

The Determination of the Elastic Constants of Nematic Liquid Crystals†

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The elastic constants K_{11} and K_{33} are calculated from the threshold field H_c associated with the Frederiks transition in a magnetic field of a uniform planar and a homeotropic layer, respectively. The elastic constant K_{22} is determined indirectly using a twisted planar layer. The errors associated with the determination of H_c are critically evaluated. In particular the anchoring conditions at the boundaries are found to have an important influence on H_c . Results for all three elastic constants of PAA and MBBA are given. In general our values for K_{11} and K_{33} are substantially higher than those reported in the literature.

1 INTRODUCTION

In the nematic liquid crystalline phase¹ the elongated molecules are, on average, aligned with their long axis parallel to a preferred direction that can be labelled by a unit vector \mathbf{n} (the director). The centres of mass of the molecules are distributed at random. In an ideal single crystal of a nematic \mathbf{n} is uniform over the whole sample. However, in many practical circumstances such an ideal configuration is not compatible with the constraints imposed by the walls of the container: \mathbf{n} will vary in space. For a distorted nematic the space variations of \mathbf{n} are small over molecular dimensions and a continuum description of the nematic liquid crystal can be used. In the bulk of a nematic sample three types of distortions can occur: splay, twist and bend. The associated elastic constants are K_{11} , K_{22} and K_{33} , respectively. The distortion-free energy (per unit volume) of a nematic is given by^{1,2}

$$F_d = \frac{1}{2}[K_{11}(\text{div } \mathbf{n})^2 + K_{22}(\mathbf{n} \cdot \text{rot } \mathbf{n})^2 + K_{33}(\mathbf{n} \times \text{rot } \mathbf{n})^2]. \quad (1)$$

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Much of the interest in liquid crystals is associated with the fact that the orientation of the director can easily be influenced by external stimuli. In the description of these effects the free energy due to the distortion always plays a central role. Consequently, knowledge of elastic constants of various liquid crystalline materials is of fundamental importance. Nevertheless, relatively little attention has been paid so far to the determination of the elastic constants.^{3–7} Moreover, values from different sources of an elastic constant of a specific compound differ often by amounts up to 20 or 100 per cent (see for example Tables 3.1 and 3.2 of Ref. 1). In this paper we shall critically evaluate the determination of the elastic constants via the so-called Frederiks transition, *i.e.* the onset of the deformation of a uniform nematic layer in a magnetic field. This, together with an accurate determination of the anisotropy of the magnetic susceptibility, makes it possible to give a complete set of elastic constants for the nematic temperature range of *p*-azoxyanisole (PAA) and N-(*p*-methoxybenzylidene-*p*-*n*-butylaniline) (MBBA).

The theory of the Frederiks transition has been described extensively elsewhere.^{4,8} In the presence of an external magnetic field \mathbf{H} the elastic free energy F_d must be supplemented by a term F_m describing the diamagnetic response of the material:

$$F_m = -\frac{1}{2}\Delta\chi(\mathbf{n} \cdot \mathbf{H})^2. \quad (2)$$

χ_{\parallel} and χ_{\perp} are the (dimensionless) volume susceptibilities parallel and perpendicular to \mathbf{n} , respectively. In nematics the difference $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ is usually positive; the situation with $\mathbf{n} // \mathbf{H}$ corresponds to minimum energy. Consider a magnetic field perpendicular to the director of a uniform nematic layer of thickness d . We assume fixed boundary conditions, *i.e.* the orientation of the director at the substrates is not influenced by the field (strong anchoring). Then the director pattern will be distorted only above a threshold field H_c .^{4,8} Using Eqs. (1) and (2) H_c can be calculated to be given by

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

where $i = 1, 2$ and 3 for the respective situations depicted in Figure 1a, 1b and 1c. If the upper boundary of a uniform planar layer (Figure 1a) is rotated over an angle ψ , a twisted planar layer is obtained. This situation is depicted for $\psi = \pi/2$ in Figure 1d. The threshold field now is given by⁹

$$\Delta\chi H_c^2 d^2 = (K_{11} + \frac{1}{4}K_{33} - \frac{1}{2}K_{22})\pi^2. \quad (4)$$

Eqs. (3) and (4) can be used to determine the elastic constants of a given material, provided that the distortion of the director pattern can somehow be measured accurately.

