

GUEST-HOST INTERACTIONS IN NEMATIC *p*-CYANO-*p'*-ALKYLPHENYLCYCLOHEXANES

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Studies of the temperature dependence of the guest order parameter for binary mixtures of the dichroic azo dye in the homologous series of the *p*-cyano-*p'*-alkylphenylcyclohexane were performed. Odd-even effect for the order parameter value was observed. A correlation between the shift in the nematic-isotropic transition temperature after dye addition and the orientation of the guest molecules in the nematic host was discussed.

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1. Introduction

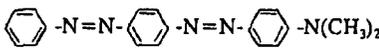
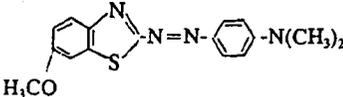
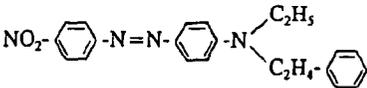
The phenomenon of the orientation of dichroic dye molecules in nematic liquid crystals ("guest-host" effect [1, 2]) has found many applications. In practice, this effect can be utilized to the construction of the colour and black-white electrooptical displays [3-7], which in comparison with the conventional liquid crystal displays have such advantages as the wider viewing angle and the higher image brightness. From scientific point of view dye-liquid crystal mixtures are very interesting, because they can be used in the optical spectroscopy for determination of the absorption and emission bands polarization of the dye molecules [8-13] as well as to obtain information about the molecular interactions between guest molecules and their liquid crystal environment [14-18].

Of many liquid crystals that can be used as matrices in guest-host mixtures the *p*-cyano-*p'*-alkylphenylcyclohexanes (PCH n), discovered by Eidenschink and collaborators [19] have many advantages, such as the low temperature range, colourlessness (they are transparent down to *ca.* 290 nm), photochemical stability and the strong positive dielectric anisotropy arising from the cyanine group attached to the molecules.

In this paper we have presented the results of our studies on the seven members of the homologous series of *p*-cyano-*p'*-alkylphenylcyclohexane ($n = 3-9$) doped with three dichroic azo dyes. The molecules of the azo dyes used are cylindrically shaped and therefore, due to their resemblance to liquid crystal molecules, would seem to be suitable for use as guests in liquid crystal matrix. The aim of the paper is to examine the molecular orientation in the guest-host mixtures and the influence of the guest on the nematic-isotropic phase transition temperature for different alkyl chain length of the nematic host.

2. Experimental

M a t e r i a l s: The nematogen liquid crystals *p*-cyano-*p'*-alkylphenylcyclohexanes — PCH n ($C_nH_{2n+1}-C_6H_{10}-C_6H_6-CN$) for $n = 3$ to 9 were synthesized by Prof. R. Dąbrowski from Military Technical Academy, Warsaw, Poland and used without further purification: the observed transition temperatures were in good agreement with those reported in literature [19-21]. As guest species three azodyes with the following chemical structure were used:

Dye code	Molecular structure
I	
II	
III	

The dye I (D2) was obtained from BDH Ltd. (UK), the dyes II and III were synthesized and chromatographically purified in Institute of Dyes, Łódź Technical University, Poland. The guests were doped to the liquid crystals at the concentration of 0.3%wt.

A p p a r a t u s: The polarized absorption spectra of the guest-host mixtures in the visible spectral region were measured 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 μ m in thickness. The temperature of the cells was regulated and controlled with the accuracy of $\pm 0.1^\circ$. After changing the measurement temperature the cell was left for approximately 20 minutes to reach thermal equilibrium. The planar orientation of molecules was achieved by treatment of the glass surfaces with polyimide and by additional rubbing process. This procedure gives a good homogeneous orientation of the liquid crystal and dye molecules in a thin layer, which was controlled with the aid of the crossed polarizers. The absorption of the dyes dissolved in the liquid crystals

was recorded at two positions of the cell: the orientation axis of the liquid crystal sample created the angles 0° and 90° with respect to the polarization plane of the light beam. Additionally, the base lines for pure liquid crystals 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 as a result.

The temperature of the phase transitions, both for the pure liquid crystals and the dye-liquid crystal mixtures was determined by means of a polarizing microscope equipped with a heating stage with an accuracy of $\pm 0.1^\circ$.

3. Results and discussion

3.1. Order parameter

The long-range orientational order which is characteristic of liquid crystals in nematic phase is usually described by the order parameter defined by [22]:

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

where θ is the angle between the long molecular axis and the optical axis of the liquid crystal.

