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Intermolecular interactions in mixtures of dichroic dyes with *n*-alkyl-4-(4-isothiocyanatophenyl)bicyclo[2,2,2]octanes

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On the basis of the polarized absorption spectra, the guest order parameter as a function of temperature for five dichroic azo dyes dissolved in four members (pentyl to octyl) of the homologous series of *n*-alkyl-4-(4-isothiocyanatophenyl)bicyclo[2,2,2]octanes has been evaluated. Moreover, the influence of the dichroic dye addition on the nematic–isotropic phase transition temperature has been examined. The relation between the molecular geometry of the guest, its orientation efficiency in the nematic host and the clearing temperature of the azo dye–liquid crystal mixtures has been determined. The experimental results have been compared in some detail with calculations performed on the basis of the mean field theory for binary mixtures.

1. Introduction

The use of dichroic dyes as guests in liquid crystal hosts is now well established, and various liquid crystal display (LCD) devices based on the guest–host effect, first described by Heilmeier and Zanoni [1], have been developed [2–7]. The most important advantages of guest–host (GH) displays are the omission of one of the polarizers (or both) resulting in higher environmental stability and lower costs, as well as a contrast virtually independent of viewing angle [8]. However, in order to construct GH LCD, competitive with conventional twisted nematic (TN) devices, a number of factors must be taken into account.

It had been previously found that a dichroic dye added to a liquid crystal affects its orientational order [9–12] and moreover, the orientation of both host and guest molecules depends on the dye concentration [9,11,13]. It had been also observed [9,11–16] that addition of a dichroic dye to a liquid crystal matrix changes the nematic–isotropic phase transition temperature with respect to that of the pure host, causing either an increase (stabilization of the mesophase) or a decrease (destabilization of the mesophase).

In this paper we have investigated the orientational order of mixtures of some azo dyes with four members of the homologous series of *n*-alkyl-4-(4-isothiocyanatophenyl)bicyclo[2,2,2]octanes, as well as the influence of the dye on the clearing temperature of the liquid crystalline host.

It had been found that dichroic azo dyes are in general not stable enough in UV light, but most of them have many other attributes, such as high order parameter, good solubility, high absorption coefficient and favourable spectral properties with respect to saturated colours [11,17–21]. These advantages mean that azo dyes can be considered suitable for application in GH LCDs which are not continuously exposed to light. Bicyclo[2,2,2]octane derivatives with an NCS terminal group, because of their low viscosity, low melting enthalpies and broad range nematic phases, are however highly useful as components of technologically important liquid crystal mixtures [22,23].

2. Experimental

Five azo dyes of various molecular sizes and shapes were used as guest species. The molecular structure, the wavelength of absorption maximum, λ_{max}, the molecular weight, *M* and the ratio of molecular length to breadth, *l*/*d* for the dyes investigated are given in table 1. All the dyes were synthesized and chromatographically purified in the Institute of Dyes, Łódź University of Technology, Poland.

The nematic liquid crystal hosts *n*-alkyl-4-(4-isothiocyanatophenyl)bicyclo[2,2,2]octanes, (LC*n*) with $n=5$ to 8, were synthesized in the laboratory of Professor R. Dąbrowski, Military Academy of Technology, Warsaw, Poland and used without further

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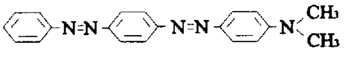
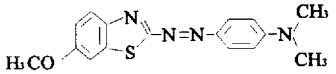
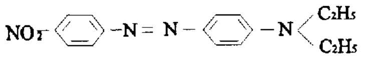
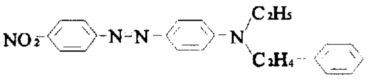
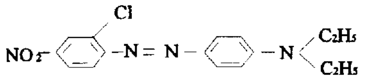
Table 1. Dyes used in experiments

Dye code	Molecular structure	M	λ_{max}/nm	l/d
1		329	475	2·54
2		328	499	2·60
3		298	511	2·43
4		375	499	2·73
5		332	491	2·51

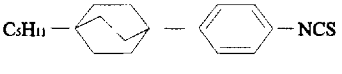
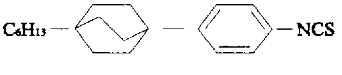
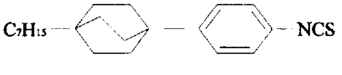
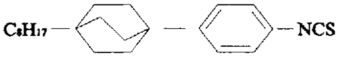
purification: the observed transition temperatures were in good agreement with those reported in the literature [23]. The molecular structures of the liquid crystal materials studied, as well as the ranges of the mesophases and l/d values are given in table 2.