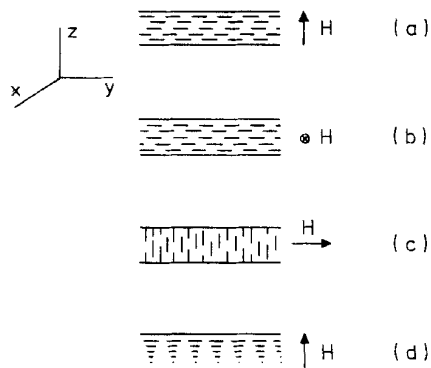


FIGURE 1 Various configurations for a Frederiks transition.

2 EXPERIMENTAL

In principle any physical quantity that has a different value along and perpendicular to the director can be used to detect variations of the director. A simple and convenient method is to make use of the anisotropy of the refractive index and to detect the transition optically. We consider the situation of Figure 1a and calculate the phase difference δ between normally incident light that is linearly polarized along the x axis and along the y axis, respectively.^{4,8} The optical path of light polarized in the x direction depends for all values of H on the ordinary refractive index n_o . The effective index n_{eff} for the light polarized in the y direction depends on the deformation angle θ , n_o and the extraordinary index n_e :

$$n_{\text{eff}} = n_e n_o (n_e^2 \sin^2 \theta + n_o^2 \cos^2 \theta)^{-1/2}. \quad (5)$$

The phase difference δ is given by

$$\delta = \frac{1}{\lambda} \left| \int_0^d (n_o - n_{\text{eff}}) dz \right|, \quad (6)$$

where λ is the wavelength of the light. With increasing field starting at $H = H_c$ a series of maxima and minima is found until $n_{\text{eff}} = n_o$ for $H \gg H_c$. The case of a homeotropic layer can be treated similarly. The determination of K_{22} , however, is somewhat more complicated. In the situation shown in Figure 1b $\delta = 0$ for all values of the field. The sample can be divided into two halves that give an equal contribution to δ but of opposite sign. In order to detect the transition one has to use light incident at a relatively large angle.^{10,11} In

practice this is fairly complicated if the sample is to be thermostated. Therefore we used an over $\pi/2$ twisted planar layer (Figure 1d and Eq. (4)) from which the value of $(K_{11} + \frac{1}{4}K_{33} - \frac{1}{2}K_{22})$ can be determined. As K_{11} and K_{33} are known it is thus possible to calculate K_{22} .

If the refractive indices of the compound under investigation are known, it is possible to obtain either K_{11} or K_{33} from the threshold value of the field, and K_{11}/K_{33} from a least-squares fit of the experimental and theoretical curve of $\delta(H) - \delta(0)$ versus H .^{6,12} We found that in practice the quality of the fit is not very sensitive to small variations of $\Delta n = n_e - n_o$, while the ratio K_{11}/K_{33} varies strongly with Δn . This makes this method rather inaccurate.^{5,13}

The monochromatic light source used is a Spectra-Physics He-Ne laser (model 133P, $\lambda = 632.8$ nm, output 1.8 mW, 500:1 polarized). The nematic sample is placed between the poles of a magnet in an electronically thermostated oven, constructed on the lines of the inner part of the Mettler FP52 heating stage. The temperature stabilization is of the order of 0.1°C. The current through the magnet is stabilized to better than 0.1% and provides a maximum magnetic field of 13 kOe over a gap of 35 mm. Depending on the orientation of the director, the light beam is lead directly through the sample via two small holes in the oven, or indirectly via two mirrors. The intensity of the chopped light beam is measured with a photosensitive diode, amplified with a synchronous amplifier and fed to the y axis of an xy recorder. The continuously variable magnetic field is measured with a Hall probe; the Hall voltage is fed to the x axis of the recorder. The field is calibrated against an NMR unit. This is essential because commercial field-strength meters often have calibration errors of the order of 3–5 per cent. The first part of a typical run is shown in Figure 2. The laser, the oven and the optical accessories are mounted on an optical bench. Using micromanipulators the director of the sample in the oven can be positioned perpendicular to the field with a high precision.

