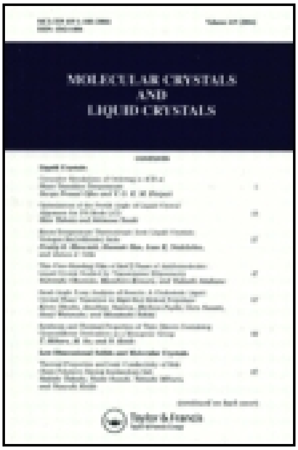

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Optical and Thermodynamic Properties of Mixtures of Pleochroic Dye with Some Alkyl-Cyanobiphenyl Liquid Crystals

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Optical and Thermodynamic Properties of Mixtures of Pleochroic Dye with Some Alkyl-Cyanobiphenyl Liquid Crystals

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The temperature dependence of the refractive indices, guest and host order parameters as well as the melting and clearing points for the binary mixtures of the pleochroic dye in some members of the homologous series of the alkyl-cyanobiphenyl have been measured. Odd-even effect in some thermodynamic properties of the mixtures investigated was observed. A good compatibility between the shift in the nematic–isotropic transition temperature after dye addition and activity coefficient ratio on the one hand and the mutual connection between guest and host order parameter in the vicinity of the clearing point on the other have been found. The experimental results were compared in some details with calculations done on the basis of the Maier-Saupe theory for binary mixtures. It was demonstrated a good agreement between experiment and theory taking into account the flexibility of the end-chain of the host.

Keywords: guest-host system, alkyl-cyanobiphenyl, refractive index, order parameter, phase transition temperature

INTRODUCTION

The pleochroic dye-liquid crystal mixtures (guest-host systems) were recently extensively investigated to get information about the influence of the guest on some physical properties of the liquid crystal on the one hand and to find the best guest-host mixture to application in the liquid crystal display devices on the other.[1–12] Of many liquid crystals that have been used in display devices the alkyl-cyanobiphenyls ($C_nH_{2n+1} \cdot \phi \cdot \phi \cdot CN$), discovered by Gray and collaborators[13] have many advantages, such as the low temperature nematic range, colorless, photochemical stability and the strong positive dielectric anisotropy arising from the cyanin group attached to the molecules. They are also very good matrices for the pleochroic dyes.[3,4,6,9–12] One from the members of the homologous series, 5CB was previously used as a host in the investigation of the optical, thermodynamic and dielectric properties of the dye-liquid crystal mixtures.[3,4,9–12] It was found that addition of the dye to 5CB changes the range of its nematic phase, causing a decrease of the melting point[9,10] and either a decrease or an increase of the clearing point.[3,6,9,10,12] The later changes are dependent on the size and the shape of the dye molecule as well as on the mutual intermolecular interaction between guest and host.[10] Moreover, the influence of the dye on the dielectric constants, the dielectric anisotropy and also on the host order parameter of 5CB was observed.[6,10,11,14] It was also found that order parameter of the guest dissolved in a liquid crystalline matrix depends strongly on the guest concentration.[9,10,12] However, up to now a little data is available concerning guest-host systems using the other member of the homologous series as nematic hosts.[4,14]

The purpose of the present work is an examination of the optical and thermodynamic properties of a dye in the alkyl-cyanobiphenyl family of liquid crystals as a function of the alkyl chain length and the dye concentration as well. The series of the liquid crystals from $n = 6$ to $n = 8$ is studied and results are compared with those obtained for 5CB in Reference 10.

EXPERIMENTAL

The cyanobiphenyls used in this study were supplied by BDH Ltd. and used without further purification: observed transition temperatures were mostly in agreement with those reported in literature[15–17] (Table I). The measurements were made only in the nematic phase of these compounds even though one of them exhibits a smectic A phase below the nematic state.

The bis-azo dye D2 (BDH) was used as a guest. This dye was chosen because its absorption region, high dichroic ratio,[2,10] good solubility and satisfactory photostability make it suitable for application in liquid crystal displays.

The refractive indices *versus* temperature were measured for sodium D light using a Leitz-Jelley microrefractometer with rubbing-induced homogenous alignment of the liquid crystal molecules. On the basis of the refractive indices data the host order parameter $\langle P_2\rangle_H$ for pure liquid crystals and dye-liquid crystal mixtures were estimated using Vuks approximation.[18] The $\bar{a}/\Delta a$ values which are required to estimate the order parameter from the refractive index data were assumed according to Reference 19 and they are presented in Table I. Here $\bar{a}$ is the mean polarizability and Δa is the anisotropy of polarizability of a perfectly oriented medium with $\langle P_2\rangle_H = 1$.

