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THERMOTROPIC, REFRACTING AND THERMO-OPTICAL PROPERTIES IN THREE HOMOLOGS OF 4-N-ALKYL-4'-CYANOBIPHENYLS

A. Nesrullajev

Department of Physics, Faculty of Science, Mugla Sitki Koçman University, 48000 Kötekli Muğla, Turkey
E-mail: arifnesr@mu.edu.tr

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Investigations of temperature behaviour of the mean refractive index n, ordinary n_o and extraordinary n_e refractive indices, and birefringence Δn have been carried out for three homologues of 4-n-alkyl-4'-cyanobiphenyls (n = 8, 10, 12). The principal polarizabilities α_0 and α_e, effective geometry parameter α_{eg} and average polarizability α_{ave} have been calculated using the isotropic internal field model (Vuks approach). Temperature behaviour of the order parameter in regions of the *smectic A–nematic*, *nematic–isotropic liquid* and *smectic A–isotropic liquid* is discussed. All of the optical and orientational parameters, which have been obtained in this work, are in good agreement with the theoretical approach.

Keywords: liquid crystals, refractive properties, optical birefringence, phase transitions

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1. Introduction

Liquid crystals (LCs) are partially ordered and physical anisotropic materials. These materials are very sensitive to different external effects, e. g. electric, magnetic and thermic fields, surfaces, boundary conditions, flows etc. Most applications of these materials in LCs technique and LCs technology depend upon their thermo-optical, electro-optical and magneto-optical properties [1–4]. These properties exhibit a very interesting behaviour in both regions of liquid crystalline mesophases and the regions of phase transitions. For the technical and technological applications of LCs, information about the optical anisotropy, refractive and polarization properties, and also about their temperature behaviour is important.

The knowledge of the optical anisotropy and the refractive indices n, n_o, and n_e of liquid crystalline mesophases is essential for calculating of the order parameter of mesophases and polarizabilities of molecules [5–9]. Such calculations using the Vuks model (Vuks approach) [10, 11] or using the Neugebauer model (Neugebauer approach) have been made [12]. 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 [5, 7, 13–15]. Besides, one of the most known methods for calculating the order parameter without considering of the internal field is the Haller approximation method [16–18]. In this method the orientational order parameter can be determined only from the refractometric dates of liquid crystalline mesophase.

In this work the objects of investigations were three homologues of 4-n-alkyl-4'-cyanobiphenyls (n = 8, 10, 12). 4-n-alkyl-4'-cyanobiphenyls are stable mesogenic compounds, exhibit smectic A and nematic mesophases and have good (photo)chemical stability. Therefore they are sufficiently interesting objects for scientific investigations and very perspective materials for technical and technological applications. Numerous reports on the optical properties of the above-mentioned mesogenic compounds are known. Namely, phase transformations for 6CB, 7CB, 8CB and 10CB by positron annihilation spectroscopy were studied in [19]; temperature dependences of the optical birefringence and refractive indexes for 5CB, 6CB, 7CB and 8CB were investigated in [20]; the frequency dependences of the refractive indexes for 5CB in the THz frequency range were investigated in [21];

the optical birefringence of 12CB at the p-Al_2O_3 interface was investigated in [22]; the temperature dependences of the refractive indices and transmission losses for 5CB were studied in [23]; the optical birefringence for 5CB, 6CB, 7CB and 8CB were studied in [24]. But comparative investigations of the refracting and birefringent properties for high homologues of 4-n-alkyl-4'-cyanobiphenyls (n = 8, 10, 12) have not been carried out. Besides, comparative investigations of the connection between the refractive and birefringent properties with the polarizabilities (principal polarizabilities, average polarizability and effective geometry parameter) in 4-n-alkyl-4'-cyanobiphenyls have not been studied.

In this work, behaviour 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 the regions of the *smectic A–nematic*, *nematic–isotropic liquid* and *smectic A–isotropic liquid*, for three homologues of 4-n-alkyl-4'-cyanobiphenyls (n = 8, 10, 12). Based on these dates, the order parameter Q, principal polarizabilities α_0 and α_e, average polarizability α_{ave} and effective geometry parameter α_{eg} have been determined, using the isotropic internal field model.

2. Theoretical background

LCs are physically anisotropic materials and are characterized by various optical, diamagnetic, dielectric, viscous-elastic etc. parameters. Optical parameters of liquid crystalline materials include the refractive index n, ordinary refractive index n_o, extraordinary refractive index n_e and the birefringence Δn.

The refractive index n is related with the ordinary and extraordinary refractive indices as [10, 11, 25, 26]

$$n^2 = \frac{n_e^2 + 2n_o^2}{3}. \tag{1}$$

On the other hand, the ordinary and extraordinary refractive indices can be obtained as a function of the refractive index and birefringence as [8, 27, 28]

$$n_e = n - \frac{1}{3}\Delta n\,, \tag{2a}$$

$$n_o = n + \frac{2}{3}\Delta n. \tag{2b}$$

The optical birefringence is an important parameter for determination of the orientational order parameter of LCs. In [2, 28–34] it is shown that the character of temperature dependences of the Δn corresponds to the character of temperature transformation of the macroscopic order parameter Q of LCs. Besides, the character of the Δn in the oriented smectic A and nematic mesophases is in good conformity with the theoretically predicted character of the temperature dependences of this order parameter [20, 24, 29, 35].

