

# Physical studies of nematic azoxybenzenes. I. Magnetic susceptibilities and the order parameter

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The anisotropy of the magnetic susceptibility and the density of the series of nematic *p,p'*-di-*n*-alkyl and *p,p'*-di-*n*-alkoxy azoxybenzenes are reported as a function of temperature. Assuming that the molecules are effectively axially symmetric the anisotropy of the susceptibility is a direct measure of the nematic order parameter *S*. The results for *S* agree reasonably well with the predictions from Maier and Saupe's theory of the nematic phase. With increasing chain length both the order parameter and the relative volume change at the nematic-isotropic transition alternate parallel to the nematic-isotropic transition temperature and the transition entropy.

## I. INTRODUCTION

The various liquid crystalline phases<sup>1</sup> are characterized by long-range orientational ordering. The elongated molecules are, on average, aligned with their long axis parallel to a preferred direction in space. In the nematic phase (N) the molecules translate freely as in the isotropic phase (I), and the centers of mass are distributed at random. In the various smectic phases (*S<sub>A</sub>*, *S<sub>B</sub>*, etc.) the molecular centers are arranged in a series of equidistant planes. The preferred direction can be described by specifying at each point in a sample a unit vector *n*, the director. In the nematic and smectic A phase uniaxial symmetry exists around *n*, while the directions given by *n* and  $-\mathbf{n}$  are equivalent. Due to this symmetry various physical properties are anisotropic. It is the purpose of this work to investigate the anisotropy of the diamagnetic susceptibility of some nematic liquid crystals, which can be used to describe the degree of orientational order. The densities will also be reported. In a second paper the refractive indices will be discussed for the same series of compounds.

The magnetic moment *M* (per unit volume) induced by an applied field *H* is related to the field by

$$M_{\alpha} = \chi_{\alpha\beta} H_{\beta}, \quad \alpha, \beta = x, y, z, \quad (1)$$

where  $\chi_{\alpha\beta}$  is an element of the magnetic susceptibility tensor  $\chi$ . In the uniaxial nematic or smectic A phase (choosing *n* along the *z* axis)  $\chi$  is given by

$$\chi = \begin{pmatrix} \chi_{\perp} & 0 & 0 \\ 0 & \chi_{\perp} & 0 \\ 0 & 0 & \chi_{\parallel} \end{pmatrix}, \quad (2)$$

where the subscripts  $\parallel$  and  $\perp$  refer to the directions parallel and perpendicular to *n*. The average susceptibility is given by

$$\bar{\chi} = \frac{1}{3} \sum_{\gamma} \chi_{\gamma\gamma} = \frac{1}{3} (\chi_{\parallel} + 2\chi_{\perp}). \quad (3)$$

The magnetic anisotropy is defined as

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp} = \frac{3}{2} (\chi_{\parallel} - \bar{\chi}). \quad (4)$$

In the isotropic phase we have on the other hand

$$\chi_{\alpha\beta} = \chi \delta_{\alpha\beta}. \quad (5)$$

The mass susceptibility  $\chi^f$  is related to the volume sus-

ceptibility used so far by  $\chi^f = \chi/\rho$ ,  $\rho$  being the density. As diamagnetism is independent of temperature we have  $\chi^f = \bar{\chi}^f$ .

Knowledge of the diamagnetic properties of liquid crystals, and especially of the magnetic anisotropy, is important for at least two reasons:

(i) An order parameter  $Q_{\alpha\beta}$  can be defined by extracting the anisotropic part of the magnetic susceptibility<sup>2</sup>:

$$Q_{\alpha\beta} = \chi_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \sum_{\gamma} \chi_{\gamma\gamma}. \quad (6)$$

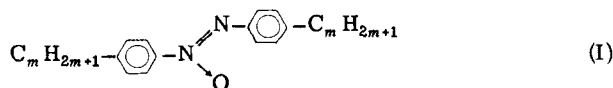
$Q$  is a second-rank tensor, which is real, symmetric, has zero trace, and vanishes in the isotropic phase. The choice of the magnetic tensor for the order parameter is convenient because the molecular diamagnetism is so small that interactions between the molecular magnetic moments can be neglected. Consequently, the internal field can be taken equal to the macroscopic field, which facilitates a molecular interpretation of the  $Q_{\alpha\beta}$ .

(ii) The response of a liquid crystal to an applied external magnetic field is largely determined by the value of  $\Delta\chi$ . Consider a field *H* at an arbitrary angle with *n*. Then the total free energy density of the nematic liquid crystal is given by<sup>3</sup>:

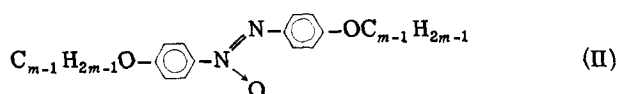
$$F = F_{\text{elastic}} - \frac{1}{2} \chi_{\perp} H^2 - \frac{1}{2} \Delta\chi (\mathbf{n} \cdot \mathbf{H})^2. \quad (7)$$

As the term  $\frac{1}{2} \chi_{\perp} H^2$  is independent of *n* it can be disregarded as far as orientation related problems are concerned, and the magnetic part of *F* depends directly on  $\Delta\chi$ . If, for example, the elastic constants  $K_{ii}$  (*i* = 1, 2, 3) of a nematic liquid crystal are determined using the deformation of a uniform layer by an orthogonal magnetic field,<sup>4</sup> what in fact is measured is  $K_{ii}/\Delta\chi$ . An independent measurement of  $\Delta\chi$  is required to obtain values for the elastic constants themselves.

