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Influence of substituent length in dichroic dye molecules on the orientational properties of guest–host liquid crystal mixtures

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The polarized absorption spectra of eight dichroic dyes, alkyl derivatives of 4-amino-(*N*-ethylnaphthalimide) dissolved in the nematic liquid crystals 5CB and 6CHBT have been measured as a function of temperature. On the basis of these spectra, the guest order parameter has been evaluated. The influence of the alkyl chain length of the dye molecule on the molecular orientation has been examined. Moreover, the nematic–isotropic transition temperatures for the dye–liquid crystal mixtures have been determined. The experimental results have been compared in some detail with calculations made on the basis of the mean field theory for binary mixtures.

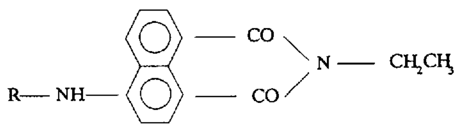
1. Introduction

Since the report of Heilmeier and Zanoni [1] of the 'guest–host' effect in nematic liquid crystals there has been much interest on phenomena associated with the addition of dichroic dyes (guests) to liquid crystalline matrices (hosts). Dye–liquid crystal mixtures have found applications in two important scientific areas, one in order to obtain information concerning the electronic spectra of the dyes [2–7], and the other to study the interactions between guest molecules and their anisotropic environment [8–13]. Furthermore, such mixtures are utilized in the construction of the electro-optical liquid crystal display (LCD) devices working both in passive and active modes [14–18]. A number of dyes of different chemical classes containing various extended chromophore systems have been examined as guests in liquid crystalline hosts [17] with the purpose of effecting improvements in colour contrast, brightness and viewing angle of LCDs. Recently, it has been found, that some derivatives of 4-amino-(*N*-ethylnaphthalimide) can be used successfully both in passive and active 'guest–host' LCD devices [19–20]. These dyes have a brilliant yellow colour, which is important not only as one of the three primary colours, but also as an ingredient for preparing a practically useful black or green colour; the dyes orientate well in technologically important liquid crystalline mixtures, have very high fluorescence quantum yields in the spectral region advantageous for the human eye, are stable to the sunlight, and do not significantly destabilize the nematic phase of the host.

In this paper, a detailed study has been made of the influence of derivatives of 4-amino-(*N*-ethylnaphthalimide) with various lengths of the alkyl chain on the orientational order and on the nematic–isotropic phase transition temperatures of the guest–host mixtures. Moreover, an attempt to find a correlation between the geometry of the guest molecules, the degree of molecular order and the mesophase existence region for the nematic liquid crystal doped with the dichroic dye has been undertaken.

2. Experimental

The alkyl derivatives of 4-amino-(*N*-ethylnaphthalimide) studied have the molecular structure:



The alkyl substituents *R*, the molecular weights M_W and

Table 1. The alkyl substituent *R*, the molecular weight, M_W and the length to breadth ratio, *l*/*d* of the dyes investigated.

Dye	*R*	M_W	*l*/*d*
1	$-CH_3$	254	1·52
2	$-CH_2CH_3$	268	1·66
3	$-(CH_2)_2CH_3$	282	1·77
4	$-(CH_2)_3CH_3$	296	1·91
5	$-(CH_2)_4CH_3$	310	2·01
6	$-(CH_2)_6CH_3$	338	2·27
7	$-(CH_2)_{11}CH_3$	407	2·83
8	$-(CH_2)_2CH(CH_3)_2$	310	1·88

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Table 2. Concentration of dye, *c*, and guest order parameter, S_G at 300 K for the dye–liquid crystal mixtures investigated.

	5CB		6CHBT	
Dye	$c[M_W/l]$	S_G	$c[M_W/l]$	S_G
1	$2{\cdot}0\times10^{-2}$	0·40	—	—
2	$2{\cdot}0\times10^{-2}$	0·34	$5{\cdot}0\times10^{-3}$	0·41
3	$3{\cdot}1\times10^{-2}$	0·32	$1{\cdot}0\times10^{-2}$	0·40
4	$4{\cdot}0\times10^{-2}$	0·37	$5{\cdot}0\times10^{-3}$	0·41
5	$4{\cdot}0\times10^{-2}$	0·40	$5{\cdot}0\times10^{-3}$	0·46
6	$4{\cdot}0\times10^{-2}$	0·40	$5{\cdot}0\times10^{-3}$	0·45
7	$4{\cdot}0\times10^{-2}$	0·42	$5{\cdot}0\times10^{-3}$	0·46
8	$4{\cdot}0\times10^{-2}$	0·34	$5{\cdot}0\times10^{-3}$	0·45