The order parameter of the guest aligned in the nematic host can also be determined from Eq. (1), but in this case θ is the angle between the long axis of the guest molecule and the direction of the host orientation. If guest molecules are chosen such that their geometric long axis corresponds to the direction of absorption polarization and the contribution to the absorption caused by molecular polarization in the perpendicular direction is small, then the order parameter can be obtained from the polarized absorption spectra of the guest-host mixture by means of the formula [23, 24]:

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}, \quad (2)$$

where A_{\parallel} and A_{\perp} are the absorbances of the light polarized, respectively, in parallel and perpendicularly to the orientation axis of the liquid crystals. Figures 1 and 2 show the order parameter of dyes I, II and III in the liquid crystals PCH6 and PCH7, respectively, as a function of the reduced temperature $T^* = T/T_{\text{NI}}$, where T_{NI} is the clearing point of the guest-host mixture and T is the temperature of measurement. For calculation of the order parameter the values of the absorbance A_k ($k = \parallel, \perp$) were taken at the wavelength corresponding to the maximum of absorption. For the dyes investigated in PCH n 's the positions of the absorption maximum do not depend on the host within the experimental uncertainty and are as follows:

dye I	$\lambda_{\text{max}} = (480 \pm 2) \text{ nm},$
dye II	$\lambda_{\text{max}} = (503 \pm 2) \text{ nm},$
dye III	$\lambda_{\text{max}} = (512 \pm 2) \text{ nm}.$

In Fig. 3 the order parameter of dyes I, II and III at $T^* = 0.98$ versus the number of carbon atoms in the alkyl chain for the homologous series of PCH n is presented.

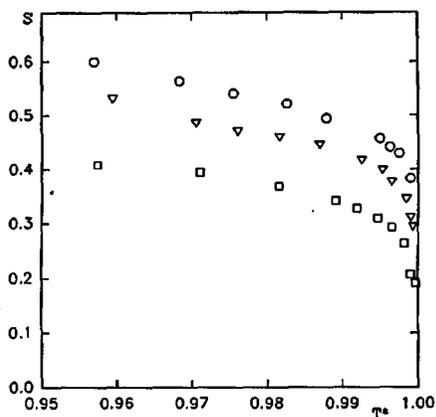


Fig. 1. Guest order parameter S as a function of reduced temperature T^* for dye-PCH6 mixtures: o — dye I, ∇ — dye II, \square — dye III.

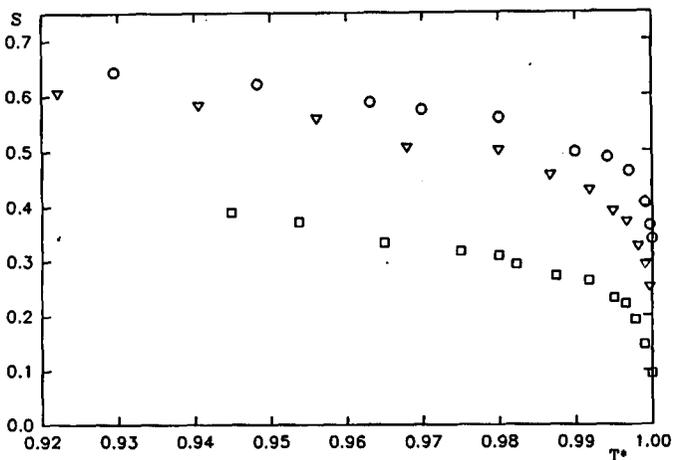


Fig. 2. Guest order parameter S as a function of reduced temperature T^* for dye-PCH7 mixtures: o — dye I, ∇ — dye II, \square — dye III.

Many authors studying the molecular orientation in guest-host mixtures [25–29] had found that there exists a correlation between the sizes of the dye molecule and its order parameter. Our results do not confirm these observations. All the dyes investigated are of the same ratio of length to breadth, $l/d \approx 2.5$. The value was estimated from the bond lengths and configuration in molecules [30] including the van der Waals radii of the terminal atoms [31]. However, the order parameters of the dyes are very different and depend on the host matrix. For dye III extremely low order parameter in all liquid crystalline hosts under investigation has been observed. Such low optical order parameter can arise either

from the direction of the electronic transition dipole moment which cannot be assumed as parallel to the long molecular axis of the dye or from the incomplete alignment of the dye molecules with respect to the orientation axis of the liquid crystal. The molecular structure of dye III suggests that one can expect non-zero angle between the transition moment and the long axis of the molecule, however, this deviation is rather small and cannot cause so strong decrease in the value of the order parameter obtained from the absorption measurements. It seems that the steric effects due to the presence of the end group connected to the benzene ring are of crucial importance. They are the source of the short-range repulsive forces which reduce the guest-host van der Waals interaction by preventing close alignment of the dye with liquid crystal molecules. As a result, the order parameter grows smaller.