The methods used for the determination of the guest order parameter $\langle P_2\rangle_G$ as well as the phase transition temperatures were described elsewhere.[10]

TABLE I

The properties of the alkyl-cyanobiphenyls R · ϕ · ϕ · CN studied.

Liquid crystal (R)	Transition temperatures [°C] K → N or K → S_A	S_A → N	N → I	$\frac{\bar{a}^{15}}{\Delta a}$	$\frac{\Delta S_{NI}}{R}$	$\frac{l}{d}$
5CB (C_5H_{11})	23.4	—	35.1	1.55	0.131	2.87
6CB (C_6H_{13})	14.5	—	29.1	1.64	0.117	3.06
7CB (C_7H_{15})	29.3	—	42.4	1.71	0.240	3.25
8CB (C_8H_{17})	21.8	33.5	40.6	1.81	0.257	3.44

In all the measurements the dye concentration has been changed from 15 to 45 mM/dm^3.

RESULTS AND DISCUSSION

Refractive indices and order parameters

Figure 1 presents the refractive indices of pure liquid crystals and dye-liquid crystal mixtures as a function of the reduced temperature $T^* = T/T_{NI}$, where T_{NI} is the clearing point either of the pure host or the guest-host mixture and T is the given temperature (in K). The dye concentration was 45 mM/dm^3.

The refractive indices of some members of the homologous series of alkyl-cyanobiphenyls have been reported by other workers[15,16] and measurements presented here are in substantial agreement with them. However, as it can be seen from Figure 1 the addition of the pleochroic dye D2 to the liquid crystalline matrix changes the values of the refractive indices and causes the increase of the birefringence. Such an effect for 5CB was already observed.[10]

On the basis of the birefringence data the host order parameter was evaluated. The values of $\langle P_2 \rangle_H$ for pure liquid crystals and liquid crystals with various concentration of the dye at $T^* = 0.977$ and in the vicinity of the nematic–isotropic

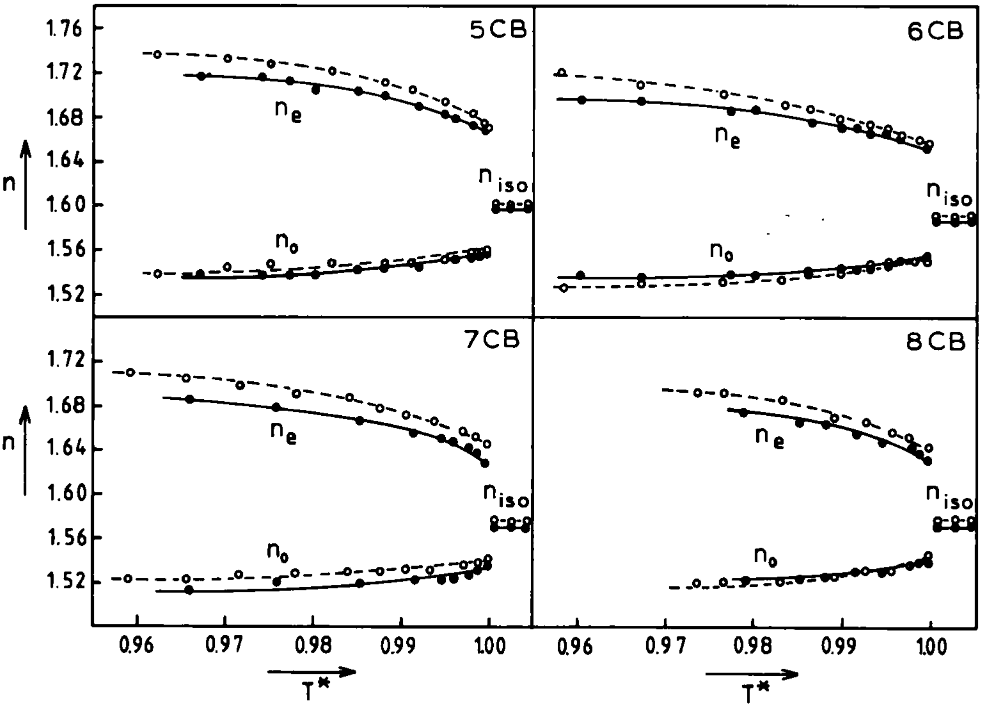

FIGURE 1 Temperature dependence of the refractive indices for the alkyl-cyanobiphenyls (solid curves) and the D2-alkyl-cyanobiphenyl mixtures (dashed curves).

