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## PHYSICAL PROPERTIES OF NEMATIC *p,p'*-DIHEPTYLAZOBENZENE

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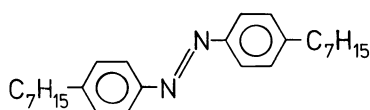
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**Résumé.** — Les coefficients élastiques, la susceptibilité magnétique, les indices de réfraction et la densité du *p,p'*-diheptylazobenzène sont mesurés. Le comportement des coefficients élastiques de cette substance non polaire ressemble beaucoup à celui des substances polaires analogues. L'anisotropie de la permittivité statique et de celle à hautes fréquences est proportionnelle à l'anisotropie de la susceptibilité, analogue aux observations de la permittivité à hautes fréquences d'autres corps nématiques.

**Abstract.** — The elastic constants, magnetic susceptibility, refractive index and density are reported for *p,p'*-diheptylazobenzene. The behaviour of the elastic constants of this non polar compound is very similar to that of related polar compounds. The anisotropy of both the static and the high-frequency permittivity is proportional to the anisotropy of the susceptibility, as observed earlier for the high-frequency permittivity of other nematogenic compounds.

1. **Introduction.** — In a nematic liquid crystal [1, 2] there is orientational order : the elongated molecules are, on average, aligned with their long axes parallel to a preferred direction (the director). On the other hand, the molecules translate freely, and there is no long-range correlation between the centres of mass. Due to the uniaxial symmetry around the director, the physical properties are in general anisotropic. In a recent series of papers [3, 4] the (anisotropic) magnetic susceptibility and refractive index were reported for the homologous series of *p, p'*-dialkyl- and dialkoxyazoxybenzenes. For these compounds, the elastic constants that describe the variation of the free energy when the director pattern is distorted have also been reported [5]. A comparison with members of the series of *p, p'*-dialkylazobenzenes [6] would be interesting, as the latter compounds are non-polar. Hence short-range interactions due to the presence of permanent dipole moments are absent, which makes them suitable as *reference* compounds. Of this series *p, p'*-diheptylazobenzene



is the only one that gives an enantiotropic nematic phase. The melting point is 40 °C, the clearing point 47 °C, while a monotropic nematic-smectic A transition is observed around 21 °C. Thermodynamic data for this compound are reported in reference [7], and the static dielectric permittivities have been given in reference [8]. In this paper we report results for the elastic constants, the magnetic susceptibility, the refractive index and the density.

2. **Experimental.** — The elastic constants  $K_{ii}$  ( $i = 1, 2, 3$ ) were obtained from the thresholds  $H_c$  for the deformation of uniform planar and homeotropic layers, respectively, in an orthogonal magnetic field (Frederiks transition).  $H_c$  is given by [9]

$$\Delta\chi H_c^2 d^2 = K_{ii} \pi^2, \quad i = 1, 2, 3, \quad (1)$$

where  $\Delta\chi$  is the anisotropy of the magnetic (volume) susceptibility and  $d$  the sample thickness. In the uniform planar case, strong anchoring of the director at the substrates was obtained by coating the glass substrates with poly-*p*-xylylene and then rubbing gently. Homeotropic samples were made with substrates coated with cetyltrimethylammonium bromide (CTAB) by dipping them in a 400 ppm solution

of CTAB in water. The thresholds were determined optically; details of the measurements of  $K_{11}$  and  $K_{33}$  are described in reference [5]. The values thus obtained for  $K_{33}/K_{11}$  were used to calculate the deformation of the director above  $H_c$  [9], which gave a reasonable fit to the experiment.  $K_{22}$  was determined as described in references [10] and [11]. In addition, the threshold of an over  $\pi/2$  twisted planar layer in an orthogonal magnetic field was determined. The threshold for this case is given by equation (1) with  $K_{ii}$  replaced by