The nematic liquid is put between two polished glass plates. The plates are thoroughly cleaned in successive solutions on Teepol, KOH, and HNO₃ plus H₂SO₄. Then an appropriate procedure is applied to obtain well-defined boundary conditions (see next section). The plates are kept apart at a fixed distance by two tungsten wires ($\varnothing 50 \mu\text{m}$) and sealed at two sides with epoxy resin. The thickness of the nematic layer is taken equal to the spacing between the two plates of the empty cell, which is measured interferometrically with an accuracy of about 0.5 per cent.

The determination of an elastic constant requires in addition to the values of H_c and d the value of $\Delta\chi$. The anisotropy of the susceptibility was obtained with an accuracy of the order of 1–2 per cent by measuring χ_{\parallel} in the nematic phase and $\bar{\chi} = (\chi_{\parallel} + 2\chi_{\perp})/3$ in the isotropic phase by the Faraday-Curie method. Details will be described elsewhere.¹⁴

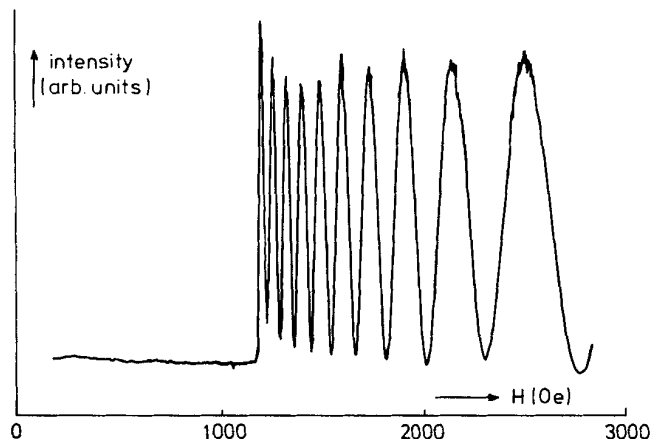


FIGURE 2 Interference pattern of a uniform planar nematic layer between crossed polarizers in monochromatic light (PAA, 131°C, $d = 47.7 \mu\text{m}$).

The following points were found to be important for an accurate determination of H_c :

a) The theory assumes strong anchoring conditions of the director at the boundaries: $\theta = 0$ for $z = 0$ and $z = d$. In practice different surface treatments were found to give different values for H_c (other conditions being equal). This indicates that in the presence of the magnetic field strong anchoring conditions are not fulfilled. There seems to be no separate method for checking the boundary coupling. However, it can be expected that the weaker the boundary anchoring the lower H_c .¹⁵

b) As the theory assumes equilibrium conditions, the variations of the field should be quasi-static. We observed that near the threshold dH/dt had to be restricted to values $\lesssim 40 \text{ Oe/min}$. For $H/H_c > 1.1$ a three times larger value could be used.

c) It was found that the accuracy with which \mathbf{H} is normal to \mathbf{n} is very important. In Figure 3 the phase difference of the run of Figure 2 is plotted against the field. H_c can be obtained by straightforward extrapolation. However, for even small angles between \mathbf{H} and the normal to \mathbf{n} there is a strong rounding off of the curve near $H = H_c$. This makes the extrapolation to obtain H_c difficult, and leads to values of H_c that are too small.¹⁶

The errors associated with the points (a) and (c) probably can account for the large apparent discrepancies found in the literature. As these errors always lead to a decrease of H_c , a high value of a specific elastic constant is to be preferred to a lower one if Eq. (3) has been used.

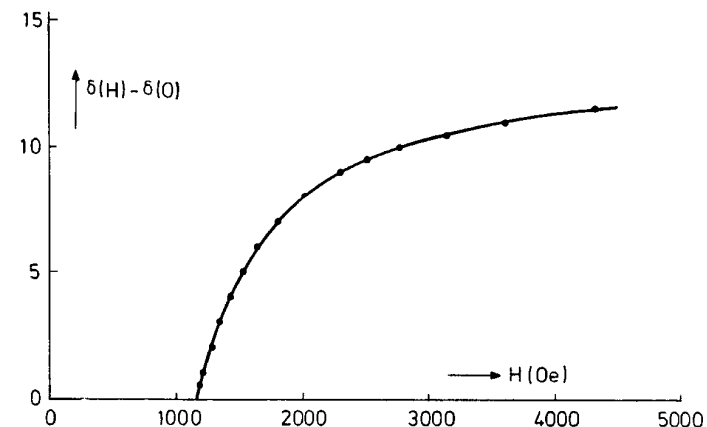


FIGURE 3 Phase-difference versus magnetic field strength for the run of Figure 2.