The parameter Q is related with Δn as [24, 34, 35, 36–39]

$$Q = \frac{\Delta n}{\Delta n_0}. \tag{3}$$

Here Δn_0 is the birefringence of liquid crystalline material in the crystalline state (at $T = 0$). At this temperature $Q = 0$ takes place. Because the Δn_0 is a constant value for each liquid crystalline material, $Q \sim \Delta n$ takes place. Thus, the character of temperature dependences of the Δn corresponds to the temperature dependences of the Q parameter. We would like to note that several tensorial properties such as the anisotropy of dielectrical, magnetical, optical and elastical properties can be used for the determination of the macroscopic order parameter in LCs. Besides, as it is noted in [7, 21, 28], study of the refractive indexes as well as the birefringence is key for fundamental studies and practical applications of LCs.

In the model, presented in [10, 11], it is accepted that the local field in crystals is the same in all directions, i. e. that this field is isotropic. In this case (so-called Vuks relations) [10, 11, 33]

$$\alpha_e = \frac{3}{4\pi N}\frac{n_e^2 - 1}{n^2 + 2}, \tag{4a}$$

$$\alpha_o = \frac{3}{4\pi N}\frac{n_o^2 - 1}{n^2 + 2} \tag{4b}$$

take place. Here N is the number of liquid crystalline molecules per cm^3. Taking into consideration that $\frac{3}{4\pi N}$ is a constant value, Eqs. 6a and 6b can be expressed as

$$k \cdot \alpha_e = \frac{n_e^2 - 1}{n^2 + 2}, \tag{5a}$$

$$k \cdot \alpha_o = \frac{n_o^2 - 1}{n^2 + 2}. \tag{5b}$$

Thus, using temperature dependences of n_e, n_0 and n, the $k \cdot \alpha_e$ and $k \cdot \alpha_0$ values can be determined. If, however, the local field is anisotropic, Neugebauer's relations

$$n_e^2 - 1 = \frac{4\pi N\alpha_e}{1 - N\alpha_e\gamma_e}, \tag{6a}$$

$$n_o^2 - 1 = \frac{4\pi N\alpha_o}{1 - N\alpha_o\gamma_o} \tag{6b}$$

can be used [12]. Here γ_e and γ_o are the internal field factors. Between the γ_e and γ_o factors the $\gamma_e + 2\gamma_0 = 4\pi$ connection takes place. Because the order parameter in LCs is temperature dependent, the γ_e and γ_o factors must also be temperature dependent. Therefore, Eqs. (8a) and (8b) may be written as [33, 40]

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3}\left(\frac{n_e^2+2}{n_e^2-1} + 2\frac{n_o^2+2}{n_o^2-1}\right). \quad (7)$$

Additionally, between n, α_e and α_o the following connection takes place [16, 33, 40]:

$$\alpha_e + 2\alpha_o = \frac{9}{4\pi N}\left(\frac{n^2-1}{n^2+2}\right). \quad (8)$$

Thus, knowing the n_e, n_o and n values, the α_e and α_o values, and also the polarizability anisotropy $(\alpha_e - \alpha_o)$ can be determined.

Ratio between n_o and n_e determines the value of the effective geometry parameter α_{eg} for liquid crystals with the positive optical anisotropy as [28, 41, 42]

$$\alpha_{eg} = \frac{n_0}{n_e}. \quad (9)$$

Because n_o and n_e are dependent on temperature, α_{eg} are also dependent on temperature. α_{eg} is an important parameter to understand the light deflection in liquid crystals. In [43, 44] it is shown that α_{eg} is connected with light travelling near disclinations and other topological defects in liquid crystals, and with the orientation of the director field.

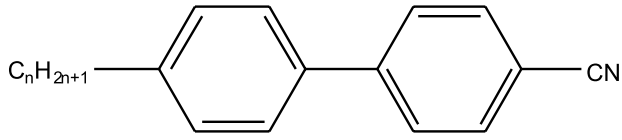
In [5, 7, 28, 33, 36, 37, 40] temperature dependences of n_e, n_0, Q, α_e, α_o, α_{eg}, $(\alpha_e - \alpha_o)$, γ_{II}, $\gamma_\perp$ and $(\gamma_{II} - \gamma_\perp)$ for various LCs have been determined and the connection between these parameters has been studied, using both the isotropic internal field model (Vuks approach) and the anisotropic internal field model (Neugebauer's approach). Liquid crystalline materials, which display smectic C, smectic A, nematic and cholesteric mesophases, have been used. In these works sufficiently good agreement between these values, estimated from these two independent methods, has been found.

