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Order Parameters and Refractive Indices of Two Carboxylate Nematic Liquid Crystals With Negative Dielectric Anisotropy

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Refractive indices of two carboxylate nematic liquid crystals have been measured throughout the nematic and isotropic phases to determine their order parameters by using the Vuks method [Vuks, M. F. (1966). Opt. Spektrosk.*, 20, 644], and characterization of anisotropic behaviors. These factors characterize anisotropic behaviors of selected liquid crystals with negative dielectric anisotropy that are essential for their applications and improvement. The temperature dependence of refractive indices, birefringence, and order parameters in the anisotropic phase have been investigated for these nematic liquid crystals. Furthermore, the alkyl substituents' effects on the order parameters of carboxylate liquid crystals were also investigated.*

Keywords Carboxylate liquid crystal; negative dielectric anisotropy; order parameter; refractive index

1. Introduction

The liquid crystals exhibit anisotropy in many of their physical properties. These properties allow their applications in display and other optical device technologies. The optical anisotropy, or birefringence, is an essential physical property for the optimization of liquid crystals for application in liquid crystal display devices [1].

Order parameter is a uniquely important parameter of a liquid crystal, which controls nearly all its physical properties [1–5]. This parameter can be used for the estimation of molecular parameters of liquid crystal substances such as molecular polarizabilities and their anisotropy [6,7]. The knowledge of temperature dependence of order parameter and refractive indices is practically important from the operating point of view [8]. The microscopic order parameter (S), first introduced by Tsvetkov [9,10], is given by

$$S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle, \tag{1}$$

where θ is the angle between the optic axis and long molecular axis of a molecule. In most of the cases, the microscopic order parameters provide an adequate description of liquid crystal systems. However, in some cases, this microscopic description is no longer

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adequate and some other means must be found for specifying the degree of order. The macroscopic properties, such as refractive index, can be used to identify the macroscopic order parameters (Q) [1–4]:

$$Q = \frac{n_e - n_o}{\Delta n_o}, \tag{2}$$

where Δn_o is the birefringence corresponding to complete alignment, and n_e and n_o are extraordinary and ordinary components of refractive indices, respectively.

Several methods have been developed for the determination of order parameters. Among these methods, optical methods are the most commonly used ones [11–14]. It is generally accepted that the data obtained by the optical measurements are one of the most accurate, precise, and convenient results that one can acquire. Thus, optical methods are normally preferred to determine order parameters. Furthermore, optical methods provide optical anisotropy data that are important for the application of liquid crystals in display devices [15].

In this work, we have studied two nematic liquid crystals with negative dielectric anisotropy. These liquid crystals have polar carboxylate linking group and attached electronegative chloro substance. In order to obtain the effect of this attractive structure on optical properties of these liquid crystals, we determined the birefringence, ordinary and extraordinary refractive indices, macroscopic and microscopic order parameters, and temperature dependence of these parameters on these liquid crystals. Thus, all the physical and optical properties of these liquid crystals with attractive structure can be calculated by using the obtained parameters.

2. Theory

2.1. Normalized Polarizabilities and Temperature Gradient of Refractive Indices

Because of the anisotropic character of liquid crystals, these matters have two refractive indices, n_e and n_o. Vuks [16] suggested a semi-empirical equation that shows relationship between microscopic molecular polarizablities and macroscopic refractive indices for the liquid crystal anisotropic medium in isotropic local field:

$$\frac{\left(n_{e,o}^2 - 1\right)}{\left(\langle n^2 \rangle + 2\right)} = \left(\frac{4\pi}{3}\right) N\alpha_{e,o}, \tag{3}$$

where, n_e and n_o are refractive indices for the extraordinary and ordinary rays, respectively, α_e and α_o are respective molecular polarizabilities, N is the number of molecules per unit volume, and $<n^2>$ is defined as

$$\langle n^2 \rangle = \frac{\left(n_e^2 + 2n_o^2\right)}{3}. \tag{4}$$

Ordinary and extraordinary refractive indices can be obtained as a function of average refractive index ($\langle n \rangle = \frac{n_e + 2n_o}{3}$) and the birefringence ($\Delta n = n_e - n_o$) [17],

