ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 4, pp. 827–832. © Pleiades Publishing, Ltd., 2015.
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Mesomorphic and Dielectric Properties of the Systems Based on Nematic Cyanobiphenyls

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Received November 17, 2014

Abstract—Nematic cyanobiphenyls have been modified with small amount of polar additives. Phase transition temperatures as a function of composition of the prepared mixtures have been determined by polarization thermomicrscopy. The dielectric constant as a function of temperature has been determined via dielcometry measurements, and the dielectric anisotropy of the studied mixtures has been revealed. Broadening of the mesophase existence temperature range and enhancement of the dielectric anisotropy of the nematic biphenyls upon addition of polar dopants results from the supramolecular self-assembly via hydrogen bonding.

Keywords: supramolecular mesogen, non-mesogen, thermal stability, dielectric anisotropy, hydrogen bonding

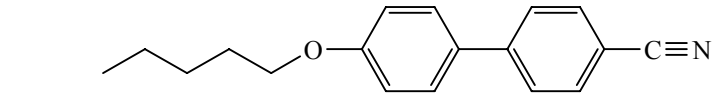
DOI: 10.1134/S107036321504009X

The development of information technology is impossible without application of high-quality, cheap, and energy-efficient means for information display, in particular, devices based on liquid-crystalline materials [1–3]. The latter are generally mechanical mixtures of calamite-type mesogens bearing different substituents, the mesogen derivatives of cyanobiphenyl (biphenyl-4-carbonitrile) being among the most promising due to a high dielectric anisotropy and excellent electrooptical properties [4–6].

Dipole-dipole antiparallel orientation of the molecules is one of the fundamental features of the systems based on mesogenic nitriles [7, 8]. Targeted influence of the doping additives on the dipole-dipole association allows enhancement of the mesogens utilitarian properties. Depending on the anisotropy, polarity, and the presence of active functional groups the dopants may induce a number of effects on the properties of the liquid-crystalline material. For example, the addition of small amounts of highly polar non-mesogenic dinitriles significantly enhances the dielectric constant anisotropy without noticeable deterioration of the viscoelastic properties [9]. The introduction of small amounts of terphenyls bearing side or terminal polar substituents (CN or F) into the nematic composites may either reduce or enhance the dielectric anisotropy (basing on the substitution pattern) simultaneously improving the elastic properties; this is of practical importance in view of adjusting flexoelectric properties of liquid-crystalline materials [10]. The addition of nanoparticles (carbon nanotubes, $Sn_2P_2S_6$, or $BaTiO_3$) alters the local electric field structure and the ordering of nematic and ferroelectric materials, thus improving the operation speed of electrooptical cells [11–13]. The unusually high positive dielectric anisotropy has been found in the case of 4'-hexylbiphenyl-4-carbonitrile mixture with salicylaldimine [14]. Furthermore, dielectric properties and electric conductivity have been studied for liquid-crystalline mixtures of biphenylcarbonitriles doped with spiropyranylazobenzoate and spiropyranylcarboxylate [15, 16].

In addition to conventional approaches to molecular design of mesogenic compounds, the development of supramolecular liquid-crystalline systems has recently emerged [17–21]. In particular, mixtures of conventional mesogenic calamites with active amphiprotic additives capable of supramolecules formation involv-

Scheme 1.



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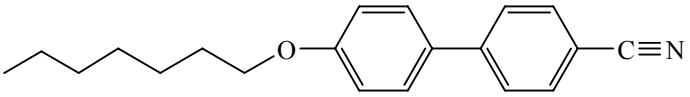

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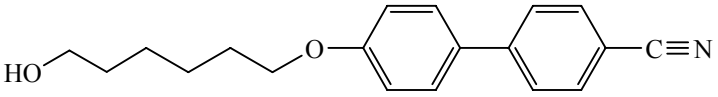

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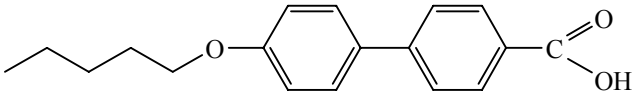

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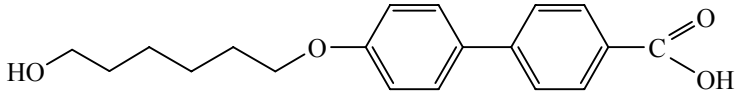

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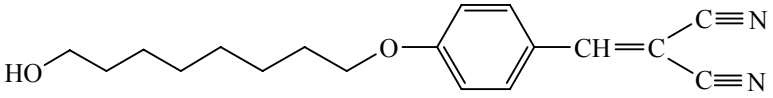

III

ing liquid-crystalline solvent have attracted considerable attention. Doping with non-mesogenic as well as liquid-crystalline substances has been recognized as a promising approach towards deep modification of the conventional liquid-crystalline systems.