3. Experimental

3.1. Materials

In this work, three even homologues of the 4-n-alkyl-4'-cyanobiphenyls series were objects of our investigations. The homologues investigated are 4-n-octyl-4'-cyanobiphenyls (8CB), 4-n-decyl-4'-cyanobiphenyls (10CB), and 4-n-dodecyl-4'-cyanobiphenyls (12CB). 4-n-alkyl-4'-cyanobiphenyls were purchased from *Merck* and used without further purification. The structural formulae of 4-n-alkyl-4'-cyanobiphenyls are given in the Diagram. These liquid crystalline materials have uniaxial molecular symmetry, are colorless, thermally stable and stable to moisture. Besides, these materials have low-temperature liquid crystalline states, display enantiotropic mesophases and thermotropic phase transitions, and also have high positive optical anisotropy.

Diagram. The structural formulae of 4-n-alkyl-4'-cyanobiphenyls. 8CB: n = 8; 10CB: n = 10; 12CB: n = 12.



3.2. Methods

In this work, the temperature dependences of the refractive indexes n, n_e and n_o for 8CB, 10CB and 12CB have been measured. For these measurements the polythermic refractometry setup, based on an Abbe's refractometer, has been used. Accuracy for the refractive indexes measurements was as 0.1%. The temperature changes of an Abbe's refractometer have been carried out using a recirculation immersion thermostat Ultraterm 200. Temperature of LCs under investigation was controlled by a digital temperature controller with an accuracy of ±0.1 K. A sketch of the experimental setup is presented in Fig. 1.

The thermotropic and thermo-morphologic properties, and temperatures of phase transitions in 8CB, 10CB and 12CB were studied using the polarizing optical microscopy technique (POM). As it is well known, the POM is a sufficiently convenient and informative method for investigation of the

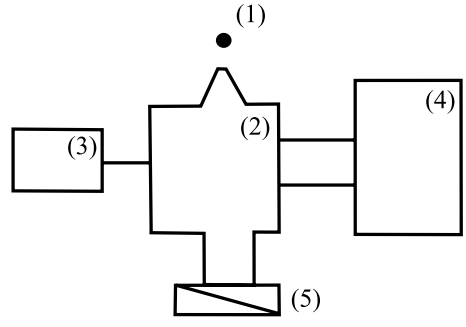


Fig. 1. Sketch of the experimental setup: (1) light source; (2) Abbe's refractometer; (3) digital temperature controller; (4) recirculation immersion thermostat; (5) polarizer.

mesomorphic and morphologic properties of liquid crystals and also for identification of liquid crystalline mesophases.

For determination of the refractive indexes n_e and n_o, peculiarities of polarizers, and homeotropic and planar alignment of liquid crystalline materials have been used. To obtain information on the alignment in a liquid crystalline state, the prisms of the refractometer were treated. The deposition of the mixture of 0.1% cetyl-trimethylammonium bromide in deionized and bidistilled water or the mixture of 1% lecithin in ethyl alcohol on the prisms provided the homeotropic orientation (yielding n_e) of 8CB, 10CB and 12CB. The deposition of a film of polyvinylalcohol, that was subsequently rubbed with velvet tissue, on the prisms induced the planar alignment (yielding n_o) of LCs under investigations. Degree of the homeotropic alignment was checked on control samples by the POM and estimations of the conoscopic pictures. The estimations showed that the mixture of 1% lecithin in ethyl alcohol provided better alignment than the mixture of 0.1% cetyl-trimethylammonium bromide in deionized and bidistilled water. In Fig. 2, the conoscopic pictures for these two cases are presented. As seen in this figure, the mixture of lecithin provides better homogeneity of the homeotropic alignment. 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

$$P = \frac{I_{max} - I_{min}}{I_{max} + I_{min}}. \quad (10)$$

Here the I_{min} is the intensity of light, transmitted from the sample, which was placed parallel to the polarizer (or analyzer); the I_{max} is the intensity of light, which was transmitted from the sandwich-cell, placed under 45° to the polarizer (or analyzer). The degree of the planar orientation for 8CB, 10CB and 12CB was estimated as $P \approx 0.90–0.92$.

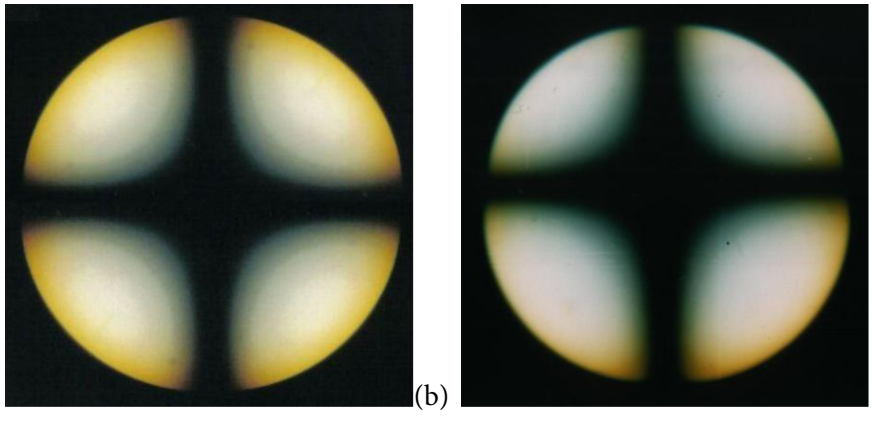
4. Results and discussion

Temperatures of phase transitions in 8CB, 10CB and 12CB were examined by observing of texture transformation, using the POM method. Heating was done at the rate of 1.0 K/min. Results of the examination are presented in the Table.