The dimensions of the liquid crystal and dye molecules were estimated from known bond lengths and molecular configurations [24], including the van der Waals radii of the terminal atoms [25]. The dyes were dissolved in the liquid crystals at a concentration of 0·3 wt %.

The order parameter of the guest, S_G, in the liquid crystal was evaluated from the dichroic absorption ratio [16,26]. The polarized absorption spectra of the dye–liquid crystal mixtures in the visible spectral region were recorded using a SPECORD M40 spectrophotometer (Carl Zeiss, Jena) equipped with polarizers. The measurements were made as a function of temperature in 'sandwich' cells of 10 μm thickness. The temperature of the cells was regulated and controlled with an accuracy of ±0·1 K. After changing the temperature, the cell was left for approximately 20 min to reach thermal equilibrium. The planar orientation of the molecules was achieved by treatment of the glass surfaces with polyimide and by an additional rubbing process. This procedure gave a good homogeneous orientation of the liquid crystal and dye molecules in a thin layer, which was monitored with crossed polarizers. The absorption spectra of the dyes dissolved in the liquid crystals were recorded for two positions of the cell: the orientation axis of the liquid crystal was set at angles of 0° or 90° with respect to the polarization plane of the incident light beam. Additionally, the base lines for the pure liquid crystal hosts at the same two positions of the cell were recorded. 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 phase transitions, both for the pure liquid crystals and the dye–liquid crystal mix-

Table 2. Chemical formulae and melting (T_{CN}) and clearing (T_{NI}) temperatures for the liquid crystals studied

LC Code	Molecular structure	T_{CN}/K	T_{NI}/K	l/d
LC5		347·2	372·7	2·87
LC6		323·7	363·0	3·06
LC7		330·2	368·2	3·25
LC8		323·7	360·7	3·44

tures were determined using a polarizing microscope equipped with a heating stage controlled with an accuracy of ±0·1 K.

3. Results and discussion

3.1. *Order parameter*

Figure 1 shows, as an example, the guest order parameter, S_G for dyes **1** and **4** dissolved in LC6 versus the reduced temperature $T^* = T/T_{NI}$. In this figure, the temperature dependence of the host order parameter, S_H, estimated from optical birefringence measurements [27], is also shown. For calculation of the order parameter from the dichroic ratio, the values of the absorbance A_k ($k = \parallel, \perp$) were taken at the wavelength corresponding to the maximum of absorption. The azo dyes used in our experiments show only one absorption band in the visible region; the maximum for each dye in LC*n* is given in table 1.

Table 3 presents the values of the order parameter, S_G for all the dye–liquid crystal mixtures investigated, obtained at the reduced temperature $T^* = 0{\cdot}92$ and in the vicinity of the nematic–isotropic transition. The error in the estimation of S_G was assessed as ±0·01. For comparison, in this table, the values of the host order parameter, S_H, of the pure liquid crystals used in our experiments [27] are also listed.

In figure 2 the guest, S_G, and host, S_H, order parameters at $T^* = 0{\cdot}92$ as a function of the number of carbon atoms, *n* in the alkyl chain of the liquid crystal hosts studied are presented.

It is seen in figures 1 and 2 and in table 3 that the order parameters of the dyes are very different and

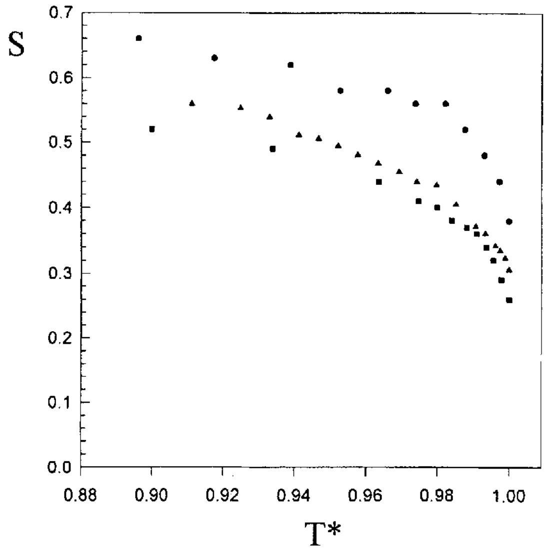


Figure 1. Order parameter versus reduced temperature for dye **1** in LC6 (●), dye **4** in LC6 (■) and for pure LC6 (▲) [27].