$$K_{\text{eff}} = K_{11} + \frac{1}{4} K_{33} - \frac{1}{2} K_{22}. \quad (2)$$

The anisotropy of the diamagnetic susceptibility was measured with the Faraday-Curie method as described in reference [3] <sup>(1)</sup>. In fact, in the nematic phase  $\chi_{\parallel}^g$  is measured, and in the isotropic phase it is  $\chi^g$  that is measured where  $\chi^g$  is the gram-susceptibility ( $\chi^g = \chi/\rho$ ,  $\rho$  being the density). As diamagnetism is independent of temperature,  $\chi^g = \bar{\chi}^g$ , where  $\bar{\chi}^g = (\chi_{\parallel}^g + 2\chi_{\perp}^g)/3$ . Hence the magnetic anisotropy is given by

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

The density was determined as a function of temperature using a digital density meter DMA 10 (Anton Paar, Graz, Austria).

Finally, the refractive index in the isotropic phase and the ordinary index  $n_{\perp}$  in the nematic phase were measured with an Abbe refractometer. In addition,  $\Delta n = n_{\parallel} - n_{\perp}$  was measured directly by means of an interference technique. A uniform planar nematic layer was placed between crossed polarizers at  $45^\circ$  with the optical axis in a monochromatic light beam. The intensity of the transmitted light was recorded for various temperatures as a function of the wavelength, and the value of  $\Delta n$  was calculated from the positions of the maxima and minima. The order of the maxima and minima was determined as described in reference [12].

**3. Results.** — The results for the elastic constants  $K_{ii}/\Delta\chi$  at various temperatures in the nematic phase are given in table I. Figure 1 shows the temperature dependence of the ratio  $K_{33}/K_{11}$ , which increases from 0.6 at low temperatures to about 0.8 near  $T_{NI}$ . This behaviour is very similar to that of p, p'-diheptyl-azoxybenzene [5]. Furthermore, the diamagnetic anisotropy and the density are given in table I. For convenience these results are reported as interpolated values at the temperatures where the elastic constants

<sup>(1)</sup> In the experimental section of ref. [3] a value

$$\chi_{\text{air}}^g = 106.3 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$$

is quoted, which is in fact the value of  $\chi_{\text{oxygen}}^g$ .

TABLE I

*Elastic constants, anisotropy of the magnetic susceptibility and density of p, p'-diheptylazobenzene.*

$t$ (°C)	$K_{11}/\Delta\chi$	$K_{33}/\Delta\chi$ (dyne)	$K_{22}/\Delta\chi$ (*)	$\Delta\chi^g$ (*) ( $10^{-7} \text{ g}^{-1} \text{ cm}^3$ )	$\rho$ (*) ( $\text{g cm}^{-3}$ )
32.1	—	10.14	5.93	1.040	0.952 2
35.0	15.30	9.57	5.53	0.998	0.949 0
38.0	13.49	8.92	5.10	0.947	0.945 8
40.6	11.98	8.20	4.70	0.893	0.943 0
42.6	10.97	7.44	4.34	0.842	0.940 9
44.1	9.94	6.92	4.06	0.793	0.939 3
45.7	8.44	6.15 (*)	3.68	0.725	0.937 2
46.3	7.90 (*)	5.86	3.50	0.682	0.935 9
46.6	7.65	—	—	0.652	0.934 8

(\*) Interpolated values.

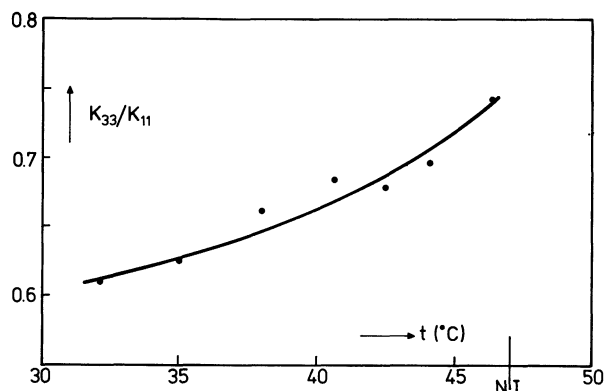


FIG. 1. — Temperature dependence of the ratio  $K_{33}/K_{11}$  of p, p'-diheptylazobenzene.