In the following we shall report on the diamagnetic anisotropy and the density of two homologous series of nematic liquid crystals as a function of temperature. The first series are the *p, p'*-di-*n*-alkylazoxybenzenes<sup>5</sup>:



for *m* = 3–8. This series will be compared with the series of the *p, p'*-di-*n*-alkoxyazoxybenzenes<sup>6</sup>:



for  $m = 2-9$ . In Sec. II we describe the experimental methods. The results are given in Sec. III. Section IV presents a concluding discussion. Using a simple rod-like model for the molecules a molecular interpretation of the  $Q_{\alpha\beta}$  can be given. The resulting values for the order parameter will be compared with the entropy changes at the NI transition.

## II. EXPERIMENTAL

The magnetic susceptibilities are measured by the classical Faraday-Curie method; a sample of volume  $v$  is placed in a strong magnetic field that has a gradient in the vertical direction ( $x$  direction),<sup>7</sup> and the total force  $K$  acting on the sample due to the magnetic field is determined.  $K$  is given by

$$K = \frac{1}{2} (\chi - \chi_1) \int_v \frac{\partial H^2}{\partial x} dv = \frac{1}{2} (\chi - \chi_1) v \left( \frac{\partial H^2}{\partial x} \right)_{av} \quad (8)$$

Here  $\chi$  is the volume susceptibility of the sample and  $\chi_1$  that of the gas driven out by the sample. If this gas itself is diamagnetic  $\chi_1$  can be neglected. Using the mass susceptibility  $\chi^e$ , Eq. (8) can then be written as

$$K = \frac{1}{2} \chi^e m \left( \frac{\partial H^2}{\partial x} \right)_{av} \quad (9)$$

The force  $K$  and the mass  $m$  can be measured directly with a sensitive balance. The values have to be corrected for those of the empty sample holder. The quantity  $(\partial H^2/\partial x)_{av}$  is determined by applying the same procedure to a reference liquid. The reference is made to occupy as closely as possible the same volume as the unknown substance at the same position between the poles of the magnet. Then to a very good approximation

$$\chi^e = \frac{K}{K_{\text{ref}}} \frac{m_{\text{ref}}}{m} \chi_{\text{ref}}^e \quad (10)$$

In our situation the measurements were carried out in air. In that case  $\chi_1 = \chi_{\text{air}}$  in Eq. (8) cannot be disregarded because air is paramagnetic owing to the oxygen. Equation (10) then must be modified to

$$\chi^e(t) = \frac{K}{K_{\text{ref}}} \frac{m_{\text{ref}}}{m} \left[ \chi_{\text{ref}}^e - \frac{\rho_{\text{air}}(t_0)}{\rho_{\text{ref}}(t_0)} \chi_{\text{air}}^e(t_0) \right] + \frac{\rho_{\text{air}}(t)}{\rho(t)} \chi_{\text{air}}^e(t) \quad (11)$$

In this expression  $\rho_{\text{air}}$ ,  $\rho_{\text{ref}}$ , and  $\rho$  are the respective densities of air, of the reference liquid, and of the nematic sample, and  $t_0$  is the temperature at which the reference measurement is carried out. Although the corrections as compared with Eq. (10) are not large ( $\sim 1\%$ ) they are important in the present situation because of the different temperature dependence of  $\chi_{\text{air}}^e(t)$  and  $\chi_{\text{nematic}}^e(t)$ .

The electromagnet used is current stabilized to better than 0.5% and provides a field of about 8 kOe over a gap of 45 mm (diameter pole caps 50 mm). The sample is placed at the edge of the pole caps where a value of  $(\partial H^2/\partial x)_{av}$  of the order of  $10^7 \text{ Oe}^2 \text{ cm}^{-1}$  is obtained. The

main field causes a uniform orientation of the director of the nematic sample parallel to  $\mathbf{H}$ . In the nematic phase, therefore,  $\chi_{11}$  will be measured. As  $\bar{\chi}$  can be measured in the isotropic phase, full information on  $\Delta\chi$  is obtained. A Mettler M5SA balance is used, which has a sensitivity of 2  $\mu\text{g}$  in combination with a relatively large allowed weight (20 g). The sample holder is a small cylinder of quartz that can contain up to about 0.6  $\text{cm}^3$  substance. It is connected to the balance with a thin quartz rod. At the lower end a thick quartz rod is attached in order to minimize the corrections for the susceptibility of the empty sample holder. Sample and quartz rods are placed in a double cylinder of glass in which a thermostated liquid is circulated. The temperature is measured near the sample in the circulated liquid with a Pt100 resistance thermometer. The temperature stabilization is of the order of 0.1  $^\circ\text{C}$  after allowing the sample enough time to reach equilibrium.