Table 3. Order parameters of liquid crystals and dyes investigated

Liquid crystal	Dye	S_H or S_G $T^* = 0{\cdot}92$	S_H or S_G at N→I transition
LC5	—	0·65[a]	0·40[a]
	1	0·67	0·43
	2	0·55	0·34
	3	0·50	0·25
	4	0·54	0·23
	5	0·47	0·25
LC6	—	0·56[a]	0·30[a]
	1	0·65	0·38
	2	0·57	0·37
	3	0·58	0·32
	4	0·51	0·26
	5	0·63	0·35
LC7	—	0·65[a]	0·38[a]
	1	0·67	0·37
	2	0·67	0·43
	3	0·59	0·30
	4	0·51	0·22
	5	0·63	0·32
LC8	—	0·62[a]	0·34[a]
	1	0·68	0·38
	2	0·68	0·40
	3	0·52	0·25
	4	0·54	0·25
	5	0·60	0·27

[a] From reference [27].

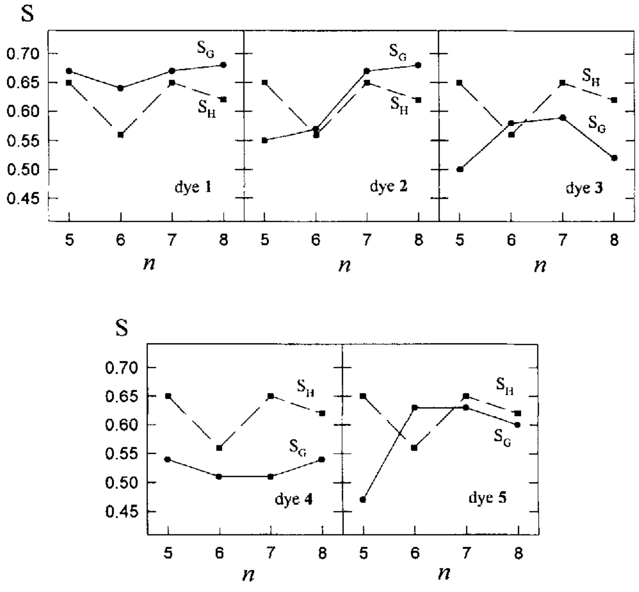


Figure 2. Guest (solid line) and host (dashed line) order parameter at $T^* = 0{\cdot}92$ versus number of alkyl chain segments in the homologous series of liquid crystals studied.

strongly depend on the host matrix. The guest order parameter for some dye–liquid crystal mixtures is greater than that of the pure host, but the opposite situation also occurs. Looking at the molecular structure of the dyes investigated, it is seen that there exists some correlation between size and shape of the guest molecule and the mutual relation between S_G and S_H. For dye **1**, which is the longest molecule, $S_G > S_H$ in all the liquid crystalline matrices, whereas for dye **4** which has an additional benzene ring in the end group, S_G is always lower than S_H. In this latter case, both lack of symmetry and the presence of a heavy terminal group reduces the guest–host van der Waals interaction by preventing close alignment of the dye with the liquid crystal molecules. The lateral Cl substituent of dye **5** does not influence strongly the efficiency of orientation of the guest molecules in the mesophase environment, except for the mixture of this dye with LC5. In the case of dyes **2** and **3**, the lowest S_G values occur also in LC5. In other liquid crystals, dye **2** has $S_G \gtrsim S_H$, whereas for dye **3**, $S_G \lesssim S_H$ is observed.

It was previously found that some physical properties of the homologous series of liquid crystal hosts show an odd–even effect [28–30], which has been explained in terms of the alternation of interaction between alkyl chains [31]. The *n*-alkyl-4-(4-isothiocyanatophenyl) bicyclo[2,2,2]octanes reveal the odd–even effect very distinctly both in the nematic–isotropic transition temperatures (table 2) and in their order parameters (figure 2): S_H for an odd member of the homologous series is always greater than that for the previous even member. No analogous effect for the guest order parameters, S_G of the mixtures investigated has been found. As is seen from figure 2, the changes in the S_G values with number of carbon atoms in the alkyl chain of the liquid crystal host are indeed observed, but they have a different character, which is different for the various dyes. These results confirm once more the crucial role in the guest–host interactions played by the molecular geometry of the guest. If the dye molecule is similar to that of the liquid crystal, the changes in S_G with n approximately follow those of S_H (dyes **1** and **2**), whereas if the geometries of the dye and liquid crystal molecules are inconsistent (dyes **4** and **5**), the dependencies of S_G and S_H on n are completely different. In the case of dye **3**, whose molecular structure is similar in size and shape to that of the liquid crystals investigated, the incompatibility between the S_G and S_H changes may be due to the terminal, polar NO_2 group, which interacts strongly with the NCS group of the liquid crystals. Such a type of interaction has been found previously in dielectric measurements of the guest–host systems [32,33]. All these observations lead to the general conclusion that the efficiency of orientation of the dye in the liquid crystal results strongly from the *individual* intermolecular interactions (attractive van der Waals forces and steric effects due to the guest molecular geometry) in the given guest–host mixture. The ratio S_G/S_H can be a measure of these interactions.

