Viscoelastic twist properties of some nematic liquid crystalline azoxybenzenes

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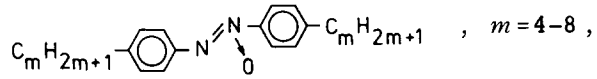
The static and dynamic behavior of the Frederiks transition for twist of a uniform planar nematic sample in an external magnetic field has been studied by monitoring the associated conoscopic figure. In particular, the decay of this figure after the field has been switched off is considered in detail in order to obtain results for the twist viscosity γ_1. Results for the twist elastic constant K_2 and for the viscosity γ_1 are reported for the homologous series of p, p'-dialkylazoxybenzenes. K_2 is found to be smaller than both K_1 and K_3, while K_2 varies little along the series. The temperature dependence of γ_1 can be described by a combination of an activated process and a term depending on the orientational order parameter.

I. INTRODUCTION

Nematic liquid crystals are anisotropic liquids in which the constituting molecules are, on average, aligned with a certain axis parallel to a preferred direction in space, given by the director **n**. In an actual sample, the orientation **n** is determined by boundary conditions and external fields. Variations of **n** in space and time, respectively, can be described by a continuum theory.[1] The elastic properties are governed by three curvature elastic constants, corresponding to the restoring torques opposing splays (K_1), twists (K_2), and bends (K_3). The hydrodynamic properties are determined by five independent viscosity coefficients. Two of these are related to reorientation of the director, without material flow being involved. Apart from the inherent interest in these properties (e.g., the elastic constants are related to the gradients of the intermolecular interactions), they are of great importance for the performance of materials in liquid crystal displays.

Measurements of the elastic constants are relatively numerous,[2] and are usually performed by determining the threshold for deformation of a uniform director pattern in an external field (Frederiks transition). The attention has been focused mainly on K_1 and K_3. Much fewer results are available for K_2,[3] probably because the deformation of the director pattern is not so easily observed in the relevant twist geometry as in the cases of K_1 and K_3. Alternatively, $K_{\text{eff}} = K_1 + \frac{1}{4}K_3 - \frac{1}{2}K_2$ has been determined from the deformation of a planar nematic layer twisted over an angle of $\pi/2$ in an external magnetic field. If K_1 and K_3 are known, then K_2 can also be obtained, though much less accurately.[2] Full information on the viscosity coefficients is only available for very few compounds.[4] For practical reasons, attention has been given mainly to the shear-alignment viscosity[5] η_s and to the viscosity γ_1.[6] The latter quantity is important for switching times of liquid crystal displays. To determine γ_1 frequently rotating field methods[2] are used, which unfortunately require a relatively large amount of material.

In this paper, we give results for K_2 and γ_1 of the homologous series of p,p'-dialkylazoxybenzenes



, $m = 4-8$,

to be indicated as mAB. K_2 is obtained from the Frederiks transition for twist of a uniform planar sample in an external magnetic field. The threshold field H_c is found from the rotation angle δ of the associated conoscopic figure, as originally proposed by Cladis[7] and developed further by Leenhouts.[8] Furthermore, γ_1 is obtained from the dynamics of the same Frederiks transition. The precision with which $\delta(t)$ can be measured at small angles, and thus the feasibility of the whole method, has been greatly improved by photographing the conoscope figure at fixed time intervals, and measuring δ from the resulting negatives. K_2 increases only slightly along the mAB series, with pronounced alternation with m in a fashion similar to that observed for K_1 and K_3. The temperature variation of γ_1 is governed by an activated process on which the dependence of the orientational order parameter is superimposed.

II. EXPERIMENTAL

When a magnetic field H is applied to a uniform planar nematic layer (**n** parallel to one direction in the plane of the substrate) such that H is parallel to the layer and perpendicular to **n**, distortion of **n** starts at the threshold field given by[1,2]

$$H_c = (\pi/d)(K_2/\Delta\chi)^{1/2} . \tag{1}$$

Here, d is the thickness of the layer and $\Delta\chi$ the anisotropy of the magnetic susceptibility. Above H_c the maximum twist angle ϕ_m in the middle of the sample is determined by the relation

$$H/H_c = (2/\pi)\,F(\tfrac{1}{2}\pi, \phi_m) , \tag{2}$$

where F is the complete elliptic integral of the first kind. The conoscopic figure associated with a uniform planar nematic layer consists of two hyperbola. When a twist deformation is applied, this pattern is rotated over an angle δ given by[7]

$$\tan 2\delta = \langle \sin 2\phi(z)\rangle / \langle \cos 2\phi(z)\rangle$$
$$= 2 \sin \phi_m / [2E(\tfrac{1}{2}\pi, \sin \phi_m) - F(\tfrac{1}{2}\pi, \sin \phi_m)] . \tag{3}$$

