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An X-ray diffraction study of a mixture of azo dyes with 4-*n*-pentyl-4'-cyano-*p*-terphenyl

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The intensities of the X-ray diffraction pattern of the aligned nematic phase of T15-azo dye mixtures have been measured as a function of temperature. Intermolecular distances as well as the monomer and associate lengths of the T15 molecules in the presence of the dyes were determined. The dimer fraction in the liquid crystal-dye mixtures were estimated and it was found that dyes with nitro groups in the para position influence particularly the monomer to dimer ratio in the liquid crystal range. The orientational distribution function, $f_0(\beta)$ and the order parameter $\langle P_2 \rangle_H$ and $\langle P_4 \rangle_H$ were calculated from the wide angle region. The perturbation of the nematic host phase by the dyes is discussed.

1. Introduction

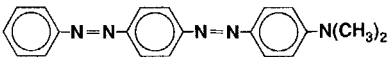
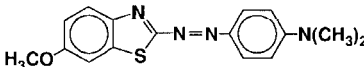
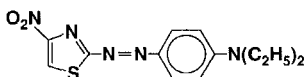
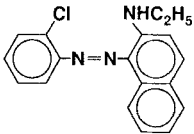
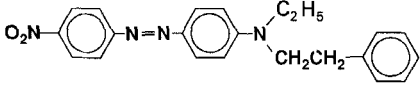
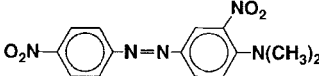
It is well-known that the presence of a guest dye in a nematic liquid crystal affects some properties of the pure host, e.g. the addition of a dye can stabilize or destroy the nematic mesophase [1-3]. Furthermore the influence of a dye on the dielectric constants [4] and on the order parameter of host has been observed [1, 2, 5] and the order parameter of guest depends strongly on the guest concentration [1, 3, 6, 7]. Although the study of the host-guest effects are, at present, very intense the microscopic mutual interactions in the host-guest system continue to be objects of speculation [1, 4, 8, 9]. We have therefore turned our attention to the X-ray diffraction technique. This has proved to be a good tool with which to obtain information about the molecular arrangement (conformation and packing) and the range of the molecular order in an aligned liquid-crystalline sample. This paper reports the determination of some parameters from the inner and outer reflections in the X-ray diffraction pattern of liquid crystal T15-azo dye mixtures.

2. Experimental

The purified nematogen 4-*n*-pentyl-4'-cyano-terphenyl (T15) which was used as a host was kindly provided by E. Merck, Darmstadt, F.R. Germany. The dyes investigated are listed in table 1 with the numbering scheme given in [1]. Dye I was obtained from BDH Ltd, Poole. The others were synthesized and chromatographically purified in the Institute of Dyes, Lodz Technical University, Poland. The concentration of the dyes in all experiments was 6×10^{-2} M/dm³.

The thermal analyses were performed using D.S.C. equipment (Du Pont 990) and a polarizing microscope (Leitz Orthoplan Pol) equipped with a Mettler FP52 hot stage. The experimental error in the melting and clearing points are $\pm 0.2^\circ$ and $\pm 0.1^\circ$,

Table 1. Molecular structure of the dyes investigated.

No.†	Molecular structure
I	
III	
V	
IX	
XI	
XIV	

† According to [1].

respectively. The temperature dependent X-ray diffraction measurements were performed with a modified STOE focussing horizontal diffractometer using monochromated $\text{CuK}\alpha$ radiation. A detailed description of the experimental set up has been given elsewhere [10]. The samples were contained in sandwich cells of thickness 1 mm [10] and oriented by an external magnetic field of about 0.8 T using two permanent magnets. The oven used was stabilized to ± 0.01 K during the measurements.

3. Results and discussions

3.1. Phase transitions

The temperature of the solid–nematic, T_{CN} , and nematic–isotropic T_{NI} , phase transitions for the liquid crystal–dye mixtures studied are given in table 2. It shows

Table 2. Solid–nematic, T_{CN} , and nematic–isotropic, T_{NI} , transition temperatures of the dye–T15 mixtures.