TABLE II

The host and guest order parameters of investigated dye-liquid crystal mixtures.

Liquid crystal	c [mM/dm^3]	$\langle P_2\rangle_H$ $T^* = 0.977$	$\langle P_2\rangle_H$ at $N \rightarrow I$ transition	$\langle P_2\rangle_G$ $T^* = 0.977$	$\langle P_2\rangle_G$ at $N \rightarrow I$ transition
5CB	0	0.560	0.350	—	—
	15	0.560	0.350	0.62	0.43
	30	0.570	0.350	0.64	0.44
	45	0.590	0.360	0.67	0.45
6CB	0	0.510	0.360	—	—
	15	0.520	0.360	0.59	0.39
	30	0.540	0.360	0.61	0.41
	45	0.570	0.370	0.65	0.43
7CB	0	0.585	0.350	—	—
	15	0.585	0.350	0.63	0.41
	30	0.590	0.360	0.64	0.43
	45	0.595	0.370	0.67	0.46
8CB	0	0.590	0.360	—	—
	15	0.590	0.370	0.66	0.42
	30	0.600	0.370	0.68	0.42
	45	0.620	0.380	0.70	0.44

transition are listed in Table II. The error in the estimation of $\langle P_2\rangle_H$ was assigned as ±0.015. The guest order parameters $\langle P_2\rangle_G$, obtained from the polarized absorption measurements are also gathered in Table II. The experimental uncertainty in this case is ±0.01.

From the summary of the results given in Table II several indications can be seen: 1) the changes of the host ordering after dye addition are rather small, but some trend to the rise of the liquid crystal molecules orientation with increasing dye concentration for all alkyl-cyanobiphenyls under investigation is observed; this rise is the largest in the case of 6CB, 2) likewise $\langle P_2\rangle_G$ rises always with increasing dye concentration, but in this case the rise is very distinct, 3) in all cases the $\langle P_2\rangle_G$ values are greater than $\langle P_2\rangle_H$ values, which means that compatibility of dye D2 with liquid crystal studied is very good.

It was previously found that the nematic–isotropic transition temperature and some other physical properties of the homologous series show the odd-even effect.[16,17,20–22] Such a behavior was explained as the alternation of interaction between alkyl chains.[23] The odd-even effect in the order parameter was observed in 5CB, 6CB and 7CB, but $\langle P_2\rangle_H$ value for 8CB is greater than that for 7CB.[16,22] This increasing was attributed to the presence of the smectic A phase below the nematic one.

It is worth noting that the change in the alternation between 7CB and 8CB was also previously observed for bend elastic constant[16] and explained through the smaller longitudinal correlation length in 8CB than in 7CB close to the clearing point.

Figure 2 shows the host order parameter of pure liquid crystal, $\langle P_2\rangle_H$ as well as the host, $\langle P_2\rangle_H$ and the guest, $\langle P_2\rangle_G$ order parameters for the D2-liquid crystal