$$n_e = \langle n \rangle + \frac{2}{3}\Delta n, \tag{5a}$$

$$n_o = \langle n \rangle - \frac{1}{3}\Delta n. \tag{5b}$$

To describe the temperature dependence of birefringence, Haller's approximation ($Q = (1 - {}^{T}/_{T_c})^{\beta}$) [18] is usually employed when the temperature is not too close to the clearing point:

$$\Delta n = \Delta n_o \left(1 - \frac{T}{T_c}\right)^{\beta}. \tag{6}$$

In Eq. (6), Δn_o is the liquid crystal birefringence in crystalline state (or at $T = 0$ K), T_c is the clearing temperature of the liquid crystal compound, and β is its material characteristic constant. Using the linear curve fitting approach on logarithmic form of Eq. (6), the values of Δn_o and β are obtained. Utilizing the experimental data of n_e and n_o, it is found that $\sqrt{\langle n^2 \rangle}$ decreases linearly with temperature as [17]

$$\sqrt{\langle n^2 \rangle} = A + BT. \tag{7}$$

Substituting Δn and $\sqrt{\langle n^2 \rangle}$ from Eqs. (6) and (7) into Eqs. (5a) and (5b), the modified four-parameter model [1,17] is acquired that describes the temperature dependence of liquid crystal refractive indices:

$$n_e = A + BT + \frac{2}{3}\Delta n_o \left(1 - \frac{T}{T_C}\right)^{\beta}, \tag{8a}$$

$$n_o = A + BT - \frac{1}{3}\Delta n_o \left(1 - \frac{T}{T_C}\right)^{\beta}. \tag{8b}$$

Equations (8a) and (8b) contain four unknown parameters ([A, B] and [Δn_o, β]). These parameters can be obtained separately by two-stage fitting the experimental data of $\sqrt{\langle n^2 \rangle}$ and Δn. To obtain [A, B], one can fit $\sqrt{\langle n^2 \rangle}$ as a function of temperature dependence using Eq. (7). Furthermore, fitting the experimental data of Δn as a function of temperature by using Eq. (6) gives the values of Δn_o and β. Moreover, variation rate of n_e and n_o with respect to temperature [1] can be expressed as

$$\frac{dn_e}{dT} = B - \frac{2}{3}(\beta(\Delta n_o)/T_C)(1 - T/T_C)^{\beta - 1}, \tag{9a}$$

$$\frac{dn_o}{dT} = B + \frac{1}{3}(\beta(\Delta n_o)/T_C)(1 - T/T_C)^{\beta - 1}, \tag{9b}$$

and the ratio of normalized polarizabilities can be expressed as [19]

$$\frac{\alpha_e}{\alpha_o} = \frac{(n_e^2 - 1)}{(n_o^2 - 1)}. \tag{10}$$

2.2. Determination of Order Parameters

Value of macroscopic order parameter can be determined by means of Haller's approximation, according to which the order parameter can be approximated as $Q = (1 - {}^{T}/_{T_c})^{\beta}$. Using this equation along Eq. (6), one can rewrite Eq. (5) as

$$n_e = \langle n \rangle + \frac{2}{3}\Delta n_o Q, \tag{11a}$$

$$n_o = \langle n \rangle - \frac{1}{3}\Delta n_o Q. \tag{11b}$$

After subtracting Eq. (11a) from Eq. (11b), Eq. (2) for the order parameter (Q) can be acquired. This method can be directly applied to the birefringence data rather than to refractive indices. In this approach, the orientational order parameter is calculated by means of the Vuks assumption [16]:

$$S\left(\frac{\Delta\alpha}{\alpha}\right) = \frac{n_e^2 - n_o^2}{\langle n^2 \rangle - 1}, \tag{12}$$