The reference substance chosen was dibutylphthalate ( $\chi^e = -0.629 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ ),<sup>8,9</sup> which is conveniently a nonvolatile liquid at room temperature. The densities of the reference liquid and the liquid crystals of series I were determined as a function of temperature with a digital density meter DMA 10 (Anton Paar, Graz, Austria). Using the magnetic susceptibility of air ( $\chi_{\text{air}}^e = 106.3 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$  at 20  $^\circ\text{C}$ ),<sup>10</sup> the tabulated density of air,<sup>11</sup> and Curie's law  $\chi_{\text{air}}^e \sim 1/T$ , the necessary corrections as given by Eq. (11) can be calculated.

In order to obtain reasonably accurate values for  $\Delta\chi(t)$ , the relative accuracy with which  $\chi_{11}(t)$  and  $\bar{\chi}$  can be obtained is particularly important. We shall discuss in some detail the two following sources of errors.

### (i) Constancy of $(\partial H^2/\partial x)_{av}$

Basic to the use of Eq. (10) or (11) is that  $(\partial H^2/\partial x)_{av}$  is equal for the reference and the nematic liquid. In practice several effects tend to counteract this requirement. Firstly the positioning of the nematic sample, the reference, and the empty sample holder is never exactly the same. This is probably the most important factor for the final reproducibility of the result (see next section). Secondly the volumes of sample and reference can only be made equal to within about 3%, while moreover the volume of the sample increases with temperature. It was found that the associated differences in  $(\partial H^2/\partial x)_{av}$  are smaller than 0.1% and can be neglected. Finally, because a mechanical balance is used, the position of the sample in the vertical direction depends on the actual weight. The influence on  $(\partial H^2/\partial x)_{av}$  can be disregarded as far as the nematic sample and the reference are concerned, but not in the case of the empty sample holder. In that case we measured the force exerted by the magnetic field for two different positions (by adding a fixed weight to the balance). Assuming a linear variation of the magnetic force with position the actual correction to the force on either the reference or the nematic sample can thus be obtained.

### (ii) Influence of dissolved oxygen

Because oxygen is paramagnetic small quantities dissolved in a diamagnetic liquid can be a significant source

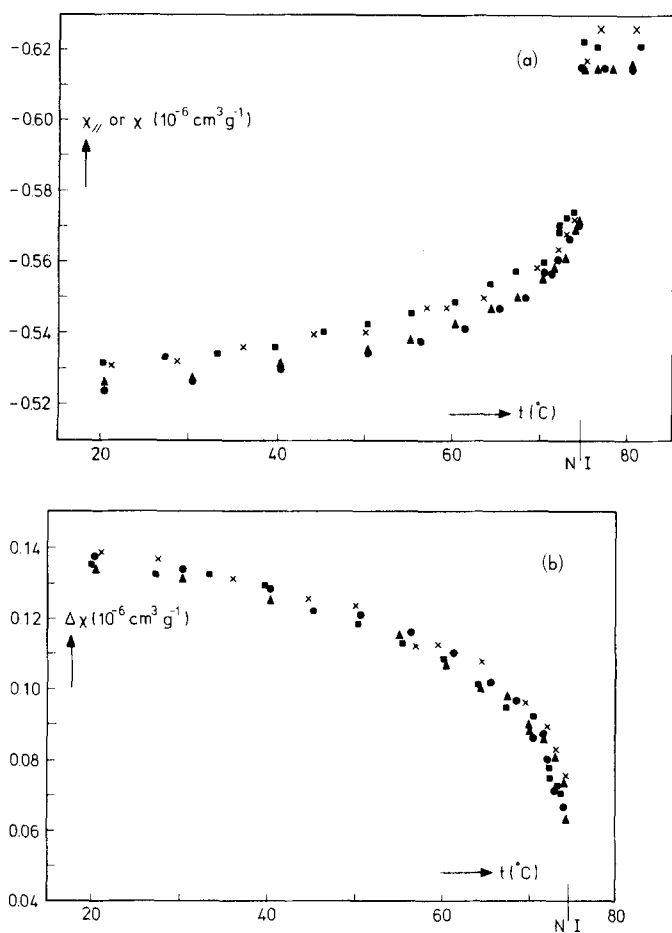


FIG. 1. Diamagnetic susceptibilities of N4. Filled symbols indicate results from three independent measurements from this work; crosses are from Ref. 13.

of errors.<sup>12</sup> Fortunately the errors due to the oxygen in the reference and in the nematic liquid counteract each other. If we denote the magnetic force on the dissolved oxygen alone by  $\delta K_{\text{ref}}$  and  $\delta K$ , respectively, the correction to  $K/K_{\text{ref}}$  in Eq. (10) is approximately given by

$$(1 + \delta K/K - \delta K_{\text{ref}}/K_{\text{ref}}) . \quad (12)$$

$K$  and  $K_{\text{ref}}$  are of the same order of magnitude. If the amount of oxygen dissolved in the nematic liquid and in the reference is not very different, the correction will be very small. For this reason we did not take the trouble of working in oxygen-free conditions, because in that case hermetic sealing would be necessary, making it impossible to use the same sample holder for the reference and for the nematic liquid.

