

FIRST- AND SECOND-ORDER NEMATIC–SMECTIC *A* PHASE TRANSITIONS IN THE SERIES OF DI-*n*-ALKYL AZOXYBENZENES

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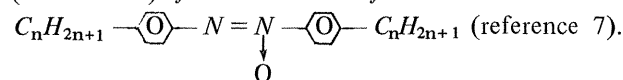
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The nematic–smectic *A* phase transitions of di-*n*-hexyl, heptyl and octyl azoxybenzene are found to be second-order, weakly first-order and first-order, respectively. This is indicated by measurements of the heats of transition and of the order parameter.

IT HAS been argued theoretically^{1,2} and there is some experimental evidence^{3–6} that the transition from the nematic to the smectic *A* mesomorphic state can be a second-order phase transition. The transition entropy is predicted to be a function of the smectic–nematic and nematic–isotropic transition temperatures, T_{SN}/T_{NI} , becoming zero when this ratio is smaller than 0.866.² In this respect some recent calorimetric data on the homologous series of di-*n*-alkyl azoxybenzenes⁷ are interesting. The hexyl, heptyl and octyl substituted members ($n = 6, 7$ and 8) exhibit a nematic and a smectic phase. From the microscopic appearance (simple fan-shaped textures)⁸ and from some miscibility studies⁸ the smectic phases could be classified as smectic *A*. As conoscopic figure a cross was obtained that remained symmetric over the whole mesomorphic range, in agreement with this assignment. The relevant calorimetric data are summarized in Table 1. For $n = 6$ the *SN* transition is practically second-order, almost no heat of transition being detectable. For $n = 7$ the *SN* transition is still only weakly first-order with a very small heat of transition; for $n = 8$ the transition is clearly first-order. In this letter we shall check this interpretation by considering the behaviour of the order parameter $S = 1 - \frac{3}{2} \sin^2 \Theta$ around T_{SN} for these three compounds. For a second-order transition there should be no discontinuity in S at T_{SN} .²

A convenient measure for S is the anisotropy of the refractive index $\Delta n = n_{\parallel} - n_{\perp}$, where the indices refer to the principal axes of the mesomorphic medium. However, S is defined in terms of the

Table 1. Transition temperatures t ($^{\circ}\text{C}$), enthalpy changes ΔH (kJ.mole^{-1}) and entropy changes ΔS ($\text{J.K}^{-1}.\text{mole}^{-1}$) of some members of the series



n		<i>mp</i>	<i>SN</i>	<i>NI</i>
6	t	24	17*	54.5
	ΔH	11.7	0.02	0.57
	ΔS	39	0.07	1.73
7	t	34	54.5	71
	ΔH	12.6	0.16	1.12
	ΔS	41	0.50	3.26
8	t	39	64.5	67
	ΔH	19.4	2.30	2.30
	ΔS	62	6.80	6.75

* monotropic transition

polarizabilities α_{\parallel} and α_{\perp} ⁹ and one has to adopt a model for the internal field in order to relate n to α .^{9,10} For the present discussion it is sufficient to note that in a first approximation Δn is proportional to S . Consequently any discontinuity in S at a phase change will lead to a jump in Δn .

In order to measure Δn the nematic or smectic sample was placed between crossed polarizers in the light beam from a He-Ne laser and the intensity of the transmitted light was recorded as a function of the temperature.¹¹ Our method differed from reference 11 in that we used thinner samples (10–100 μm) and a planar texture. With the optical axis

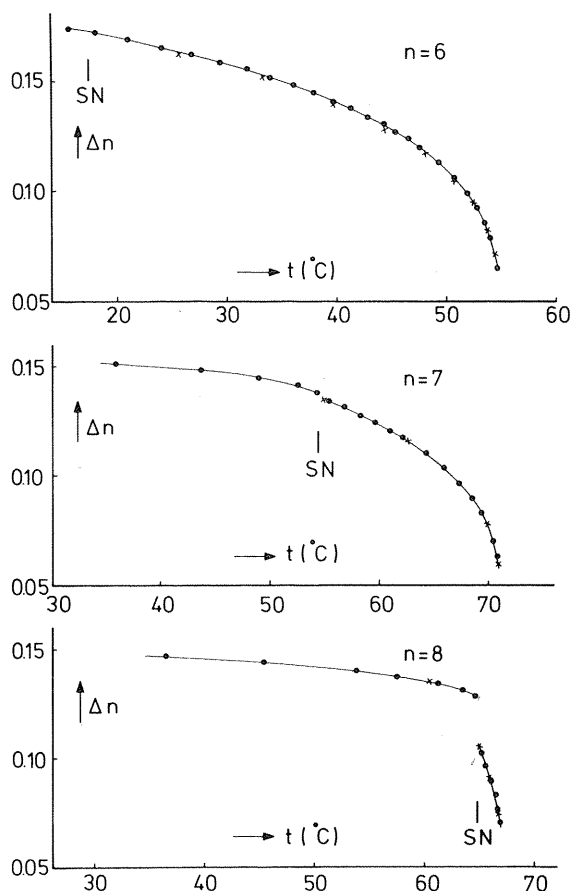


FIG. 1. Anisotropy of the refractive index at 632.8 nm of di-*n*-hexyl, heptyl and octyl azoxybenzene; crosses and circles refer to samples of different thickness.