It is well known that most macroscopic parameters of homologous series of liquid crystals show the odd-even effect [21, 32-38], which was explained as the alternation of interaction between alkyl chains [39]. From Fig. 3 it is seen that the order parameter of dyes I and II reveals the odd-even effect very distinctly. For the liquid crystals with odd number of carbon in alkyl chain S is always higher than for even members of the series. As the number of carbon rises, the effect becomes progressively smaller, which can be simply explained in terms of the increasing flexibility of the end chain [39]. Such alternation of S was also observed for other homologous series of liquid crystals [34, 37, 39]. The order parameter of dye III behaves differently. For this dye the lack of the regular alternation is observed. Moreover, for the odd members with $n = 5$ and 7 the values of the order parameter are lower than for previous even members of the series. This is probably a result of the mentioned above incomplete alignment of dye III in

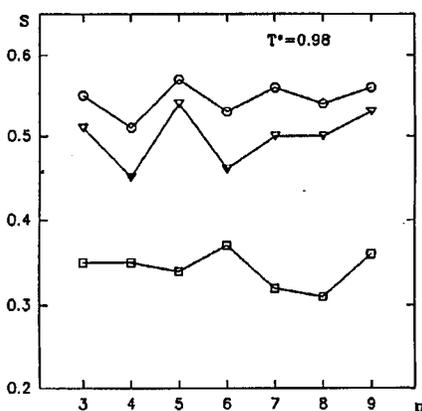


Fig. 3. Guest order parameter S at $T^* = 0.98$ versus number of alkyl chain segments in the PCH_n series: \circ — dye I, ∇ — dye II, \square — dye III.

the liquid crystals investigated, which causes that the guest does not reflect the alternation in the host orientation with the change of the carbon number in the alkyl chain.

3.2. Nematic-isotropic transition temperature

It was previously found that the addition of a dichroic dye to a nematic liquid crystal changes the nematic-isotropic transition temperature, causing either decrease or increase in the clearing point with respect to that of a pure host [18, 37, 40–42]. Moreover, it was found [18, 37, 41, 42] that the presence of the elongated dye molecules in the nematic matrix leads to the formation of a two-phase region in the vicinity of the clearing point, in which both nematic and isotropic phases coexist in equilibrium.

The temperatures of the nematic-isotropic transition for the liquid crystals and the dye-liquid crystal mixtures studied in this paper are gathered in Table I. T_I and T_N are the temperatures at which the first nematic drop appears and the last isotropic drop disappears, respectively, by cooling of the guest-host mixture; $T_I - T_N$ is the range of the two-phase region, T_{NI} is the average nematic-isotropic transition temperature and ΔT_{NI} is the average shift of the clearing point with respect to the pure liquid crystal. For dye I dissolved in all PCH n 's at such low concentration no two-phase region is observed within the experimental uncertainty. In the case of dye II-PCH n mixtures this region appears in some liquid crystals but it is relatively narrow, whereas the existence of the two-phase region after addition of dye III to nematic hosts is seen very distinctly. Dye III causes simultaneously the considerable diminishing of the nematic-isotropic phase transition temperature of all the liquid crystals, whereas in the presence of the other dyes the temperature of the clearing point in general rises (with except of dye-PCH5 and dye II-PCH7 mixtures). This means that dichroic azo dye can either destroy or stabilize the mesophase existence region of the nematic host.

As might be anticipated from the theory [43] and was found experimentally for many guest-host systems [18, 37, 42], there exists some correlation between the shift of T_{NI} and the order parameter of the dye. The results presented in Fig. 3 and in Table I indicate that for a given liquid crystal the higher is the value of S , the more positive or less negative is the shift of the clearing point. Very small order parameter for dye III in all PCH n 's is associated with the significant depression of T_{NI} . This dye added to the liquid crystal matrix causes the disordering of the nematic host molecules, reduces the region of the mesophase and leads to the formation of the broad two-phase region. However, dyes I and II, which do not affect considerably the phase transition temperature are able to correlate their long molecular axes alignment parallel (or almost parallel) to the long axes of the liquid crystal molecules. These dyes can stabilize the nematic host causing in the most cases the broadening of the mesophase region. Our observations lead to the conclusion that the nematic-isotropic transition temperature of the guest-host mixture is affected in great part by the guest order parameter, which is a measure of the intermolecular interaction with the anisotropic host, whereas the dependence of T_{NI} on the sizes of the guest molecules plays a secondary role. In the case of dye

TABLE I

Temperature data for dye-PCH*n* mixtures.