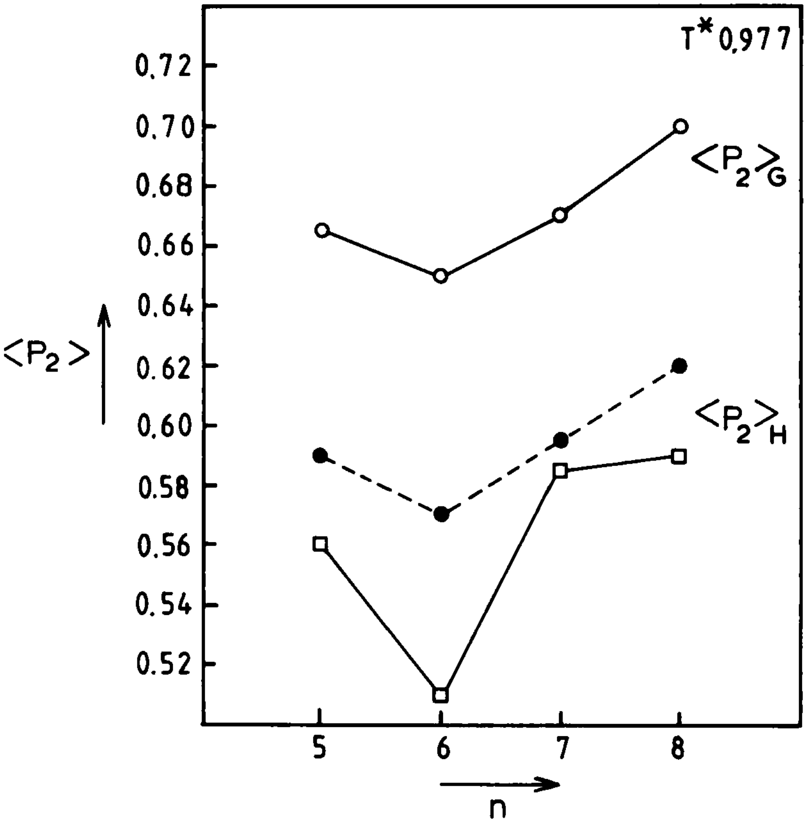

FIGURE 2 Host, $\langle P_2\rangle_H$ and guest, $\langle P_2\rangle_G$ order parameters as a function of the number of carbon atoms in the alkyl chain for the homologous series of alkyl-cyanobiphenyls ($n = 5 \rightarrow 8$). Solid line = $\langle P_2\rangle_H$ for the pure liquid crystals, dashed line = $\langle P_2\rangle_H$ for the D2 – liquid crystal mixtures.

mixtures at T* = 0.977 as a function of the alkyl chain length of the alkyl-cyanobiphenyls studied. The dye concentration was 45 mM/dm^3. The results presented in this figure indicate that addition of the dye D2 does not change the alternation observed for pure liquid crystals, but it is distinctly seen that both host and guest order parameters rise much higher for the even members than for their previous odd members of the series.

Transition temperatures of guest-host mixtures

It was previously found that the dye D2 stabilizes the nematic phase of the 5CB, causing that its clearing point is increasing.[10] Furthermore, the presence of the guest leads to the formation of a two-phase region, in which both nematic and isotropic phases coexist. In order to check the behavior of other members of the homologous series, the T_N and T_I temperatures as a function of the dye concentration have been measured. T_N and T_I are the temperatures at which the two-phase region begins (isotropic phase appears) and ends (nematic phase disappears), respectively, by heating of the guest-host mixture.

The indicator of the ability of the guest to the stabilization of the nematic phase is the positive sign of the β_N and β_I parameters, defined as follows:

$$\beta_N = \frac{dT_N^*}{dx}, \tag{1a}$$

$$\beta_I = \frac{dT_I^*}{dx}, \tag{1b}$$

where $T_N^* = T_N/T_{NI}$, $T_I^* = T_I/T_{NI}$ (here T_{NI} is the nematic–isotropic transition temperature of the pure host) and x is the guest mole fraction.

According to the literature,[24] at very low guest concentration, the limiting slopes of the nematic phase boundary line, β_N^∞ and the isotropic phase boundary line, β_I^∞ are connected with the guest activity coefficients by relations:

$$\beta_N^\infty = \left(1 - \frac{\delta_N^\infty}{\delta_I^\infty}\right)\left(\frac{R}{\Delta S_{NI}}\right), \tag{2a}$$

$$\beta_I^\infty = \left(\frac{\delta_I^\infty}{\delta_N^\infty} - 1\right)\left(\frac{R}{\Delta S_{NI}}\right), \tag{2b}$$

where R is gas constant, ΔS_{NI} is nematic–isotropic transition entropy of the pure nematic host, and δ_N^∞ and δ_I^∞ are infinite-dilution (Henry's law region) guest activity coefficients in the nematic and isotropic phases, respectively.

In order to determine the ratio of $\delta_N^\infty/\delta_I^\infty$, the experimentally obtained β_N and β_I values have been corrected for the infinite dilution using procedure described by Kronberg *et al.*[25]

The corrected values of β_N^∞ and β_I^∞ as well as ratios of $\delta_I^\infty/\delta_N^\infty$ for D2 in alkyl-cyanobiphenyls are gathered in Table IIIA. This table gives the averaged values of the β^∞ parameters over the dye concentration. The $\Delta S_{NI}/R$ values were calculated from the heat of transition given by Coles and Strazielle[26] and they are listed in Table I.

From the results presented in Table IIIA it is seen that: 1) in all cases the β^∞ values are positive, that means that dye D2 stabilizes the nematic phase of the all alkyl-cyanobiphenyls investigated and 2) the difference between β_N^∞ and β_I^∞ values occurs, which indicates the existence of the two-phase region for D2-alkyl-cyanobiphenyl mixtures.

