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Viscoelastic properties of a homologous series of nematic liquid crystalline Schiff’s bases

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1. Introduction.

Nematic Liquid Crystals (NLCs) are fluids: they differ from ordinary (isotropic) liquids only by the fact that the molecules are orientationally ordered [1, 2]. On average, in any finite volume, the elongated molecules point collectively in one direction, referred to as the nematic director no. There is a phase transition where this anisotropic behaviour disappears because the molecules become randomly oriented. This first-order phase transition occurs at a temperature T_{NI}, the so-called clearing temperature.

Most nematic liquid crystals consist of rigid elongated molecules composed of benzene or cyclohexane rings. It is often convenient to visualize these molecules as spherocylinders with length L and width W. It is advisable to look for such a dependence by comparing NLC’s which are composed of molecules that differ in length but which are otherwise quite similar. This condition is very nearly satisfied if one focuses attention on a homologous series.

The molecules of such a series are of variable length, but have the same basic structure. This length is made variable by binding, for instance, alkyl chains with different numbers of carbon atoms to the basic structure.

NLC’s exhibit strong depolarized light scattering. The light scattering can be described by fluctuations of the dielectric tensor $\epsilon(r, t)$. In NLC’s the off-diagonal elements of the dielectric tensor depend linearly on the fluctuations of the instantaneous $n(r, t)$ around its averaged value $n_0$.

The Orsay Liquid Crystal Group [3] has shown that if the director fluctuations are small and overdamped these fluctuations can be described by a set of linear (« hydrodynamic ») relaxation equations. In addition, they showed that $\delta n(r, t) = n(r, t) - n_0$ can be written as a sum of two uncoupled modes, related to three special types of deformation in the alignment pattern which are called the « splay », « twist » and « bend » distortions. These two uncoupled modes both decay exponentially and hence the optical spectrum of the light scattered by either mode should have a Lorentzian line shape. Experimentally we find that the width of these lines is very small compared to the angular frequency of the incoming field. Using the technique of homodyne photoelectric detection known as self-beat...
spectroscopy, it is possible to determine the line broadening by analysis of the noise intensity spectrum of the scattered light [4].

The noise intensity spectrum of laser light scattered by the long wavelength orientational fluctuations is a well-known function of the distortion viscoelastic properties [3]. In addition the angular distribution of the scattered light is a well-known function of the distortion elastic constants, called the Frank elastic constants [5].

Leenhouts et al. [6] investigated some physical properties of a series of nematic Schiff's bases, namely the homologues of anisylidene-p-aminophenylacetate (APAPA) as a function of temperature. They reported data for the optical and magnetic susceptibility, as well as the Frank elastic constants obtained from Fréedericksz transition measurements [7].

Here we report on the dynamical properties of the same homologous series obtained from measurements of the angular dependence of the spectral noise intensity of scattered laser light. More precisely, we present the splay, twist and bend viscoelastic ratios and the ratio of two Miesowicz viscosity coefficients, \( \eta_3/\eta_1 \) [8] as a function of temperature. In addition we give the ratios of the three Frank elastic constants obtained from measurements of the angular distribution of the scattered laser light.

We studied the compounds anisylidene-p-aminophenylacetate (APAPA or APAPA1), a number of homologues of APAPA (APAPAm; \( m = 2-5, 9 \)) and o-hydroxy-p-methoxybenzylidene-p'-butylaniline (OHMBBA). These compounds have the following structure:

\[
\text{H}_3\text{C-O-} \text{C}_n\text{H}_{2m+1} \text{N-R}_1 \text{C}_4\text{H}_9 \text{R}_2
\]

The side and end groups are \( R_1 = \text{H} \) and \( R_2 = \text{OCOC}_n\text{H}_{2m+1} \) for APAPAm respectively, whereas \( R_1 = \text{OH} \) and \( R_2 = \text{C}_4\text{H}_9 \) for OHMBBA. Note that \( m \) stands for the number of carbon atoms of the alkyl chain of the ester group \( \text{OCOC}_n\text{H}_{2m+1} \).

In table I the measured transition temperatures crystal-nematic (\( T_{KN} \)) and nematic-isotropic (\( T_{NI} \)) are listed. We also give in this table the length-to-width ratio \( L/W \) for these compounds as calculated by Leenhouts et al. [6].

In this section the results of the measurements are presented. Using the methods described in our earlier paper [11], we calculated from these results the ratios of the Miesowicz coefficients and the Leslie coefficients [12]. Finally in section 4 the results are discussed.

### 2. Experimental arrangement.

The optical arrangement used in the experiments is shown in figure 1. As this homodyne self-beat set-up is identical to the one described in an earlier paper [9] we refer the reader to that paper for details.

