samples N3 and N5 may indicate that the chosen direction of the symmetry axis a (figure 1) is close to the real direction of the greatest polarizability in LC fluorenes.

Thus, the experimental data presented show that the polar structure of LC fluorenes is determined by the dipole moments of the donor- or acceptor-substituents. The experimental determination of the dipole moment direction in these substances permits us to suppose that the macroscopic dielectric anisotropy will change in sign, being positive for the first three compounds (N1-3) and negative for the last two (N4,5) [6]. The molecular characteristics which we have determined may be used in future analyses of the dielectric and electro-optical

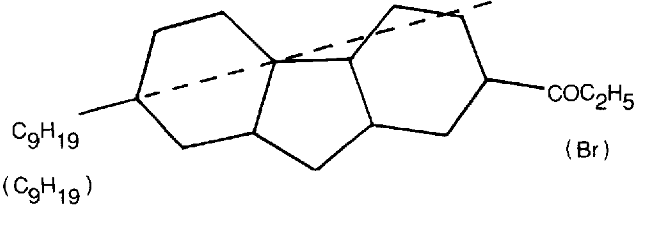

Figure 1. Molecular structure of 2-nonyl-7-propionylfluorene (and 2-nonyl-7-bromofluorene) showing (dashed line) the molecular symmetry axis (a).

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properties of low molecular mass and polymeric LCs based on fluorene derivatives.

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