In Figure 3 the shifts in the clearing (ΔT_{NI}) and melting (ΔT_{KN}) points of the dye-liquid crystal mixtures with respect to the transition temperatures of the pure nematic host and also the ratio of the activity coefficients $\delta_N^\infty/\delta_I^\infty$ *versus* number of carbon atoms of the alkyl-cyanobiphenyls are presented (T_{NI} for guest host mixtures is now the average value of the temperatures at which the two-phase region begins and ends). Here the odd-even effect for all investigated members of the homologous series is evident. Dye D2 stabilizes better the alkyl-cyanobiphenyls with the odd number of carbon atoms than those with the even number. This alternation is also observed in $\delta_N^\infty/\delta_I^\infty$ value.

TABLE III

Comparison of the experimental β_N^∞, β_I^∞ and $\delta_N^\infty/\delta_I^\infty$ values with theoretical calculations.

A. Experiment

Liquid crystal	β_N^∞	β_I^∞	$\delta_N^\infty/\delta_I^\infty$
5CB	0.58	0.63	0.923
6CB	0.26	0.27	0.965
7CB	0.40	0.44	0.906
8CB	0.24	0.25	0.940

B. Theory

Liquid crystal	$v_2/v_1 = m_2/m_1$			$v_2/v_1 = m_2/m_1$[a]		
	β_N^∞	β_I^∞	$\delta_N^\infty/\delta_I^\infty$	β_N^∞	β_I^∞	$\delta_N^\infty/\delta_I^\infty$
5CB	0.65	0.72	0.914	0.54	0.58	0.930
6CB	0.41	0.44	0.951	0.24	0.26	0.971
7CB	0.62	0.73	0.851	0.42	0.47	0.900
8CB	0.54	0.63	0.861	0.30	0.32	0.923

[a] Value considering the flexibility of the alkyl chain of the liquid crystal.

The smaller ratio $\delta_N^\infty/\delta_I^\infty$ implies greater compatibility with the nematic phase of the host and *vice versa*, thus correlation between the activity coefficients and the ordering of the guest by the host would be anticipated. Comparing the results in Figure 2 to those in Figure 3 we do not notice such a correlation. However, analysing once more the data from Table II one can see, that the changes of the order parameters with the temperature do not follow in the same way for all alkyl-cyanobiphenyls investigated. Both $\langle P_2\rangle_G$ and the ratio $\langle P_2\rangle_G/\langle P_2\rangle_H$ at N → I phase transition are larger for mixtures of D2 with 5CB and 7CB than those for D2 with 6CB and 8CB, what means that the former guest-host mixtures are more resistant to the thermal fluctuations than the later. It seems that the ratio $\delta_N^\infty/\delta_I^\infty$ and thereby the shift in the nematic–isotropic transition temperature after dye addition are affected rather by $\langle P_2\rangle_G/\langle P_2\rangle_H$ ratio than by absolute values of $\langle P_2\rangle_G$ and/or $\langle P_2\rangle_H$. It will be demonstrated also in the next section. Therefore, the correlation between $\langle P_2\rangle_G/\langle P_2\rangle_H$ at N → I transition and the thermodynamic results is very good.

The theoretical calculations of β_N^∞ and β_I^∞

On the basis of the Maier-Saupe mean field theory for binary mixture[27] the expression for the ratio of the infinite-dilution guest activity coefficients in the vicinity of the clearing point is following:

$$\ln\left(\frac{\delta_N^\infty}{\delta_I^\infty}\right) = \frac{\Delta S_{NI}}{R}\left\{\frac{v_2}{v_1} - \left(\frac{b_{12}}{b_{11}}\right)^2\right\}, \tag{3}$$