### III. RESULTS

In order to test the experimental set up we first measured the susceptibility of dibutylphthalate as a function of temperature. With  $\rho_{\text{ref}} = 1.046$  at  $20^\circ\text{C}$ ,  $d\rho_{\text{ref}}/dt = 1 \times 10^{-3} \text{ g cm}^{-3} \text{ K}^{-1}$ , and taking  $\chi^f = -0.6290 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$  at  $20^\circ\text{C}$  we found that  $\chi^f$  varied no more than 0.2% as a function of temperature. The nematic test substance chosen was N4 (E. Merck, Darmstadt), a mixture of the

two isomers of *p*-methoxy-*p'*-*n*-butylazoxybenzene (nematic range  $18\text{--}75^\circ\text{C}$ ). The results for  $\chi_{||}$  and  $\Delta\chi$  of three independent measurements are displayed in Figs. 1(a) and 1(b), respectively. The reproducibility for both is about 1%. The agreement with the results of Haller *et al.*<sup>13</sup> for the same substance is excellent. As Haller *et al.* worked with degassed samples sealed *in vacuo*, this supports our assumption that the influence of dissolved oxygen can be disregarded.

The results for  $\Delta\chi$  of the members of series I and II are given in Tables I and II, respectively. The results for *p*-azoxyanisole (PAA, series II,  $m=2$ ) have already been given elsewhere.<sup>14</sup> They agree very well with other values from the literature.<sup>14-16</sup> The value of  $\bar{\chi}$  (not given in the tables) increases for each series with increasing  $m$ , in agreement with Pascal's rules.<sup>7</sup> In some cases, however, unexpectedly low values of  $\bar{\chi}$  were observed, probably due to traces of ferromagnetic impurities. It was not always possible to remove these impurities completely, but we established that the values for  $\Delta\chi$  were not affected. For some of the members of series I results for  $\Delta\chi$  have been reported in the literature.<sup>17</sup> The agreement with our measurements is good.

The values for the densities in the nematic and isotropic phases of the substances of series I and II are also given in Tables I and II. For convenience the results in the nematic phase are given as interpolated values at the temperatures where  $\Delta\chi$  was measured. The results for series I are from this work and estimated to be accurate within  $3 \times 10^{-4} \text{ g cm}^{-3}$ . For  $m=3$  only a monotropic NI transition is observed and we did not succeed in making density measurements in the nematic phase. The values given in Table I are extrapolated from the isotropic phase, assuming a density change at the NI transition of  $0.002 \text{ g cm}^{-3}$ , by analogy with the results for the other members of the series. The results for series II are from Ref. 18. The relative volume changes  $\Delta v/v_N$ , where  $\Delta v = v_I - v_N$ , at the NI transitions, are given in Table III. Necessarily these small differences between large quantities are not very accurate (say  $\pm 0.05\%$ ).

### IV. DISCUSSION

First we shall discuss the molecular interpretation of the magnetic susceptibility  $\chi$  and its anisotropic part  $\mathbf{Q}$ . Let  $\xi, \eta, \zeta$  be the axes of a molecule-fixed coordinate system, and  $\kappa$  the tensor of the molecular magnetic polarizability. The elements of  $\kappa$  are  $\kappa_{ij}$ . Then

$$\chi_{\alpha\beta} = N \sum_{i,j} \kappa_{ij} \langle i_\alpha j_\beta \rangle, \quad \alpha, \beta = x, y, z, \quad (13)$$

$$i, j = \xi, \eta, \zeta,$$

where  $N$  is the number of molecules per unit volume, and the brackets denote a statistical average over the orientations of all molecules. An element of the tensor order parameter  $\mathbf{Q}$  [see Eq. (6)] can then be written as

$$Q_{\alpha\beta} = N \sum_{i,j} \kappa_{ij} \langle i_\alpha j_\beta - \frac{1}{3} \delta_{\alpha\beta} \delta_{ij} \rangle . \quad (14)$$

Because of the uniaxial symmetry around  $\mathbf{n}$  (taken along the  $z$  axis) and due to the fact that  $\mathbf{Q}$  has zero trace, it is sufficient to consider only one element  $Q_{\alpha\beta}$ . For

TABLE I. Temperature (°C), anisotropy of the magnetic susceptibility ( $10^{-3} \text{ cm}^3 \text{ g}^{-1}$ ) and density ( $\text{g cm}^{-3}$ ) for some members of series I.