Substance	T_I [K]	T_N [K]	$T_I - T_N$	\bar{T}_{NI}	$\Delta\bar{T}_{NI}$
PCH3	319.4	319.4	0.0	319.40	-
PCH3 + dye I	319.7	319.7	0.0	319.70	+ 0.30
PCH3 + dye II	319.6	319.4	0.2	319.50	+ 0.10
PCH3 + dye III	318.6	318.1	0.5	318.35	-1.05
PCH4	312.7	312.7	0.0	312.70	-
PCH4 + dye I	312.9	312.9	0.0	312.90	+ 0.20
PCH4 + dye II	312.8	312.8	0.0	312.80	+ 0.10
PCH4 + dye III	312.2	311.9	0.3	312.05	-0.65
PCH5	328.0	328.0	0.0	328.00	-
PCH5 + dye I	327.9	327.9	0.0	327.90	-0.10
PCH5 + dye II	327.7	327.4	0.3	327.55	-0.45
PCH5 + dye III	327.0	326.3	0.7	326.65	-1.35
PCH6	322.8	322.8	0.0	322.80	-
PCH6 + dye I	323.3	323.3	0.0	323.30	+0.50
PCH6 + dye II	323.2	323.2	0.0	323.20	+0.40
PCH6 + dye III	322.3	322.1	0.2	322.20	-0.60
PCH7	330.6	330.6	0.0	330.60	-
PCH7 + dye I	330.8	330.8	0.0	330.80	+0.20
PCH7 + dye II	330.6	330.5	0.1	330.55	+0.05
PCH7 + dye III	330.1	329.8	0.3	329.95	-0.65
PCH8	327.6	327.6	0.0	327.60	-
PCH8 + dye I	327.9	327.9	0.0	327.90	+0.30
PCH8 + dye II	327.9	327.6	0.3	327.75	+0.15
PCH8 + dye III	326.9	326.3	0.6	326.60	-1.00
PCH9	331.3	331.3	0.0	331.30	-
PCH9 + dye I	331.9	331.9	0.0	331.90	+0.60
PCH9 + dye II	332.0	331.7	0.3	331.85	+0.55
PCH9 + dye III	331.2	330.6	0.6	330.90	-0.40

III, for example, the unfavourable steric interaction causing the perturbation of the host ordering seems to be the dominant factor determining the magnitude of the depression of the nematic-isotropic phase transition by the guest. It is worth noting, however, that the correlation between T_{NI} and S is indirect, because the shift in clearing point of PCH*n*'s after addition of the dye does not show the alternation, which was observed for the order parameter.

In order to compare the experimentally obtained and theoretically predicted [18, 42, 43] relation between the properties of the dye-liquid crystal mixture at nematic-isotropic transition and the order parameter of the guest, some additional data are needed, i.e. the length to breadth ratio of the liquid crystal molecule l/d , the nematic-isotropic transition entropy of the pure host ΔS_{NI} and the ratio of the order parameters of the guest and of the host at T_{NI} . Unfortunately, a complete set of these data is not available for all members of the PCII*n* series. Therefore, in the following the attempt to make some estimation only for the dye-PCH7 mixtures will be undertaken. The l/d ratio for PCH7 molecule was calculated similarly as for the dye molecules [30, 31] and for the full extended form (assuming zigzag conformation) it is equal to 3.25. The value of the host order parameter for PCH7 at T_{NI} , $S = 0.33$, was taken from Ref. [42], whereas the guest order parameters at T_{NI} are as follows (see Fig. 2):

dye I	$S = 0.34$,
dye II	$S = 0.25$,
dye III	$S = 0.10$.

Now, using the method described in Ref. [18] and assuming that $\Delta S_{NI}/R$ (where R is gas constant) is equal to 0.418 (i.e. the value predicted by the mean field theory of nematics [43,44]), we are able to calculate the values of $\Delta T_I = T_I - T_{NI}$ and $\Delta T_N = T_N - T_{NI}$, where T_{NI} is the clearing temperature of the pure host, and T_I and T_N are boundary temperatures of the two-phase region for the guest-host mixture. The data gathered in Table II indicate that the sign and the magnitude of

TABLE II
Comparison of experimental shifts of clearing point after addition of guest with theoretical calculations.

Substance	Experiment		Theory	
	ΔT_I	ΔT_N	ΔT_I	ΔT_N
PCH7 + dye I	+0.2	+0.2	+0.2	+0.2
PCH7 + dye II	-0.0	-0.1	-0.1	-0.1
PCH7 + dye III	-0.5	-0.8	-0.4	-0.6

the shift in the clearing point as well as in prediction of the range of the two-phase coexistence region obtained in our experiments are in good agreement with the theoretical predictions.

Finally, it should be underlined that the investigations of the guest-host mixtures contribute not only to the better understanding of the interaction between molecules in anisotropic systems, but allow also to assess the effect of additives used in liquid-crystalline displays on nematic phase stability.

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