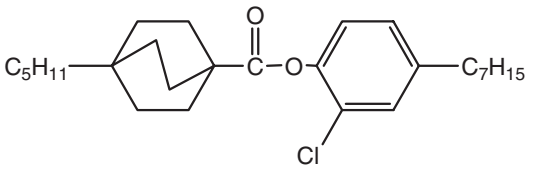
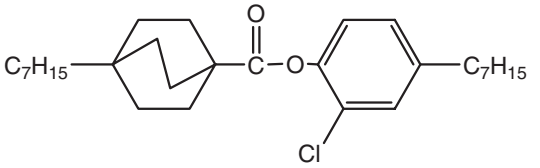
where $\Delta\alpha$ ($= \alpha_{II} - \alpha_{\perp}$) is the anisotropy of polarizability and α is the mean molecular polarizability. To determine ($\frac{\Delta\alpha}{\alpha}$), plot linear part of $\ln[\frac{3(n_e^2 - n_o^2)}{n_e^2 + 2n_o^2 - 3}]$ against $\ln(1 - {}^{T}/_{T_c})$ and extrapolate to $T = 0$ K. The intercept at $T = 0$ K, where complete ordered structure exists, i.e., $S = 1$, gives the value of scaling factor ($\frac{\Delta\alpha}{\alpha}$). Assuming that the value of ($\frac{\Delta\alpha}{\alpha}$) remains fixed for all temperatures, and substituting into Eq. (12), one can obtain values of order parameters at different temperatures. Thus, the smaller scaling factors and the larger values of ($\frac{n_e^2 - n_o^2}{\langle n^2 \rangle - 1}$) render higher values for the microscopic order parameter.

3. Experimental

3.1. Materials

The liquid crystalline materials (7CP5BOC and 7CP7BOC) were synthesized in the Institute of Chemistry of the Military Technical Academy, Warsaw, Poland. The chemical structures of these compounds are shown in Table 1. The nematic to isotropic transition temperatures (clearing temperatures) for these nematogens were measured by using differential scanning calorimetry (DSC) and polarized microscopy methods, and are given in Table 1.

Table 1. Chemical structures and clearing temperature, T_C, of carboxylate nematic liquid crystalline compounds.

Abbreviated name	Compounds	T_C (°C)
7CP5BOC	 2-chloro-4-heptylphenyl 4-pentylbicyclo[2.2.2]octane-1-carboxylate	43.6
7CP7BOC	 2-chloro-4-heptylphenyl 4-heptylbicyclo[2.2.2]octane-1-carboxylate	47.3

3.2. Refractive Index Measurements

Refractive index is measured using Abbe's refractometer having an accuracy of 0.00001 in the range of 1.2 to 1.74 (Bellingham Stanley Abbe 60ED). A polarizer sheet is introduced at Abbe's refractometer ocular to block extraordinary ray. This clears the contrast of boundary line. The temperature of Abbe's refractometer was controlled by circulating water in a water bath temperature controller. The temperature was measured by placing a thermometer in close vicinity of the sample with an accuracy of $\pm 0.01^{\circ}$C, and the ordinary and extraordinary refractive indices, n_o and n_e, are measured directly in the nematic phase.

4. Results and Discussion

4.1. Birefringence, Refractive Indices, and Their Temperature Dependence

The temperature variation of experimental data for ordinary and extraordinary refractive indices (n_e, n_o) and birefringence (Δn) are given in Figs 1 and 2 for liquid crystals. The unknown constants (A, B, β, and Δn_0) of the modified four-parameter model by fitting experimental data of Δn and $\sqrt{\langle n^2 \rangle}$ into Eqs. (6) and (7) were obtained. The fitting parameters for investigated samples are listed in Table 2.

In Fig. 1, the obtained values via curve fitting and the experimental results for investigated liquid crystals show good agreement. Furthermore, these liquid crystals show positive optical anisotropy (i.e., $n_e > n_o$) over the entire nematic phase. The ordinary refractive index (n_o) increases slightly, while the extraordinary refractive index (n_e) decreases sharply with increase in temperature. At the nematic–isotropic phase transition point, the value of refractive indices change abruptly. The birefringence values also show a sharp decrease with increase in temperature. On the other hand, small temperature fluctuations in the range of nematic–isotropic phase transition cause a large change in birefringence. In isotropic phase, the birefringence (Δn) is zero and refractive index decreases with increase in temperature.

The same molecular skeletons and odd number of CH_2 groups in the chain of investigated liquid crystals cause the values of the optical parameters, such as refractive index and birefringence, show a similar amount. Although the small alkyl chain in 7CP5BOC as compared with 7CP7BOC, five in case of 7CP5BOC and seven in case of 7CP7BOC, causes the higher number of 7CP5BOC, molecules exist per unit volume and exhibit a higher ordinary and extraordinary refractive index in all the nematic range as compared with 7CP7BOC liquid crystals. The two additional CH_2 groups in the case of 7CP7BOC give fluctuation in contributions to the polarizability of the long axis, which results in decrease in birefringence as compared with 7CP5BOC.

