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Thermotropic, refracting and birefringent properties in homogeneous mixtures of 4-n-alkyl-4′-cyanobiphenyl mesogens

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ABSTRACT

In this work, studies of the thermotropic and thermo-optical properties in five homogeneous mixtures of 4-n-alkyl-4′-cyanobiphenyl mesogens have been carried out. Temperature behavior of the mean refractive index n, ordinary n_o and extraordinary n_e refractive indices has been investigated. The principal polarizabilities α_0 and α_e, effective geometry parameter α_{eg} and average polarizability α_{ave} were calculated using the internal field model (Vuks approach). Behavior of the birefringence Δn and the anisotropy of polarizability $\Delta\alpha$ as a function of temperature, and the order parameter in regions of the *smectic A–nematic*, *nematic–isotropic liquid* and *smectic A–isotropic liquid* phase transitions are discussed.

1. Introduction

Liquid crystalline materials have the ordering properties of solid crystalline materials but they are fluid like liquids. Therefore, liquid crystals are partially ordered, viscous elastic and physically anisotropic materials. These materials exhibit various mesophases, which are characterized by the orientational, translational and positional orders [1–5]. A lot of interest in liquid crystals came from their scientific, technical and technologic applications.

Most applications of liquid crystals in technique and technology (liquid crystalline display, indicators, multimatrix elements, systems of information registration and reading, thermography, etc.) depend upon their thermo-optical, electro-optical, magneto-optical and acousto-optical properties [6–10]. These properties exhibit very interesting behavior in both the liquid crystalline mesophase regions and the regions of phase transitions. For technical and technological applications of liquid crystalline materials, information about their optical anisotropy, refractive and polarization properties, and also about thermal behavior and temperature states of mesophases are sufficiently important.

Besides, the knowledge of the optical anisotropy and the refractive properties of liquid crystalline mesophases are essential for calculating of the order parameter of mesophases and polarizabilities of molecules [11–15]. Such calculations using the Vuks model (Vuks approach) [16–18] or the Neugebauer model (Neugebauer approach) [19] have been made by various scientists for individual liquid crystals. In the Vuks approach the isotropic internal field model and in the Neugebauer approach the anisotropic internal field models are taken into consideration. These two approaches lead to values of the refractive properties and order parameter of liquid crystalline mesophases, which are in sufficiently good agreement [11,13,20–22]. Additionally, one of the most known methods for calculating of the order parameter without considering of the internal field is the Haller approximation method [23–25]. In this method the orientational order parameter can be determined only from the refractometric data of liquid crystalline mesophase.

For technical and technologic applications, liquid crystalline materials with various mesophases, various mesomorphic degrees, different widths of thermal interval and different phase transition temperatures are necessary. Besides, for these applications, liquid crystalline materials with definite physical and physico-chemical properties, especially the thermo-optical and thermotropic properties, are requested. Therefore, over the past decade investigations of physical properties of liquid crystalline mixtures attract the intent attention of scientists [26–32]. The point is that liquid crystalline mixtures display physical and physical–chemical properties, which are not displayed in individual liquid crystals.

In this work the objects of investigations were homogeneous binary mixtures of 4-n-alkyl-4′-cyanobiphenyls. The thermotropic properties and behavior of the mean refractive index n, ordinary n_o and extraordinary n_e refractive indices, and birefringence Δn have been studied in a large temperature region, especially in regions of the *smectic A–nematic*, *nematic–isotropic liquid* and *smectic A–isotropic liquid* phase transitions. Based on these data, temperature dependences

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Table 1
Features of thermotropic behavior in **8CB** + **10CB** mixtures.

Sample	Concentration of components, wt.%	Phase transition temperatures, K			
		Cr–SmA	SmA–N	N–I	SmA–I
LC1	80.00 wt.%**8CB** + 20.00 wt.%**10CB**	278.3	310.9	315.6	–
LC2	65.00 wt.%**8CB** + 35.00 wt.%**10CB**	277.0	314.5	317.1	–
LC3	50.00 wt.%**8CB** + 50.00 wt.%**10CB**	276.4	316.7	318.0	–
LC4	35.00 wt.%**8CB** + 65.00 wt.%**10CB**	276.1	–	–	316.1
LC5	20.00 wt.%**8CB** + 80.00 wt.%**10CB**	274.1	–	–	313.3

of the principal polarizabilities α_0 and α_e, polarizability anisotropy $\Delta\alpha$, average polarizability α_{ave} and effective geometry parameter α_{eg} have been determined, using the isotropic internal field model.

2. Experimental

2.1. Materials

In this work, five homogeneous mixtures of 4-n-octyl-4′-cyanobiphenyl (**8CB**) with 4-n-decyl-4′-cyanobiphenyl (**10CB**) have been used. Compositions of these mixtures are presented in Table 1 as **LC1**, **LC2**, **LC3**, **LC4** and **LC5**. 4-n-alkyl-4′-cyanobiphenyls were purchased from Merck and used without further purification. The structural formula of 4-n-alkyl-4′-cyanobiphenyls is given in Scheme 1.

4-n-alkyl-4′-cyanobiphenyls are mesogenic compounds, which have uniaxial molecular symmetry, and good photo(chemical) stability, and are thermally stable and stable to moisture. Besides, these materials have low-temperature liquid crystalline states, display enantiotropic nematic and smectic A mesophases, and the thermotropic phase transitions. Molecules of 4-n-alkyl-4′-cyanobiphenyls can be considered as rigid rods, which have the cylindrical symmetry about the axis of maximum polarizability. Besides, these liquid crystals have large dipole moment and can easily form textures with the homeotropic and planar alignment. Therefore, 4-n-alkyl-4′-cyanobiphenyls are important materials for scientific investigation, and technical and technological applications.