3.2. *Nematic–isotropic transition temperatures*

As mentioned previously, the addition of the dichroic dye to the liquid crystal host changes the nematic–isotropic transition temperature, causing either a decrease or an increase in the clearing point with respect to that of the pure host [9,11–16]. Moreover, it was observed that in the dichroic dye–liquid crystal mixtures, a two-phase region is formed in which both nematic and isotropic phases coexist in equilibrium [11,16,30,34].

Table 4 shows the results of the phase transition temperature measurements of the dye–liquid crystal mixtures investigated. Here T_I and T_N denote the temperatures at which, on cooling, the two-phase region begins (the first nematic drop appears) and ends (the isotropic phase entirely disappears), respectively. ΔT_N and ΔT_I denote the shifts of T_N and T_I with respect to the T_{NI} value of the pure liquid crystal.

The data presented in table 4 indicate that the azo dyes added to the *n*-alkyl-4-(4-isothiocyanatophenyl)bicyclo[2,2,2]octanes can both decrease and increase the temperature of clearing. As the melting point of the liquid crystal does not change, within the experimental uncertainty, after the dye addition, this means that in some cases the dye narrows the mesophase

Table 4. Temperature data for dye–liquid crystal mixtures investigated

Liquid crystal	Dye	T_N	ΔT_N	T_I	ΔT_I
LC5	**1**	373·0	+0·3	373·2	+0·5
	2	372·3	−0·4	372·4	−0·3
	3	371·8	−0·9	371·9	−0·8
	4	371·4	−1·3	371·6	−1·1
	5	371·9	−0·8	372·1	−0·6
LC6	**1**	362·9	+0·7	362·4	+1·0
	2	362·4	+0·2	363·5	+0·5
	3	362·3	+0·1	364·2	+0·3
	4	361·5	−0·7	362·8	−0·5
	5	362·6	+0·4	363·6	+0·6
LC7	**1**	368·0	−0·2	368·9	−0·1
	2	368·7	+0·5	370·2	+0·6
	3	367·7	−0·5	367·9	−0·3
	4	367·1	−1·1	367·3	−0·9
	5	367·8	−0·4	367·9	−0·3
LC8	**1**	361·1	+0·4	361·3	+0·6
	2	361·6	+0·9	361·7	+1·0
	3	360·3	−0·4	360·4	−0·3
	4	360·0	−0·7	360·3	−0·4
	5	360·3	−0·4	360·4	−0·3

region of the nematic host, whereas in the others a broadening of the mesophase region is observed. Comparing the results in table 4 with those in table 3, it can be seen that for the dye–liquid crystal mixtures which show $S_G > S_H$, the shifts of the nematic–isotropic transition temperatures are positive (with only one exception). In such cases the dye molecules have a good parallel correlation of alignment of their long axes with the long axes of the liquid crystal molecules and stabilize the nematic phase of the host, as observed in the broadening of the mesophase region. However, for the mixtures where $S_G < S_H$, the dye added to the liquid crystal decreases the clearing temperature, leading to a destabilization of the host mesophase. The region of two-phase coexistence for the dye–liquid crystal mixtures investigated is narrow; for the most part it is equal to 0·1–0·2 K, but in spite of the measurement error of ±0·1 K, this region is detectable.

Measures of the destabilization or stabilization of the nematic phase by the guest molecules are given by the slopes of the reduced temperature T_N^* and T_I^* lines with change in the solute mol fraction, defined as follows:

$$\beta_N = \frac{dT_N^*}{dx} \qquad (1)$$

and

$$\beta_I = \frac{dT_I^*}{dx} \qquad (2)$$

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 destroy the orientational order in the host nematic phase.

According to Martire [35], at very low guest concentrations, the limiting slopes of the nematic phase boundary line, β_N^∞ and the isotropic phase boundary line, β_I^∞ are connected with the solute activity coefficients by the relations:

$$\beta_N^\infty = \left(1 - \frac{\gamma_N^\infty}{\gamma_I^\infty}\right)\left(\frac{R}{\Delta S_{NI}}\right), \qquad (3)$$

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

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.

The smaller the ratio of $\gamma_N^\infty/\gamma_I^\infty$, the greater is the compatibility of the guest with the nematic host and vice versa; thus a correlation between the activity coefficients and the orientation of the guest by the host would be anticipated.

