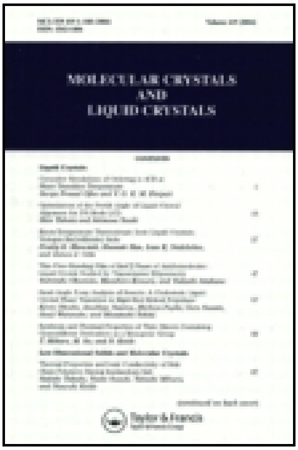

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THE SMECTIC A LIQUID CRYSTAL ELECTROCONDUCTIVITY ANISOTROPY AND ITS CONNECTION TO A MOLECULAR STRUCTURE

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Abstract This work studies the influence of polar and nonpolar dopants with different structures on the electroconductivity anisotropy $\sigma_\perp/\sigma_\parallel$ of the smectic A liquid crystal and establishes a relationship between the electroconductivity anisotropy and the concrete molecular structure.

INTRODUCTION

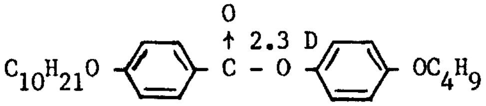
The growing interest in smectic liquid crystals is in general due to the following factors. First, various important electrooptical effects have been discovered which permit the reproduction of the optic information with a high resolving ability, a long-time memory and a great contrast, etc. in the liquid crystals[1-5].

Second, the mechanisms of the smectic liquid crystal effects have not been revealed in full. The mechanism and characteristics of the electrooptical effects are in general determined by such important smectic liquid crystal parameters as the electroconductivity anisotropy $\Delta\sigma=\sigma_\parallel-\sigma_\perp$ and the dielectric anisotropy $\Delta\varepsilon=\varepsilon_\parallel-\varepsilon_\perp$ ($\varepsilon_\parallel$ and $\varepsilon_\perp$ are the components measured parallel and perpendicular to the initial orientation of the long molecular axis).

That is why it is important to determine these general parameters. In order to change the dielectric anisotropy a liquid crystal is doped by a suitable dopant. In this case an additive law – $\Delta\varepsilon=\Sigma c_i \Delta\varepsilon_i$ is valid[6]. The increase of the electroconductivity anisotropy $\Delta\sigma$ was achieved by doping with conductive dopants. A general technique ensuring the variation of $\Delta\sigma$ (in particular, the decrease) has not yet been elaborated.

Our investigations show that due to the inherent character of the smectic liquid crystal structure it is possible to vary its electroconductivity anisotropy by doping with neutral molecules, which permits to relate the smectic liquid crystals electroconductivity anisotropy to the molecular structure of the liquid crystal.

In this paper we study the influence of both polar and nonpolar dopant with different structures on the smectic A liquid crystal electroconductivity anisotropy value and we establish a relation between the electroconductivity anisotropy and the concrete molecular structure. A substrate with a structural formula has been used as a matrix:

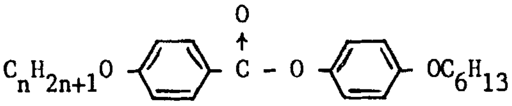


It has the following phase transition temperatures

$$C \xleftarrow{34^{o}C} S_B \xleftarrow{54^{o}C} S_C \xleftarrow{59^{o}C} S_A \xleftarrow{83^{o}C} N \xleftarrow{93^{o}C} I$$

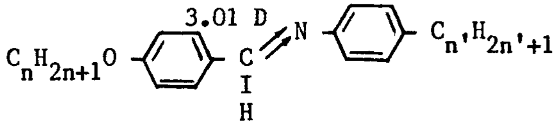
The substances with the following formulas are used as dopants:

A.



with n=7,8,9

B.

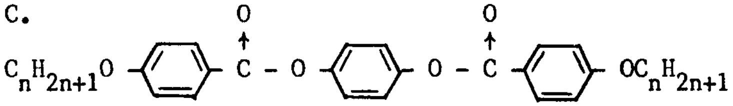


with n'=1 and n=2-7

n'=2 and n=4,6-8

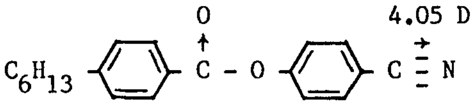
n'=4 and n=1,2,6,7

C.



with n=9-12

D.



The dopants were chosen after the following considerations:

1. in order to be a liquid crystal by its structure and its geometric form the dopant molecule should be similar to the matrix molecules. This is important for the good mixing and to form a smectic mesophase with a layered structure.

2. The dopant molecules should be distinguished by the molecular length, by the polar and nonpolar, transversal or longitudinal (central or end) molecular fragment content and by the number of the carbon atoms in the end alkyl chain. The concrete molecular fragment's dipole moment of the substance is marked by arrows on the figure.

