

## First- and Second-order Smectic-A to Nematic Phase Transitions in $p,p'$ -Dialkylazoxybenzenes studied by Birefringence

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The birefringence of mixtures of homologues from the terminally non-polar series of  $p,p'$ -dialkylazoxybenzenes has been studied. The birefringence is used as a probe of the orientational order parameter, which is coupled to the translational (smectic) order parameter. The tricritical nematic to smectic-A point which results from this coupling is found at a McMillan ratio  $T_{AN}/T_{NI} = 0.977$ . This is similar to the values reported for terminally polar systems and is higher than predicted by theory. The critical exponent for the variation of the order parameter across the  $S_A$ -N phase transition obeys the expected trend.

Despite considerable experimental<sup>1</sup> and theoretical<sup>2</sup> effort several aspects of the nematic (N) to smectic-A ( $S_A$ ) phase transition remain poorly understood. The critical behaviour that results from de Gennes's phenomenological theory<sup>3</sup> is subject to controversy. Experimentally, non-universal critical exponents are observed for the specific heat, the correlation lengths and the layering susceptibility. In this paper, we adhere to problems around a more microscopic approach. In this case complications arise owing to the strong coupling between the orientational (nematic) and the translational (smectic) order parameter. In the microscopic theory of Kobayashi<sup>4</sup> and McMillan,<sup>5</sup> this coupling makes the phase transition first-order when the ratio of smectic-nematic and nematic-isotropic transition temperatures,  $T_{AN}/T_{NI}$ , exceeds a specific value. For McMillan's choice of potential for the molecular interaction, this value is  $T_{AN}/T_{NI} = 0.87$ ,<sup>5</sup> where a tricritical point occurs. Experimentally, this point is found at values of  $T_{AN}/T_{NI}$  between 0.94 and 0.994.<sup>6-11</sup> In all cases reported so far, the elongated molecules are either weakly or strongly asymmetric in the end-groups. In McMillan's theory, however, the molecules are implicitly assumed to be symmetric. Thus it seemed worthwhile to investigate the tricritical point in the case of symmetric molecules, or at least molecules as symmetric as possible. We used the homologous series of  $p,p'$ -dialkylazoxybenzenes<sup>12-16</sup> for this purpose. The molecules are symmetric in the end-groups and almost symmetric in the central part. The alkyl number  $n$  was continuously varied using mixtures of  $n = 7$  (7AB) and  $n = 8$  (8AB). The first- or second-order nature of the  $S_A$ -N phase transition was determined using the birefringence  $\Delta n = n_{\parallel} - n_{\perp}$ , which probes the orientational order parameter  $S = \langle P_2(\cos \theta) \rangle$ . The indices  $\parallel$  and  $\perp$  refer to the director  $n$ , which is the principal axis of the medium. Although the relation between  $\Delta n$  and  $S$  is complicated by the internal field problem, it is sufficient for the present discussion to note that to a first approximation they are proportional.<sup>16-18</sup> At a first-order  $S_A$ -N phase

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transition, the discontinuity in the smectic order parameter will lead to a jump in  $S$  through their mutual coupling, and hence to a jump in  $\Delta n$ . The method proves to be an accurate and relatively easy way to determine the order of an  $S_A$ -N phase transition, as compared to adiabatic calorimetry and critical X-ray scattering experiments.