Substance	$T_{\text{CN}}/^\circ\text{C}$	$T_{\text{NI}}/^\circ\text{C}$
Pure T15	131.6†	240.0†
Dye I + T15	130.0	241.7
Dye III + T15	139.0	240.8
Dye V + T15	128.8	234.2
Dye IX + T15	127.6	236.0
Dye XI + T15	129.5	235.3
Dye XIV + T15	128.2	234.5

† From [11].

that the addition of the dyes to T15 leads to a change of the melting and clearing points. The melting point decreases in all cases except for dye III; however because of the small amount of the dye III no further investigation was made. Moreover, the clearing point increases or decreases in the presence of the dye, in good agreement with the results obtained previously [1, 3, 11].

3.2. The inner reflection

As has been shown by Brownsey and Leadbetter [12] and by Haase *et al.* [13] that the inner reflection of T15 consists of two maxima (see figure 1). The X-ray diffraction of T15-azo dye mixtures also revealed two inner maxima whose intensity ratio changed with increasing temperature. In table 3 the ratio of the intensity maxima of peak 1 to peak 2 are presented (see figure 2) for all T15-dye mixtures. For comparison the data for pure T15 [13] at two reduced temperatures are also shown. The reduced temperature is defined by

$$T^* = \frac{T}{T_{N1}}, \quad (1)$$

where T_{N1} is the clearing point either of the pure host or of the host-guest mixture.

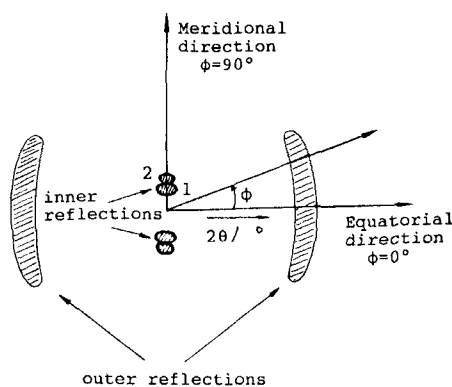


Figure 1. Schematic representation of the X-ray diffraction patterns for the nematic phase of T15.

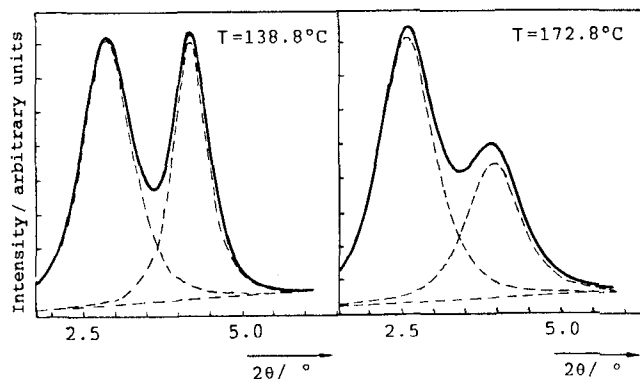


Figure 2. The intensity profiles of the inner reflections in the X-ray diffraction patterns for T15 ($\phi = 90^\circ$).

Table 3. Parameters derived from the inner reflections in the X-ray diffraction pattern of the oriented dye-T15 mixture.

Substance	T^*	$l/\text{\AA}$	$d_D/\text{\AA}$	$d_M/\text{\AA}$	I_D/I_M	x_D
Pure T15	0.815	21.7	30.7†	20.7†	1.35	0.57
	0.890		31.5†	20.7†	2.15	0.68
Dye I + T15	0.815	22.1	31.5	21.8	1.28	0.56
	0.890		32.1	21.6	2.31	0.70
Dye III + T15	0.815	20.0	31.4	21.7	0.99	0.50
	0.890		32.2	21.8	1.95	0.66
Dye V + T15	0.815	18.0	32.2	22.0	1.10	0.52
	0.890		33.1	22.2	1.76	0.64
Dye IX + T15	0.815	14.0	31.5	20.8	1.28	0.56
	0.890		32.1	20.7	1.99	0.67
Dye XI + T15	0.815	22.0	31.0	21.3	1.00	0.50
	0.890		32.1	21.2	1.78	0.64
Dye XIV + T15	0.815	17.1	31.4	21.7	1.21	0.55
	0.890		32.2	21.5	1.78	0.64

† From [11] and $\delta d = \pm 0.02 \text{\AA}$.