The unfocused but polarized laser light from a 5 mW He-Ne laser is scattered by the NLC contained in a flat sample holder. At a variable angle \( \Theta_1 \) the depolarized scattered light is detected by a photomultiplier tube (PMT). The fluctuating anode current of the PMT is fed into a real-time frequency analyser (Bruel and Kjaer, type 3347) which displays the noise spectrum in the frequency range 12.5 Hz to 63 kHz.

The sample holders we used consisted of two glass plates kept 25 \( \mu \)m apart by tungsten ribbon and glued with epoxy resin. We ascertained that the glass plate spacing does not affect the experimental results by varying the spacing between 10 and 50 \( \mu \)m.

The degreased glass walls were rubbed with cotton Webrill wipes in order to ensure uniform planar alignment of any NLC contained in the sample holder.

### In table I — List of nematic liquid crystals studied and their measured transition temperatures. \( T_{KN} \) and \( T_{NI} \) are the solid nematic and the nematic isotropic transition temperatures respectively. \( L/W \) is the length-to-width ratio of the molecules, as calculated by Leenhouts et al. [6].

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T_{KN}(^\circ\text{C}) )</th>
<th>( T_{NI}(^\circ\text{C}) )</th>
<th>( L/W )</th>
</tr>
</thead>
<tbody>
<tr>
<td>APAPA</td>
<td>82</td>
<td>109.00</td>
<td>3.25</td>
</tr>
<tr>
<td>APAPA2</td>
<td>72</td>
<td>110.87</td>
<td>3.46</td>
</tr>
<tr>
<td>APAPA3</td>
<td>53</td>
<td>112.57</td>
<td>3.68</td>
</tr>
<tr>
<td>APAPA4</td>
<td>61</td>
<td>100.45</td>
<td>3.87</td>
</tr>
<tr>
<td>APAPA5</td>
<td>83</td>
<td>104.36</td>
<td>4.02</td>
</tr>
<tr>
<td>APAPA9</td>
<td>76</td>
<td>97.05</td>
<td>4.43</td>
</tr>
<tr>
<td>OHMBBA</td>
<td>44</td>
<td>65.00</td>
<td></td>
</tr>
</tbody>
</table>

In section 2 the experimental light scattering arrangement is described. In this section we also discuss in some detail the quality control of our samples. Section 3 deals with the experimental methods and the analysis of the experimental data.

Fig. 1. — Experimental set-up.
Further details about these samples are given in section 2.1. The samples were placed between two heating stages (Mettler FP 52), which kept the temperature constant to within 0.01 K. Two holes in the heating stages made it possible for the incident and scattered light to be transmitted.

The director \( n_0 \) as well as the direction of the polarizer \( (i) \) and analyser \( (f) \) could be chosen at will. As is pointed out in section 3 a judicious choice of \( n_0, i \) and \( f \) with respect to the scattering plane makes it easier to determine the viscoelastic properties of the NLC.

### 2.1 QUALITY CONTROL OF THE SAMPLE CONTAINING NLC.

- Rubbing the surfaces of the clean glass plates in one direction causes small parallel grooves. In contact with the glass walls the NLC aligns parallel to these grooves, since this alignment is most favourable in terms of the distortion free-energy density.

- The uniformity of the alignment was checked with the help of two techniques, namely
  1. Examining the local optical axis of the NLC;
  2. Examining the diffraction pattern of the depolarized scattered light.

Since the optical axis of the birefringent NLC is parallel to the director, an examination of this optical axis yields direct information concerning the alignment. To this end we applied a microprojection technique with the above set-up. With this technique one can study the part of the sample by which the laser light is scattered. The laser light transmitted by the NLC is focused on a screen or a photographic film presenting an image of the NLC as if it were a slide. The direction of polarization of the incident light with respect to the director could be chosen at will by means of the polarizer. The polarization of the transmitted light was examined with the help of an analyser.

Since NLC's are birefringent, the transmitted light can only be extinguished if the polarizer and analyser are crossed and are parallel or perpendicular with respect to the optical axis of the NLC. If the NLC is not uniformly aligned in parallel not all transmitted light can be extinguished, since locally the optical axis is not parallel to the mean optical axis of the sample.

We found that it was always possible to achieve complete extinction of the transmitted light. However, it turned out that the angle between polarizer and analyser at complete extinction differed systematically from 90°. For all compounds studied, the direction of polarization was rotated by about 3°-5° in a clockwise direction (for nematic layers of 25 µm thickness (cf. Fig. 2)). These angles were determined by comparing the directions of the polarization and analyser at complete extinction in both the nematic and the isotropic phase. Since the compounds studied are not optically active we are tempted to ascribe this effect to some impurity-induced cholesteric behaviour. Note that the rubbed glass walls should force the NLC to align in a purely planar fashion. Therefore the degree of rotation of the director will depend on the anchoring conditions. Clearly the anchoring achieved by rubbing is not entirely satisfactory. Unfortunately, many of the superior methods of preparing high quality planar samples do not work at temperatures above 100°. We therefore corrected our light scattering results for the small optical rotations found.