Table 2. Fitting parameters for the average refractive index and birefringence of the studied liquid crystals.

	7CP5BOC	7CP7BOC
A	1.63605	1.63494
B	-4.12×10^{-4} (K^{-1})	-4.17×10^{-4} (K^{-1})
Δn_0	0.08788	0.103
β	0.1474	0.1981

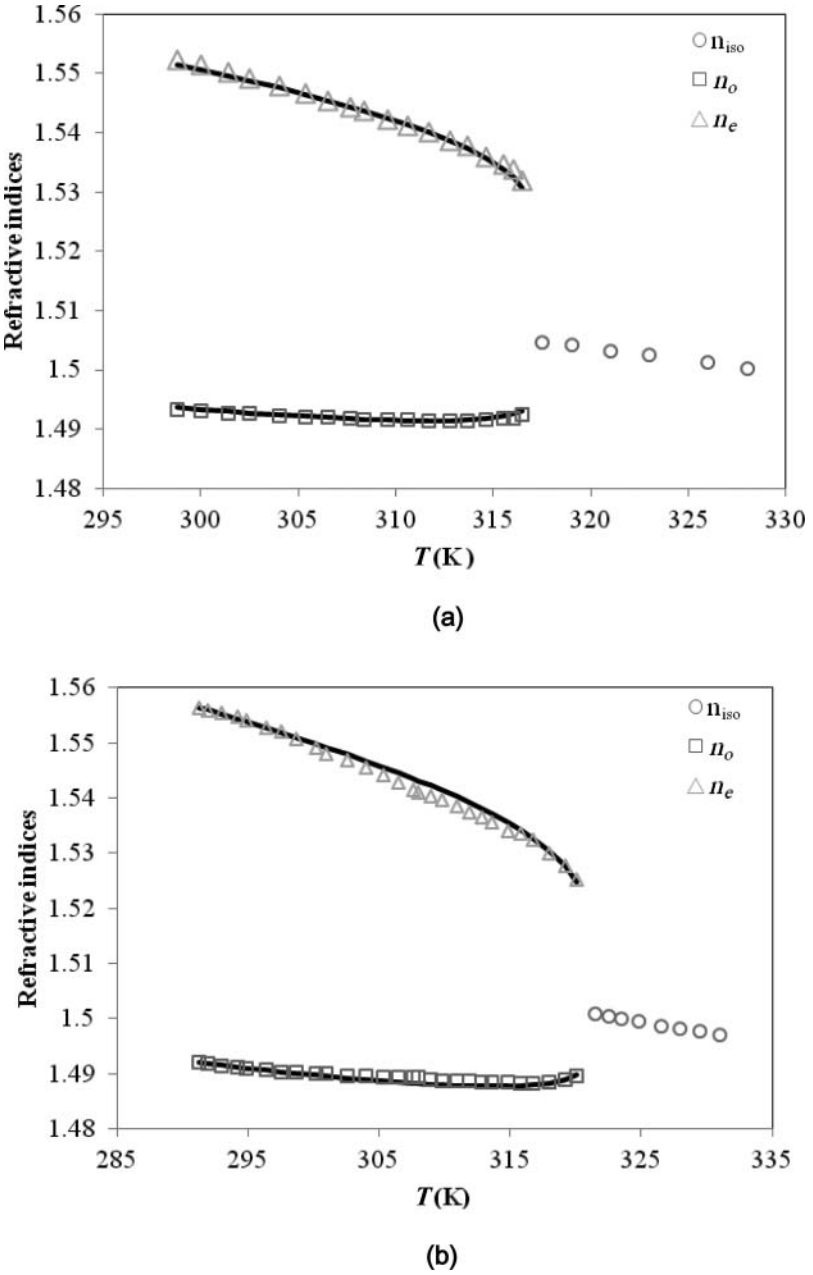


Figure 1. Temperature dependence of refractive indices (n_e, n_o). Marker represents the experimental data of (n_e, n_o, and n_{iso}) for liquid crystals. Solid lines are the fitting curves using four-parameter model. (a) 7CP5BOC (b) 7CP7BOC.