have been measured. The accuracy of  $K_{ii}/\Delta\chi$  ( $i=1, 2, 3$ ) is of the order of 3%. The values of  $\Delta\chi$  are estimated to be accurate to within 2%. The temperature variation of these quantities is of course obtained with greater precision. In table II the measured values of  $K_{\text{eff}}/\Delta\chi$  are compared with those calculated from equation (2) and the data of table I. The agreement is excellent. Similar results were obtained by Karat and Madhusudana for p-heptyl-p'-cyanobiphenyl [13].

TABLE II

*$K_{\text{eff}}/\Delta\chi$  as determined experimentally and as calculated from the data of table I*

$t$ (°C)	$K_{\text{eff}}/\Delta\chi$ (dyne)	
	experimental	calculated
35.0	14.4	14.9
38.0	12.8	13.2
40.6	11.4	11.7
42.6	10.2	10.7
44.1	9.3	9.6
45.7	8.0	8.1

Using the data of table I, one can calculate the reduced elastic constants which are defined as

$$C_{ii} = K_{ii} V^{7/3} / S^2, \quad (4)$$

where  $V$  is molar volume and  $S$  the order parameter. Assuming that the molecules can be considered to be effectively axially symmetric,  $S$  is given by

$$S = (\chi_{\parallel}^e - \chi_{\perp}^e) / (\chi_{\parallel}^e - \chi_{\perp}^e). \quad (5)$$

Here,  $\chi_{\parallel} - \chi_{\perp}$  is the anisotropy of the magnetic susceptibility for a perfectly ordered sample ( $S = 1$ ). For this quantity we take the value of  $55 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ , which is about the average value observed in the solid state of various compound which have two benzene rings [3]. The results thus obtained are displayed in figure 2. We note that the  $C_{ii}$  are not independent of temperature. The ratio  $K_{33}/K_{22}$  is, however, approximately constant, contrary to  $K_{33}/K_{11}$  (see Fig. 1).

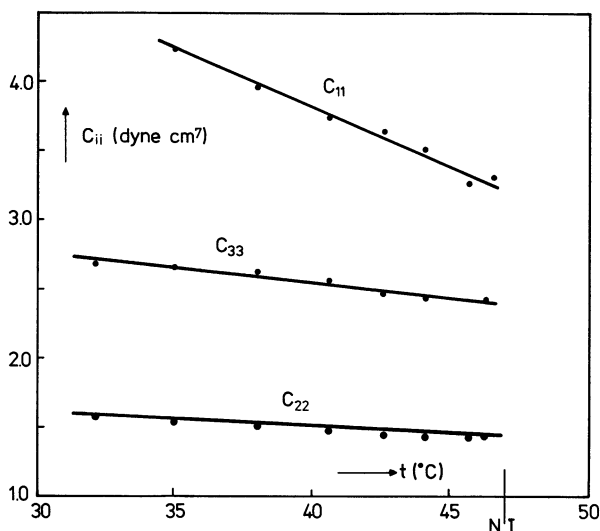


FIG. 2. — Temperature dependence of the reduced elastic constants of p, p'-diheptylazobenzene.