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Here $\phi(z)$ is the twist angle of $\mathbf{n}$, and $z = \pm\frac{1}{2}d$ defines the boundaries of the nematic layer where strong anchoring ($\phi = 0$) is assumed. In Eq. (3), the brackets denote an average, while E is the complete elliptic integral of the second kind. For $H \gg H_c$ one finds that $\phi_m \to \frac{1}{2}\pi$ and also $\delta \to \frac{1}{2}\pi$. As discussed by Leenhouts,[8] if H is perpendicular to $\mathbf{n}$, the conoscopic pattern can rotate either clockwise or counterclockwise. In practice, both of these will occur simultaneously in different regions of the sample, which makes an accurate determination of δ impossible. This problem can be overcome by orienting H at an angle of $(90° - \phi_0)$ to $\mathbf{n}$. In this case, the deformation already starts at $H = 0$, and Eqs. (2) and (3) have to be replaced by[8]

$$H/H_c = (2/\pi)\int_{\psi_0}^{\pi/2} d\psi(1 - \sin^2\phi_m \sin^2\psi)^{-1/2} , \tag{4}$$

$$\tan 2\delta = \frac{2(\sin^2\phi_m - \sin^2\phi_0)^{1/2}\cos 2\phi_0 - H(\psi_0, \phi_m)\sin 2\phi_0}{2(\sin^2\phi_m - \sin^2\phi_0)^{1/2}\sin 2\phi_0 + H(\psi_0, \phi_m)\cos 2\phi_0} . \tag{5}$$

Here $\sin\psi_0 = \sin\phi_0/\sin\phi_m$ and $H(\psi_0, \phi_m)$ is given by

$$H(\psi_0, \phi_m) = 2\int_{\psi_0}^{\pi/2} d\psi(1 - \sin^2\phi_m \sin^2\psi)^{1/2} \times - \int_{\psi_0}^{\pi/2} d\psi(1 - \sin^2\phi_m \sin^2\psi) . \tag{6}$$

In practice ϕ_0 is restricted to a few degrees and is only known within approximately one degree. The angle δ is recorded as a function of H. By making a nonlinear least-square fit to Eqs. (4) and (5), values for H_c and ϕ_0 are obtained. With Eq. (1), H_c leads finally to values for K_2, while the constancy of ϕ_0 with temperature gives an indication of the quality of the fitting procedure.

If a field $H > H_c$ is switched on, the dynamic equation for $\phi(z, t)$ is given by[9]

$$K_2\partial^2\phi/\partial z^2 + \sin\phi\cos\phi\Delta\chi H^2 = \gamma_1\partial\phi/\partial t . \tag{7}$$

The general solution for $\phi(z, t)$ can be expressed as a power series

$$\phi(z, t) = \sum_n C_n(t)\cos[(2n+1)\pi z/d] . \tag{8}$$

Equating the left-hand side of Eq. (7) to zero gives the equilibrium values for $\phi(z)$. If the field is now switched off, the eigenfunctions of $\phi(z, t)$ decay with characteristic time constants

$$\tau_n^{-1} = (K_2/\gamma_1)[(2n+1)\pi/d]^2 . \tag{9}$$

The time constant τ_0 gives the slowest decay corresponding to the least distorted solution. Provided $\phi_m(0)$ is not too large, one expects a simple exponential decay

$$\phi(z, t) = \phi(z, 0)\exp(-t/\tau_0) , \tag{10}$$

with

$$\phi(z, 0) = \phi_m\cos(\pi z/d) \tag{11}$$

and

$$\tau_0 = \gamma_1 d^2/(\pi^2 K_2) = \gamma_1/(\Delta\chi H_c^2) . \tag{12}$$

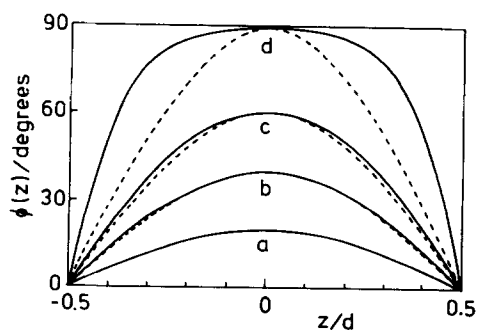

FIG. 1. Twist angle $\phi(z)$ for values of ϕ_m of 20°, 40°, 60°, and 89°, respectively (a, b, c, d). Full lines: complete theory, broken lines: approximation of Eq. (11).