Systematic studies of mesomorphic, anisotropic, and orientation properties of various supramolecular liquid-crystalline systems and their mixtures with non-mesogens (4-nitroaniline, 4-hydroxybenzonitrile, 4-aminobenzonitrile, 4'-hydroxybiphenyl-4-carbonitrile, etc.) have been performed in our group as well [22–26]. The most important fundamental and practical results obtained in the studies of individual supramolecular mesogens and their hydrogen-bonded mixtures with non-mesogens have been generalized in [27].

In this work we discuss the effect of polar additives [4-(pentyloxy)biphenyl-4'-carboxylic acid (**I**), 4-(6-hydroxyhexyloxy)biphenyl-4'-carboxylic acid (**II**), and 4-(8-hydroxyactyloxy)-1-(2,2-dicyanoethenyl)benzene (**III**)] on mesomorphic and dielectric properties of 4'-(pentyloxy)biphenyl-4-carbonitrile (**LC-1**), 4'-(heptyloxy)biphenyl-4-carbonitrile (**LC-2**), and 4'-(6-hydroxyhexyloxy)biphenyl-4-carbonitrile (**LC-3**) (Scheme 1).

Liquid-crystalline solutions with various additives possessed mesomorphic properties over certain temperature and concentration ranges. The additives effect on the nematic–isotropic phase transition was mainly determined by the nature of the intermolecular interactions. The compositions and mesomorphic properties of the studied mixtures are collected in Table 1.

When analyzing the experimental data, the molecules shape and size as well as the presence of functional groups should be taken into consideration. Monocyclic non-mesogen **III** destabilized the **LC-2** mesophase as reflected in the reduced T_{NI} with the increasing additive fraction; simultaneously, the temperature range of the mesophase existence was narrowed.

The effect of nematic biphenylcarbonitriles doping with bicyclic additives was the opposite. In particular,

increasing the concentration of acid **I** or **II** in the mixture enhanced the thermal stability of mesophase of liquid-crystalline compounds **LC-1** and **LC-3**, the range of the mesophase existence being widened. We believe that the mentioned effects may result from the capability of the additive to be incorporated into the structure of the liquid-crystalline solvent due to similar geometry and polarity parameters; furthermore, the formation of the hydrogen-bond complexes between the liquid-crystalline compound and the mesogen yields the supramolecule containing a rigid elongated core favoring the orientation ordering. On top of that, the change of association state of the antiparallel mesogenic nitriles could play a role.

The analysis of mesomorphic properties of the studied systems containing the mesogen and the non-mesogen revealed that the temperatures of liquid crystal phase transition were governed by a combination of several factors, the hydrogen bonds-assisted formation of supramolecules being the most important one; the hydrogen bonding was in turn depending on the structural features of both the non-mesogen and the liquid-crystalline solvent. Evidently, the formation of such supramolecular structures should have altered various physical properties of the system, in particular, the dielectric anisotropy.

The dielectric constant is among the fundamental properties of liquid-crystalline materials, as utilitarian properties of the electrooptical cells are governed by the anisotropy of dielectric properties of the mesogen. The introduction of various additives is generally accompanied by changes both in the dielectric constant and the related parameters: threshold voltage and the turnon/turnoff times of the electric cells.

Figures 1 and 2 show the experimentally determined components of dielectric permittivity of the studied systems in the nematic and the isotropic liquid phases as a function of temperature. Since the T_{NI} of the solutions depended on their composition, the data were rescaled as a function of ($T_{red} = T - T_{NI}$), the equal reduced temperatures thus corresponding to the similar nematic ordering. As follows from the analysis of the data (Table 2), the studied liquid-crystalline solutions showed a positive dielectric anisotropy and fairly high components of dielectric permittivity. The influence of the non-mesogen additives on anisotropy of dielectric constant of the liquid-crystalline materials increased in the series **I** < **III** < **II**.