EXPERIMENT

All the measurements have been made with a device constructed around a polarizing microscope.

A smectic A homeotropic texture with aligned smectic layers parallel to the electrooptical cell electrodes has been obtained through heating a sample until its nematic phase and the subsequent cooling into the smectic A phase or through parallel shifting of the cell glasses against each other. The suitable geometry permits to measure the components $\sigma_{\parallel}$, $\varepsilon_{\parallel}$.

A planar texture where the layers align perpendicular to the cell electrodes, has been obtained from the homeotropic-planar transition[8] which permits to measure the components $\sigma_{\perp}$, $\varepsilon_{\perp}$.

Using the above-mentioned dopants 3% (by weight) mixtures into the matrix were prepared.

The mixture parameters are measured at the temperature $t = t_{N-S_A} - 5^{o}C$ where t_{N-S_A} is a mixture phase transition from the nematic phase to the smectic A phase.

The effective area and the cell thickness are equal to 1 cm^2, and 30 μm, respectively.

The accuracy of the measuring of the phase transition and of the cell thermostabilization is $\pm 0.1^{o}C$.

RESULTS

Fig.1 shows the dependence of the nematic-smectic A (t_{N-S_A}) phase transition of the earlier-mentioned mixtures on the homologous number (n).

It is shown that the thermostability of the smectic A phase improves when increasing the dopant molecular length, which is valid for the mixtures with the dopant A (curve 1), B (curves 2,3,4). The dependence on the homologous number can be seen in dopant B (n'=1) (curve 1). In the case of the dopant C (curve 5) one notices the smectic mesophase thermostability aggravation when lengthening the alkyl chain till n=11; and at n=12 there is again an increase of t_{N-S_A} as

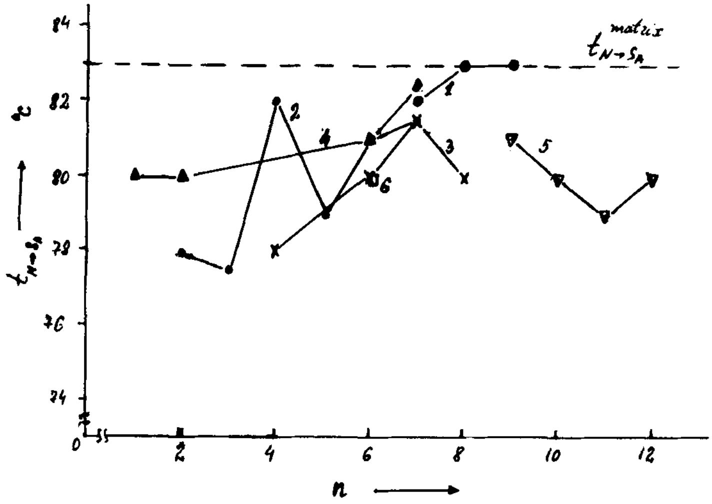


FIGURE 1. The n dependence of the nematic-smectic A phase transition temperatures for matrix + dopant mixtures: 1 - dopant A; 2 - dopant B (n'=1); 3 - dopant B (n'=2); 4 - dopant B (n'=4); 5 - dopant C; 6 - dopant D

compared with n=11. In this diagram the point 6 indicates t_{N-S_A} for the mixture with the dopant D.

Fig.2 gives the dependence of the mixtures' electroconductivity anisotropy, determined as a ratio between the electroconductivity transversal component and the longitudinal one ($\sigma_\perp/\sigma_\parallel$) on the homologous number (n) of the homologous series of the dopants.

The figure shows that $\sigma_\perp/\sigma_\parallel$ increases when n increases for the mixtures with dopant A (curve 1) and C (curve 5). But in the case of C the increase is valid as far as n=11. For n=12, $\sigma_\perp/\sigma_\parallel$ decreases unlike for n≤11.

$\sigma_\perp/\sigma_\parallel$ decreases slightly for the mixture with the dopant B (curves 2,3,4) and besides one observes the even-odd effect, when increasing the number of the homologue for