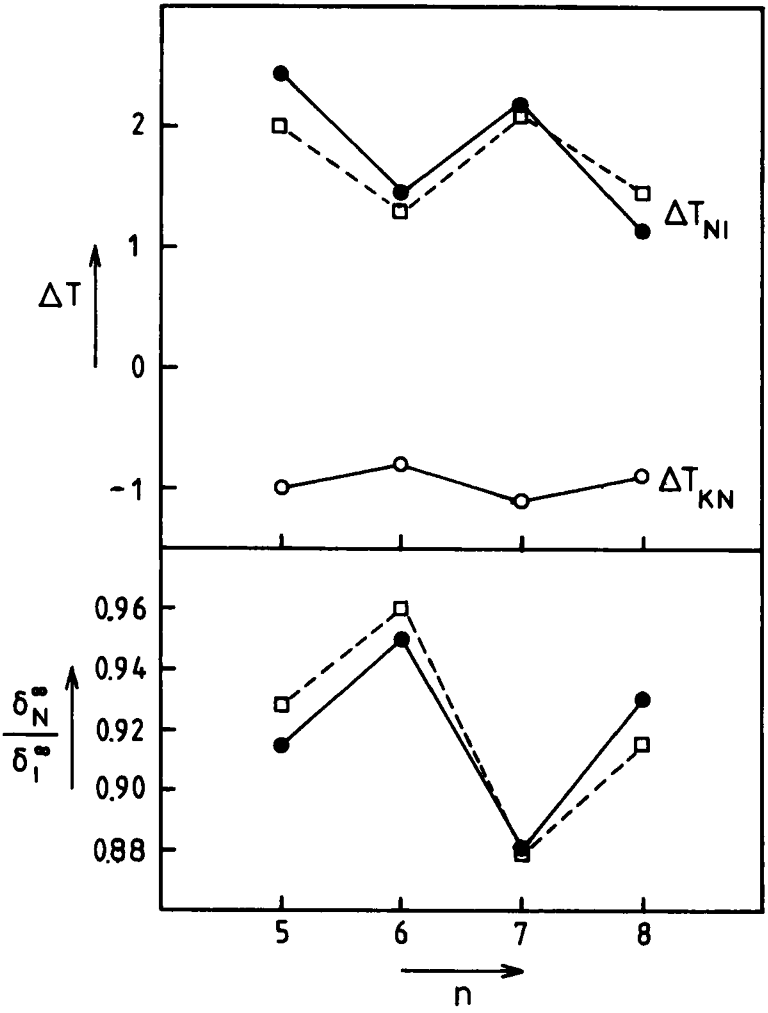

FIGURE 3 Shift in melting, ΔT_{KN} and clearing, ΔT_{NI} points after dye addition (c = 45 mM/dm^3) and the activity coefficients ratio, $\delta_N^\infty/\delta_I^\infty$ *versus* the alkyl chain length for the homologous series of the alkylcyanobiphenyls. Solid lines = experimental results, dashed lines = theoretical calculations.

where v_1 and v_2 are, respectively, the host and guest molecular volumes, while ratio b_{12}/b_{11} is a measure of the relative strength of the guest-host and host-host molecules interactions. The b_{12}/b_{11} ratio can be easily estimated from the measurements of the $\langle P_2\rangle_G/\langle P_2\rangle_H$ in the vicinity of the nematic–isotropic transition.[27] Knowing the $\delta_N^\infty/\delta_I^\infty$ values, the slopes β_N^∞ and β_I^∞ can be calculated from equations (2a) and (2b), respectively.

Similarly as in the previous paper[10] the ratio of the molecular length (l) to breadth (d) was used as a measure of the host and the guest sizes. It was assumed that $v_2/v_1 = m_2/m_1$, where $m = l/d$. The sizes of the D2 and liquid crystal molecules were estimated from the known bond lengths and the configuration in molecules[29] including van der Waals radii of the terminal atoms.[29] The *l*/*d* value for D2 is equal 2.5,[10] the values of *l*/*d* for liquid crystal molecules in the fully extended form (assuming zig-zag conformation) are given in Table I.

Table IIIB summarizes the calculated values of β_N^∞, β_I^∞ and $\delta_N^\infty/\delta_I^\infty$ for D2 in homologous series of alkyl-cyanobiphenyls. The data presented in this table are averaged values of over the dye concentration (considering the concentration dependence of $\langle P_2 \rangle$—Table II). The results of the calculations revealed, that the correlation between experimental and calculated data is very poor for both β^∞ and $\delta_N^\infty/\delta_I^\infty$ parameters as well as for the breadth of the two-phase region, where the difference between β_N^∞ and β_I^∞ is a measure of this breadth. Therefore the flexibility of the alkyl chain of the liquid crystal molecules in the next fitting on was taken into account and the *l*/*d* values for all investigated alkyl-cyanobiphenyl were assigned as 2.5[10] taking $n = 3$.[5,30] The results are presented in Table IIIB (the averaged values) and in Figure 3 (for the dye concentration $c = 45$ mM/dm^3). In this case the much better correlation between calculations and experiment is achieved, what demonstrates that the theoretical model which takes into account the host end-chain flexibility can provide a good description of the behavior of the guest-host mixture at the nematic–isotropic phase transition.

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