Table 1. Mesomorphic properties of liquid-crystalline solvents and their mixtures

System	Phase transition temperature, °C		Mesophase existence temperature range, °C
	T_{CN}	T_{NI}	
LC-1	53.0	67.5	14.5
LC-1 + 1 wt % **I**	46.6	67.0	21.0
LC-1 + 5 wt % **I**	50.3	68.8	18.5
LC-2	53.5	75.0	21.5
LC-2 + 3 wt % **III**	54.7	73.1	18.4
LC-2 + 7 wt % **III**	55.3	68.0	12.7
LC-2 + 10 wt % **III**	51.0	63.5	12.5
LC-3	91.5	98.0	6.5
LC-3 + 1 wt % **II**	91.3	101.3	10.0
LC-3 + 3 wt % **II**	91.3	102.3	11.0
LC-3 + 5 wt % **II**	86.0	102.4	16.4

The increase in the dielectric parameters could be ascribed to the formation of the molecular associates via hydrogen bonding between the hydroxy and the nitrile groups. The formation of the hydrogen bond stabilized complexes should enhance the non-mesogen incorporation into the liquid crystal matrix and thus increase the total dipole moment along the mesogen optical axis, increasing the parallel component of the dielectric permittivity $\varepsilon_{||}$. Moreover, the association should prevent the formation of the antiparallel systems.

Temperature dependences of $\varepsilon_{||}$ and $\varepsilon_{\perp}$ of the binary mixtures of supramolecular biphenylcarbonitrile **LC-3** and the biphenylcarboxylic acid **II** (Fig. 2) significantly differed from those of conventional biphenylcarbonitrile and their mixtures. The dielectric permittivity and its anisotropy were significantly enhanced (Table 2) in the case of the supramolecular system, and the curves shape was changed. The unusual curves shape was related likely to the heat-assisted cleavage of hydrogen bonds. Upon heating, two processes may occur at different rates: the hydrogen bonds cleavage (in other words, destruction of the linear associates) and the antiparallel orientation of the molecular dipoles.

The degree of liquid-crystalline solvent modification was largely dependent on the ability of the doping additive to form the supramolecules with the mesogen via hydrogen bonding. The additive influence on the nematic–isotropic phase transition and the range of the mesophase existence was determined by the presence

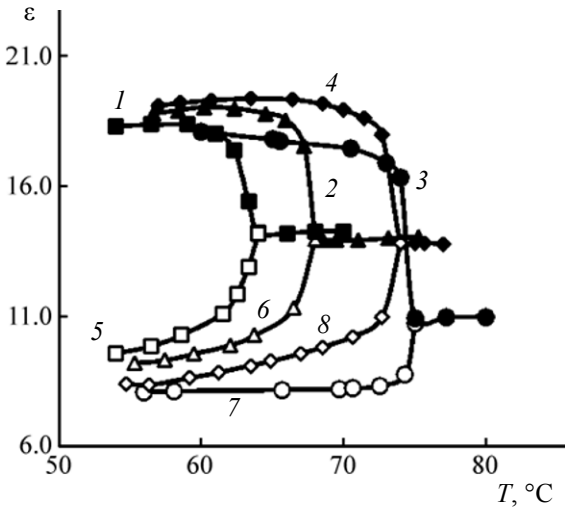

Fig. 1. Dielectric permittivity as a function of temperature for pure liquid-crystalline solvent **LC-2** (*1*, *5*) and for **LC-2** doped with compound **III**: LC-2 + 3 wt % **III** (*2*, *6*); **LC-2** + 7 wt % **III** (*3*, *7*); **LC-2** + 10 wt % **III** (*4*, *8*). $\varepsilon_{||}$ (*1–4*), $\varepsilon_{\perp}$ (*5–8*).

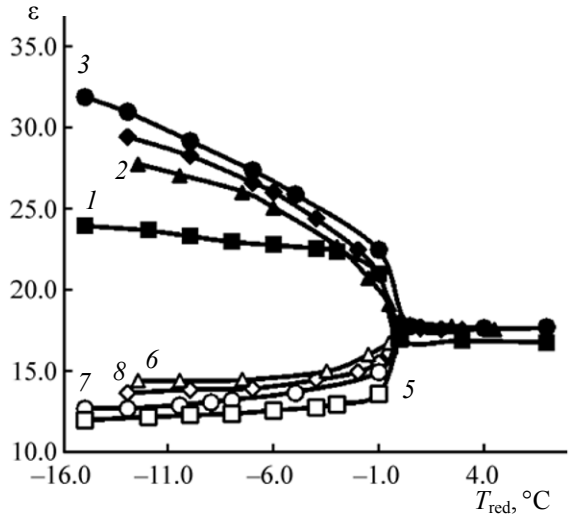

Fig. 2. Dielectric permittivity as a function of temperature for pure liquid-crystalline solvent **LC-3** (*1*, *5*) and for **LC-3** doped with compound **II**: LC-2 + 1 wt % **II** (*2*, *6*); **LC-3** + 5 wt % **II** (*3*, *7*); **LC-3** + 3 wt% **II** (*4*, *8*). $\varepsilon_{||}$ (*1–4*), $\varepsilon_{\perp}$ (*5–8*).