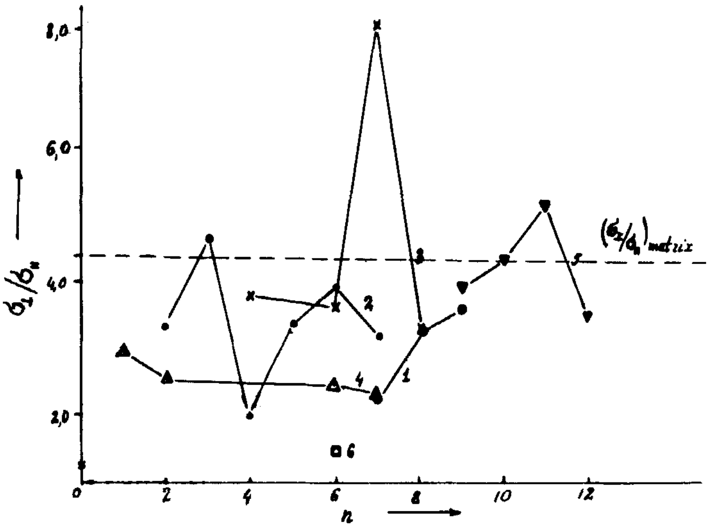


FIGURE 2. The n dependence of the electroconductivity anisotropy for mixtures matrix + dopant: 1 - dopant A; 2 - dopant B (n'=1); 3 - dopant B (n'=2); 4 - dopant B (n'=4); 5 - dopant D. All data are measured on mixtures containing 3% (by weight) of the respective dopant at a temperature 5°C below the nematic - smectic A transition temperature.

the dopant with n'=1. But for n'=2 and n=7, $\sigma_\perp/\sigma_\parallel$ takes large magnitude. We observed a strong decrease of $\sigma_\perp/\sigma_\parallel$ (point 6) for the mixture with the dopant D.

DISCUSSION

The following model can give a qualitative explanation of the experimental results obtained.

The liquid crystals are weak electrolytes whose conductivity (σ=10^{-8}-10^{-11} cm^{-1}ohm^{-1}) is essentially due to the additive ions which remain in the liquid crystal even after its careful deionization. When an electric field E is applied to a liquid crystal the ion is subjected to a local field E^*:

$$E^* = E + p/3\varepsilon_o \tag{1}$$

where ε_o is an electric constant, p is the medium polarization.

Then we take into account the permanent and induced dipole contribution in the medium polarization:

$$p = N\varepsilon_o \cdot \left(\alpha + \frac{\mu^2}{3\varepsilon_o kT}\right)E^* \tag{2}$$

where N is the concentration, α is the polarizability, μ is the permanent dipole moment of a molecule, k is the Boltzmann constant, T is the medium temperature. Furthermore, we have:

$$E^* = \left(1 - \frac{N}{3}\left(\alpha + \frac{\mu^2}{3\varepsilon_o kT}\right)\right)^{-1} \tag{3}$$

Later on we write the equation of the ion movement under an electric field E^* in the medium with the friction coefficient β:

$$m\frac{dv}{dt} = -ZeE^* - \beta v \tag{4}$$

where m is the mass, Ze is the charge, v is the ion velocity.

Let a harmonic electric field $E = E_o e^{i\omega t}$ be applied. In this case we solve the ion motion equation and use the Ohm's law $j = Zenv = \sigma E$ (where n is the ion concentration). Thus we obtain this expression for the liquid crystal electroconductivity σ:

$$\sigma = Z^2 e^2 n\beta\left[(\beta^2 + m^2\omega^2)\left(1 - \frac{N}{3}\left(\alpha + \frac{\mu^2}{3\varepsilon_o kT}\right)\right)\right]^{-1} \tag{5}$$

As the spherical forms of ions for the liquid-crystalline medium have $\beta = 6\pi\eta a$ (where a is the ion radius, η is the smectic A viscosity), and having in mind that $\beta \geq m\omega$ ($\omega \simeq 1$kHz) we find out the electroconductivity components ratio of $\sigma_\perp/\sigma_\parallel$:

$$\frac{\sigma_\perp}{\sigma_\parallel} = \frac{\eta_\parallel}{\eta_\perp} \frac{1 - \frac{N}{3}\left(\alpha^\parallel + \frac{\mu^{\parallel 2}}{3\varepsilon_o kT}\right)}{1 - \frac{N}{3}\left(\alpha^\perp + \frac{\mu^{\perp 2}}{3\varepsilon_o kT}\right)} \tag{6}$$

which is valid for a mixture with $N = N_m + N_d$ (where N_m and N_d are the molecule concentrations of the matrix and of the dopant, respectively). At small concentration of the dopant $N_d \ll N_m \cong N$ ($\eta_N^{\parallel,\perp} \simeq \eta_{Nm}^{\parallel,\perp}$) the expression (6) can be viewed as:

$$\frac{\sigma_\perp}{\sigma_\parallel} = \frac{\eta_\parallel}{\eta_\perp} \frac{1 - \frac{N_m}{3}\left(\alpha_m^\parallel + \frac{\mu_m^{\parallel 2}}{3\varepsilon_o kT}\right) - \frac{N_d}{3}\left(\alpha_d^\parallel + \frac{\mu_d^{\parallel 2}}{3\varepsilon_o kT}\right)}{1 - \frac{N_m}{3}\left(\alpha_m^\perp + \frac{\mu_m^{\perp 2}}{3\varepsilon_o kT}\right) - \frac{N_d}{3}\left(\alpha_d^\perp + \frac{\mu_d^{\perp 2}}{3\varepsilon_o kT}\right)} \tag{7}$$