$m=3$			$m=4$			$m=5$			$m=6$			$m=7$			$m=8$				
$t$	$\Delta\chi^e$	$\rho^a$	$t$	$\Delta\chi^e$	$\rho$	$t$	$\Delta\chi^e$	$\rho$	$t$	$\Delta\chi^e$	$\rho$	$t$	$\Delta\chi^e$	$\rho$	$t$	$\Delta\chi^e$	$\rho$		
55.6	102.6	1.029	17.3	101.8	1.0352	25.3	123.6	1.0192	17.0	S <sub>A</sub> N		36.3	113.1	0.9908	40.1	99.0	0.9773		
56.8	99.3		8	20.2		31	30.3		50	18.3	111.0	1.0067	40.0	110.4	0.9887	50.1	98.0	04	
57.8	94.5		7	22.7		11	35.6		08	20.5	109.6		56	110.2	50	55.5	97.0	0.9662	
58.9	89.4		65	25.2	1.0291	40.0	118.4	1.0087	25.1	105.4	29	49.6	107.0		18	59.5	93.8	29	
59.7	84.3		60	27.2		77	44.9		48	30.0	101.6	0.9995	52.0	105.6	0.9797	61.5	93.3	11	
60.1	79.5		55	29.3		55	50.5		04	35.2	97.5		56	104.6	83	62.8	92.6	0.9593	
60.4	NI			30.3		46	54.9	0.9968	39.6	94.5	23	53.9	S <sub>A</sub> N			63.6	91.5	85	
61.0		1.0225		30.8		41	57.9		38	42.1	90.7	05	54.3	100.5	0.9769	64.0	91.2	70	
63.0		15		31.3		36	61.5	93.3	02	44.5	86.0	0.9884	56.3	95.2		49	64.4	89.8	50
64.5		00		31.6		32	63.0	88.2	0.9887	47.1	82.0		64	60.3	04	64.5	S <sub>A</sub> N		
66.0		1.0185		31.8		30	64.7	81.2	68	50.1	73.0	35	65.3	80.6	0.9647	64.8	77.7	0.9525	
				31.9	NI		66.0	76.0	53	50.9	71.2	27	68.2	75.3		15	65.3	72.1	20
				32.1		1.0218	67.0	67.4	40	52.0	68.1	15	68.8	69.8	08	65.6	68.8	12	
				32.5		14	67.5	NI		52.8	63.9	06	69.7	63.6	0.9598	66.0	63.6	06	
				33.8		02	67.6		0.9810	53.2	62.2	03	70.1	61.5	92	66.7	NI		
				38.6		1.0166	68.8		03	53.8	58.0	0.9794	70.3	59.0	90	67.2		0.9458	
				46.7		01	69.7		0.9792	54.0	50.1	91	70.5	56.4	85	69.3		37	
							72.4		70	54.2	NI		70.6	NI		71.3		17	
							75.2		36	54.3		0.9778	71.0		0.9540	73.3		0.9397	
										55.6		61	71.8			33			
										59.2		30	72.6			24			
										65.9		0.9680	74.8			06			
										74.6		19							

<sup>a</sup>Values in the nematic phase are estimated (see text).

$\alpha = \beta = z$  Eqs. (6) and (14) reduce to

$$Q_{zz} = \frac{2}{3} (\chi_{\parallel} - \chi_{\perp}) = \frac{2}{3} N \sum_{ij} \kappa_{ij} S_{ij}, \quad (15)$$

where the generalized order parameter  $S_{ij}$  has been introduced:

$$S_{ij} = \frac{1}{2} \langle 3 i_x j_x - \delta_{ij} \rangle. \quad (16)$$

We shall now choose the coordinate system  $\xi, \eta, \zeta$  such that  $S_{ij}$  is diagonal. As  $\mathbf{S}$  has zero trace there are two independent order parameters. Taking the  $\zeta$  axis as the long molecular axis we choose  $S = S_{\zeta\zeta}$  and  $D = S_{\xi\xi} - S_{\eta\eta}$ . Then Eq. (15) reduces to<sup>22</sup>

$$(\chi_{\parallel} - \chi_{\perp})/N = [\kappa_{\zeta\zeta} - \frac{1}{2}(\kappa_{\xi\xi} + \kappa_{\eta\eta})]S + \frac{1}{2}(\kappa_{\xi\xi} - \kappa_{\eta\eta})D. \quad (17)$$

$S$  is the usual order parameter, which can have a value between 0 and 1:

$$S = \frac{1}{2} \langle 3 \xi_z^2 - 1 \rangle = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle, \quad (18)$$

where  $\theta$  is the  $(z, \xi)$  angle. Furthermore

$$D = \frac{3}{2} \langle \xi_z^2 - \eta_z^2 \rangle = \frac{3}{2} \langle \sin^2 \theta \cos 2\psi \rangle, \quad (19)$$

where  $\psi$  is the Euler angle specifying the rotation around the  $\zeta$  axis.  $D$  measures the difference in tendency of the two transverse molecular axes to project on the  $z$  axis. For PAA at  $120^\circ$   $D \approx 0.07$  has been estimated from nuclear magnetic resonance (NMR) measurements.<sup>23</sup> However, we found that this value depends strongly on the particular physical method considered. Using data from various methods we estimate for PAA at  $120^\circ$   $D = 0.05 \pm 0.10$ ; there is no conclusive evidence as to whether  $D$  is of importance at all. Because of these uncertainties we shall assume in the following  $D = 0$ ; the molecules are taken as effectively axially symmetric.