TABLE III

Refractive indices of p, p'-diheptylazobenzene at three wavelengths (interpolated values)

$T - T_{NI}$	546 nm		589 nm		633 nm	
	$n, n_{\perp}$	$\Delta n$	$n, n_{\perp}$	$\Delta n$	$n, n_{\perp}$	$\Delta n$
5	1.567 7	—	1.564 8	—	1.556 8	—
3	9 0	—	5 9	—	7 9	—
1	1.571 4	—	6 9	—	8 9	—
-0.5	1.526 5	0.154 1	1.522 2	0.141 2	1.515 6	0.136 0
-1	3 5	61 5	1.519 6	50 4	3 5	43 5
-2	1.519 9	74 7	6 6	61 1	0 6	54 3
-3	7 6	84 0	4 5	70 5	1.508 7	61 6
-5	4 2	97 1	1 5	82 3	6 4	71 9
-7	2 0	0.206 1	1.509 5	91 0	4 8	81 4
-10	0 1	17 1	7 6	0.201 4	2 8	91 5
-13	1.508 7	27 6	6 1	10 7	1 2	0.200 1

Finally, table III gives interpolated values of the ordinary refractive index and the birefringence of p, p'-diheptylazobenzene for three wavelengths. The absolute accuracy of  $n_{\perp}$  is about  $\pm 0.000 5$ , and that of  $\Delta n$  about 1 %. Again the relative accuracy is much better.

4. Discussion. — First we shall discuss the elastic constants. If the nematic distortion free energy is restricted to terms of the order  $S^2$ , it is found theoretically that  $K_{ii} \sim S^2$  and  $K_{11} = K_{33}$  [1, 5]. The results of figures 1 and 2 show that for p, p'-diheptylazobenzene this is not the case. Hence terms in the free energy of higher order than  $S^2$  are necessary for a correct description of the elasticity. This is in agreement with the results of reference [5] where it was found that the equality  $K_{11} = K_{33}$  holds only for one or two compounds out of a homologous series. With increasing temperature  $S$  decreases, and the errors due to the neglect of higher order terms become smaller. The temperature dependence of  $K_{33}/K_{11}$  is indeed such that with increasing temperature, the values of  $K_{33}$  and  $K_{11}$  approach each other (Fig. 1).  $C_{22}$  is the smallest of the three elastic constants, as has always been found up to now. We conclude that the elastic constants of the non-polar compound p, p'-diheptylazobenzene behave very much in the same way as in related polar compounds.

For the magnetic susceptibility and the refractive indices we find that  $\Delta \epsilon_{\infty} = n_{\parallel}^2 - n_{\perp}^2 \sim \Delta \chi$ , as observed earlier for other nematics. Using results from reference [8], the same type of proportionality is found between  $\Delta \chi$  and the anisotropy of the static permittivity  $\Delta \epsilon$  (Fig. 3). These experimental proportionalities were used in reference [4] to derive an expression for the internal field, thus relating the macroscopic permittivities  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  to the principal elements  $\alpha_1$

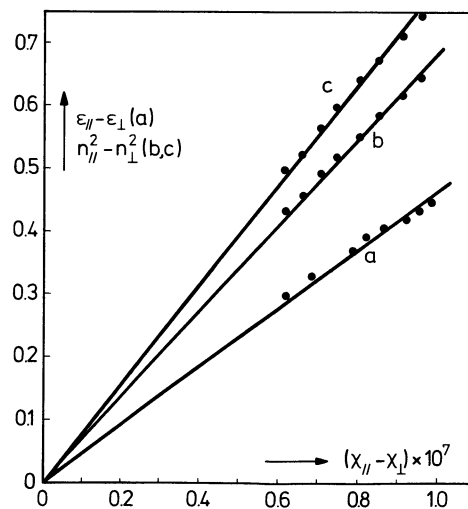


FIG. 3. — Proportionality between the anisotropy of the permittivity and of the susceptibility of p, p'-diheptylazobenzene; (a) static permittivity, (b)  $\lambda = 632.8 \text{ nm}$ , (c)  $\lambda = 546.1 \text{ nm}$ .