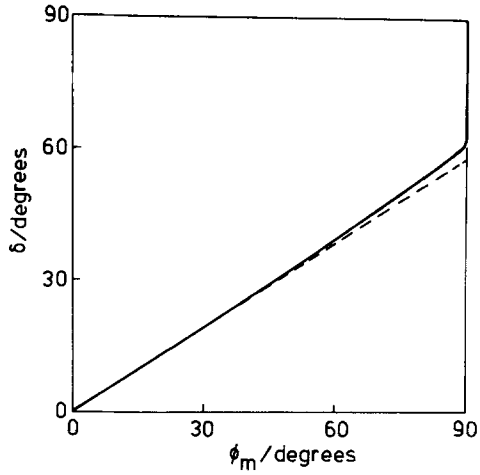

FIG. 2. Rotation angle δ of the conoscopic figure vs ϕ_m: full and broken lines as in Fig. 1.

In Fig. 1, the full solution (8) is compared with the approximation (11). Experimentally, we measure the rotation angle $\delta(t)$ of the conoscopic figure instead of $\phi(z, t)$. The relation between δ and ϕ_m is shown in Fig. 2, again for the approximation (11) and the full solution. From these results, we conclude that for $\phi_m \lesssim 40°$ it is sufficient to do a simple measurement of τ_0 on $\delta(t)$, which then gives in turn γ_1.

The *mAB* compounds were synthesized at the Philips Research Laboratories (Eindhoven) as described in Ref. 10. The transition temperatures [nematic–isotropic (NI)] are given in Table I. Uniform planar samples were made by using two glass plates coated with para-xylylene,[11] first rubbed gently in one direction. The glass plates were kept apart by tungsten ribbon of 100 μm thickness. The exact thickness, determined by interferometry on the empty cell, was usually somewhat higher.

The conoscope used has been described in Ref. 8. Conoscope and oven with sample are both placed in the gap of a Bruker BE15 electromagnet that provides a maximum field of 1.1 T over 50 mm. By means of crosswires mounted in the focal plane of the ocular, the rotation angle δ of the conoscopic pattern can be determined using a graduated scale attached to the ocular tube. The oven with glass windows is contained in a copper jacket. Using a PID controller (Eurotherm 093)

TABLE I. Values of K_2 and γ_1 of the *mAB* series.

$m=4$			$m=5$			$m=6$		
t/°C	$K_2/10^{-12}$ N	$\gamma_1/10^{-3}$ Pa s	t/°C	$K_2/10^{-12}$ N	$\gamma_1/10^{-3}$ Pa s	t/°C	$K_2/10^{-12}$ N	$\gamma_1/10^{-3}$ Pa s
20.2	2.79	•••	30.1	7.77	94.8	30.1	4.83	78.3
21.2	•••	64.2	39.8	6.60	68.9	35.4	4.17	61.7
23.4	2.54	55.0	45.3	5.91	55.2	39.8	3.71	52.8
25.4	2.29	45.7	49.6	5.27	42.3	45.3	2.71	33.1
26.5	•••	42.7	55.2	4.58	34.4	47.5	2.41	•••
27.7	1.97	33.6	59.4	3.82	25.6	48.7	2.19	25.6
28.8	1.62	29.5	61.8	3.40	21.7	49.6	2.04	23.5
30.9	NI	•••	64.0	2.81	16.8	50.8	1.84	21.2
			65.0	2.44	16.3	52.0	1.47	18.7
			66.0	1.94	13.3	53.2	NI	•••
			66.6	NI	•••			

$m=7$			$m=8$		
t/°C	$K_2/10^{-12}$ N	$\gamma_1/10^{-3}$ Pa s	t/°C	$K_2/10^{-12}$ N	$\gamma_1/10^{-3}$ Pa s
54.2	7.11	54.3	64.0	3.79	38.8
57.3	5.95	40.0	65.0	2.68	27.0
59.4	5.37	38.4	66.2	NI	•••
61.8	4.62	•••			
62.9	•••	32.0			
64.0	4.05	•••			
66.0	3.43	23.3			
67.1	3.07	18.3			
68.2	2.70	23.5			
69.4	2.03	16.0			
70.1	NI	•••			

the temperature is kept constant within 0.1 °C. To record the decay of $\delta(t)$ after the field has been switched off, photographs were taken using a Wild MPS 51S automatic camera in combination with a homebuilt electronic timer. The minimum time interval between two exposures is determined by the motor drive of the film transport, and is about 1 s. Using a mercury light source with interference filter at 546 nm and high-speed film, exposure times as short as 0.01 s can be obtained.