With  $\chi_i^M = N_A \kappa_{\zeta\zeta}$  and  $\chi_i^M = \frac{1}{2} N_A (\kappa_{\xi\xi} + \kappa_{\eta\eta})$ ,  $N_A$  being Avogadro's number, we then derive from Eq. (19) Tsvetkov's expression for the order parameters  $S^{24,25}$ :

$$S(\chi_{\parallel}^M - \chi_{\perp}^M)/(\chi_{\parallel}^M - \chi_{\perp}^M), \quad (20)$$

where  $\chi^M = \chi^e M$  is the molar susceptibility,  $M$  being the mass number.

Information about  $\chi_{\parallel}^M - \chi_{\perp}^M$  can in principle be obtained from measurements on a solid single crystal. Such measurements have been performed for PAA,<sup>15</sup> which crystallizes in the monoclinic system.<sup>26</sup> We shall identify the  $\zeta$  axis with the axis through the outer carbon atoms of the azoxybenzene part of the molecule. This axis makes angles of  $\pm 6.1^\circ$  with the mirror plane of the unit cell, while the projections on this plane are parallel.<sup>26</sup> The direction of the largest susceptibility is in the mirror plane<sup>15</sup> at an angle of  $8.8^\circ$  with the  $\zeta$  axis as assumed above. If we approximate the PAA crystal by a uniaxial system we thus obtain

$$\chi_{\parallel}^M - \chi_{\perp}^M = 61.2 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}.$$

Two benzene rings positioned similarly to the benzene rings in PAA would give<sup>7</sup>

$$\chi_{\parallel}^M - \chi_{\perp}^M = 59.7 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}.$$

We conclude that the anisotropy of the susceptibility is almost completely due to the benzene rings with their delocalized  $\pi$  electrons. This makes it possible to estimate from the benzene values

$$\frac{1}{2} (\chi_{\xi\xi}^M - \chi_{\eta\eta}^M) = 57 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}.$$

Consequently the error made when disregarding  $D$  in Eq. (17) is of the order of  $D/S$ . For related molecules with two benzene rings usually somewhat smaller values for  $\chi_{\parallel}^M - \chi_{\perp}^M$  are found (of the order of 50 to  $55 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ ).<sup>27</sup> Attempts have been made to obtain a value

for  $\chi_i - \chi_t$  by extrapolation of the results for  $\chi_{||} - \chi_{\perp}$  to  $T=0$  and assuming at zero temperature  $S=1$ .<sup>13,28</sup> However, this method leads to values of  $\chi_i - \chi_t$  that fluctuate along a homologous series, indicating that the results cannot be expected to be very reliable.

In order to calculate  $S$  from Eq. (20) we use for all the members of series I the value for  $\chi_i^M - \chi_t^M$  estimated from two benzene rings, and for series II the PAA value. This procedure may lead to an underestimation of  $\chi_i^M - \chi_t^M$  for the higher members of the series. However, the associated error is not likely to be more than a few percent as the susceptibility of a paraffinic chain is not very anisotropic.<sup>29</sup> The results are displayed in Fig. 2 as a function of the reduced temperature  $\tau = (T/T_{NI})(v/v_{NI})^2$ . The theoretical curve for  $S$  as obtained from Maier and Saupe's theory of the nematic phase<sup>20</sup> is indicated as a broken line. We see that in general the theory gives a reasonable estimate for  $S$ . The experimental results differ mainly in the temperature dependence near  $T_{NI}$ , which is somewhat stronger than predicted theoretically, while in addition the whole curve for  $S$  is sometimes shifted.

For PAA and PAP (*p*-azoxyphenetole; series II,  $m=3$ ) the results for  $S$  can be compared with the values obtained from NMR measurements. Values for  $S$  from both the *ortho* proton-proton coupling<sup>30</sup> and from the *para* carbon-13 chemical shift<sup>31</sup> are available (see Fig. 3). For PAA the values from the three methods agree reasonably well. As the *ortho* proton-proton coupling is practically independent of  $D$ , this supports the idea that  $D$  can be taken as effectively zero. For PAP the

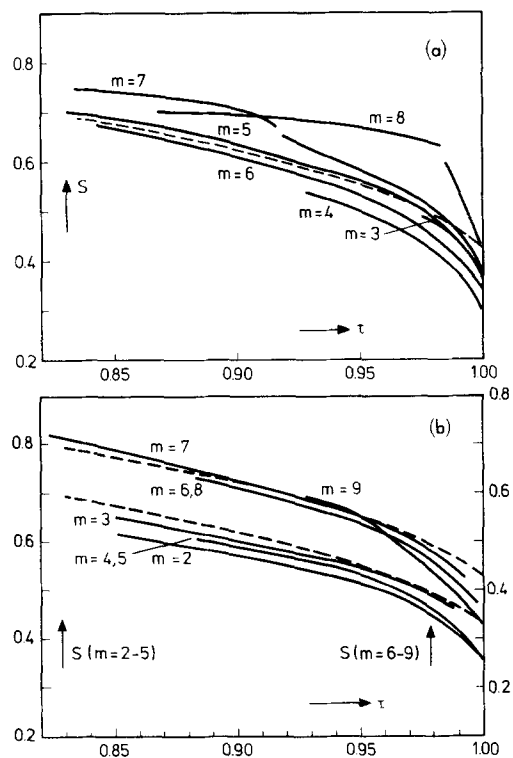


FIG. 2. Order parameter versus reduced temperature for series I (a) and series II (b). Broken line is from Maier and Saupe's theory (Ref. 20). Note the change of scale with  $m$  in Fig. 2(b).