Table. Temperatures of phase transitions in 8CB, 10CB and 12CB.

Sample	Phase transition temperatures, K			
	Cr–SmA	SmA–N	N–I	SmA–I
8CB	294.3	306.8	313.8	–
10CB	317.1	–	–	323.5
12CB	321.3	–	–	331.7

The temperature dependences of the refractive indices n, n_e and n_o for 8CB, 10CB and 12CB are presented in Figs. 3–5. As seen in these figures, temperature dependences of n for liquid crystals under investigation exhibit practically linear behaviour with slight fluctuations in the region of the phase transitions. However, as the temperature increases, the refractive indices n_e and n_o show different behaviour. The refractive index n_e strongly depends on the temperature and decreases in the smectic A mesophase range with an increase in temperature for 10CB and 12CB. The refractive index n_o shows weak temperature dependence in the mesophase region but some increase of this index near the clearing temperature for these liquid crystals. In the *smectic A–isotropic liquid* (SmA–I) phase transition region, a disappearance of the refractive indices n_e and n_o takes place (Figs. 4, 5). This effect is connected with disappearance of the optical anisotropic properties and appearance of the optical isotropic properties in liquid crystalline materials at the clearing temperature. Then, in the isotropic liquid state the refractive index n decreases slightly with an increase in temperature, like other liquid crystalline materials for the *nematic–isotropic liquid* (N–I) and *cholesteric–isotropic liquid* (Ch–I) phase transitions [33, 37, 40, 45].



(a) (b)

Fig. 2. Conoscopic pictures of homeotropic oriented samples: (a) orientation by lecithin; (b) orientation by cetyl-trimethylammonium bromide.

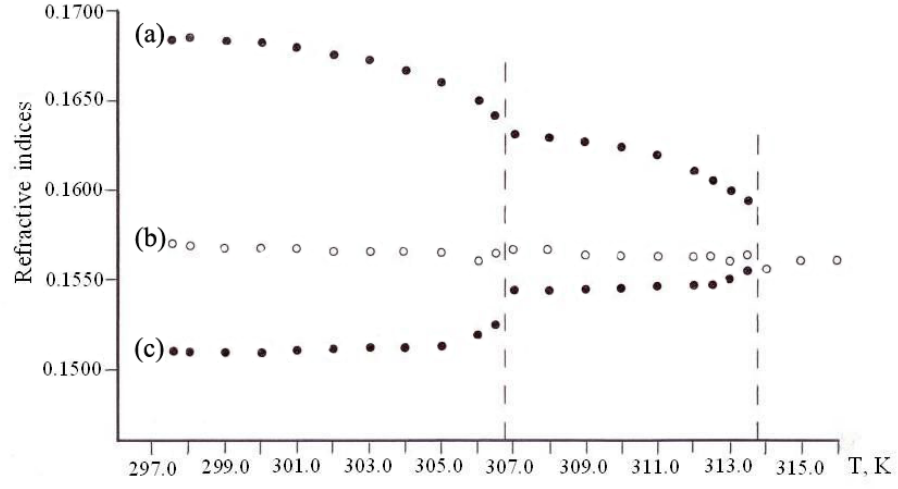


Fig. 3. The temperature dependences of the n_e (a), n (b) and n_o (c) refractive indexes for 8CB.

As seen in Fig. 3, the refractive indices n_o and n_e undergo abrupt changes twice: in the *smectic A–nematic* (SmA–N) and N–I phase transition regions. A similar interesting behaviour of the refractive indexes for liquid crystals in the *smectic A–cholesteric* (SmA–Ch) and *cholesteric–isotropic liquid* (Ch–I) phase transitions was also observed in [33, 40]. Such character of the temperature dependences of the above-mentioned