the ratios of the molecular length to the breath, *l*/*d* of each of the dyes investigated are listed in table 1. The sizes of the dyes were estimated from the known bond lengths and the configurations of the molecules [21] including the van der Waals radii of the terminal atoms [22]. The dyes were synthesized and chromatographically purified in the Institute of Dyes at Łodź Technical University, Poland. The details of the synthesis are given in [19, 23]. The commercial nematogens 5CB (4-*n*-pentyl-4′-cyanobiphenyl), (K15, Merck Ltd, UK) and 6CHBT (4-trans-4′-*n*-hexylcyclohexyl)isothiocyanotobenzene), (POCH, Lublin) were used without further purification as host matrices. The dyes were initially screened for their solubility in the liquid crystal in the nematic phase and were dissolved in 5CB and 6CHBT at the concentrations given in table 2.

The polarized absorption spectra of the guest–host mixtures in the visible spectral region were obtained using a SPECORD M40 (Carl Zeiss Jena) double beam spectrophotometer equipped with neutral polarizers. The measurements were made as a function of temperature using 'sandwich' cells of 20 μm (dye–5CB mixtures) and 80 μm (dye–6CHBT mixtures) thickness. The temperature of the cells was regulated and controlled with a practical accuracy of ± 0·1° using a Temperature Controller 660 (UNIPAN). After changing the measurement temperature, the cell was left for approximately 20 min to reach thermal equilibrium. The planar orientation of the guest and host molecules was achieved by treatment of the glass surfaces of the cells with polyimide and by an additional rubbing process. This procedure gives a good homogeneous molecular orientation in a thin layer, and this was controlled with the aid of the crossed polarizers. The absorption spectra of the dyes dissolved in the liquid crystals were recorded for two positions of the cell, that is, with the orientation axis of the liquid crystal sample at angles of 0° and 90° with respect to the polarization plane of the light beam. Additionally, the base line spectra for the pure liquid crystals were recorded for the same two positions of the cell. After correction for the base line, two components of absorbance, $A_\parallel$ and $A_\perp$, as a function of the wavelength were obtained.

The temperatures of the nematic–isotropic phase transition, both for the pure liquid crystals and the dye–liquid crystal mixtures were determined with an accuracy of ± 0·1° by means of a polarizing microscope, BIOLAR PI (PZO, Warsaw), equipped with a heating stage.

3. Results and discussion

3.1. *Order parameter of dyes in liquid crystals*

The long range orientational order which is a characteristic feature of the nematic phase of liquid crystal materials can be described by the order parameter, as proposed many years ago by Zwetkoff [24] who suggested

$$S = \tfrac{1}{2}(3\langle\cos^2\theta\rangle - 1). \qquad (1)$$

Equation (1) is valid, assuming the liquid crystal molecules to be cylindrically symmetric objects. θ is the angle between the molecular long axis of one of these objects and the preferred direction of the molecular alignment (the director).

The order parameter of the guest oriented in the nematic host, S_G can also be determined from equation (1), but in this case θ means the angle between the director and the long axis of the guest molecule. Experimental evaluation of S_G is possible through measurement of the polarized absorption spectra of the guest dissolved in the nematic host. The absorption of light by the guest in relation to a certain electronic transition is determined by the transition moment $\boldsymbol{\mu}$. If we assume for simplicity that there is a single transition from the ground to the excited state and that the direction of this transition deviates from the direction of the molecular axis at an angle α, the order parameter, S_G can be obtained from the measured absorbance for the incident polarized light using the following formula [25, 26]

$$S_G = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp}\cdot\frac{2}{3\cos^2\alpha - 1}, \qquad (2)$$

where $A_\parallel$ and $A_\perp$ are the absorbances of the light polarized, respectively, parallel and perpendicular to the director.

In equation (2) it is implicitly assumed that the guest molecules are cylindrically symmetric. For non-cylindrical molecules, there exists a more complicated relation between S_G and the absorbance measured in the experiment. In the case of biaxial guest molecules for example, the second order parameter, D_G, which depends on the angle of rotation about the director should be introduced [27, 28]. An investigation of the order parameters of dichroic dyes with molecular structures similar to that of the dyes studied in this paper has shown that the values of

D_G are small with respect to S_G [7]; therefore we neglect the biaxiality order parameter D_G in our considerations.