When the treatment of the substrates includes rubbing, the boundary conditions are often not exactly tangential. If the angle between the director and the substrate is θ_0 , this leads to either a uniform tilt angle in the sample (Figure 4a) or to a tilt angle that varies from $-\theta_0$ to θ_0 (Figure 4b). In the case of a twisted planar layer these two situations are connected with opposite twist directions, and can occur in the same sample. For small values of θ_0 this difference in tilt angle does not influence the value of H_c , provided the direction of the magnetic field is carefully optimized to give the highest possible threshold. In the case of a twisted planar layer of MBBA consistent values of H_c were only obtained if the sample was cooled down from the isotropic phase in presence of a magnetic field parallel to the glass plates and at an angle with the rubbing directions. This ensured a correct uniform twist over the sample.

If the angle between \mathbf{H} and \mathbf{n} is 90° or very close to this value there are two equivalent possibilities for the director to tilt in the direction parallel to \mathbf{H} . Between two regions with different tilt angles inversion walls occur. These walls do not contribute to the interference pattern but only scatter light. This effect depends strongly on the quality of the original uniform texture. If this texture is really uniform no walls occur.

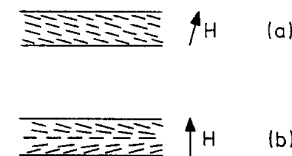


FIGURE 4 The two possible director patterns if the boundary conditions are not exactly tangential.

3 RESULTS AND DISCUSSION

When the methods described above are used to determine K_{11} , K_{22} and K_{33} the anchoring energy at the surface turns out to be the most uncertain factor. Various possible surface treatments have been tested for samples of PAA. Rinsing of the substrate with chromic/sulphuric acid is the classical method of obtaining homeotropy. Using this method the values for $K_{33}/\Delta\chi$ of PAA reported by Tsvetkov³ and by Saupe⁴ could be reproduced very well (see Figure 5). Higher thresholds were found using substrates that were

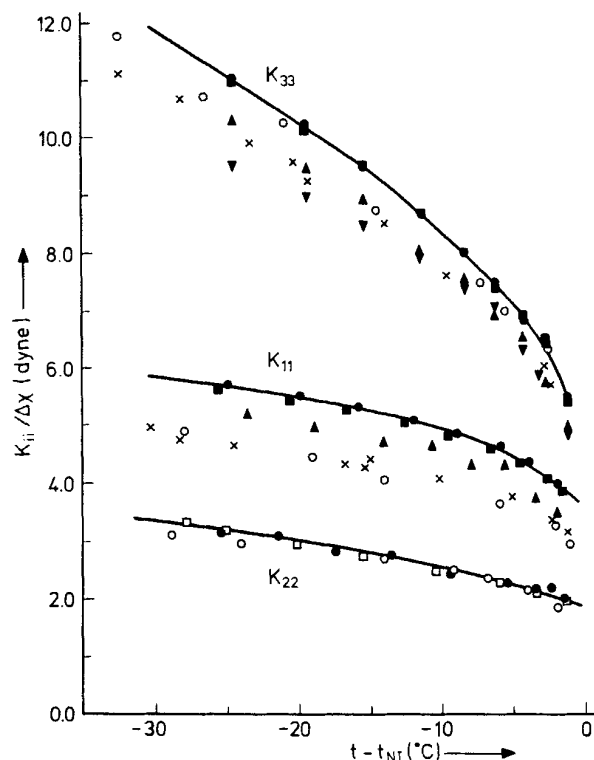


FIGURE 5 Elastic constants $K_{ii}/\Delta\chi$ for PAA.
 ○ Tsvetkov (Ref. 3),
 × Saupe (Ref. 4),
 □ Madhusudana *et al.* (Ref. 11),
 Filled symbols: this work, surface treatments:
 ● K_{33} : 1-dodecanol,
 ■ K_{22} , K_{11} : polymer film + rubbing,
 ▲ K_{33} : chromic/sulphuric acid,
 ◻ K_{11} : rubbing + cremophor O,
 ▼ K_{33} : CTAB.

exposed for about 30 minutes to 1-dodecanol at 200°C and degreased with isopropanol afterwards. When additionally 0.1% (by weight) cetyltrimethylammoniumbromide (CTAB) was added to the liquid crystal a lower threshold was obtained.