Insufficient rubbing of the glass plates causes local differences in the degree of anchoring. This implies that the nematic layer is not uniformly strongly anchored. Small local differences (\(< 1°\)) will occur in the rotating of the director, because of the supposed small cholesteric tendencies. In that case not all transmitted light can be extinguished by the analyser and the remaining transmitted light could be mistaken for depolarized scattered light.

In these cases it turned out that there was still a good correlation of the directions of alignment in the rubbing direction. In fact insufficient rubbing only caused differences in the alignment in a direction perpendicular to the rubbing direction.

This effect works like a diffraction grating, but with the parallel scratches at random distances. As a consequence the effect causes a diffraction pattern of light polarized perpendicular to the transmitted laser light. An example of such a diffraction pattern is shown in figure 3. Obviously this diffraction effect will influence angular dependent light scattering experiments, especially at small scattering angles and in the configuration where the director is perpendicular to the scattering plane. Note that measurements of the angular dependence of the spectral noise intensity of the scattered light may be influenced, since the diffracted (unmodulated) light will mix with the scattered light (heterodyne mixing).

As a consequence great care was taken to avoid making measurements with samples where such a diffraction effect occurred.
Fig. 3. — Diffraction pattern of an insufficiently rubbed sample. The mean direction of alignment of the NLC is indicated by an arrow. The very weak darkening on the background is caused by depolarized scattering. Good rubbed and aligned samples will not show such diffraction.

2.2 QUALITY CONTROL OF THE NLC ITSELF. — Thermal decomposition of the molecules decreases the purity of the NLC. As a consequence $T_{NI}$ drops slowly with time (max. 0.05 °C/hour at $T \approx T_{NI}$). Therefore measuring $T_{NI}$ regularly is a good method of checking the purity of the NLC. Another method of checking the quality of the NLC is to observe the characteristics of the nematic-isotropic transition with the help of the above-mentioned microprojection technique. The temperature range at which the transition takes place is important, so are the kinetics and morphology of the transition. On average it turned out that our samples were of good quality for at least four hours.

In figures 4 a-c the nematic-isotropic phase transition is shown for the compound APAPA. These photographs show the part of the sample illuminated by the laser beam, as observed through the holes in the heating stage. Due to the presence of these holes the

Figs. 4a-c. — Typical example of an isotropic to nematic phase transition for the compounds studied. In this example with APAPA at a temperature of $T = 109.00$ °C the lighter nematic areas come into existence (a), increase (b; $T = 108.90$ °C), and finally the (darker) isotropic areas disappear (c; $T = 108.80$ °C).
temperature in the centre of this part is approximately 0.01 °C lower than at its edges. Absorption of the incident light was found to have a negligible effect on the sample temperature. Therefore, at the isotropic-to-nematic transition the first nematic domains will be observed in the centre of the scattering volume.

A quite different and rather remarkable transition behaviour was observed for APAPA2 and -4. Such a transition is shown in figures 5a-e. By decreasing the temperature some domains develop and grow in the same way as described above (Fig. 5a). However, these areas show no birefringence at all, since the transmitted light can be extinguished completely by means of crossed — but otherwise unaligned — polarizers. Hence the molecules in these domains are not orientationally ordered. These domains then coalesce to form one domain (Fig. 5b). When the temperature is lowered by a few hundredths of a degree, the centre of this domain becomes birefringent (Fig. 5c). Note that there is a sharp interface between the non-birefringent and birefringent domains, suggesting that these represent distinct phases. At a temperature of about 0.2 °C below the first transition effects this alignment becomes uniformly planar oriented and any disorder disappears (Fig. 5e). We do not believe that the intermediate phase could be a chiral impurity-induced cholesteric blue phase. At present we can offer no explanation for the observed phenomenon.

Figs. 5a-e. — Isotropic-nematic transition for APAPA2. At $T = 110.90$ °C areas come into existence (a) which are not anisotropic, in contrast to what we expect. At $T = 110.88$ °C these areas become one non-birefringent area (b) in which at $T = 110.85$ °C anisotropic behaviour appears (c), which has birefringent properties, as is demonstrated by crossing the polarizers (d). At $T = 110.80$ °C the disordering disappears and the sample becomes uniformly planar aligned (e).
3. Optical determination of the viscous and elastic properties.

In earlier papers [9, 10] we described the experimental techniques used to determine the viscous and elastic properties of NLC’s by laser light scattering. In summary,

1) viscoelastic data can be obtained by measuring the angular dependence of the spectral noise intensity of the scattered light;
2) elastic data can be obtained by measuring the angular distribution of the scattered light.