It is well-known from other X-ray diffraction measurements [15], N.M.R. [16] and dielectric studies [4, 18–20] that samples with a *p*-cyano end group exhibits anti-parallel dipole–dipole association which is revealed by smaller 2θ values in diffraction and are normally interpreted as a dimer. The molecular length d can be calculated using the Bragg formula [14].

$$2d \sin \theta = n\lambda.$$

Because of the low concentration of dye molecules their contribution to the scattering can be neglected. The calculated lengths d corresponding to both maxima are gathered in table 3. As pure T15 [13] the monomer length d_M of the given host–guest mixtures is nearly independent of temperature but after addition of the dye it increases somewhat. The dimer length d_D increases with temperature. Moreover, the increase of d_D occurs after addition of the dye. Considering the molecular lengths l of the dyes, calculated from standard bond lengths and angles [21] including van der Waals radii [22], it can be seen that long dye molecules enlarge the d_M value of the pure host. We could believe that hard rod-like dye molecules stiffen the liquid crystal molecules, especially their alkyl-chains. But the question is, in what way can so low concentration of the guest (1 molecule of the dye per 50 molecules of T15) affect the d_M value so strongly. On the other hand it is known that even small amounts of the guest can cause very large changes of liquid crystal properties [1, 4, 12].

The dimer fraction x_D and its change can be calculated from the intensity ratio, I_D/I_M . Assuming I_D/I_M is proportional to n_D/n_M , we obtain n_M as the number of monomers and n_D the number of dimers where

$$x_D = \frac{I_D/I_M}{1 + I_D/I_M}. \quad (2)$$

In order to obtain the separate intensities I_D and I_M , the diffraction curves were fitted to the second power of the Lorentz function using the STOE-Package computer

program. In figure 2 the inner reflection for pure T15 at two temperatures is shown as an example. The calculation of the separate intensities was done using a planimeter. The x_D values for all T15-dye mixtures at two temperatures are listed in table 3. The systematic error of x_D was estimated to be ± 0.01 .

It is evident from the results in table 3 that some dyes cause a reduction of the dimer fraction, x_D . Such an effect was also observed for dyes with the polar end group $-\text{NO}_2$ during the study of the dielectric permittivity of the liquid crystal-azo dye mixtures [4]. Considering the molecular structure of the dyes (see table 1) we can see that x_D is reduced by those dyes which have the $-\text{NO}_2$ group in the 4-position of the thiazolic sulphur atom (dye V) or in the *p*-position (dye XI). The reduction of x_D for dye XIV, which possesses the $-\text{NO}_2$ group in the *p*-position, is less distinct and may be due to the second $-\text{NO}_2$ group in the *o*-position of the phenyl ring. The strong reduction of x_D for dye III at the low temperatures can be explained by its high melting temperature. Figure 3 presents the inner reflections for dye V and dye XI in T15, while figure 4 shows the temperature dependence of the dimer fraction for dye I and dye XI in T15. In both figures the differences between the influence of the dyes without the $-\text{NO}_2$ group (dye I and IX) and with the $-\text{NO}_2$ group (dye V and XI) on the dimer fraction of T15 are seen very clearly.