and  $\alpha_t$  of the molecular polarizability tensor ( $\alpha_l$  being along the long molecular axis) :

$$\varepsilon_{\parallel} = 1 + \frac{4}{3} \pi N \left[ \frac{\alpha_l(2S+1)}{1-4\pi N\alpha_l\Omega_l} + \frac{\alpha_t(2-2S)}{1-4\pi N\alpha_t\Omega_t} \right], \quad (6a)$$

$$\varepsilon_{\perp} = 1 + \frac{4}{3} \pi N \left[ \frac{\alpha_l(1-S)}{1-4\pi N\alpha_l\Omega_l} + \frac{\alpha_t(2+S)}{1-4\pi N\alpha_t\Omega_t} \right]. \quad (6b)$$

Here  $N$  is the number of molecules per unit volume and  $\Omega_l$  and  $\Omega_t$  are shape factors that depend only on the axes ratio of the molecular spheroid. This ratio is calculated to be 4.5 for *p, p'*-diheptylazobenzene, taking the length to be equal to that calculated from a model of the all-stretched molecule, and the width such that the volume of the spheroid is equal to that available to a molecule in the nematic phase at  $T_{NI}$ . The data of tables I and III and equation (6) can then be used to calculate  $\alpha_l$  and  $\alpha_t$ . The results are given in table IV. Static values of the electronic polarizabilities can be obtained by extrapolation, using the dispersion formula  $\alpha = \text{const.}/(\omega_0^2 - \omega^2)$ . This procedure is valid if the frequency  $\omega_0$  where the nearest optical absorption takes place is sufficiently high [14]. For the present case this condition is only approximately fulfilled for  $\alpha_l$ , leading to some uncertainty in the extrapolated value for  $\alpha_l$ . In table IV the results are compared with the polarizabilities obtained from the static dielectric permittivity. The latter results are larger because they contain a contribution from the ionic polarizability which is not included in the optical

polarizabilities. This contribution is often estimated to be about 10 %, which is quite correct for the present case.

It has been stated that reasonable estimates of the electronic polarizabilities of a molecule can often be obtained from the addition of tabulated bond polarizability data [15]. Unfortunately, this method does not work very well for conjugated systems where the polarizability can be much larger than the value obtained from such an additivity scheme. For example, using the polarizabilities of benzene [16] ( $12.3 \text{ \AA}^3$  and  $6.7 \text{ \AA}^3$ , respectively) and the values for the CN- and NN-bond [17] one calculates for azobenzene

$$\alpha_l = 25 \text{ \AA}^3, \quad \alpha_t = 19 \text{ \AA}^3.$$

From measurements of the Kerr-effect of azobenzene it has been estimated that [17]

$$\alpha_l = 34 \text{ \AA}^3, \quad \alpha_t = 20 \text{ \AA}^3.$$

Even if the uncertainties in the interpretation are taken into account, it is evident that the conjugation in the longitudinal direction has led to a strong increase in the value of  $\alpha_l$ . The polarizabilities of a C-C bond are quoted as  $1.0 \text{ \AA}^3$  and  $0.25 \text{ \AA}^3$  parallel and perpendicular to the bond direction, respectively; and for a C-H bond as  $0.67 \text{ \AA}^3$  in both directions [15]. Assuming that the alkyl chains are in the planar all-trans *zig-zag* conformation, we thus calculate for *p, p'*-diheptylazobenzene :

$$\alpha_l = 63 \text{ \AA}^3, \quad \alpha_t = 44 \text{ \AA}^3.$$

Emphasizing again the uncertainties of such an estimate, we note that especially the result for  $\alpha_l$  is rather smaller than the value from the spheroidal model given in table IV. The anisotropy of the molecule is probably somewhat overestimated as a result of the procedure chosen to estimate the axes ratio  $a/b$ .

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TABLE IV

Polarizabilities of *p, p'*-diheptylazobenzene ( $10^{-24} \text{ cm}^3$ )

$\lambda$ (nm)	$\alpha_l$	$\alpha_t$
546.1	103	39.8
589.3	99.3	39.7
632.8	96.8	39.5
$\infty$	80 (*)	38.5 (*)
static values	89.4	42.1

(\*) Extrapolated optical values.

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