For the coupling of the nematic order parameter  $S$  with the smectic order parameter  $\Psi$  de Gennes postulated the mean-field form<sup>19</sup>  $S - S_0 \sim \langle |\Psi|^2 \rangle$  for  $T < T_{AN}$ . Here  $S_0$  is the hypothetical nematic order parameter in the absence of smectic ordering. With the inclusion of short-range  $S_A$  fluctuations in the nematic phase, this form is modified into<sup>20</sup>  $\tilde{S} - S_0 \sim \langle |\Psi|^2 \rangle$ . The mean-square smectic order parameter  $\langle |\Psi|^2 \rangle$  has been measured directly by X-ray scattering, for a number of compounds with second-order  $S_A$ -N phase transitions<sup>21</sup> and fitted to the form  $\langle |\Psi|^2 \rangle = L + M^\pm |t|^\alpha$ , where  $t = (T - T_{AN})/T_{AN}$  is the reduced temperature and  $M^+$  and  $M^-$  are constants above and below  $T_{AN}$ , respectively. It was demonstrated that the critical exponent  $\alpha$  is not equal to  $1 - \alpha$  ( $\alpha$  is the specific heat exponent) as predicted for the Landau-de Gennes free energy.<sup>22</sup> The discrepancy is largest for materials with long nematic ranges, which are expected to be described best by de Gennes's model. This observation raises questions about the validity of the Landau-de Gennes free energy. Assuming the relation  $S - S_0 \sim \langle |\Psi|^2 \rangle$  we can independently determine  $\alpha$  from our  $\Delta n(T)$  curves and compare the values with those obtained from X-ray scattering.

### Experimental

In the optical method used the phase difference  $\Delta\varphi = 2\pi d/\lambda\Delta n$  is measured between the ordinary ( $\parallel$ ) and extraordinary ( $\perp$ ) waves travelling through a planar liquid-crystalline sample of thickness  $d$ . Uniform planar orientation is achieved by treating the boundaries (two parallel glass plates) with a polyimide coating. The coated glass plates were rubbed gently to make the orientation uniform, with  $n$  in the direction of the rubbing. The glass plates were kept apart by tungsten spacers of thickness  $d$  between 17 and 60  $\mu\text{m}$ . The exact thickness of the empty cell was determined interferometrically. The transmitted intensity exhibits maxima as a function of the wavelength at  $k\lambda = 2d$  ( $k = 1, 2, \dots$ ) because of interference between the direct and the doubly reflected beam.

The optical part of the set-up is similar to that described by Lim and Ho;<sup>20,23</sup> the essentials are shown in fig. 1. Light from an He-Ne laser ( $\lambda = 632.8 \text{ nm}$ ) passes through a polarizer, the sample, a quarter-wave plate and a rotating polaroid (angular frequency  $\omega \approx 10 \text{ s}^{-1}$ ) before it reaches a photodiode. The polarizer and the quarter-wave plate are both oriented at an angle of  $45^\circ$  to the director. A reference beam from an LED passes through the rotating polaroid and an analyser onto another photodiode. Thus the two signals are modulated with an angular frequency  $2\omega$ . Their phase difference  $\Delta\varphi + \varphi_0$  ( $\varphi_0$  is an instrumental constant) is recorded by a phasemeter (Brüel and Kjær type 2971) with a sensitivity of 0.01 rad. In this way the method is independent of the non-linear response of the photodiode. The resolution in  $\Delta n$  is  $ca. 2 \times 10^{-5}$  for  $d = 35 \mu\text{m}$ . If the angles of the polarizer and the  $\lambda/4$  plate with  $n$  are  $\pi/4 + \delta$  and  $\pi/4 + \epsilon$ , the recorded phase difference is  $\Delta\varphi + \varphi_0 - \arg[1 + 2A \tan(2\delta) - A^2]$  with  $A = \tan \epsilon \exp(i\Delta\varphi)$ . It follows that the relative angles of the optical parts have to be set with an accuracy of  $ca. 3^\circ$  to keep the deviation in  $\Delta\varphi$  within 0.01 rad.

The sample was placed in a two-stage oven. The outer stage was kept typically 1 K below the desired sample temperature by a thermostatted water bath. The inner stage was heated electrically. The heating was driven by a lock-in amplifier measuring the output of an a.c. Wheatstone bridge, comparing the signal from a thermistor in the oven with that from a reference resistor. This provided an accurate temperature control with a stability of  $ca. 10^{-3} \text{ K}$  at the position of the thermistor. The temperature could be varied automatically at different speeds while  $\Delta\varphi$  and  $T$  were recorded at regular intervals.