The alkyl derivatives of 4-amino-(*N*-ethylnaphthalimide) have only one absorption band in the visible region. The position of the maximum of this band does not depend on the length of the alkyl chain within the experimental uncertainty, and is equal to $\lambda_{max} = 435$ nm in 5CB and $\lambda_{max} = 425$ in 6CHBT. This means that the origin of the absorption is the central part of the dye molecules and the transition results from charge transfer between the nitrogen atom at the substituent *R* (donor) and the imide carbonyl oxygen atoms (acceptors). The difference in the λ_{max} position in the two liquid crystals is caused by the different polarities of the solvents. Therefore, the terminal groups should not affect the direction of the transition moment, μ and will influence only the order parameter, S_G. This allows us to assume for simplicity that the direction of the transition moment is parallel to the director, although the symmetry group of the dyes investigated is not high enough to fix $\alpha = 0°$. We do not know, however, up to now the angle α for the novel synthesized dyes studied in this paper. However, it seems that although we cannot determine the absolute value of S_G, we can compare values for the dyes with different terminal substituents.

Figures 1 and 2 show the order parameters, S_G of the chosen dyes in 5CB (see figure 1) and 6CHBT (see figure 2) as a function of the reduced temperature $T^* = T/T_{NI}$, where T_{NI} is the average clearing temperature of the guest–host mixture and *T* is the temperature of the measurement in K. Additionally, the temperature dependence of the host order parameter, S_H for pure 5CB and 6CHBT, estimated on the basis of the refractive index measurements [12, 29], are presented in the figures. For the calculation of S_G from equation (2), the values of the absorbance were taken at the wavelength corresponding to the absorption maximum. At least three and usually five cells were used to determine each order parameter. The results presented here are average values. The uncertainty in the determination of S_G is estimated to be ± 0·01.

From figures 1 and 2, it is seen that the order parameter changes with temperature and drops to 0·15–0·38 just below the nematic–isotropic transition. This transition is first order, and in the isotropic phase the value of the order parameter is zero. The temperature dependence of S_G in the nematic phase is different for the various dye–liquid crystal mixtures. This suggests that the mixtures investigated are differently resistant to thermal fluctuations (vibrations, librations, and possible internal reorientations of the molecules) and indicates strong individual solute–solvent interactions. The latter is confirmed by the significant difference between the S_G and S_H values at the same reduced temperature.

Table 2 summarizes the guest order parameters, S_G obtained at room temperature (300 K) for all the mixtures that have been studied, whilst figures 3 and 4 present the dependence of S_G on the alkyl chain length of the substituent *R* at the reduced temperatures 0·967, 0·985 and at the nematic–isotropic phase transition temperature for 5CB and 6CHBT, respectively. Dye **1** does not dissolve in 6CHBT at a concentration sufficient to measure the

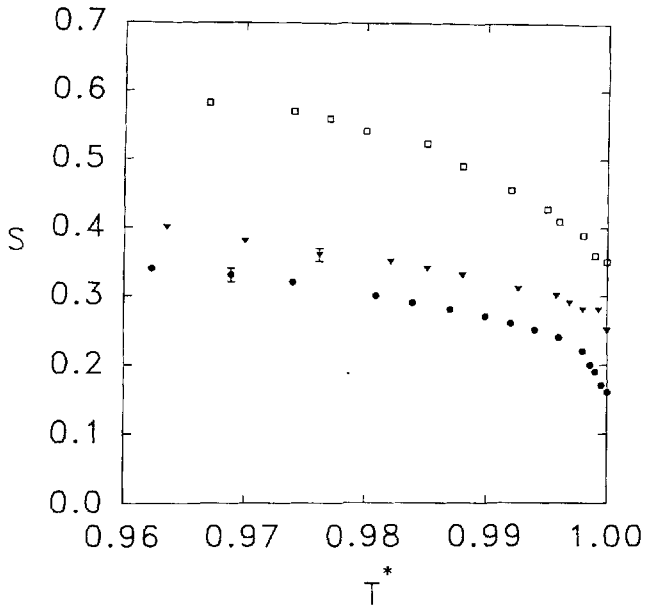

Figure 1. Order parameter as a function of reduced temperature, T^* for pure 5CB [12] (squares), dye **2** in 5CB (circles) and dye **6** in 5CB (triangles). $T^* = T/T_{NI}$.