To obtain uniform planar samples of PAA the classical rubbing technique was used, while in addition the surfactant $\text{CH}_3(\text{CH}_2)_{15}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$ (cremophor O, BASF) was added. The highest thresholds were obtained, however using substrates coated with a polymer film of $(-\text{CH}_2-\text{Ph}-\text{CH}_2-)_n$ (poly-*p*-xylylene) and gently rubbed afterwards. The values of $K_{11}/\Delta\chi$ thus obtained are approximately 20 per cent higher than those reported by Tsvetkov or by Saupe (see Figure 5). Rubbing with cremophor O gives intermediate results for PAA. However, this seems to be due to the relatively high temperature used. For MBBA and other substances at temperatures below 80°C the thresholds obtained using poly-*p*-xylylene and cremophor O were found to coincide. Substrates coated with obliquely evaporated SiO were found to give lower thresholds.

Using substrates coated with poly-*p*-xylylene twisted planar samples of PAA were made. With the threshold for this situation and the new values of $K_{11}/\Delta\chi$ and $K_{33}/\Delta\chi$ values are obtained for $K_{22}/\Delta\chi$ using Eq. (4). These values agree very well with results reported in the literature (see Figure 5). These latter values were obtained using the configuration of Figure 1b. Evidently it is relatively easy to obtain in the case of PAA strong anchoring conditions for a rotation of the director parallel to the substrate. Hence earlier results for $K_{22}/\Delta\chi$ are probably more trustworthy than those for $K_{11}/\Delta\chi$ and $K_{33}/\Delta\chi$.

Samples of MBBA were made using the surface treatments with 1-dodecanol (homeotropic) and poly-*p*-xylylene or cremophor O (uniform and twisted planar). The results for $K_{ii}/\Delta\chi$ are given in Figure 6. Again our values for K_{11} and K_{33} are substantially higher than those reported in the literature. The results obtained for $K_{22}/\Delta\chi$ are slightly higher than the values from Ref. 17. As $K_{22}/\Delta\chi$ is obtained indirectly using Eq. (4) the highest values are now not necessarily the best ones. The difference with Ref. 17 is probably within the experimental accuracy.

In Figures 7 and 8 we give results for $\Delta\chi^g = \Delta\chi/\rho$, where ρ is the density, of PAA and MBBA. For PAA our data agree very well with values reported earlier in the literature.^{18,19} For MBBA there is considerable disagreement between the various authors. Our values agree essentially with those of Haller *et al.*²⁰, and also within 5 per cent with those of Sigaud and Gasparoux.²¹ Earlier results from Gasparoux *et al.*¹⁹ give a rather different temperature dependence of $\Delta\chi^g$. These measurements should probably be disregarded because of the rather low NI transition temperature of the MBBA used. It is not clear why the values for $\Delta\chi^g$ of Poggi *et al.*²² are so much higher than those of the others. Results from the literature for $\Delta\chi^g$ of PAA and MBBA obtained