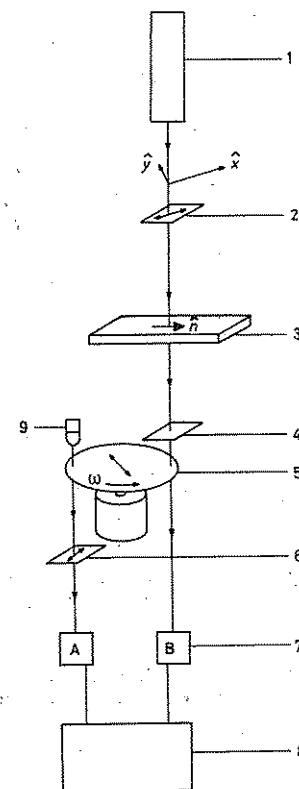


Fig. 1. The optical part of the set-up: 1, He-Ne laser; 2, polarizer; 3, sample; 4,  $\lambda/4$  plate; 5, rotating polaroid; 6, analyser; 7, photodiodes; 8, phasemeter; 9, LED.

### Results and Discussion

The phase diagram of the  $nAB$  series is shown in fig. 2. The transition temperatures (table 1) were determined from the  $\Delta n(T)$  curves shown in fig. 3. Naturally, the phase difference  $\Delta\varphi$  can only be determined apart from an arbitrary multiple ( $2\pi k$ ) of  $2\pi$ . The resulting arbitrariness in  $\Delta n$  is removed by measuring samples of different thickness. For 7AB, samples with  $d = 50.9$  and  $17.4 \mu\text{m}$  have been used; for 8AB,  $d = 60.7$ ,  $51.0$  and  $18.9 \mu\text{m}$ . For the mixtures (b)-(e), only one thickness was used. Here the order  $k$  is interpolated from the requirement that  $\Delta n$  on the nematic side of the N-I phase transition should not vary abruptly as a function of the 8AB mole fraction  $c_{8AB}$ . Fig. 4 shows the behaviour of  $\Delta n - \Delta n_{AN}$  vs.  $T - T_{AN}$  in the vicinity of the  $S_A$ -N phase transition of the mixtures (a)-(f) (see table 1).  $\Delta n_{AN}$  is the birefringence at the  $S_A$ -N transition or, in case the transition is first-order, the mean value of  $\Delta n$  at both sides of the transition. The transition is continuous for  $c_{8AB} = 0.465$  [mixture (c)], whereas there is a jump for  $c_{8AB} = 0.573$  [mixture (d)], indicating a first-order transition. The tricritical point is estimated to occur at  $c_{8AB} = 0.52 \pm 0.05$  with a McMillan ratio  $T_{AN}/T_{NI} = 0.977 \pm 0.001$ . This is well within the range of values reported for less symmetric

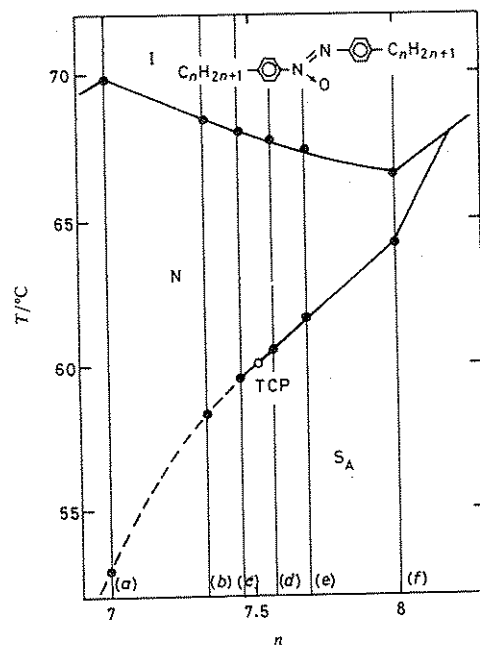


Fig. 2. Partial phase diagram of the  $nAB$  series. Solid lines are first-order, broken lines second-order phase transition lines; TCP is the approximate location of the tricritical point. Thin lines indicate the mixtures (a)-(f).

