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> OTHER PROBLEMS OF PHYSICAL CHEMISTRY

# Effects of Nonmesomorphic Substituted Benzonitriles on the Dielectric Properties of Cyanobiphenyl Liquid Crystals

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**Abstract**—The effects of the cyano-substituted aromatic nonmesomorphic additives N-(3,4-dicyanophenyl)-4'-nonyloxybenzamide (I), 3,4-dicyanophenyl-4'-nonyloxybenzoate (II), 3,4-dicyanophenyl-3',4',5'*tris*-(4''-undecyloxyphenylbenzoate)benzoate (III), and 4-(6-hydroxyhexyloxy)benzonitrile (IV) on the dielectric properties of 4-hexyloxy-4'-cyanobiphenyl and a liquid-crystal mixture E3 were studied. Dielectric anisotropy, birefringence, and orientational ordering were studied to show that monocyano derivative IV most strongly increased the dielectric anisotropy of mesomorphic compositions because of its effective incorporation into the liquid crystal matrix.

DOI: 10.1134/S0036024408070285

### INTRODUCTION

Because of their unique properties (fluidity combined with anisotropy of physical properties), liquid crystals (LCs) have found wide use in various fields of engineering, research, and technology. LCs hold special position as materials used in optoelectronic devices for mapping information. The problem of reducing control voltages by decreasing the threshold of LC reorientation is a challenge. It can be solved by increasing dielectric anisotropy with maintaining other service characteristics at an acceptable level [1]. These problems cannot be solved by methods of molecular design alone because the set of potential synthons (fragments) for the design of rodlike mesogens (rings, bridging groups, and lateral and terminal substituents) is limited [2]. Profound modification of mesomorphic and physical properties can also be achieved via selective doping with special additives, both liquid-crystalline and nonmesomorphic [3]. Thus, it was shown [4] that the anisotropy of dielectric permittivity could be significantly increased without decreasing viscosity and elasticity characteristics by introducing small amounts of high-polarity nonmesogenic dinitriles. However, the effects of polar nonmesogens on the physical characteristics of LC compositions have not been investigated.

The aim of the present work was to study the effects of small amounts of cyano-substituted aromatic nonmesomorphic admixtures on the dielectric properties of the nematic LC



where R = C<sub>6</sub>H<sub>13</sub>O (4-hexyloxy-4'-cyanobiphenyl, 6OCB) ( $Cr \rightarrow 54^{\circ}C \rightarrow N \rightarrow 76^{\circ}C \rightarrow I$ ) and R = C<sub>5</sub>H<sub>11</sub> (55%), C<sub>5</sub>H<sub>11</sub>O (15%), C<sub>7</sub>H<sub>15</sub>O (13%), C<sub>8</sub>H<sub>17</sub>O (17%) in a liquid-crystal mixture based on cyanobiphenyls E3 that forms the nematic phase over a wide temperature range [5] ( $Cr \rightarrow -2^{\circ}C \rightarrow N \rightarrow 56^{\circ}C \rightarrow I$ ). N-(3,4-dicyanophenyl)-4'-nonyloxybenzamide (I), 3,4-dicyanophenyl-4'-nonyloxybenzoate (II), 3,4-dicyanophenyl-3',4',5'-*tris*-(4''-undecyloxyphenylbenzoate)benzoate (III), and 4-(6-hydroxyhexyloxy)benzonitrile (IV) were used as modifiers:



Compound	μ, D	Compound	μ, D
6OCB	5.4	II	8.3
E3	5.1 [5]	III	9.9
Ι	9.8	IV	5.3

 
 Table 1. Dipole moments of LCs and nonmesogenic substances





## **EXPERIMENTAL**

Compounds I–III were prepared and purified by a procedure similar to that described in [6]; 4-(6-hydrox-yhexyloxy)benzonitrile (IV) was synthesized by boiling 4-hydroxybenzonitrile and 6-chloro-1-hexanol in DMF in the presence of potassium carbonate. The product was purified by recrystallization from a mixture of ethanol and water. 4-*n*-Alkoxy-4'-cyanobiphenyls of



**Fig. 1.** Dependences of the components of dielectric permittivity on reduced temperature for (1) the E3 mixture and its modifications (E3 + 3% modifier: (2) I, (3) II, (4) III, and (5) IV) on reduced temperature.

ch. d. a. (pure for analysis) grade were used without additional purification.

The dipole moments ( $\mu$ ) of the mesogen molecules were calculated using the Guggenheim–Smith equation [7] and the experimental permittivities and refraction indices of dilute solutions of LCs in benzene at 25°C. The error in dipole moments did not exceed 0.01D. Permittivities were measured at a frequency of 10 kHz using an LCR-817 (INSTEK) instrument in a temperature-controlled (±0.01 K) plane parallel cell with a gap of 0.2 mm in a magnetic field of 0.2 T. The error in  $\varepsilon$  did not exceed ±0.02.

The order parameter was determined as described in [8] from the <sup>1</sup>H NMR spectra obtained on a Bruker AC-200 spectrometer equipped with a BVT3000 temperature accessory. Birefringence  $\Delta n = n_{\parallel} - n_{\perp}$  was measured by refractometry at a wavelength of 589 nm to an accuracy of  $\pm 0.02$ . The refractive indexes of the ordinary beam  $(n_0 = n_\perp)$  in mesomorphic and isotropic liquid states  $(n_{is})$  were directly measured on an Abbe temperature-controlled refractometer at 589 nm  $(\pm 0.0005)$ . The prism surface of the refractometer was preliminarily polished for sample orientation with an LC surface. The refractive index of the extraordinary beam  $(n_e = n_{\parallel})$  was determined from the equation for the mean value,  $n^2 = (n_e^2 + 2n_o^2)/3$ , evaluated by extrapolating  $n_{is}$  to the nematic phase region taking into account the temperature dependence of the density of LC.