The expression for the noise intensity spectrum derived by van Eck et al. [4] is given by

\[ S_{\text{nf}}(\omega, q) = \beta^2 \left\{ \frac{G_1^2 G_2^2}{K_1(q) K_2(q)} \times \right. \\
\left. \times \frac{1/\tau_1 + 1/\tau_2 + \sum G^4_s}{\omega^2 + (1/\tau_1 + 1/\tau_2)} \right\}, \]

where \( \beta \) is a function of the dielectric anisotropy, the scattering volume, the distance between this volume and the point of observation, the incoming electric field and absolute temperature \( T \). (At constant temperature, \( \beta \) is a constant; this information is not needed for the determination of the viscoelastic properties.) The optical geometry factor \( G \) is defined by \( G = (\mathbf{i} \cdot \mathbf{q}) + (\mathbf{k} \cdot \mathbf{q}) \), where the vectors \( \mathbf{i} \) and \( \mathbf{k} \) are the polarization vectors of the incoming and scattered light respectively. The vector components are considered with respect to an orthonormal coordinate system defined by the following base vectors \( \mathbf{e}_3 \equiv \mathbf{n}_0 \), \( \mathbf{e}_2 \equiv (\mathbf{n}_0 \times \mathbf{q})/|\mathbf{n}_0 \times \mathbf{q}| \), \( \mathbf{e}_1 \equiv \mathbf{e}_2 \times \mathbf{e}_3 \), where \( \mathbf{q} \) is the scattering wave vector, \( \mathbf{q} = \mathbf{k} - \mathbf{k}_s \). Note that \( q_s = 0 \). The elasticity function is given by

\[ K_s(q) = K_s q_1^2 + K_s^3 q_1^2 \]  

(2)

where \( K_s \) is a distortion elastic constant, which depends only on the physical properties of the NLC. The elastic constants associated with the splay (\( K_1 \)), twist (\( K_2 \)), or bend (\( K_3 \)) deformation are often referred to as the Frank constants [5]. The components \( q_{11} \) and \( q_{12} \) of the scattering wave vector are parallel and normal to the director \( \mathbf{n}_0 \) respectively.

The relaxation time \( \tau_\alpha \) in equation (1) is given by [3]

\[ \tau_\alpha = \frac{\eta_{\text{eff}}(q)/K_s(q)}{\eta_{\text{eff}}(q)} \]  

(3)

The viscosity function \( \eta_{\text{eff}}(q) \) has the dimension of viscosity and is given by

\[ \eta_1(q) = \gamma_1 - (\alpha_3 q_1^2 - \alpha_2 q_1^2)/\eta_2 q_1^2 + (\eta_1 + \eta_2 + \eta_13) q_1^2 q_1^2 + \eta_1 q_1^2 \]  

\[ \eta_2(q) = \gamma_2 - (\alpha_3 q_1^2)/\eta_3 q_1^2 + \eta_1 q_1^2 \]  

(4)

where \( \gamma_1 \) is the rotational (or twist) viscosity, \( \eta_{\text{eff}}(\alpha = 1, 2, 3) \) is a (positive) Mie\-słowicz coefficient and \( \alpha_\ell \) is a Leslie coefficient [1, 12].

In the special cases where \( q_{11} = 0 \) or \( q_{12} = 0 \), \( \eta_{\text{eff}}(q) \) is independent of \( q \) and related to the distortion viscosities[10], i.e.

\[ \eta_1(q; q_{12} = 0) = \eta_{\text{sl}} \]  

\[ \eta_2(q; q_{12} = 0) = \eta_{\text{tw}} \]  

(5)

and

\[ \eta_1(q; q_{11} = 0) = \eta_{\text{sl}}(q; q_{11} = 0) = \eta_{\text{bend}} \]  

(6)

Hence,

\[ \eta_{\text{sl}} = \gamma_1 - \alpha_3 q_1^2/\eta_2 \]  

\[ \eta_{\text{tw}} = \gamma_1 \]  

\[ \eta_{\text{bend}} = \gamma_1 - \alpha_3 q_1^2/\eta_1 \]  

(7)

The angular distribution of the time averaged intensity of the scattered light, i.e. the differential cross section \( \text{d}^\circ \) per solid angle \( \text{d}^\Omega \), is given by

\[ I(\theta) = \frac{d^\circ(q)}{d^\Omega} = \frac{1}{\beta} \sum_{\alpha = 1, 2} \frac{G^2}{K_s(q)} \]  

(8)

In an earlier paper [10] we described in some detail the two optical configurations which are best suited for the determination of the distortion viscoelastic and elastic ratios. These configurations (cf. Fig. 6) are used in the present experiments and will be referred to as configuration 1 and configuration 2. Note that with these two configurations the rather complicated equations (1, 4) are reduced to simpler forms.