Table 1. The mole fraction  $c_{8AB}$  of 8AB in the 7AB-8AB mixtures,  $S_A$ -N and N-I phase transition temperatures, McMillan ratios, the jump in  $\Delta n$  at the  $S_A$ -N transition and the critical exponents  $x$  as derived from fig. 5

mixture	$c_{8AB}$	$T_{AN}/^\circ\text{C}$	$T_{NI}/^\circ\text{C}$	$T_{AN}/T_{NI}$	$\Delta(\Delta n)$	$x$
(a) (7AB)	0	52.86	69.85	0.9504	0	$0.64 \pm 0.06$
(b)	0.345	58.34	68.39	0.9706	0	$0.61 \pm 0.05$
(c)	0.464	59.71	68.02	0.9757	0	$0.51 \pm 0.05$
(d)	0.573	60.49	67.75	0.9787	0.004	
(e)	0.689	61.55	67.42	0.9828	0.010	
(f) (8AB)	1	64.20	66.50	0.9932	0.022	

molecules, and consequently far above the theoretical value of 0.87. Hence we conclude that the molecular asymmetry has no significant effect on the location of the  $S_A$ -N tricritical point.

Finally, we discuss the critical exponent  $x$ . For this purpose, the data are shown in a double logarithmic plot of  $|\Delta n - \Delta n_{AN}|$  vs.  $|T - T_{AN}|$  in fig. 5. For each mixture, the curves for  $T < T_{AN}$  and  $T > T_{AN}$  seem to converge towards a common asymptote on approaching the  $S_A$ -N phase transition. In the region  $|T - T_{AN}| < 0.1$  K they practically coincide. For the second-order phase transitions [mixtures (a)-(c)] the slopes of the

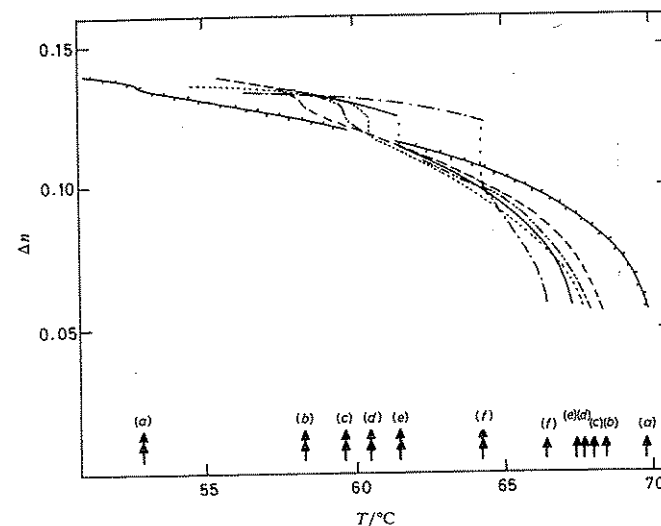


Fig. 3. The birefringence,  $\Delta n$ , of the mixtures vs. temperature, for the mixtures (a)-(f) (see table 1). The  $S_A$ -N and N-I phase transitions are indicated by double and single arrows, respectively. (---) (a), (---) (b), (---) (c), (---) (d), (---) (e), (---) (f).