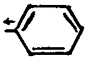
Formula (7) is a general formula expressing the relation between the smectic A liquid crystal electroconductivity anisotropy and its molecular structure. For example, this model shows that the decrease of the smectic A liquid crystal electroconductivity anisotropy ($\sigma_\perp/\sigma_\parallel$) can only be achieved after doping with its dopant consisting of molecules with great permanent longitudinal dipole moment ($\mu_d^\parallel$) or with great longitudinal polarizability ($\alpha_d^\parallel$) and with small transversal components at small dopant concentration. On the other hand, in order to increase $\sigma_\perp/\sigma_\parallel$ it is necessary to use a dopant with a great $\mu_d^\perp$ or $\alpha_d^\perp$ and with small longitudinal components of these quantities.

This model gives qualitative interpretations of the carried out experiments as (Fig.1, Fig.2).

1. The lengthening of the alkyl chain for dopant A mixtures causes a longitudinal dipole moment decrease; this is due to the fact that the dipole O  of the direct bond between the oxygen atoms and the benzene ring is stronger isolated[9] due to the increase of n in the fragment C_nH_{2n+1}. The result is that the interaction between the ends of the molecules decreases. That is why the nematic phase thermostability aggravates (Fig.1, curve 1). After the decrease of the total longitudinal dipole moment $\mu_d^{\parallel}$ and of the total longitudinal polarizability $\alpha_d^{\parallel}$, according to equation (7), the electroconductivity anisotropy $\sigma_{\perp}/\sigma_{\parallel}$ (Fig.2, curve 1) decreases.

2. For dopant B mixtures the increase of the carbon atoms n in the end alkyl chains causes first, the isolation of the longitudinal dipole O  and, second, the weakening of the interaction between the end-methyl group and the central transversal dipole $C\overset{+}{=}N$.

This interaction is stronger at the n-odd, as in this case the end methyl group of the zigzag alkyl chain makes an angle with the molecule longitudinal axis[9].

In all the three cases (n'=1,2,4) the n-increasing causes a noticeable isolation of the longitudinal dipole O . Consequently the molecular interaction between the molecule ends weakens and the nematic phase thermostability weakens, too (Fig.1, curves 2,3,4).

When the alkyl chain is lengthened, the strength of the interaction between the end methyl group and the transversal dipole $C\overset{+}{=}N$ decreases, the effective transversal dipole moment of dopant molecules decreases too, which itself causes the diminution of $\sigma_{\perp}/\sigma_{\parallel}$ according to formula (7) (Fig.2, curves 2,3,4). At the n'=2 dopant for n=7 homologous number (odd) the anomalous great value of $\sigma_{\perp}/\sigma_{\parallel}$ is explained by the stronger interaction between the end-methyl group and the central dipole as compared to the n-even ($\mu_d^{\perp}$(odd)>$\mu_d^{\perp}$(even)). Here the nematic phase thermostability improves (Fig.1, the peak in the curve 3).

3. The dopant molecule length is larger than the matrix molecule length for the dopant C mixtures (l_m=32.46 Å; l_d=44.08-52.72 Å). That is why the end-methyl groups of dopant molecules interact strongly with the central transversal dipole of the matrix molecule, which improves the nematic phase thermostability (Fig.1, curve 5). The intermolecular lateral interaction between the dopant molecules and the matrix decreases when n is further increased. For example: (t_{N-S_A}(n=12)>t_{N-S_A}(n≤11)). The above-mentioned strong interaction causes an increase of the obtained dipole moment $\mu_m^{\perp}$ and as a consequence an increase of $\sigma_{\perp}/\sigma_{\parallel}$ according to formula (7) (Fig.2, curve 5).

At n=12 $\mu_m^{\perp}$ decreases due to this interaction, thus causing $\sigma_{\perp}/\sigma_{\parallel}$ to decrease.

4. The end chain group of the dopant molecules ($\mu_d^{\parallel}$=4.05 D) is strongly polar according to (7) (Fig.2, dopant D). In this connection intermolecular end interactions are intensified, thus the nematic phase thermostability (Fig.1, dopant D) is increased. Thus, the smectic A liquid crystal electroconductivity anisotropy can be varied on will by adding of suitable polar or nonpolar dopants in it. This knowledge is important to determine the mechanism of the electrooptical effects of this substance and permits to optimize the parameters of the liquid-crystalline compositions which are used as a working medium, and as devices for storage and processing of optic information.

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