The effects of the tail length in the contribution to the polarizability of investigated liquid crystals can be explained in the way similar to birefringence. The variations in the ratio of normalized polarizabilities $\frac{\alpha_e}{\alpha_o}$ with temperature show the same performance of birefringence of the carboxylate nematic liquid crystals (Fig. 3). The ratio of normalized

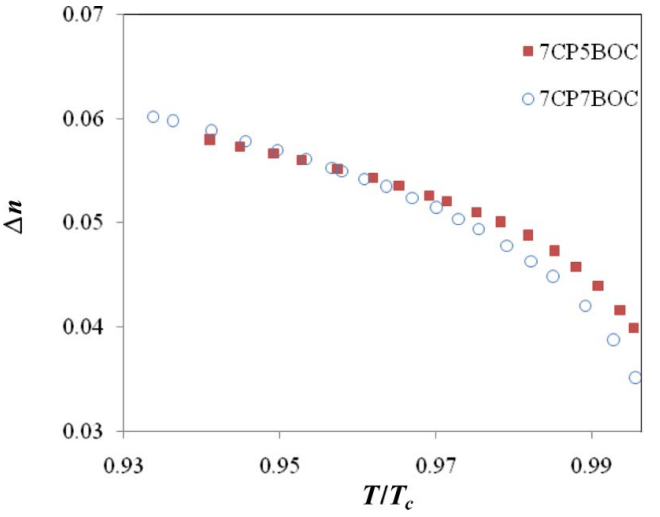


Figure 2. Temperature-dependent birefringence of carboxylate nematic liquid crystals.

polarizabilities decreases as the temperature increase, and near the clearing temperature, the value of $\frac{\alpha_e}{\alpha_o}$ goes to one (see Eq. (10)).

By using the listed parameters in Table 2, one can calculate $\frac{dn_e}{dT}$ and $\frac{dn_o}{dT}$ for these liquid crystals. The temperature dependence of $-\frac{dn_e}{dT}$ and $\frac{dn_o}{dT}$ for carboxylate nematic samples is shown in Fig. 4. The extraordinary refractive index decreases with increase in temperature; therefore, its negative temperature gradient $(-\frac{dn_e}{dT})$ always remains positive for all liquid crystal samples throughout their nematic range. The ordinary refractive index of these liquid crystals increases with increase in temperature. The temperature gradient $(\frac{dn_o}{dT})$ show

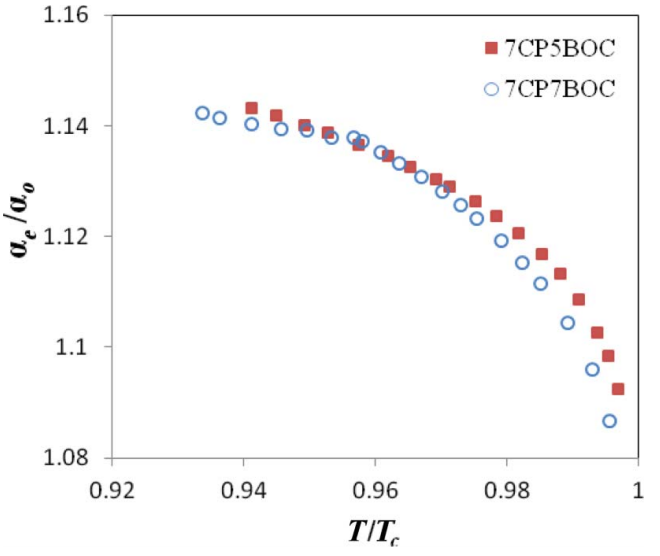


Figure 3. The variation of ratio of normalized polarizabilities $\frac{\alpha_e}{\alpha_o}$ with temperature.