In configuration 1, where \( q_{11} = 0 \), equations (4) reduce to equations (5) and equation (8) reduces to

\[ I(\theta) \sim \sum_{\alpha = 1, 2} \frac{G^2}{K_s(q)} q_{11}^2 \]  

(9)

Using configuration 1 light scattering that is due only to a combination of splay and twist distortion fluctuations will be observed. In configuration 2 we have \( G_s = 0 \) and equation (1) reduces to one Lorentzian (\( \alpha = 2 \)) which has only one bandwidth \( \omega_1 = 2/\tau_2 \). Equation (8) now becomes

\[ I(\theta) \sim 1/(K_2 q_{11}^2 + K_3 q_{11}^2) \]  

(10)

Fig. 6. — Schematic diagrams of the optical configurations (indicated by 1 and 2 respectively) used in experiments.
Note that in both configurations the relative contributions caused by two different types of distortion in each configuration depend on the ratios $G_1/G_2$ (in configuration 1) and $q_1/q_2$ (in configuration 2). As a consequence, since $G_\alpha$ ($\alpha = 1, 2$) and $q$ are well-known functions of the scattering angle $\theta$, the relative contributions can be varied by changing the scattering angle $\theta$. Angle dependent measurements of optical properties of the scattered light now make it possible to unravel these particular contributions with the help of computer procedures [10].

By fitting the measured angular distributions of the scattered light to equation (8), we determined the ratios of the splay, twist and bend elastic constants with an error of 2\% (cf. refs. [9, 10]). Experimental results for the angular dependences of the spectral noise intensity $S_\omega(\omega)$ were analysed by computer fitting, as discussed in ref. [10]. These analyses yield the splay, twist and bend viscoelastic ratios as well as the ratio of two Mie\-\-sowicz coefficients, $\eta_3/\eta_1$. Figures 7 to 12 show the experimental results for the splay, twist and bend elastic and viscoelastic ratios and for $\eta_3/\eta_1$ as a function of the reduced temperature $T/T_N$. The statistical error in the elastic and viscoelastic ratios is about 2\%. The statistical error in $\eta_3/\eta_1$ is about 5\%. These results have also been collected in tables II a-f.

4. Discussion.

4.1 ELASTICITY. — Our experimental data of the elastic ratios can now be compared with the data obtained by Leenhouts [6] who used the Fr\-\-édericksz transitions method. In table III we have listed our

![Fig. 7. — Experimental results for the splay/twist elastic ratios, $K_1/K_2$ versus the reduced temperature, $T/T_N$ (●: APAPA, ▲: APAPA2, ▼: APAPA3, ■: APAPA4, ×: APAPA5, +: APAPA9, *: OHMBBA).](image)

![Fig. 8. — Experimental results for the bend/twist elastic ratios, $K_3/K_2$ versus the reduced temperature, $T/T_N$ (●: APAPA, ▲: APAPA2, ▼: APAPA3, ■: APAPA4, ×: APAPA5, +: APAPA9, *: OHMBBA).](image)

![Fig. 9. — Experimental results for the splay viscoelastic ratios, $\eta_{splay}/K_1$ versus the reduced temperature, $T/T_N$ (●: APAPA, ▲: APAPA2, ▼: APAPA3, ■: APAPA4, ×: APAPA5, +: APAPA9, *: OHMBBA).](image)

values for $K_1/K_2$ and $K_3/K_2$ and those of Leenhouts, measured at a reduced temperature of $T/T_N = 0.96$. It is obvious that our data of both ratios are systematically about 10\% higher than those of Leenhouts. The reason for this difference is not understood at present.

Figure 13 shows the bend/splay elastic ratios at $T/T_N = 0.96$ for the compounds APAPAm ($m = 1-5, 9$), calculated from the above ratios. For comparison we have added the corresponding data
of Leenhouts. The results are seen to agree rather well. In contrast to experimental results for series of rigid molecules (cf. e.g. ref. [6]), i.e. molecules without flexible chains, it turned out that $K_3/K_1$ is not proportional to $L/W$ (cf. Fig. 13). On the basis of experimental results for homologous series of nematic azoxybenzenes with flexible chains, de Jeu et al. [13] attributed this effect qualitatively to a short-range smectic-like correlation that increases with increasing alkyl chain length. This idea has been worked out in a more quantitative fashion in a recent publication by van der Meer et al. [14]. Note that de Vries [15] already demonstrated some smectic-like behaviour in NLC (cybotactic nematics).

From our elastic data we calculated the reduced values of $K_i$, i.e. $K_i^R = (K_i - \bar{K})/\bar{K}(i = 1, 2, 3)$ where $\bar{K}$ is the average value of $K_i$. Table IIa.