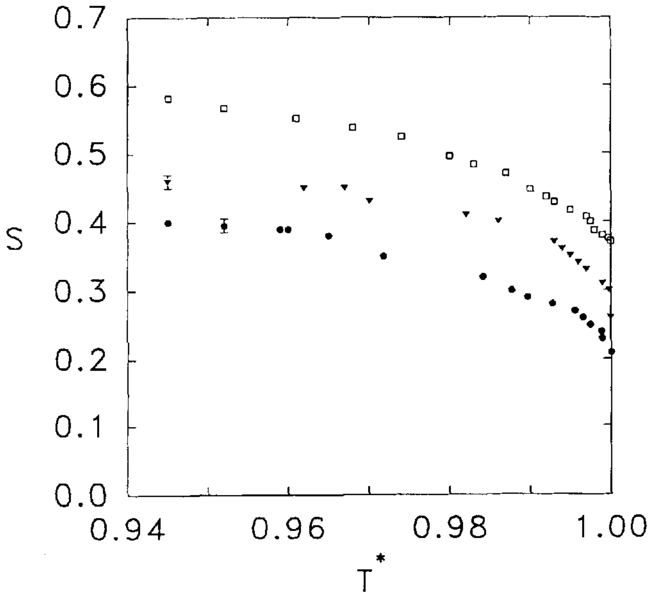

Figure 2. Order parameter as a function of reduced temperature, T^* for pure 6CHBT [28] (squares), dye **3** in 6CHBT (circles) and dye **7** in 6CHBT (triangles). $T^* = T/T_{NI}$.

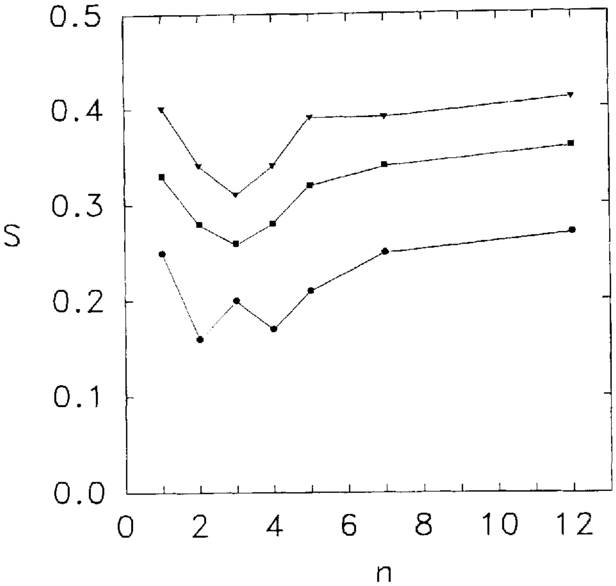

Figure 3. S_G versus alkyl chain length of dye molecules dissolved in 5CB at three reduced temperatures: 0·967 (triangles), 0·985 (squares) and 1·0 (circles).

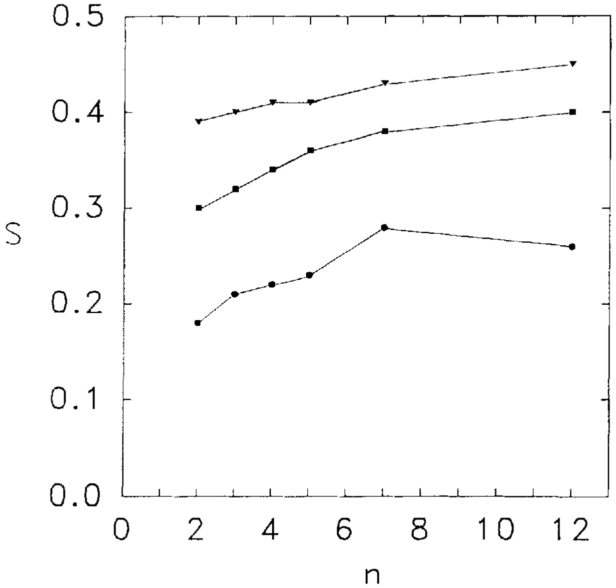

Figure 4. S_G versus alkyl chain length of dye molecules dissolved in 6CHBT at three reduced temperatures: 0·967 (triangles), 0·985 (squares) and 1·0 (circles).