TABLE II. Temperature (°C), anisotropy of the magnetic susceptibility ( $10^{-8}$  cm<sup>3</sup> g<sup>-1</sup>), and density (g cm<sup>-3</sup>, from Ref. 18,  $m=9$  from Ref. 19) for some members of series II.

t	m=3			m=4			m=5			m=6			m=7			m=8			m=9			
	$\Delta\chi^f$	$\rho$	t	$\Delta\chi^f$	$\rho$	t	$\Delta\chi^f$	$\rho$	t	$\Delta\chi^f$	$\rho$	t	$\Delta\chi^f$	$\rho$	t	$\Delta\chi^f$	$\rho$	t	$\Delta\chi^f$	$\rho$	t	
130.4	141.8	1.1080	109.0	111.0	1.072	109.6	110.7	1.0386	98.8	102.1	1.0271	82.7	115.8	1.0231	97.3	93.0	0.9971	111.7	80.7	0.979		
135.9	137.4	22	112.3	107.6	1.067	117.4	105.1	12	102.3	99.9	36	85.8	113.1	1.0180	102.4	88.6	23	114.0	80.0	7		
140.4	135.6	1.0986	115.4	102.6	3	121.8	102.2	1.0269	106.4	96.6	05	89.3	111.0	65	106.5	85.6	0.9884	116.5	77.7	5		
145.5	128.5	32	117.9	96.6	1.0585	126.7	95.4	22	109.5	92.9	1.0167	95.2	106.5	08	110.4	83.6	46	118.4	71.9	3		
150.4	126.3	1.0882	119.8	90.0	58	130.3	89.6	1.0188	112.1	89.2	38	99.4	104.0	1.0072	113.3	79.8	19	120.3	67.3	1		
154.0	120.8	45	121.1	84.6	35	133.3	77.3	45	115.8	82.2	01	105.7	99.0	15	116.1	75.3	0.9792	122.1	62.3	0.969		
158.1	116.7	02	121.7	76.3	24	134.4	71.2	28	117.5	78.0	1.0085	109.0	95.3	0.9987	118.1	71.8	73	123.6	58.5	6		
161.1	110.0	1.0771	122.1	72.8	14	135.3	68.4	19	120.0	70.8	60	115.0	90.3	29	120.5	65.7	50	124.9	51.1	9		
163.4	105.8	46	122.6	NI	1.0477	135.5	62.6	16	121.2	58.1	48	120.2	85.3	0.9884	121.8	59.7	39	125.9	47.1	2		
167.0	88.4	11	122.8	NI	61	136.3	NI	1.0073	121.8	NI	42	123.0	80.4	59	123.0	56.0	24	126.3	NI			
167.7	NI	124.2	124.2	61	136.3	61	136.3	61	122.6	62	122.6	125.5	73.4	36	123.9	NI	0.9688	128.7	0.958			
169.0	169.0	1.0589	126.2	46	137.4	46	137.4	62	122.6	0.9983	127.3	127.3	NI	17	124.2	NI	0.9688	137.3	0			
175.6	175.6	40	129.2	20	140.8	20	140.8	30	126.0	0.9757	129.3	129.3	NI	30	125.3	81	0.9688	137.3				
184.7	184.7	1.0455	132.1	1.0394	144.9	1.0394	144.9	0.9985	131.8	34	129.6	129.6	34	129.6	127.5	46	0.9688	137.3				
											132.6	132.6	132.6	132.6	131.1	19	0.9688	137.3				
											137.0	137.0	137.0	137.0	136.5	19	0.9558	137.3				
											141.8	141.8	141.8	141.8	136.5	50	0.9558	137.3				

TABLE III. Relative volume changes at the nematic-isotropic transitions.

$m$	$\Delta v/v_N$ (%)	
	series I	series II
2	...	0.35 <sup>a</sup>
3	...	0.60 <sup>b</sup>
4	0.10	0.30
5	0.26	0.34
6	0.21	0.30
7	0.39	0.36
8	0.41	0.26

<sup>a</sup>Reference 20.<sup>b</sup>Reference 21.

values from both NMR methods roughly agree, still in agreement with  $D \approx 0$ , but are higher than those from the magnetic susceptibilities. Probably this indicates that the value for  $\chi_i - \chi_t$  we have used is somewhat too high. If we take for  $\chi_i^N - \chi_t^N$  a value between  $50$  and  $55 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  the agreement with the NMR data is good for both substances. For the higher homologues only *para* carbon-13 chemical shift measurements are available for a comparison.<sup>32</sup> The values for  $S$  from the latter method have systematically a somewhat stronger alternation with  $m$  than the results for  $S$  from our susceptibility measurements. At present no adequate explanation for this difference is available.