2.2. Methods

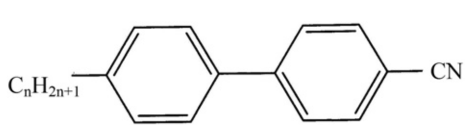
In this work, temperature dependences of the refractive indices n, n_e and n_o for **LC1**–**LC5** liquid crystalline mixtures have been measured using the polithermic refractometry setup (PR). For these measurements an Abbe's refractometer with a digital temperature control system has been used. An accuracy for the refractive index measurements was as 0,05%. The temperature changes of Abbe's refractometer have been carried out using a thermostat with circulating water. Temperature of liquid crystalline materials was controlled by digital temperature control system and Cu–Co thermocouple, placing in close vicinity of the samples with an accuracy of ±0.1 K.

The thermotropic properties and temperatures of phase transitions in **LC1**–**LC5** were studied using the polarizing optical microscopy technique (POM) and the capillary temperature wedge device (CTW).

For determination of the n_e and n_o refractive indices, peculiarities of polarizers, and the homeotropic and planar aligned textures of liquid crystals under investigations have been used. For obtaining of alignment in liquid crystalline mesophase, the prisms of the refractometer were treated. The deposition on the prisms of refractometer mixture of 0.1% cetyl-trimethylammonium bromide in deionized and bidistilled water or the mixture of 1.0% lecithin in ethyl alcohol provided the homeotropic alignment (yielding n_e) of 4-n-alkyl-4′-cyanobiphenyl mixtures. The deposition on the prism films of polyvinylalcohol, that was subsequently rubbed with velvet tissue, induced the planar alignment (yielding n_o) of 4-n-alkyl-4′-cyanobiphenyl mixtures. As is known, the light which is polarized parallel to the optic axis of liquid crystalline mesophase gave the extraordinary ray ($n_e = n_{||}$); the light which is polarized perpendicular to the optic axis gave the ordinary ray ($n_o = n_{\perp}$). Degree of the homeotropic alignment was checked on control samples by POM and estimations of view of the conoscopic images. Estimations showed that the mixture of 1.0% lecithin in ethyl alcohol provided better homeotropic alignment than the mixture of 0.1% cetyl-trimethylammonium bromide in deionized and bidistilled water. Homogeneity of the planar alignment has been examined by the POM and estimated by the optical polarization (OP) degree. The value of the OP degree has been determined as

$$P = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}. \quad (1)$$

Here I_{min} is the intensity of light, transmitted from the sample, which was placed parallel to the polarizer (or analyzer); and I_{max} is the intensity of light, transmitted from the sandwich-cell, placed under 45° to the polarizer (or analyzer). The degree of the planar alignment for 4-n-alkyl-4′-cyanobiphenyl mixtures was estimated as $P \approx 0.91 \div 0.93$.



Scheme 1. The structural formula of 4-n-alkyl-4′-cyanobiphenyls. **8CB**: $n = 8$; **10CB**: $n = 10$.

3. Results and discussion

8CB + **10CB** mixtures exhibit nematic (N) and smectic A (SmA) mesophases. These mesophases display by classic textures, which are presented in Fig. 1. As seen in Fig. 1a, texture of SmA mesophase consists of the confocal and polygonal formations. Availability of such formation is typical for mesophase with the D_∞ symmetry. As seen in Fig. 1b, texture of N mesophase consists of the thread-like formations and separate regions with definite alignment. Such texture is typical for mesophase with the $D_{\infty h}$ symmetry. Type of textures, which are presented in Fig. 1a,b, is well known for SmA and N mesophases, accordingly [33–35].

Investigations of the thermotropic properties showed that an increase of **10CB** concentration in **8CB** + **10CB** mixtures leads to a decrease of the *crystal–smectic A* (Cr–SmA) phase transition temperatures in **LC1**–**LC5**, to an increase of the *smectic A–nematic* (SmA–N) phase transition temperatures in **LC1**–**LC3**, to an increase of the *nematic–isotropic liquid* (N–I) phase transition temperatures in **LC1**–**LC3** and to a decrease of the *smectic A–isotropic liquid* (SmA–I) phase transition temperatures in **LC4** and **LC5** (Table 1). Besides, by an increase of **10CB** concentration in the mixtures, a decrease of nematic mesophase temperature interval has been observed. N mesophase has not been observed in **LC4** and **LC5**. In Fig. 2 state diagram of **8CB** + **10CB** mixtures is presented.

In this work the thermo-optical properties and temperature behavior of the n, n_o and n_e refractive indices have been investigated for **LC1**–**LC5**. As is known, in the optically positive liquid crystals the refractive index n is connected with the ordinary and extraordinary refractive indices as [16,17,36,37]

$$n^2 = \frac{n_e^2 + 2n_o^2}{3}. \quad (2)$$

As an example, the temperature dependences of the refractive indices n, n_e and n_o for **LC1**, **LC3** and **LC5** are presented in Figs. 3–5. As is seen in these figures, the temperature dependences of the n for the liquid crystals under investigation exhibit practically linear behavior with slight fluctuations in the regions of the phase transitions. Similar