III. RESULTS

The results for both K_2 and γ_1 of the *mAB* series are given in Table I. Figure 3 shows a typical plot of the decay of δ vs time when the field is switched off, starting at approximately $\delta \approx 45°$. As one can see, the scatter of experimental points around the straight line increases at small values of δ, due to increased relative error in the determination of δ. Figure 4 shows plots of K_2 vs the reduced temperature. In order to obtain K_2 from H_c, data for the anisotropy of the magnetic susceptibility are required, which were taken from Ref. 12. For 4*AB* and 7*AB*, the values of K_2 agree reasonably well with the less accurate values obtained earlier from the threshold of a twisted nematic layer.[13] For 5*AB* and 6*AB*, there are considerable differences. Finally, in Fig. 5, Arrhenius type plots of $\ln\gamma_1$ vs $1/T$ are shown. As we see, no straight lines are obtained, indicating a more complicated dependence on the temperature.

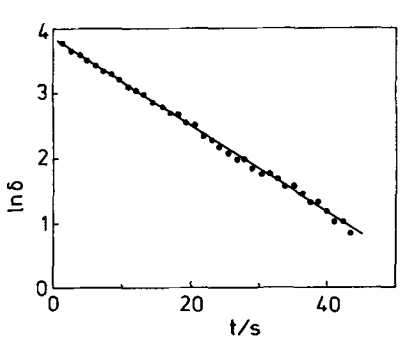

FIG. 3. Typical decay of the rotation angle δ of the conoscopic figure.

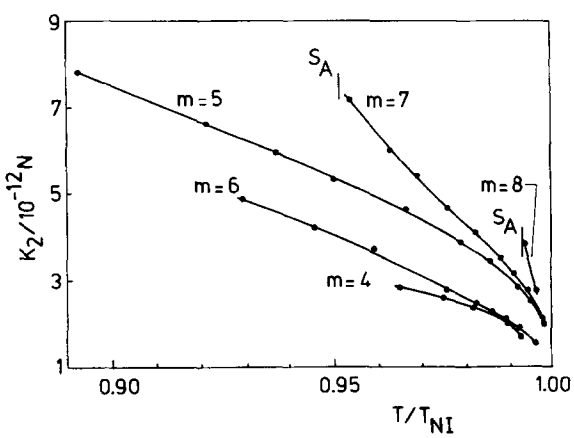

FIG. 4. Twist elastic constants K_2 of the *mAB* series.

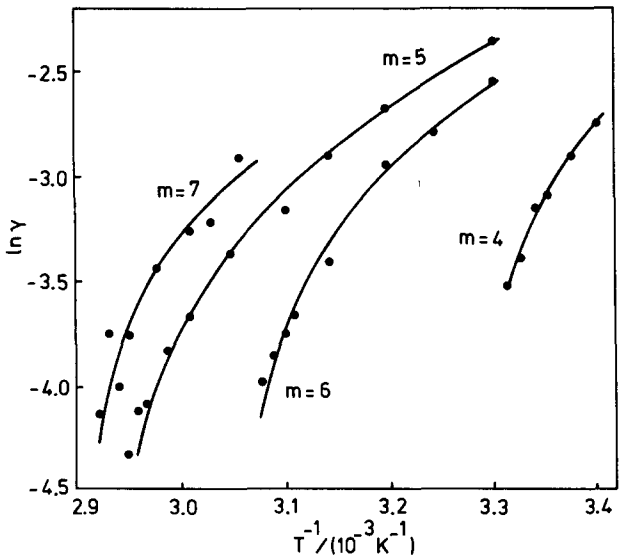

FIG. 5. Twist viscosity γ_1 vs inverse temperature for the *mAB* series; full lines give least-square fits of the data to Eq. (14).