The NI transition entropies  $\Delta\Sigma$  have been reported for

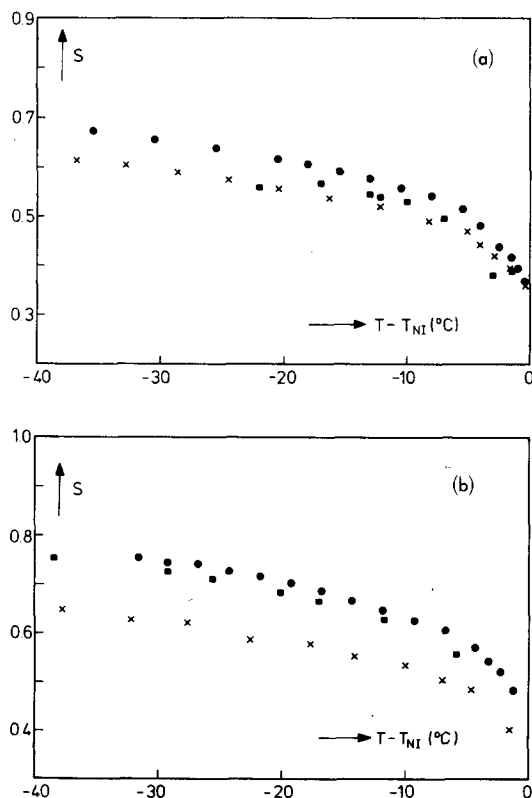


FIG. 3. Order parameter as determined via different methods for PAA (a) and PAP (b); ● *ortho* proton-proton splitting (Ref. 30); ● *para* carbon-13 chemical shift (Ref. 31); × magnetic susceptibility (this work).

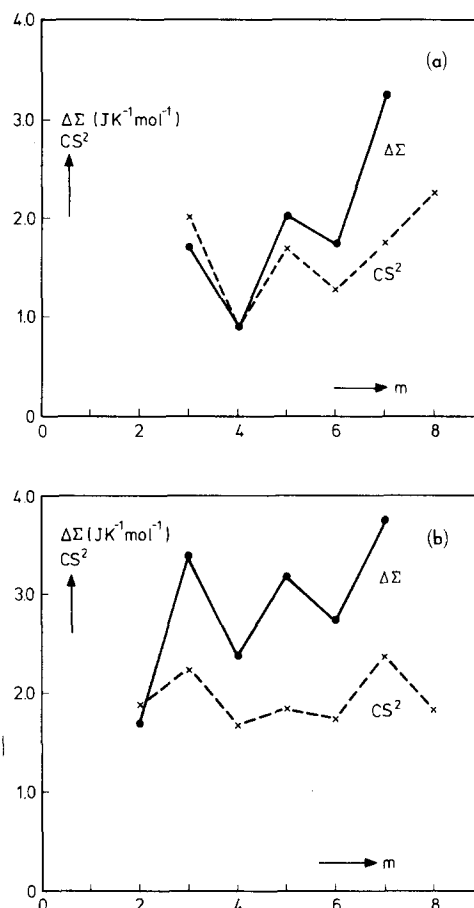


FIG. 4. Order parameter at NI transition and transition entropy for series I (a) and series II (b);  $CS^2$  is normalized to  $\Delta\Sigma$  for series I,  $m=4$ .

both series of compounds,<sup>5,6,33</sup> and are found to alternate with increasing chain length parallel to the well-known alternation of  $T_{NI}$ . It has been suggested that this is mainly due to an alternation of  $S$  at  $T_{NI}$ ,<sup>5</sup> because a simple Landau theory of the NI transition predicts  $\Delta\Sigma \sim S^2$ . In Fig. 4 the results for  $\Delta\Sigma$  and  $CS^2$  of both series are compared, where  $CS^2$  is normalized to  $\Delta\Sigma$  for series I,  $m=4$ . For series I the alternation of  $S^2$  can explain to a large extent the results for  $\Delta\Sigma$ . The difference for large  $m$  can be attributed to a contribution of smectic short-range ordering to the entropy of the nematic phase. For series II there is already a relatively large difference between  $\Delta\Sigma$  and  $CS^2$  for small  $m$  (except for  $m=2$ ). Probably the use of one proportionality factor between  $\Delta\Sigma$  and  $S^2$  for both series is incorrect, as is also indicated by the approximately two times larger values for  $\Delta\Sigma$  of series II as compared with series I. Although theoretical models for the alternation of  $\Delta\Sigma$  and  $S$  have been proposed,<sup>34</sup> it does not yet seem possible to conclude whether other contributions to  $\Delta\Sigma$  ought to be taken into account.

Finally we note that for each of the series the relative volume change  $\Delta v/v_N$  alternates parallel to  $\Delta\Sigma$  (see Table III and Fig. 4). Moreover both quantities are somewhat higher for series II than for series I. Using the Clausius-Clapeyron equation this indicates that  $dT_{NI}/d\rho$  too should not vary much for the various com-

pounds studied. The experimental results for series I,  $m = 4-7$  and series II,  $m = 2$  show that this is indeed in the case.<sup>35,36</sup>

#### ACKNOWLEDGMENT

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