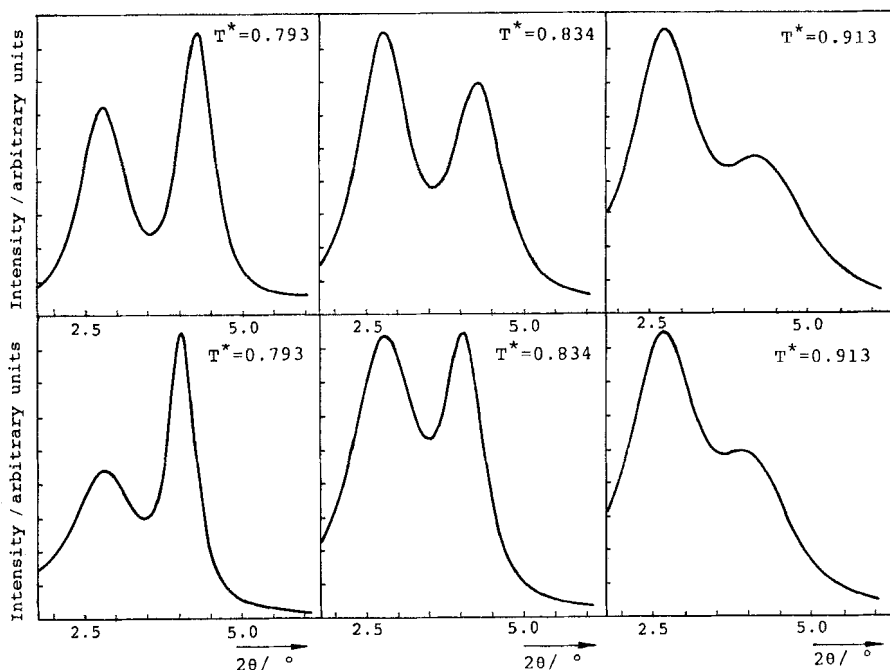


Figure 3. Inner reflections for the T15-dye IX mixture (upper) and T15-dye V mixture (bottom) at $\phi = 0^\circ$.

The results obtained from the inner reflections confirm the previous assumption [4] that the $-\text{NO}_2$ polar end group of the dye interacts strongly with the polar CN-group or the phenyl ring of the *p*-cyano substituted liquid crystal hosts and leads to a change of the dimer fraction, x_D .

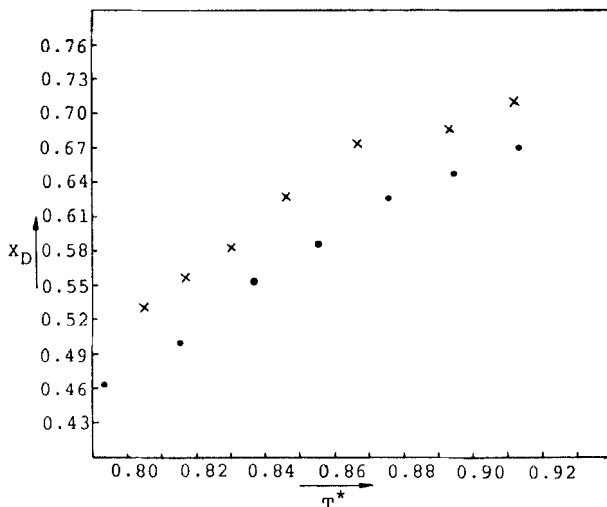


Figure 4. Temperature dependence of the solvent dimer fraction. Circles: dye T15-dye XI mixture; Crosses: T15-dye I mixture.

3.3. *The outer reflection*

The outer reflection of the X-ray diffraction pattern was studied in detail for the T15-dye I mixture. The measurements were made at various angles ϕ (see figure 1). In figure 5 the outer reflection of the T15-dye I mixture and of pure T15 at $T^* = 0.815$ for $\phi = 0^\circ$ are shown. From the position of the maximum the intermolecular distance, D was calculated from [14, 17]

$$2D \sin \theta = 1.117 \lambda.$$

It was found that the D value of this sample remains unchanged after addition of the dye and is equal to $5.10 \pm 0.03 \text{ \AA}$. With increasing temperature the distance D in the T15-dye I mixture increases slightly, which was also observed from X-ray diffraction studies of other systems [23-26].

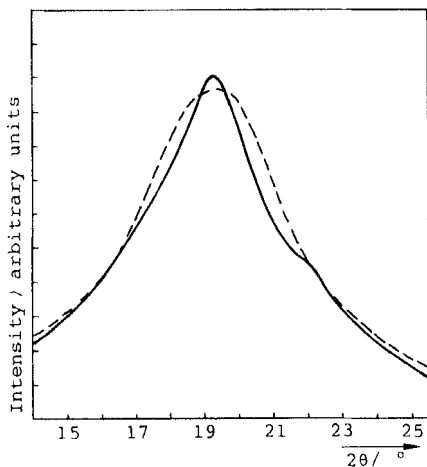


Figure 5. Outer reflections (2θ scan at $\phi = 0$; $T^* = 0.815$). Solid line: pure T15; dashed line: T15-dye I mixture.