absorption in the thin layer. From the results presented in table 2 and figures 3 and 4, it follows that the values of the order parameter, S_G for the various dyes in the same liquid crystal matrix are different, and this illustrates some influence of the end groups on the orientation of the guest in the nematic host. For dyes **1–7** dissolved in the liquid crystals, we had expected the occurrence in the changes of the order parameter with alkyl chain length of the so-called odd–even effect [30], due to alternation of the interaction between the terminal groups of the dye and liquid crystal molecules: the guest order parameter for the dyes with an odd number of carbons in the alkyl chain should be greater than that for the preceding even member of the series. The results presented in figures 3 and 4 show that the dyes investigated do not reveal an odd–even effect. As the temperature rises, the odd–even effect begins to appear only for 5CB. Generally, however, some tendency to an increase of S_G with lengthening of the dye molecule is observed. The lack of regular alternation in the S_G values can be attributed either to a flexibility of the alkyl chain caused by rotation about its single bonds [31] or to the incomplete alignment of the dyes in the liquid crystal matrices. This latter can be confirmed by the relatively low values of S_G for the 4-amino-(*N*-ethylnaphthalimide) derivatives in the liquid crystals used.

3.2. *Nematic–isotropic transition temperatures of guest–host mixtures*

Recently, results in many papers [11–13, 18–20, 32, 33] have shown that addition of a dichroic dye to a liquid crystal matrix changes the range of the mesophase of the nematic host, caused by either a decrease or an increase in the clearing temperature of the pure liquid crystal. As has been shown in [12], the change of the nematic–isotropic transition temperature is dependent on the size and shape of the dye molecule and on the dye concentration, as well as up on the mutual intermolecular interactions among the guest and host molecules. Moreover, according to thermodynamic laws and the first-order nature of the nematic–isotropic phase transition [34], in the vicinity of the clearing point, a two-phase region for binary dye–liquid crystal mixtures appears. In this region both nematic and isotropic phases coexist in equilibrium.

Tables 3 and 4 present the results of the temperature investigations of the dye-liquid crystal mixtures. Here T_N is the temperature at which the first drop of the isotropic liquid appears, T_I is the temperature at which the last trace of the nematic disappears on sample heating; (T_I-T_N) is the range of two-phase region and ΔT_N and ΔT_I are the shifts of T_N and T_I with respect to T_{NI} of the pure liquid crystal. The average nematic–isotropic transition temperature $\bar{T}_{NI}$ for the mixtures studied is also given.

Data presented in tables 3 and 4 indicate that the derivatives of 4-amino-(*N*-ethylnaphthalimide) decrease the temperature of clearing with respect to T_{NI} of the pure liquid crystal, which means that after dye addition, destabilization of the nematic phase occurs. The destabilization is greater in the case of 6CHBT, for which very small amounts of the dye (about one order smaller than in 5CB) cause significant changes in T_{NI}. The appearance of

Table 3. Thermal data for the dye–5CB mixtures.

Substance	T_N/K	T_I/K	T_I/T_N	ΔT_N	ΔT_I	$\bar{T}_{NI}$
5CB	308·3	308·3	0·0	—	—	308·30
5CB + **1**	308·2	308·3	0·1	−0·1	0·0	308·25
5CB + **2**	307·6	307·9	0·3	−0·7	−0·4	307·75
5CB + **3**	307·1	307·4	0·3	−1·2	−0·9	307·25
5CB + **4**	306·6	306·8	0·2	−1·7	−1·5	306·70
5CB + **5**	306·7	307·0	0·3	−1·6	−1·3	306·85
5CB + **6**	306·5	306·9	0·4	−1·8	−1·4	306·70
5CB + **7**	307·3	307·5	0·2	−1·0	−0·8	307·40
5CB + **8**	306·6	307·2	0·6	−1·7	−1·1	306·90

Table 4. Thermal data for the dye–6CHBT mixtures.