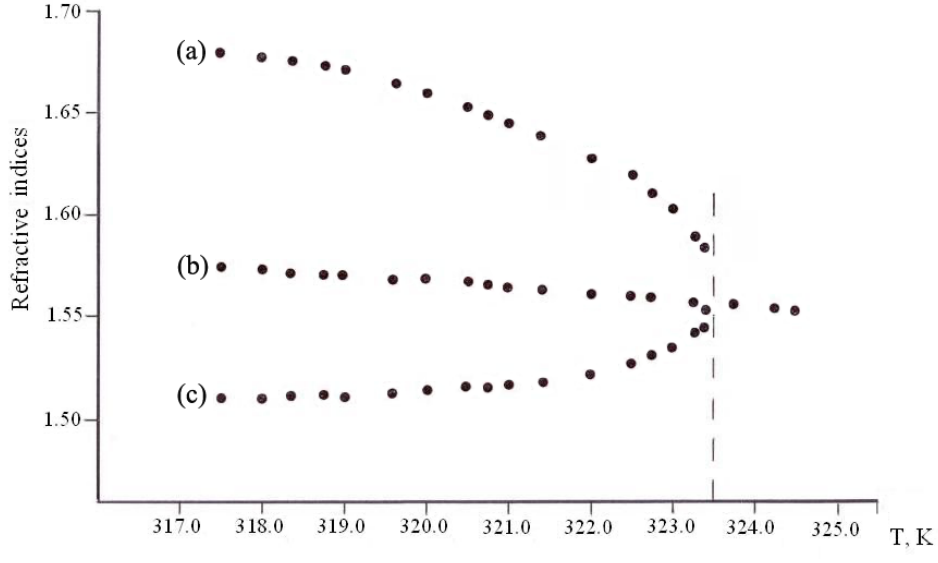


Fig. 4. The temperature dependences of the n_e (a), n (b) and n_o (c) refractive indexes for 10CB.

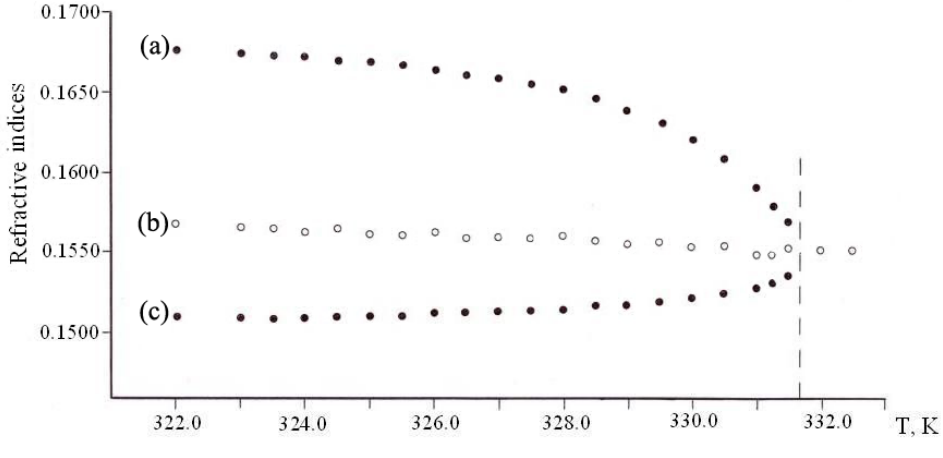


Fig. 5. The temperature dependences of the n_e (a), n (b) and n_o (c) refractive indexes for 12CB.

refractive indices is due to decreased orderedness, which results in a decrease of the optical anisotropy in the nematic mesophase as compared with the smectic A mesophase.

The temperature dependences of α_e and α_0 for the liquid crystals under investigation are presented in Figs. 6–8. As seen in these figures, the temperature dependences of α_e and α_0 exhibit a similar behaviour for 8CB, 10CB and 12CB. These figures demonstrate that as temperature increases, α_e decreases and α_0 increases. A break in α_e and α_0 is observed at the SmA–N and N–I phase transitions for 8CB and at the SmA–I phase transitions for 10CB and 12CB. In the isotropic liquid state $\alpha_o = 0$ and $\alpha_e = 0$ takes place. That fact indicates disappearance of the principal polarizabilities of the liquid crystalline mesophase in the directions of the ordinary and extraordinary rays. Using the α_e and α_0 values, the average polarizability α_{ave} was determined by