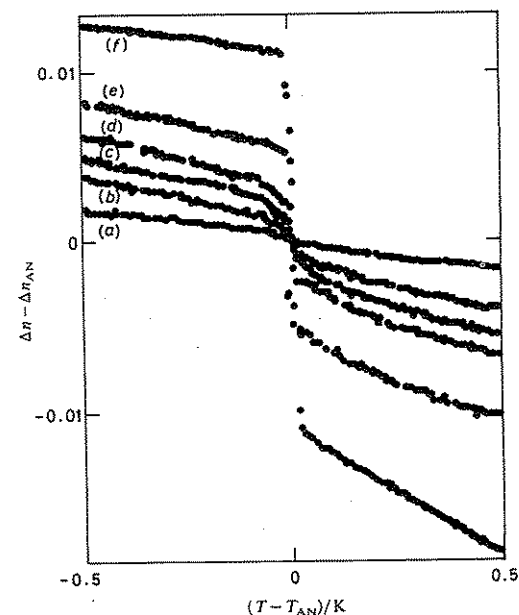


Fig. 4. Detailed plot of  $\Delta n - \Delta n_{AN}$  vs.  $T - T_{AN}$  for mixtures (a)-(f) (see table 1).  $\Delta n_{AN}$  is the birefringence at the  $S_A$ -N transition or, in the case that the transition is first-order, the mean value of  $\Delta n$  on both sides of the transition.

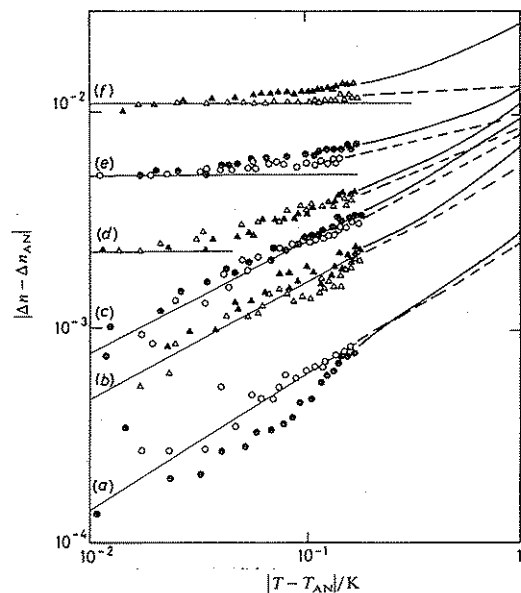


Fig. 5. Double logarithmic plot of  $|\Delta n - \Delta n_{AN}|$  vs.  $|T - T_{AN}|$  for the mixtures (a)-(f) (see table 1).  $\Delta n_{AN}$  is the birefringence at the  $S_A$ -N transition or, in the case the transition is first-order, the mean value of  $\Delta n$  on both sides of the transition. Open (closed) symbols and broken (full) lines refer to  $T < T_{AN}$  ( $T > T_{AN}$ ). The thin lines through the data of the second-order transitions (a), (b) and (c) have slopes  $x = 0.64$ ,  $0.54$  and  $0.51$ , respectively.

asymptotes give the critical exponents  $x = d(\log |\Delta n - \Delta n_{AN}|) / d(\log |T - T_{AN}|)$ . The exponents are listed in table 1. They evolve from  $x = 0.64 \pm 0.06$  for pure 7AB to  $x = 0.51 \pm 0.06$  for the mixture (c) closest to the tricritical point. These values are obtained from data in slightly more than one decade on the reduced temperature scale, and we cannot really exclude the possibility of a crossover to other values of  $x$  in the region closer to the phase transition. Bearing this in mind, it is interesting to note that the values are in excellent agreement with those obtained from X-ray scattering,<sup>21</sup> where it was found that  $x$  evolves from ca. 0.5 for a tricritical point (9CB) to 0.7 for materials with small McMillan ratios (ca. 0.93). In all these cases, the empirical scaling relation  $x = \frac{1}{2}(\nu_{\parallel} + \nu_{\perp})$ , with  $\nu_{\parallel}$  and  $\nu_{\perp}$  being the correlation length exponents, was satisfied instead of the Landau-de Gennes relation  $x = 1 - \alpha$ . Unfortunately, none of the exponents  $\nu_{\parallel}$ ,  $\nu_{\perp}$  and  $\alpha$  are available for the 7AB-8AB system, so that a direct check of these relations cannot be made in our case. Nevertheless, it is striking that the critical exponent  $x$  obtained from the birefringence fits so well into the trend established from X-ray scattering.

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