Substance	T_N/K	T_I/K	T_I/T_N	ΔT_N	ΔT_I	$\bar{T}_{NI}$
6CHBT	316·0	316·0	0·0	—	—	316·00
6CHBT + **1**	—	—	—	—	—	—
6CHBT + **2**	315·8	315·9	0·1	−0·2	−0·1	315·85
6CHBT + **3**	315·3	315·6	0·3	−0·7	−0·4	315·45
6CHBT + **4**	315·5	315·7	0·2	−0·5	−0·3	315·60
6CHBT + **5**	315·4	315·6	0·2	−0·6	−0·4	315·50
6CHBT + **6**	315·6	315·7	0·1	−0·4	−0·3	315·65
6CHBT + **7**	315·7	315·8	0·1	−0·3	−0·2	315·75
6CHBT + **8**	315·1	315·3	0·2	−0·9	−0·7	315·20

the two phase region in all investigated binary mixtures is also observed.

The indicators of the destabilization or stabilization of a nematic phase by a guest are the slopes of the changes in the reduced temperatures, T_N^* and T_I^* with change in the solute mol fraction, x, defined in the following way:

$$\beta_N = \frac{dT_N^*}{dx}, \qquad (3a)$$

and

$$\beta_I = \frac{dT_I^*}{dx}, \qquad (3b)$$

where $T_N^* = T_N/T_{NI}$ and $T_I^* = T_I/T_{NI}$.

A positive β means the ability of a guest to improve, and a negative β to disrupt the long range orientational order in the nematic phase.

From thermodynamics it follows [34] that the limiting slopes $(x \rightarrow 0, T^* \rightarrow 0)$ of the nematic and isotropic boundary lines, β_N^∞ and β_I^∞, respectively, are given by

$$\beta_N^\infty = \left(1 - \frac{\gamma_N^\infty}{\gamma_I^\infty}\right)\left(\frac{R}{\Delta S_{NI}}\right), \qquad (4a)$$

and

$$\beta_I^\infty = \left(\frac{\gamma_I^\infty}{\gamma_N^\infty} - 1\right)\left(\frac{R}{\Delta S_{NI}}\right), \qquad (4b)$$

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

In order to determine the ratio of $\gamma_N^\infty/\gamma_I^\infty$, the experimentally obtained β values have been corrected to infinite dilution using the procedure described by Kronberg *et al.* [35]. The corrected β_N^∞ and β_I^∞ values, as well as the ratios $\gamma_N^\infty/\gamma_I^\infty$ for the dye-liquid crystal mixtures investigated are listed in tables 5 and 6. The $\Delta S_{NI}/R$ value for 5CB was assumed to be 0·253, following [36] and for 6CHBT it was estimated from the heat of transition to be 0·267 [37].

A smaller ratio $\gamma_N^\infty/\gamma_I^\infty$ implies a greater compatibility with the nematic host and vice versa; thus a correlation between the activity coefficients and the degree of order of the guest in the liquid crystal matrix would be anticipated. From tables 5 and 6 it is seen that for all the mixtures investigated, $\gamma_N^\infty/\gamma_I^\infty > 1$, which means that the derivatives of 4-amino-(*N*-ethylnaphthalimide) when added to 5CB and 6CHBT cause destabilization of the nematic phase. This effect correlates well with the relatively low values of the order parameter of these dyes, S_G, which are in all the cases smaller than the values of the

Table 5. Comparison of experimental values of β_N^∞,β_I^∞ and $\gamma_N^\infty/\gamma_I^\infty$ with results of theoretical calculations for dye–5CB mixtures.

	Experiment			Theory		
Dye	β_N^∞	β_I^∞	$\gamma_N^\infty/\gamma_I^\infty$	β_N^∞	β_I^∞	$\gamma_N^\infty/\gamma_I^\infty$
1	−0·07	0·00	1·02	−0·10	−0·10	1·03
2	−0·46	−0·27	1·12	−0·48	−0·43	1·12
3	−0·51	−0·38	1·13	−0·40	−0·36	1·10
4	−0·55	−0·49	1·14	−0·57	−0·49	1·14
5	−0·52	−0·42	1·13	−0·47	−0·42	1·12
6	−0·59	−0·46	1·15	−0·42	−0·38	1·11
7	−0·33	−0·26	1·08	−0·57	−0·50	1·15
8	−0·55	−0·36	1·14	−0·58	−0·51	1·15

Table 6. Comparison of experimental values of β_N^∞,β_I^∞ and $\gamma_N^\infty/\gamma_I^\infty$ with results of theoretical calculations for dye–6CHBT mixtures.