of the active substituents capable of specific intermolecular interaction. The studies of dielectric parameters showed that doping of mesogenic nitriles with polar non-mesogens capable of hydrogen bonds formation increased the dielectric constant. One of the reasons for that could be the decreased degree of antiparallel association of the mesogen due to the self-assembly of the supramolecules and supramolecular linear associates.

Table 2. Dielectric properties of the studied mesogens and their mixtures at T_{red} – 10°C

System	$\varepsilon_{||}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
LC-1	18.1	9.0	9.1
LC-1 + 1 wt % **I**	19.2	10.0	9.1
LC-1 + 5 wt % **I**	17.2	9.8	7.4
LC-2	15.1	8.1	7.0
LC-2 + 3 wt % **III**	19.3	9.1	10.2
LC-2 + 7 wt % **III**	18.8	9.3	9.5
LC-2 + 10 wt % **III**	18.3	8.9	9.4
LC-3	24.4	12.1	12.3
LC-3 + 1 wt % **II**	27.1	14.6	12.5
LC-3 + 3 wt % **II**	28.3	13.9	14.4
LC-3 + 5 wt % **II**	29.2	13.1	16.1

EXPERIMENTAL

Biphenylcarbonitrile derivatives **LC-1** and **LC-2** ("analytically pure" grade) were used without purificatrion. The **LC-3** mesogen was prepared via alkylation of 4'-hydroxybiphenyl-4-carbonitrile (Aldrich) with 6-chlorohexan-1-ol in DMF in the presence of K_2CO_3 and was purified by recrystallization from ethanol and 12 h maintaining at the residual pressure of 200 Pa at the temperature of the mesophase existence. The purity of the liquid-crystalline solvents was judged from the constant temperature of nematic–isotropic transition (T_{NI}) in the repeated purification cycles, the absence of layering into the nematic and the isotropic phases upon the phase transition, and the correspondence of the melting points to the reference values [28].

Biphenylcarboxylic acids **I** and **II** were prepared as described in [29] and purified by recrystallization from 80 wt % acetic acid followed by 12 h maintaining at the residual pressure of 200 Pa at 150°C. Compound **III** was prepared as described in [30].

Liquid-crystalline mixtures were prepared by mechanical mixing of the precisely weighed components (±0.05 mg) in the isotropic liquid state during 1 h.

Phase transition temperature of the studied systems were determined by means of thermomicroscopy using a Polam R211 polarization microscope equipped with a temperature stage allowing for heating at the rate of 0.1–3.5 deg/min in the range of 0–500°C and maintaining the constant temperature. The accuracy of temperature determination (±0.1°C) was ensured by calibration with a set of melting point references.

Dielectric permittivity of the liquid-crystalline materials was measured using a cell consisting of two parallel plates (S = 19.6 mm^2 and the gap of 0.25 mm, the specimen being put between the plates), a 2000 Gs electromagnet assisting the specimen orientation, a capacity reading device (LCR-817, INSTEK), and a thermostat (±0.1°C). The measurements were run at 10 kHz and 1 V. The cell was calibrated using the dielectric constant references. The specimen dielectric constant was calculated as follows.

$$\varepsilon = \frac{C_X - C_M}{C_W}, \quad (1)$$

where C_X being capacitance of the cell with the studied specimen; C_M being wiring capacitance as determined from the cell calibration; and C_W being capacitance of the cell working distance from the calibration.

In order to estimate the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, we performed the measurements parallel ($\varepsilon_{\parallel}$) and perpendicular ($\varepsilon_{\perp}$) to the nematic liquid crystal director. The relative error of dielectric constant measurement was 1%, the dielectric anisotropy was determined with the error of 3%.

ACKNOWLEDGMENTS

The study of mesomorphic properties of liquid-crystalline materials was financially supported by Russian Foundation for Basic Research (project no. 12-03-00370-a). The study of dielectric properties was performed in the frame of governmental contract of Ministry of Education and Science of Russian Federation.

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