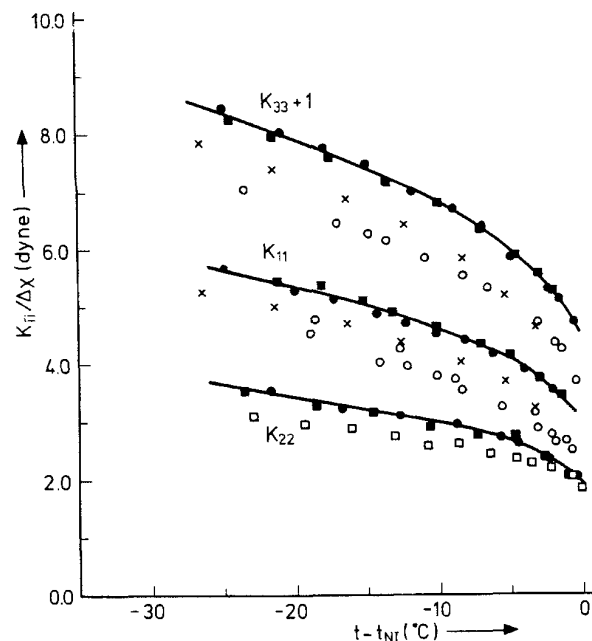


FIGURE 6 Elastic constants $K_{ii}/\Delta\chi$ for MBBA.
 ○ Haller (Ref. 5),
 × Greulich *et al.* (Ref. 7),
 □ Leenhouts *et al.* (Ref. 17),
 Filled symbols: this work.

with rotating field methods²⁴ are considerably lower than the values given in Figures 7 and 8.

Finally we give in Tables I and II a series of values of the elastic constants of PAA and MBBA. These were calculated with data for $K_{ii}/\Delta\chi$ and $\Delta\chi^g$ obtained via interpolation using the full curves in Figures 5–8. From the reproducibility of the results for different samples it is estimated that $K_{ii}/\Delta\chi$ ($i = 1, 3$) can be determined with an accuracy of about 2 per cent. This leads to an accuracy of the order of 4 per cent for K_{11} and K_{33} and of about 10 per cent for K_{22} . The temperature dependence of K_{ii} of a single compound is obtained more accurately. It is difficult to estimate whether systematic errors are still present. In principle it cannot be excluded that other methods of surface treatment may give a higher anchoring energy and possibly higher elastic constant values. However, the good agreement of our values for $K_{22}/\Delta\chi$ with other work indicates that this situation is not likely to occur.

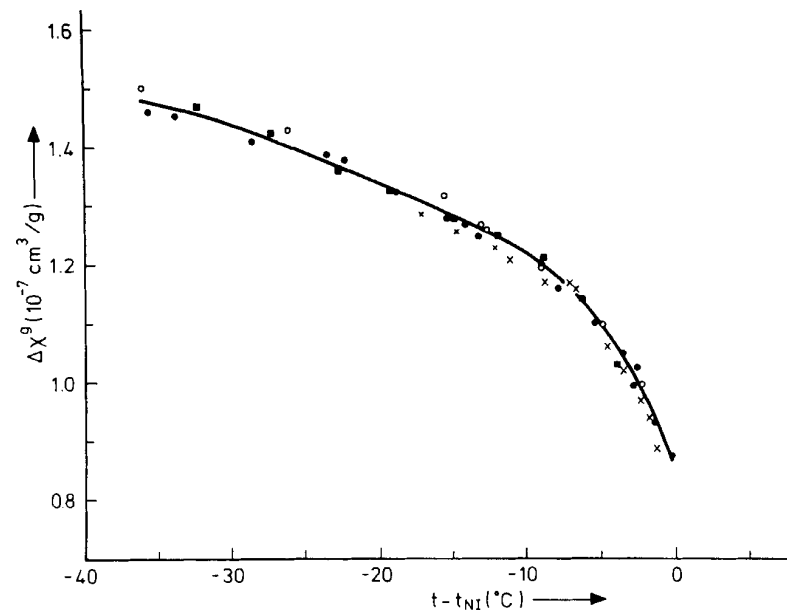


FIGURE 7 Diamagnetic anisotropy of PAA.
 ○ Foëx (Ref. 18),
 × Gasparoux *et al.* (Ref. 19),
 ●■ this work.

TABLE I
 Elastic constants of PAA ($t_{NI} = 135^\circ\text{C}$)