The width of the diffraction along the equatorial plane is related to the regularity of the molecular packing; that is the more constant the distance between adjacent molecules, the narrower is the diffraction peak. Thus, the broadening of the diffraction for the mixture with respect to that for the pure liquid crystal (see figure 5), indicates the disordering of the molecular packing of T15 after addition of the dye and with increasing temperature.

The integral intensity of the outer reflection, $I(\phi)$, is related to the orientational distribution function $f_d(\beta)$ by [13, 27]

$$I(\phi) = K \int_{\phi}^{\pi/2} f_d(\beta) \sec^2 \phi \frac{\sin(\beta) d\beta}{\sqrt{[\tan^2(\beta) - \tan^2(\phi)]}}. \quad (3)$$

Here β is the angle between the long molecular axis and the director direction, whereas $f_d(\beta)$ describes the distribution function for the orientation β of a local cluster of more than 10 molecules with respect to the director.

From the distribution, $f_d(\beta)$, the order parameter $\langle P_2 \rangle$ and $\langle P_4 \rangle$, where $P_L(\cos \beta)$ ($L = 2, 4$) are Legendre polynomials, can be calculated from

$$\langle P_L \rangle = \frac{\int_0^{\pi/2} P_L(\cos \beta) f_d(\beta) \sin(\beta) d\beta}{\int_0^{\pi/2} f_d(\beta) \sin(\beta) d\beta}. \quad (4)$$

The numerical calculation of $f_d(\beta)$ and then $\langle P_L \rangle$ using the experimental values of $I(\phi)$ were made using a computer program described in [13]. Figure 6 shows $\langle P_2 \rangle_H$ and $\langle P_4 \rangle_H$ (subscript H refers to the host order parameter) as a function of the reduced temperature for the T15-dye I mixture and for pure T15. The solid lines are calculated on the basis of the Maier-Saupe molecular field theory [28, 29]. A comparison of our results with those obtained from the Maier-Saupe model shows that this model does not predict very well the absolute values of $\langle P_L \rangle_H$; we have obtained in most cases larger values. Such a difference occurs because the molecular

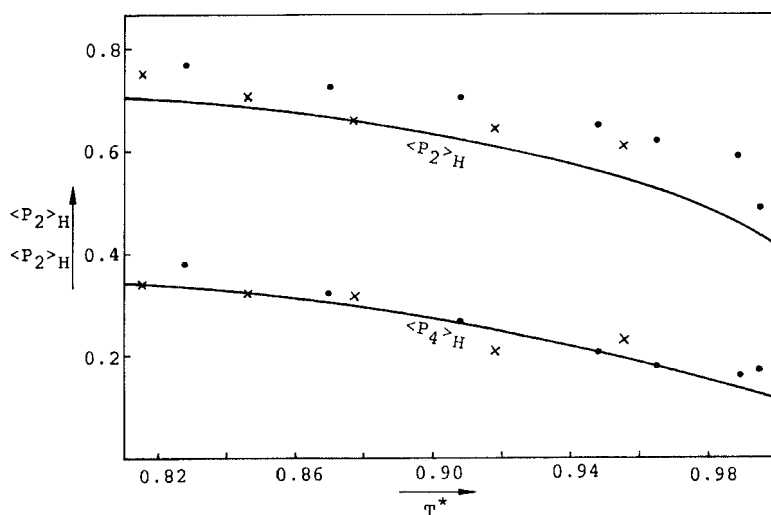


Figure 6. $\langle P_2 \rangle_H$ and $\langle P_4 \rangle_H$ versus reduced temperature. Circles: pure T15 [11]; crosses: T15-dye I mixture; solid line: Maier-Saupe theory.

field theory does not take into account the short range interactions between the liquid crystal molecules. None the less, the agreement of the temperature dependence of $\langle P_L \rangle_H$ found in our experiment and the prediction of the Maier-Saupe theory is satisfactory. It was found, on the basis of refractive index measurements, that dye I added to the liquid crystal K15 improves the ordering of the nematic host and this order effect is greater as the concentration increases [1, 2]. Looking at the results in figure 6 we notice that dye I perturbs somewhat the molecular order of T15.

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