### Table IIa. — Experimental results for the splay/twist elastic ratios $K_1/K_2$.

<table>
<thead>
<tr>
<th></th>
<th>$\eta_{\text{twist}}/K_2$</th>
<th>$\eta_{\text{bend}}/K_3$</th>
<th>$\eta_{\text{in}}/\eta_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>APAPA</td>
<td>0.9990 1.45</td>
<td>0.9994 1.355</td>
<td>0.9994 1.396</td>
</tr>
<tr>
<td>APAPA</td>
<td>0.9980 1.48</td>
<td>0.9978 1.39</td>
<td>0.9988 1.424</td>
</tr>
<tr>
<td>APAPA</td>
<td>0.9951 1.53</td>
<td>0.9947 1.41</td>
<td>0.9960 1.53</td>
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<td>APAPA</td>
<td>0.9915 1.58</td>
<td>0.9927 1.43</td>
<td>0.9916 1.549</td>
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<td>APAPA</td>
<td>0.9899 1.48</td>
<td>0.9798 1.463</td>
<td>0.9842 1.565</td>
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<td>APAPA</td>
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<td>OHMBBA</td>
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<td>0.9015 1.699</td>
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<td>OHMBBA</td>
<td>0.9098 1.660</td>
<td>0.8704 1.765</td>
<td>0.9000 1.915</td>
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</table>

Fig. 10. — Experimental results for the twist viscoelastic ratios, $\eta_{\text{twist}}/K_2$ versus the reduced temperature, $T/T_{NI}$ (O : APAPA, D : APAPA2, V : APAPA3, A : APAPA4, X : APAPA5, + : APAPA9, * : OHMBBA).

Fig. 11. — Experimental results for the bend viscoelastic ratios, $\eta_{\text{bend}}/K_3$ versus the reduced temperature, $T/T_{NI}$ (O : APAPA, D : APAPA2, V : APAPA3, A : APAPA4, X : APAPA5, + : APAPA9, * : OHMBBA).

Fig. 12. — Experimental results for the ratios of two Mięsowicz viscosity coefficients, $\eta_3/\eta_1$ versus the reduced temperature, $T/T_{NI}$ (O : APAPA, D : APAPA2, V : APAPA3, A : APAPA4, X : APAPA5, + : APAPA9, * : OHMBBA).
### Table IIb. — Experimental results for the bend/twist elastic ratios \( K_3/K_2 \).

<table>
<thead>
<tr>
<th>APAAP</th>
<th>APAAP2</th>
<th>APAAP3</th>
<th>APAAP4</th>
<th>APAAP5</th>
<th>APAAP6</th>
<th>OCHMBA</th>
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</thead>
<tbody>
<tr>
<td>T/( T_{\text{RT}} )</td>
<td>( K_3/K_2 )</td>
<td>T/( T_{\text{RT}} )</td>
<td>( K_3/K_2 )</td>
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### Table IIc. — Experimental results for the splay viscoelastic ratios \( \eta_{\text{splay}}/K_1 \times 10^9 \text{ sm}^{-2} \).

### Table IId. — Experimental results for the twist viscoelastic ratios \( \eta_{\text{twist}}/K_2 \).

### Table IIe. — Experimental results for the bend viscoelastic ratios \( \eta_{\text{bend}}/K_3 \times 10^9 \text{ sm}^{-2} \).
Table III. — The splay/twist and bend/twist elastic ratios at $T/T_{NI} = 0.96$, obtained (1) from measurements of the angular distribution of the scattered light and (2) from the Fréedericksz transitions method (Leenhouts et al. [6]).

\[
\begin{array}{cccccc}
\text{Compound} & \frac{K_1}{K_2} & \frac{K_1}{K_2} & \frac{K_1}{K_2} \\
\text{(1)} & \text{(2)} & \text{(1)} & \text{(2)} \\
\text{APAPA} & 1.660 & 1.597 & 2.200 & 2.950 \\
\text{APAPA2} & 1.345 & 1.363 & 2.470 & 2.444 \\
\text{APAPA3} & 1.645 & 1.528 & 2.570 & 2.574 \\
\text{APAPA4} & 1.800 & 1.601 & 2.280 & 2.051 \\
\text{APAPA5} & 1.920 & 1.702 & 2.950 & 2.399 \\
\text{APAPA6} & 2.200 & 2.013 & 2.310 & 1.934 \\
\text{OHMBBA} & 2.040 & 1.642 & 1.835 & 1.735 \\
\end{array}
\]

$K$ stands for the arithmetic mean value of $K_i$, i.e. $K = \frac{1}{3} \sum K_i$. Figure 14 shows that $K_2^R$ is independent of the alkyl chain length, $m$. $K_1^R$ and $K_2^R$ approach each other as $m$ is increased. Apparently, only splay and bend distortions are affected by a change in the length of the alkyl chains. Priest [16] predicted on the basis of a mean field theory that

\[
\begin{align*}
K_1^R &= \Delta - 3 \Delta' \left( \frac{\langle P_4 \rangle}{\langle P_2 \rangle} \right) \\
K_2^R &= -2 \Delta - \Delta' \left( \frac{\langle P_4 \rangle}{\langle P_2 \rangle} \right) \quad (11) \\
K_3^R &= \Delta + 4 \Delta' \left( \frac{\langle P_4 \rangle}{\langle P_2 \rangle} \right),
\end{align*}
\]

where $\Delta$ and $\Delta'$ are constants depending on molecular properties. The quantities $\Delta$ and $\Delta'$ can be calculated if the molecules can be represented as spherocylinders interacting via hard core repulsions [16] (Onsager model). Note, however, that any attractive interaction is neglected in this model. It turned out that the values of $K_3^R$ predicted by this model are in disagreement with the experimental data [6, 11].