$$\alpha_{ave}^2 = \frac{\alpha_e^2 + 2\alpha_0^2}{3}. \tag{11}$$

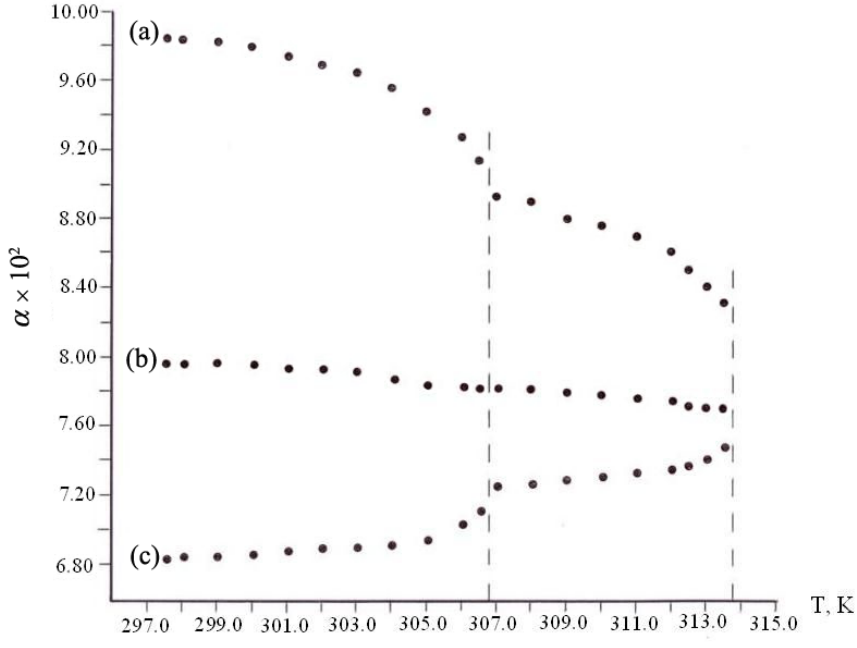


Fig. 6. The temperature dependences of α_e (a), α_{ave} (b) and α_0 (c) for 8CB.

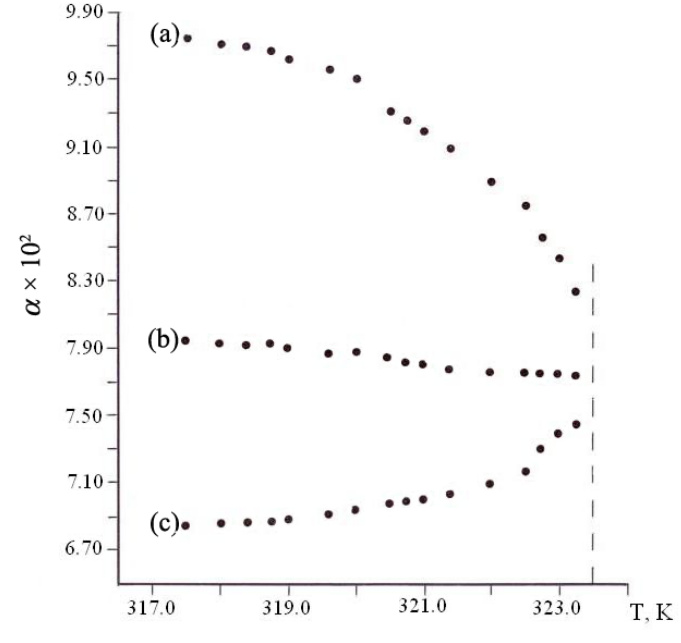


Fig. 7. The temperature dependences of α_e (a), α_{ave} (b) and α_0 (c) for 10CB.

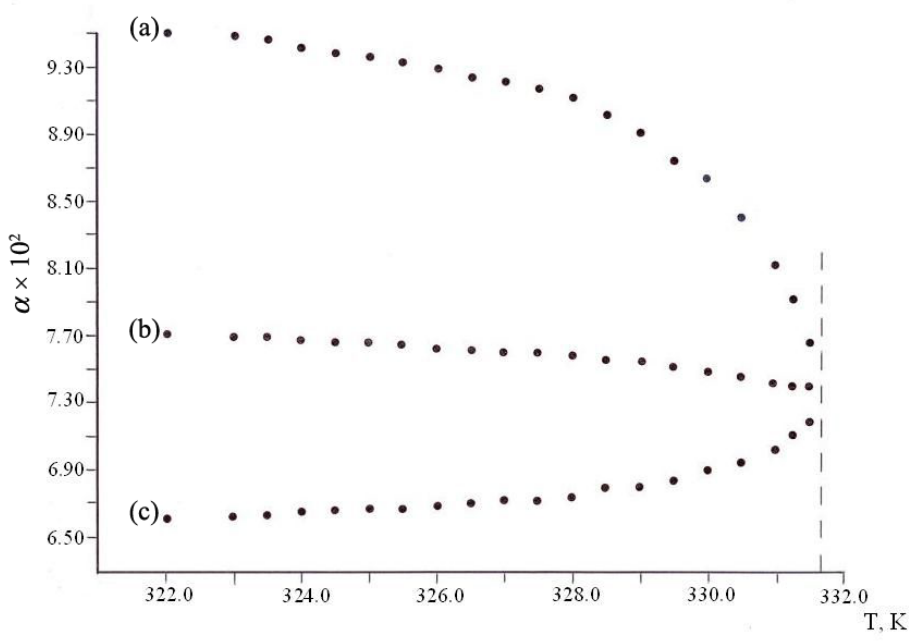


Fig. 8. The temperature dependences of α_e (a), α_{ave} (b) and α_0 (c) for 12CB.

As seen in Figs. 6–8, α_{ave} is almost constant in both nematic and smectic A mesophases for the liquid crystals under investigations. Such behaviour of α_{ave} corresponds to the temperature behaviour of the optical isotropic parameter, i. e. the behaviour of n.