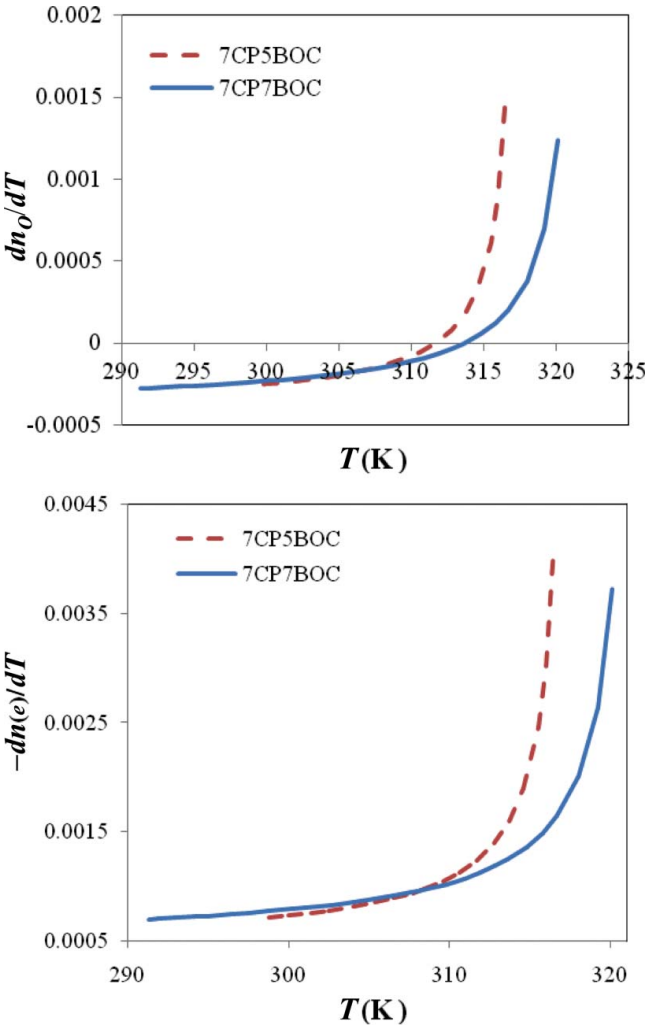


Figure 4. The temperature dependencies of $-\frac{dn_e}{dT}$ and $\frac{dn_o}{dT}$ for liquid crystals.

positive value for carboxylate nematic liquid crystals behind the crossover temperature, T_o [20]. It was known, based on Eq. (9b), that low clearing temperature and high birefringence are two important factors for achieving a large $\frac{dn_o}{dT}$ [20,21]. When T approaches T_c, both $\frac{dn_e}{dT}$ and $\frac{dn_o}{dT}$ changes significantly (Fig. 4). In other words, in the vicinity of phase transition temperature, a small temperature fluctuation would cause a big change in $\frac{dn_o}{dT}$ and $\frac{dn_o}{dT}$.

4.2. Order Parameter of Carboxylate Liquid Crystals

The microscopic order parameters (S) of investigated carboxylate liquid crystals were calculated from refractive indices data and the Vuks approach [16], Eq. (12), with estimating the scaling factors for these liquid crystal substances. The macroscopic order parameters (Q) can be obtained from birefringence (Eq. (2)). Macroscopic and microscopic order parameters show good agreement (Fig. 5).

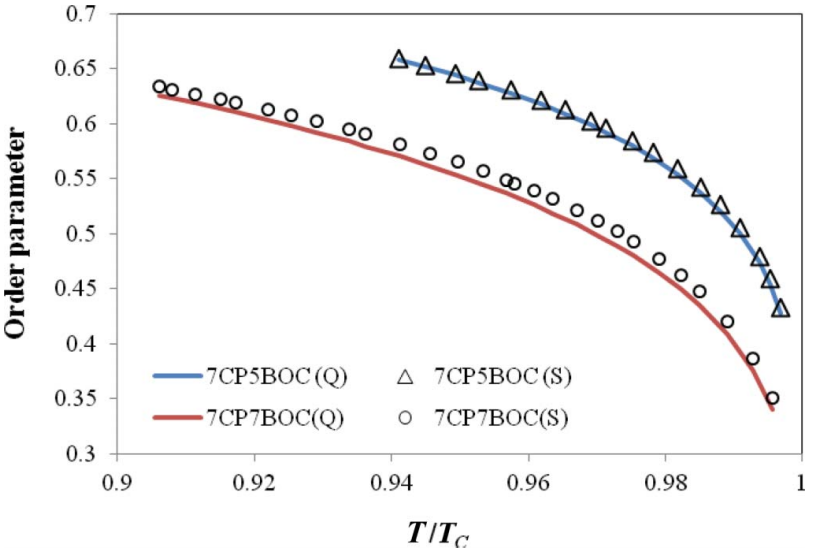


Figure 5. Temperature dependence of microscopic (S) and macroscopic (Q) order parameters for liquid crystals.