Van der Meer et al. [17] derived expressions for $\Delta$ and $\Delta'$ using pair interactions of non-axially sym-
They found where the dimensionless coefficients $j_1$ and $\mu_1$ are related to attractive and to repulsive interactions respectively. In order to fit our data to these predictions we calculated $A$ and $\Delta' \left( \frac{\langle P_4 \rangle}{\langle P_2 \rangle} \right)$ according to (cf. Eq. (11))

$$A = (4 K_3^R + 3 K_3^S)/\gamma,$$

$$\Delta' \left( \frac{\langle P_4 \rangle}{\langle P_2 \rangle} \right) = (K_3^R - K_3^S)/\gamma. \quad (13)$$

The results for $\Delta$ are shown in figure 15. The curves through the data points are the best fits to equation (12). In table IV we give the ratios of $j_1$ and $\mu_1$ obtained by these fittings. Since no accurate values of $\left( \frac{\langle P_4 \rangle}{\langle P_2 \rangle} \right)$ are available at present it was not possible to fit equation (12) to our data of $\Delta' \left( \frac{\langle P_4 \rangle}{\langle P_2 \rangle} \right)$ in an accurate way. In table V we collected the experimental values of $\Delta' \left( \frac{\langle P_4 \rangle}{\langle P_2 \rangle} \right)$, calculated according to equation (13) at a reduced temperature of $T/T_{NI} = 0.96$. We also give these values at equal values of the experimental order parameters (from Leenhouts [18]).

The distortion viscoelastic ratios on $m$. In fact the different viscoelastic ratios have the same order of magnitude at all values of $m$ (at a certain $T$). As the distortion elastic ratios are known it is possible to calculate the distortion viscous ratios, $\eta_{splay} : \eta_{twist} : \eta_{bend}$, from the measured viscoelastic ratios. Figure 16 shows the results of these calculations for $\eta_{splay} / \eta_{twist}$ and $\eta_{bend} / \eta_{twist}$. Note that these data satisfy the conditions $\eta_{splay} / \eta_{twist} \leq 1$ and $\eta_{bend} / \eta_{twist} \leq 1$ (cf. Eq. (7)).


\begin{table}[h]
\centering
\caption{The ratios $j_1/j_0$, $\mu_1/j_1$ and $\mu_0/j_0$ determined by fitting the experimental data of $A$ to Eq. (12).}
\begin{tabular}{|c|c|c|}
\hline
\text{Compound} & $j_1/j_0$ & $\mu_1/j_1$ \\
\hline
APAPA & 0.2101 & 0.9867 \\
APAPA2 & 0.2246 & 0.9643 \\
APAPA3 & 0.2132 & 0.9838 \\
APAPA4 & 0.2328 & 0.9551 \\
APAPA5 & 0.2356 & 0.9828 \\
APAPA6 & 0.2678 & 0.9847 \\
OHMBBA & 0.2194 & 0.9882 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{The values for $\Delta' \left( \frac{\langle P_4 \rangle}{\langle P_2 \rangle} \right)$, calculated according to Eq. (13) at temperatures where $\langle P_2 \rangle = 0.55$.}
\begin{tabular}{|c|c|c|}
\hline
\text{Compound} & $\Delta' \left( \frac{\langle P_4 \rangle}{\langle P_2 \rangle} \right)$ & $T/T_{NI}$ \\
\hline
APAPA & 0.102 & 0.9695 \\
APAPA2 & 0.083 & 0.9546 \\
APAPA3 & 0.062 & 0.9773 \\
APAPA4 & 0.034 & 0.9702 \\
APAPA5 & 0.055 & 0.9797 \\
APAPA6 & 0.002 & 0.9813 \\
OHMBBA & -0.034 & 0.9701 \\
\hline
\end{tabular}
\end{table}
We also calculated in accordance with reference [11] the values for the reduced Miesowicz viscosity coefficients \( \eta_i \) (i = 1, 2, 3), i.e. \( \eta_i^R = (\eta_i - \bar{\eta})/\bar{\eta} \) (cf. Fig. 17) as well as the values for \( |\alpha_3/\alpha_2| \) (cf. Fig. 18). The viscosity \( \bar{\eta} \) is defined by \( \bar{\eta} = \frac{1}{2} \sum \eta_i \). Note that the ratios of the Miesowicz coefficients can be calculated quite easily from our experimental values of \( \eta_3/\eta_1 \) and \( \eta_{\text{play}}/\eta_{\text{bend}} \); since \( \eta_{\text{play}}/\eta_{\text{bend}} = \eta_1/\eta_2 \) [11]. The values of \( |\alpha_3/\alpha_2| \) were calculated with the help of the relation \( (\alpha_3/\alpha_2)^2 = (\eta_{\text{twist}}/\eta_{\text{play}} - 1)/(\eta_{\text{twist}}/\eta_{\text{bend}} - 1) \) (cf. Eq. (7) and Ref. [11]). For a more detailed discussion of the above-mentioned ratios of APAPA as a function of temperature we refer to reference [11].