In Fig. 9, the temperature dependences of α_{eg} are presented. As seen in this figure, it is found that α_{eg} fluently increases with a temperature increase in the nematic mesophase region for 8CB and in the smectic A mesophase region for 8CB, 10CB and 12CB. The value of α_{eg} aspires to unity in the isotropic liquid state for these liquid crystals. When α_{eg} reaches unity, this means that in this temperature region there is not any orientational order in liquid crystalline material and the value of the order parameter is therefore zero. Such behaviour of α_{eg} is related with the fact that differences between n_e and n_o, and accordingly the Δn value are decreased with an increase in temperature (Eq. 9). A similar behaviour of α_{eg} was predicted in [43] and was also observed by various researches for different liquid crystalline materials in [15, 28, 41].

The behaviour of Δn, as the behaviour of other tensorial parameters (e. g. anisotropy of dielectric properties, anisotropy of viscosity, etc.), corresponds to the behaviour of the order parameter. As it is noted in [33], the measurements of $\Delta n = \Delta n(T)$ provide a more direct method to obtain a fairly ac-

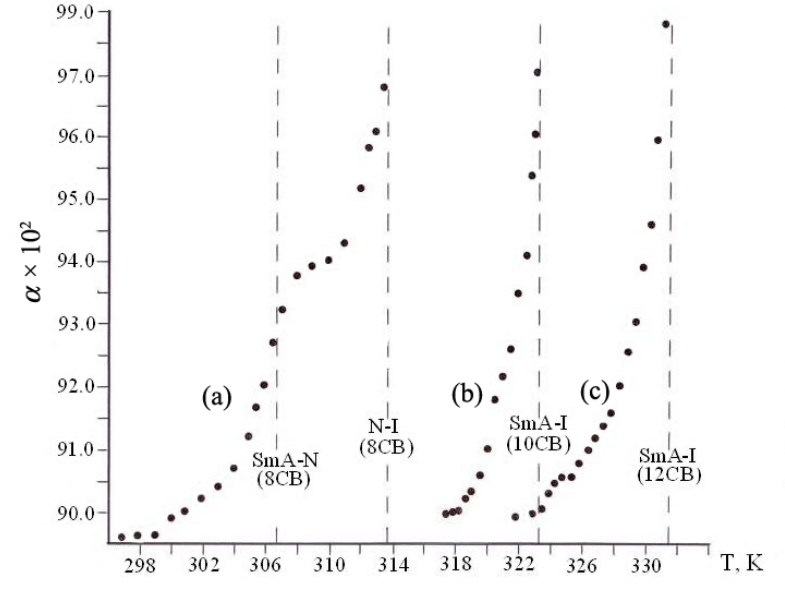


Fig. 9. The temperature dependences of α_{eg} for 8CB (a), 10CB (b) and 12CB (c).

curate value of the order parameter. Therefore, a behaviour of the order parameter in a large number of liquid crystalline materials has been reported, using the Δn data [7, 8, 15, 20, 24, 31, 35, 40, 45–47]. In Fig. 10, the temperature dependences of the birefringence for 8CB, 10CB and 12CB are shown. From these figures it is observed that longer homologues display distinctly smaller optical anisotropy. This fact may be attributed to the higher clearing temperature for the longer homologues. Such peculiarity for other homologues was also observed in various liquid crystalline materials in [7, 15, 20]. Besides, as seen in Fig. 10, a fluent decrease of Δn with an increase of temperature and jump-like change of this parameter in the region of the SmA–N phase transition takes place for 8CB.

As it is known, the character of the SmA–N phase transition is determined by the orientational order parameter Q and translational order parameter $|\psi|$. The parameter $|\psi|$ describes correlation of the gravity centers of molecules in smectic layers [30, 48, 49]. In the nematic mesophase $|\psi| = 0$ and in the smectic mesophase $|\psi| \neq 0$ takes place. Deviation of the order parameter $Q(T)$ in the smectic A mesophase from this parameter $Q_0(T)$ in the nematic mesophase is determined by

$$\delta Q = Q - Q_0 = \kappa C|\psi|^2. \quad (12)$$

Here κ is a function, which is dependent on difference between temperatures of the SmA–N (T_{AN}) and N–I (T_{NI}) phase transitions; C is a constant. For the first order SmA–N phase transition $\delta Q \neq 0$, for the second order SmA–N phase transition $\delta Q = 0$. In the microscopic theory, the numerical criterion for the SmA–N phase transition is presented [30, 48, 50]. This criterion is connected with the above-mentioned T_{AN} and T_{NI} transition temperatures. For $\frac{T_{AN}}{T_{NI}} = \beta > 0.87$ the first order transition, for $\frac{T_{AN}}{T_{NI}} = \beta < 0.87$ the second order transitions take place. As it is seen in the Table, the ratio between T_{AN} and T_{NI} is as $\frac{T_{AN}}{T_{NI}} \approx 0.95$ for 8CB. Thus, jump-like behaviour of the Δn and value of the β criterion indicates the first order transition between smectic A and nematic mesophases in 8CB.