of the sample at 45° with the polarizers this leads to almost complete extinction when

$$\Delta n d = k\lambda, \quad k \text{ integer}, \quad (1)$$

where d is the thickness of the sample. For d we used the thickness of the empty cell which was measured interferometrically. Planar textures were obtained by uni-directional rubbing of the surfaces of the cell using also a surfactant with several polar groups at different positions. These textures were preserved when the sample was cooled down to below the SN transition. The sample was placed on the optical bench in a Mettler FP52 heating stage and heated or cooled at a rate of $1^\circ/\text{min}$. As Δn changes discontinuously at T_{NI} the integer value that has to be assigned to k in equation (1) for a certain minimum is not known. However, then k can be measured by placing the nematic sample at a fixed temperature in a magnet.

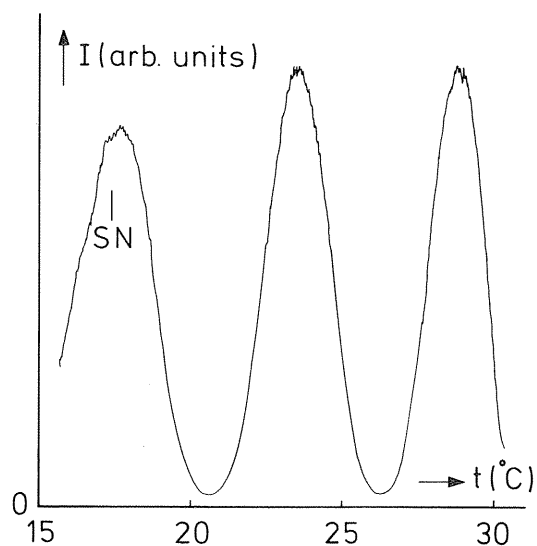


FIG. 2. Interference pattern around the nematic-smectic A transition of di-*n*-hexyl azoxybenzene ($\lambda = 632.8 \text{ nm}$, $d = 90 \mu\text{m}$, I is the intensity of the transmitted light).

When the field (perpendicular to the surface) is varied from 0 to about 10 kOe, k is given by the number of minima in the transmitted light between the planar and the homeotropic situation. The magnitude of the jump in Δn at T_{SN} could be determined accurately by comparing the interference curves around T_{SN} for samples of various thickness. The final results are given in Fig. 1.

The results for Δn (Fig. 1) confirm the expectations. For $n = 8$ there is a jump in Δn at T_{SN} of ~ 0.02 in agreement with the first-order nature of the transition. For $n = 7$ the jump is very small (~ 0.002) but clearly visible in the interference patterns. For $n = 6$ no discontinuity in Δn is observed, as expected for a second-order transition. This is once more illustrated in Fig. 2 where the interference figure in the relevant temperature range is shown. In this situation a discontinuity in Δn of 0.1% would still have been clearly visible. The SN transition being monotropic we did not succeed in cooling further than 2° below T_{SN} . Therefore it was not possible to get information about a possible discontinuity at T_{SN} of the derivative of Δn . For $n = 6$ and $n = 7$ the values of T_{SN}/T_{NI} are 0.887 and 0.952 respectively, both higher than the theoretical upper limit for a second-order SN transition of 0.866.² Around a second-order (or almost

second-order) *SN* transition strong pre-transitional effects can be expected.¹² Such results for the dielectric

constants and the electrical conductivities of di-*n*-heptyl azoxybenzene will be reported elsewhere.¹³

REFERENCES

1. KOBAYASHI K.K., *J. Phys. Soc. Japan*, **29**, 101 (1970).
2. MCMILLAN W.L., *Phys. Rev. A***4**, 1238 (1971).
3. DOANE J.W., PARKER R.S., CVIKL B., JOHNSON D.L. and FISHEL D.L., *Phys. Rev. Lett.* **28**, 1694 (1972).
4. DUREK D., BATURIC-RUBCIC J., MARCELJA S. and DOANE J.W., *Phys. Lett.* **A43**, 273 (1973).
5. MCMILLIAN W.L., *Phys. Rev.* **A7**, 1419 (1973).
6. CABANE B. and CLARK W.G., *Solid State Commun.* **13**, 129 (1973).
7. VAN DER VEEN J., DE JEU W.H., WANNINKHOF M.W.M. and TIENHOVEN, C.A.M., *J. Phys. Chem.* **77**, 2153 (1973).
8. SACKMANN H. and DEMUS D., *Mol. Cryst.* **2**, 81 (1966).
9. SAUPE A. and MAIER W., *Z. Naturf.* **16a**, 816 (1961).
10. VUKS M.F., *Opt. Spectr.* **20**, 361 (1966).
11. BALZARINI D.A., *Phys. Rev. Lett.* **14**, 914 (1970).
12. See for example: DE GENNES P.G., *Solid State Commun.* **10**, 753 (1972).
13. DE JEU W.H. and LATHOUWERS Th. W., to be published.

Les transitions de phase, nématique-smectiques A, du di-*n*-hexyl, heptyl et octyl azoxybenzene sont trouvées comme étant respectivement, du second ordre, faiblement du premier ordre et du premier ordre. Ces conclusions sont fournies par des mesures du paramètre d'ordre et des chaleurs de transition.