According to Eq. (12), the microscopic order parameters depend on scaling factor ($\frac{\Delta\alpha}{\alpha}$) and values of ($\frac{n_e^2-n_o^2}{\langle n^2\rangle-1}$). The lower amount of scaling factor and the higher amount of ($\frac{n_e^2-n_o^2}{\langle n^2\rangle-1}$) lead to higher microscopic order parameter. Here, the value of scaling factors equals to 0.21 and 0.24 for 7CP5BOC and 7CP5BOC respectively. In Fig. 6 the values of ($\frac{n_e^2-n_o^2}{\langle n^2\rangle-1}$) against the reduced temperature for investigated liquid crystals are shown. The values of

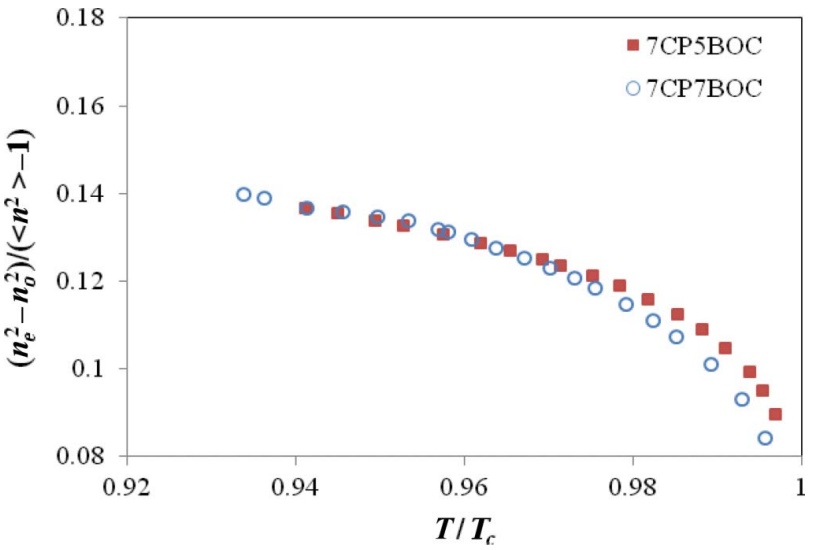


Figure 6. Temperature dependence of ($\frac{n_e^2-n_o^2}{\langle n^2\rangle-1}$) for investigated liquid crystals.

$(\frac{n_e^2 - n_o^2}{\langle n^2 \rangle - 1})$ in investigated carboxylate show the same amount. 7CP7BOC shows lesser order parameter values as compared to 7CP5BOC carboxylate liquid crystals. In addition, the highest amount of scaling factors in 7CP7BOC causes it to have the lowest values of order parameter.

5. Conclusions

Many of ordinary liquid crystal molecules have polar functional groups in head or tail part of molecular structure. Also, the order parameters are controlled with variation pattern in scaling factor and refractive indices. In other words, competitions between the directional functions of these liquid crystals render different variation patterns for order and other optical parameters [1].

The investigated liquid crystals in this work have polar carboxylate linking group and attached electronegative chloro substitute. Furthermore, the existing high polar functional groups in central part of the molecular structure lead to negative dielectric anisotropy in such structures, and variations in dependent parameters to ordinary and extraordinary functions are decreased.

The same molecular skeletons and odd number of CH_2 groups in the chain of investigated liquid crystals cause the values of the optical parameters, such as refractive index and birefringence, show the similar amount. Used carboxylate liquid crystals show a positive anisotropy (i.e., $n_e > n_o$) in the nematic phase. The ordinary refractive index (n_o) increases slightly, while the extraordinary refractive index (n_e) decreases sharply as the temperature increases. The chain group in investigated carboxylate liquid crystals controls variations of refractive indices, birefringence, and order parameters. The highest amount of polarizability anisotropy in 7CP5BOC causes to have the highest amount of normalized polarizabilities and birefringence, as well as the order parameter. 7CP7BOC shows the lowest amount of order parameters. It may be concluded that for investigated carboxylate LCs, low scaling factor controls the microscopic order parameter values.

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