As seen in Fig. 10, the abrupt changes of the Δn in the region of the SmA–I phase transition take place for 10CB and 12CB. Such behaviour of Δn vs. temperature indicates the first order SmA–I phase transition. A similar behaviour of Δn for the first order transition has been also observed in [47, 48]. The direct SmA–I phase transition has attracted increasing attention because that is transition from the layering organized structure to the disordered physically isotropic state. Peculiarities of the SmA–I phase transition have been experimentally studied by various scientists for different liquid crystalline materials in [22, 51–58]. In these works the SmA–I phase transition as the first order transition was found. Besides, this transition is more strongly first order than the N–I transition, which is known to be a sufficiently weak first order transition. The SmA–I phase transition within a phenomenological Ginzburg-Landau and Landau-de Gennes approaches has been theoretically investigated in [59–66]. In this work the above-mentioned transition is found to be the strong first order. Besides, in [66] this result is compared with a wide variety of phenomena including effects of nonmesogenic impurities and electric field,

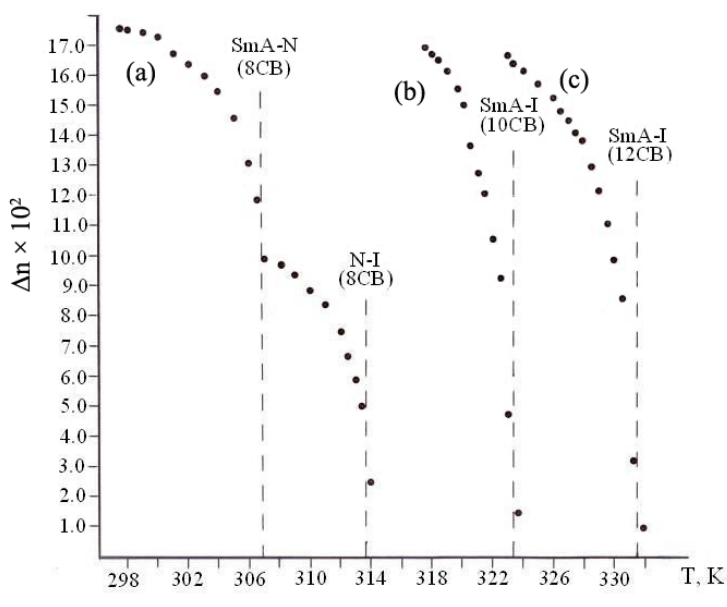


Fig. 10. The temperature dependences of Δn for 8CB (a), 10CB (b) and 12CB (c).

hydrodynamics, fluctuations, and the elastic theory of liquid crystalline elastomers. Thus, the results, obtained in the present study, are in well conformity with experimental results, obtained in [22, 51–58], and with theoretical predictions, obtained in [59–66].

5. Conclusions

In this work, the thermotropic, refracting and thermooptical properties of the 4-n-alkyl-4'-cyanobiphenyls (n = 8, 10, 12) have been studied. Investigations have been carried out for the planar alignment, homeotropic alignment and non-alignment samples. Results showed that the longer homologues of the 4-n-alkyl-4'-cyanobiphenyls displayed distinctly smaller optical anisotropy. Namely, the maximum birefringence values are as $\Delta n = 0.1760$ for 8CB, $\Delta n = 0.1700$ for 10CB and $\Delta n = 0.1680$ for 12CB. This fact may be attributed to the higher clearing temperature for the longer homologues ($T = 306.8$ K for 8CB, $T = 317.1$ K for 10CB and $T = 321.3$ K for 12CB).

Investigations show that the extraordinary refractive index (n_e) and the α_e principal polarizability decrease sharply while the ordinary refractive index (n_o) and the α_o principal polarizability increase slightly as the temperature increases. The breaks in n_e, α_e and n_o, α_0 are observed at the SmA–N and N–I phase transitions for 8CB and at the SmA–I phase transitions for 10CB and 12CB. These breaks are related with abrupt changes in the optical anisotropy of liquid crystalline mesophase and in the polarizability of molecules in the phase transition regions.

The temperature behaviour of n and α_{ave} indicates thermal stability of the refractivity and polarizability of 8CB, 10CB and 12CB. In this work the extrapolated average refractive index (n_{ave}) has been obtained by the extrapolation of the refractive index of isotropic liquid (n_{iso}) into the nematic and smectic A mesophases for 8CB and into the smectic A mesophase for 10CB and 12CB. The results, which have been obtained by extrapolating, entirely coincide with the results, which have been obtained by the refractometric method.

The character of temperature changes of Δn in the phase transition coincides with the character of temperature changes of the order parameter. The $\Delta n = \Delta n(T)$ dependences indicate the first order SmA–N and N–I phase transitions in 8CB and the first order SmA–I phase transitions in 10CB and 12CB.

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TRIJŲ 4-N-ALKIL-4'-CIANOBIFENILŲ TERMOTROPINĖS, ATSPINDŽIO IR TERMOOPTINĖS SAVYBĖS

A. Nesrullajev

Mugla Sitki Koçman universiteto Mokslo fakulteto Fizikos katedra, Kötekli Muğla, Turkija