$t_{NI} - t$ ($^\circ\text{C}$)	$K_{ii}/\Delta\chi$			$\Delta\chi^g$ ($10^{-7} \text{ cm}^3/\text{g}$)	ρ^a (g/cm^3)	K_{ii}		
	$K_{11}/\Delta\chi$	$K_{22}/\Delta\chi$	$K_{33}/\Delta\chi$			(10 ⁻⁷ dyne)		
25	5.67	3.12	11.08	1.392	1.1737	9.26	5.1	18.1
21	5.51	2.99	10.46	1.351	1.1703	8.71	4.7	16.5
17	5.32	2.84	9.78	1.307	1.1667	8.11	4.3	14.9
13	5.10	2.68	9.05	1.261	1.1630	7.48	3.9	13.3
10	4.90	2.53	8.42	1.221	1.1601	6.94	3.6	11.9
7	4.68	2.38	7.71	1.158	1.1572	6.27	3.2	10.3
5	4.46	2.25	7.12	1.100	1.1551	5.67	2.9	9.05
3	4.19	2.10	6.43	1.010	1.1528	4.93	2.5	7.56
2	4.02	2.02	5.98	0.975	1.1516	4.51	2.3	6.71
1	3.83	1.93	5.45	0.920	1.1504	4.05	2.1	5.77

^a Ref. 23

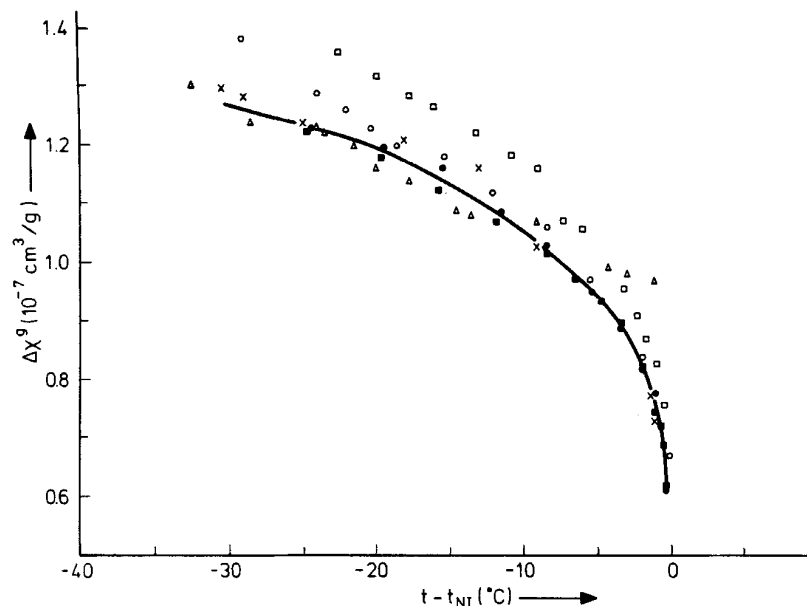


FIGURE 8 Diamagnetic anisotropy of MBBA.
 △ Gasparoux *et al.* (Ref. 19),
 ○ Sigaud and Gasparoux (Ref. 21),
 × Haller *et al.* (Ref. 20),
 □ Poggi *et al.* (Ref. 22),
 ● this work.

TABLE II

Elastic constants of MBBA ($t_{NI} = 45^\circ\text{C}$)

$t_{NI} - t$ ($^\circ\text{C}$)	$K_{11}/\Delta\chi$ $K_{22}/\Delta\chi$ $K_{33}/\Delta\chi$			$\Delta\chi^9$ (10^{-7} cm ³ /g)	ρ (g/cm ³)	K_{11} K_{22} K_{33}		
	(dyne)					(10 ⁻⁷ dyne)		
26	5.76	3.62	7.46	1.236	1.050	7.48	4.7	9.68
22	5.49	3.45	7.10	1.210	1.046 ⁵	6.95	4.4	8.99
18	5.22	3.30	6.73	1.170	1.043 ⁵	6.37	4.0	8.22
14	4.94	3.14	6.32	1.116	1.040	5.73	3.6	7.34
11	4.69	3.01	5.98	1.070	1.037	5.20	3.3	6.64
8	4.42	2.86	5.55	1.013	1.034 ⁵	4.63	3.0	5.82
6	4.21	2.70	5.21	0.967	1.033	4.20	2.7	5.20
4	3.94	2.50	4.78	0.916	1.031 ⁵	3.72	2.4	4.52
2	3.52	2.24	4.29	0.847	1.030 ⁵	3.07	2.0	3.74
1	3.18	2.10	3.95	0.745	1.029 ⁵	2.44	1.6	3.03

The methods described here were used to investigate the elastic constants of some homologous series of nematic liquid crystals. These results and a possible microscopic interpretation of the elastic constants will be published in the near future.

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