According to the model based on the mean-field theory of nematics [36,37] and the extension proposed by Humphries *et al.* [38] for binary mixtures, the expression for the ratio of the infinite-dilution guest activity coefficients at the nematic–isotropic transition temperature has the following form:

$$\ln\left(\frac{\gamma_N^\infty}{\gamma_I^\infty}\right) = \frac{\Delta S_{NI}}{R}\left[\frac{\vartheta_2}{\vartheta_1} - \left(\frac{b_{12}}{b_{11}}\right)^2\right], \qquad (5)$$

where ϑ_1 and ϑ_2 are, respectively, the host and guest molecular volumes, and b_{12}/b_{11} is a measure of the relative strength of the guest–host and host–host intermolecular interactions. The b_{12}/b_{11} can be easily estimated from the ratio of S_G/S_H in the vicinity of the clearing point [38].

Because of the lack of molecular volume data for the substances investigated, we used the ratios of the molecular length (l) to breadth (d) instead of ϑ_1 and ϑ_2 values. It has been shown previously [11,30,39] that $l/d = m$ can be successfully used as a measure of the host and guest molecular sizes and therefore, in the present calculations, we assumed also that $\vartheta_2/\vartheta_1 = m_2/m_1$. As the values of $\Delta S_{NI}/R$ for the liquid crystals investigated are unknown, it was assumed that $\Delta S_{NI}/R$ is constant for all the substances and is equal to 0·418, i.e. the value predicted by the mean-field theory of nematics [36,38].

Table 5 summarizes the calculated values of β_N^∞, β_I^∞ and $\gamma_N^\infty/\gamma_I^\infty$ for all the dye–liquid crystal mixtures investigated. ΔT_N and ΔT_I obtained from β_N^∞ and β_I^∞ on the

Table 5. Calculated values of $\gamma_N^\infty/\gamma_I^\infty$, β_N^∞, β_I^∞ and ΔT_N, ΔT_I .

Liquid crystal	Dye	$\gamma_N^\infty/\gamma_I^\infty$	β_N^∞	β_I^∞	ΔT_N	ΔT_I
LC5	**1**	0·96	+0·10	+0·12	+0·2	+0·2
	2	1·12	−0·29	−0·26	−0·3	−0·3
	3	1·24	−0·57	−0·45	−0·7	−0·5
	4	1·32	−0·77	−0·57	−0·7	−0·5
	5	1·25	−0·60	−0·48	−0·6	−0·5
LC6	**1**	0·76	+0·57	+0·77	+0·6	+0·8
	2	0·79	+0·50	+0·64	+0·5	+0·7
	3	0·89	+0·26	+0·29	+0·3	+0·3
	4	1·08	−0·19	−0·19	−0·2	−0·2
	5	0·83	+0·41	+0·50	+0·4	+0·5
LC7	**1**	0·95	+0·12	+0·12	+0·1	+0·1
	2	0·84	+0·38	+0·45	+0·4	+0·5
	3	1·07	−0·17	−0·14	−0·2	−0·2
	4	1·24	−0·57	−0·48	−0·6	−0·5
	5	1·04	−0·10	−0·10	−0·1	−0·1
LC8	**1**	0·87	+0·45	+0·56	+0·5	+0·6
	2	0·84	+0·55	+0·71	+0·7	+0·8
	3	1·16	−0·17	−0·16	−0·2	−0·2
	4	1·21	−0·26	−0·24	−0·3	−0·2
	5	1·13	−0·10	−0·09	−0·1	−0·1

basis of equations (1) and (2) are also given in this table. From comparison of the 'theoretical' data with the experimental results (table 4) there is good accordance of the ΔT_N and ΔT_I signs determined. However, the agreement between the experimentally obtained and calculated values of the ΔT is less satisfactory; in some cases large differences occur. Nevertheless, from the calculations presented in table 5 it is seen that at such small dye concentrations as those used in our investigations, the two phase region cannot be broader than 0·1–0·2 K; this is what has been observed experimentally.

Finally, it can be concluded that calculations based on the model which considers the geometry of molecules in binary mixtures $(\vartheta_2/\vartheta_1)$ as well as the anisotropic guest–host interactions (b_{12}/b_{11}) allow prediction of both the sign and approximate magnitude of ΔT_{NI} after the guest addition, as well as the occurrence of the two phase coexistence region. This information, together with the values of the guest order parameter, S_G, is of fundamental importance to the selection of suitable dye–liquid crystal mixtures for GH LCDs.

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