# **RESULTS AND DISCUSSION**

Since the dielectric properties of LCs depend strongly on the polarity of nonmesomorphic modifiers, we used the second Debye method [7] to measure the dipole moments of compounds I-IV presented in Table 1. An analysis of these data shows that the introduction of the second nitrile substituent into the aromatic ring is accompanied by an increase in the polarity of the nonmesogen. Figure 1 shows the temperature dependences of the components of the permittivity of the LC mixture E3 and compositions based on it containing 3% admixtures I-IV in the nematic and isotropic phases. Since the introduction of nonmesomorphic admixtures changes phase transition temperatures, we used the scale of reduced temperatures ( $T_{red} = T - T_{NI}$ ), which represent deviations from the nematic-isotropic phase transition point.

An analysis of the data presented in Fig. 1 shows that admixtures have a pronounced effect on the permittivity of LC. In the isotropic phase, phenyl benzoate II was the only compound that produced an appreciable effect, while in the nematic phase, all modifiers increased both permittivity components,  $\varepsilon_{\perp}$  and  $\varepsilon_{\parallel}$  (the latter increased to a greater extent). This led to an increase in the dielectric anisotropy  $\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$  (Fig. 2) in the series IV > II, III > I. A comparison of these

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results with the data from Table 1 shows that the effect of the nonmesomorphic compounds on the dielectric properties of LCs does not correlate with their polarity. Moreover, monocyano derivative IV, which had the lowest dipole moment, increased the dielectric anisotropy of the LC mixture to the greatest extent (Fig. 2).

Therefore, it is of interest to consider the behavior of the mean permittivity  $\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$  of the mesophase and the  $\epsilon_{extr}$  values extrapolated from the isotropic liquid state. As is known,  $\bar{\epsilon} < \epsilon_{extr}$  [9] for the cyano derivatives of LCs [9] because of the antiparallel dipole– dipole association of polar molecules. An analysis of Table 2 shows that the addition of nonmesogens I and IV decreases  $\delta \epsilon = \epsilon_{extr} - \bar{\epsilon}$ . This is evidence of a decrease in the degree of association of cyanobiphenyls in the mesophase. At the same time, for nonmesogens II and III,  $\delta \epsilon$  changes sign.

The unexpectedly strong effect of low-polarity IV on the dielectric properties of the LC mixture can be attributed to an increase in orientational ordering of the mixture caused by doping or to a change in the preferred orientation of dipoles. Measurements of the orientation order parameters (*S*) of mixed LCs involves serious difficulties [8], and we therefore obtained the temperature dependences of *S* for pure LC 60CB and its mixture with nonmesogen IV (3%) and the temperature dependences of birefringence (Fig. 3). The order parameters were measured by NMR, and the refractive indexes, by refractometry.

An analysis of these data shows that admixture effects on the above-mentioned characteristics are very insignificant. This is evidence that, first, the nonmesogen is effectively incorporated into the LC matrix **Fig. 2.** Dependences of dielectric anisotropy on reduced temperature for the system based on E3 ((1-5) see Fig. 1 for notation).

without destabilizing it, and, secondly, an increase in orientational order cannot be the reason for a substantial increase in dielectric anisotropy.

Modifier IV is the only nonmesogen that has a proton-donor hydroxyl group and can therefore in principle participate in specific interactions with electrondonor fragments, primarily with the cyano groups of LCs. In our opinion, the formation of the hydrogenbonded complexes



accompanied by an increase in the net dipole moment along the optical axis of an LC and, accordingly, an

CN

LC	ā	ε <sub>extr</sub>	δε	ε <sub>ll</sub>	$\epsilon_{\perp}$	Δε
E3	10.15	11.00	0.85	15.98	7.24	8.75
E3 + I	10.62	10.76	0.14	16.90	7.50	9.5
E3 + II	10.68	10.21	-0.47	17.59	7.78	9.81
E3 + III	11.1	10.99	-0.11	17.6	7.85	9.75
E3 + IV	11.40	11.52	0.12	18.17	8.01	10.16
6OCB	10.35	10.77	0.42	15.94	7.56	8.38
60CB + IV	10.58	10.83	0.25	16.79	7.47	9.32

 $CN - HO - (CH_2)_6$ 

**Table 2.** Dielectric properties of LC compositions at  $T_{\rm red} = -10$  K





Fig. 3. Dependences of the order parameter S and birefringence  $\Delta n$  on reduced temperature for (1) 6OCB and (2) a 6OCB–IV mixture.

increase in the parallel permittivity component  $(\varepsilon_{||})$ . In addition, intermolecular H-bonding can be treated as an interaction that competes with the antiparallel association of mesogen molecules, which is known [10] to balance dipoles and reduce the  $\Delta \epsilon$  effective value. Note that the formation of H-bonded complexes of this kind should be accompanied by the effective incorporation of a nonmesogen into an LC matrix. This is indirectly confirmed by the observation that the orientational order parameter and birefringence of nonmesomorphic modifier IV remain unchanged (Fig. 3).

# ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research, project no. 05-03-32571a, and the program of the Department of Chemistry and Materials Science of the Russian Academy of Sciences, project no. 20Kh.

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