IV. DISCUSSION

From Fig. 4, we note that along the homologous series K_2 increases somewhat, superimposed on a pronounced alternation with m. This behavior is compared for all three K_i in Fig. 6. Apart from the alternation, the variation of K_2 is rather small. This is similar to the behavior in some other homologous series.[3(e),8(b)]

From a simple Landau theory of the NI transition, one obtains in the lowest-order approximation[2]

$$K_1 = K_3 = 2S^2(L_1 + \tfrac{1}{2}L_2) ,$$
$$K_2 = 2S^2 L_1 . \tag{13}$$

Here $S = \langle \frac{3}{2}\cos^2\beta - \frac{1}{2} \rangle$ is the usual nematic order parameter, where β is the angle between the long molecular axis and the director, and L_1 and L_2 are coefficients in the second-order gradient terms in the Landau expansion in the order parameter. For the *mAB* series, S is known to be higher for the members with odd m compared to the even valued ones,[12] which explains the observed alternation of the K_i. As K_2 is the smallest of the three constants, we conclude from Eq. (13) that L_2 is positive. This seems to be a general result for various types of compounds. Using the relation $\Delta\chi \sim S$—which holds, provided the molecules can be treated as effectively cylindrically symmetric—the proportionality between K_i and S^2 can be checked by considering $K_i/\Delta\chi^2$. This quantity is displayed in Fig. 7 for K_2. The proportionality holds especially well for $m = 4$ where $K_1 \approx K_3$. Evidently, in this case the lowest-order approximation given by Eq. (13) is fully adequate.

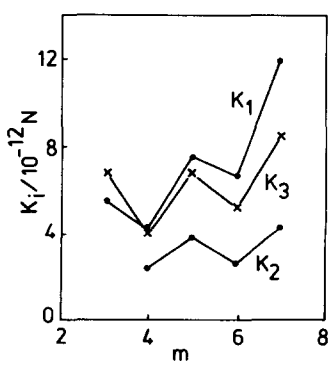

FIG. 6. Variation of the elastic constants with the chain length at $T = 0.98\ T_{NI}$.

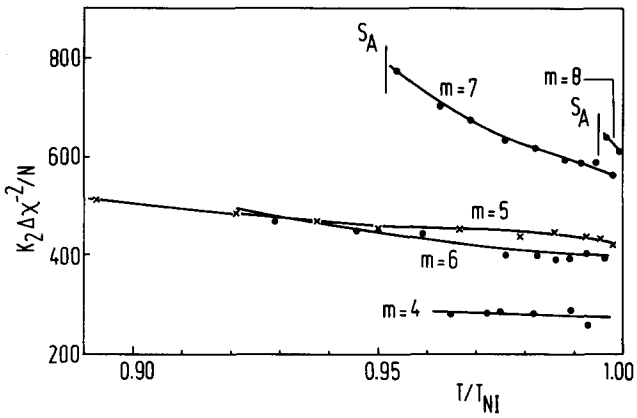

FIG. 7. Plot of $K_2/\Delta\chi^2$ vs reduced temperature for the *mAB* series.

The results for γ_1 of the *mAB* series (Fig. 5) do not show the simple exponential dependence on the inverse temperature often observed in an isotropic liquid. Evidently, some indirect dependence on T via the order parameter $S(T)$ is involved. In the literature, various proposals have been given to account for the total thermal behavior of γ_1.[14] Our data can be fitted reasonably well to the formula proposed by Martins *et al.*[14(a)]

$$\gamma_1 = cS^2 \exp(ES/k_B T) . \tag{14}$$

The full curves in Fig. 5 correspond to a least-square fit of Eq. (14) to the data, with S taken again from Ref. 12 and values of c and E as given in Table II. There has been some disagreement about the actual temperature dependence of γ_1. As a consequence of the relatively limited variation of S in combination with an activated process, it is difficult to exclude formulas other than Eq. (14). The exponential form of Eq. (14) does not allow a meaningful comparison of γ_1 values at the same reduced temperature. Taking the (extrapolated) values of γ_1 at a fixed absolute temperature not too close to the nematic–isotropic transition, it is clear that γ_1 increases with increasing chain length m.

TABLE II. Values of the coefficients c and E in Eq. (14) for various members of the *mAB* series.

m	c	E(eV)
4	0.025	0.087
5	0.017	0.097
6	0.037	0.078
7	0.045	0.060

In conclusion, the conoscopic method to monitor the Frederiks transition for twist has been used to complete the results of the elastic constants of the *mAB* series. In addition, it has been shown that the decay of the rotation of the conoscopic figure provides a convenient practical method to determine γ_1 on small samples.

ACKNOWLEDGMENTS

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