	Experiment			Theory		
Dye	β_N^∞	β_I^∞	$\gamma_N^\infty/\gamma_I^\infty$	β_N^∞	β_I^∞	$\gamma_N^\infty/\gamma_I^\infty$
1	—	—	—	—	—	—
2	−0·41	−0·21	1·08	−0·55	−0·48	1·15
3	−0·73	−0·41	1·16	−0·51	−0·45	1·14
4	−1·03	−0·62	1·24	−0·55	−0·48	1·15
5	−1·24	−0·83	1·31	−0·57	−0·49	1·15
6	−0·83	−0·62	1·21	−0·49	−0·43	1·13
7	−0·62	−0·41	1·15	−0·88	−0·71	1·24
8	−1·86	−1·45	1·57	−0·42	−0·38	1·11

host order parameter, S_H at the same reduced temperature (see figures 1 and 2). This suggests that the ratio $\gamma_N^\infty/\gamma_I^\infty$ and thereby the shift in the clearing temperature are affected by the mutual orientation of the guest and host molecules and indicates that the molecules of the derivatives of 4-amino-(*N*-ethylnaphthalimide) are not able to correlate completely the alignment of their long axes parallel to the long axes of the liquid crystal molecules.

3.3. *Comparison of experimental results with theoretical predictions*

In this section, the relation between the behaviour of the guest–host mixtures at the nematic–isotropic phase transition and the order parameter, as well as the molecular geometry of the guest, is examined theoretically, and the results are compared with those obtained experimentally.

According to the model based on the mean field theory of nematics [38, 39] and proposed for binary mixtures by Humphries, James and Luckhurst [40], the ratio of the infinite-dilution guest activity coefficients in the vicinity of the clearing point can be calculated from the following expression:

$$\ln\left(\frac{\gamma_N^\infty}{\gamma_I^\infty}\right) = \frac{\Delta S_{NI}}{R}\left[\frac{v_2}{v_1} - \left(\frac{b_{12}}{b_{11}}\right)^2\right], \qquad (5)$$

where v_1 and v_2 are, respectively, the host and guest molecular volumes, while the ratio b_{12}/b_{11} is a measure of the relative strength of the guest–host and host–host molecular interactions. The ratio b_{12}/b_{11} can be easily estimated from the ratio S_G/S_H at the nematic–isotropic phase transition [40].

Knowing $\gamma_N^\infty/\gamma_I^\infty$ values, the slopes β_N^∞ and β_I^∞ can be calculated from equations (4 *a*) and (4 *b*), respectively.

It has been shown previously [12, 41] that instead of molecular volume values, the ratio of the molecular length (l) to the breadth (d) can be used successfully as a measure of the host and guest sizes. Therefore, in the present calculations, it was also assumed that $v_2/v_1 = m_2/m_1$, where $m = l/d$. The values of m_1 for the monomeric molecules of 5CB and 6CHBT were estimated similarly to those for the dye molecules (see table 1) and are equal to 2·5 and 2·2, respectively.

Tables 5 and 6 summarize the values of β_N^∞ and β_I^∞, as well as those for $\gamma_N^\infty/\gamma_I^\infty$ obtained from experiment and theoretical predictions. The data presented indicate that for the 5CB–dye mixtures, assuming $v_2/v_1 = m_2/m_1$, one can obtain satisfactory agreement between the theoretical and the experimental results, both in the determination of the sign and the magnitude of the β values, as well as in the prediction of the range of the two-phase coexistence region, measured from the difference between β_N and β_I. However, the expected direct correlation between the guest order parameter, S_G and the ratio $\gamma_N^\infty/\gamma_I^\infty$ is not observed, indicating the significance of the relative geometries of the guest and host molecules.

For the 6CHBT–dye mixtures, the agreement between theory and experiment is considerably worse than in the case of the 5CB–dye mixtures. This disagreement is difficult to explain. Perhaps due to the very poor solubility of the dyes in 6CHBT and the necessity of using low concentrations, the changes in T_N and T_I after the dye addition are obtained with the greater uncertainty than for 5CB. The neglect of the flexibility of the alkyl chains, both in the dyes and the 6CHBT molecules, may be an additional reason for the very poor correlation between the experimental and calculated data.

In conclusion, it is worth noting that the results presented in this paper provide a new experimental approach for the investigation of guest–host interactions on the one hand, and for assessing the effect of additives used in LCDs on nematic phase stability on the other. Our study also provides evidence of the important role of repulsive forces (steric effects) in the mutual orientation of guest and host molecules.

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