It turned out (cf. Figs. 16, 17) that the ratios of the distortion viscosity coefficients as well as the reduced Miesowicz viscosity coefficients are rather similar for the various compounds. These results are somewhat counterintuitive. One would be inclined to expect that an increase in the length of a molecule will cause an increase in the anisotropic behaviour of the NLC. Apparently, however, the dynamical properties of the compounds studied are rather independent of the size of the alkyl chains. Similar independence was also found in the viscosities of some compounds of the series of cyanobiphenyls and azoxybenzenes as measured by Knepper et al. [19] using shear flow techniques. Note that their data on \( \eta^R \) are very similar to ours. In contrast to Knepper et al., however, we find that \( \eta_2^R \approx \eta_3^R \).

Although the above viscosity coefficients show no obvious dependence on the sizes of the molecules, the values for \( |\alpha_3/\alpha_2| \), shown in figure 18 are of interest since Helfrich predicted that [20]

\[
\alpha_3/\alpha_2 \approx (W/L)^2. \tag{14}
\]

By considering table VI, where we collected the values for \( |\alpha_3/\alpha_2| \) and \((W/L)^2\) for the compounds studied (at \( T/T_{NI} = 0.96 \)), we can conclude that equation (14) is satisfied to within an order of magnitude. The predicted trend that \( \alpha_3/\alpha_2 \) will decrease with \( m \) seems to be fulfilled, except in the case of APAPA9.

Since our optical experiments yield only ratios of viscosity and elasticity coefficients we are not able to determine the absolute values of these coefficients. However, from the Frédéricksz transitions Leenhouts [6] determined the absolute values of the distortion elastic constants. Now that we know these constants, we are able to calculate from our viscoelastic data the absolute values of the distortion viscosity coefficients. In a previous publication (Ref. [9]) we found \( \eta_{\text{twist}} \sim \langle P_2 \rangle/T \). With this result in mind we have plotted in \( \eta_{\text{twist}} \) versus \( \langle P_2 \rangle/T \) in figure 19, where we have used the data of \( \langle P_2 \rangle \)

| Table VI. | The determined values of \( |\alpha_3/\alpha_2| \) at \( T/T_{NI} = 0.96 \) and the values for \((W/L)^2\) (from Leenhouts [6]) of the compounds studied. |
|-----------|-----------------|-----------------|
| Compound  | \( |\alpha_3/\alpha_2| \) | \((W/L)^2\) |
| APAPA     | 0.145           | 0.095           |
| APAPA2    | 0.134           | 0.084           |
| APAPA3    | 0.087           | 0.074           |
| APAPA4    | 0.0617          | 0.067           |
| APAPA5    | 0.0469          | 0.062           |
| APAPA9    | 0.131           | 0.051           |
| OHMBBA    | 0.25            |                 |

Fig. 17. — The reduced Miesowicz coefficients versus the reduced temperature (1 : APAPA, 2 : APAPA2, 3 : APAPA3, 4 : APAPA4, 5 : APAPA5, 9 : APAPA9, OH : OHMBBA).
Fig. 19. — The natural logarithm of the rotational or twist viscosity versus $P/T_0$ (●: APAPA, ▲: APAPA2, ▼: APAPA3, ■: APAPA4, ×: APAPA5, +: APAPA9, *: OHMBBA).

from reference [18]. From the figure it can be seen that for the homologous series studied the rotational viscosity can be approximated by

$$\eta_{\text{twist}} = \gamma_1 = \text{const.} e^{(P_2)/\eta_2 T}, \quad (15)$$

where the constant $\varepsilon$ is generally called an activation energy. For all compounds we found $\varepsilon = 0.20 \pm 0.02$ eV.

The compound MBBA differs from OHMBBA only by the fact that the OH-chain is replaced by a single H-atom. As a consequence the molecules of these two compounds will have the same length but will differ somewhat in width.

Table VII. — Viscosities of OHMBBA and MBBA (from refs. [21, 22]) at $T/T_{NI} = 0.9431$.

| Compound | $\eta_1^R$ | $\eta_2^R$ | $\eta_3^R$ | $|\alpha_3/\alpha_2|$ | $\gamma_1$ [Pa.s] |
|----------|------------|------------|------------|-----------------|-----------------|
| OHMBBA   | 1.06       | -0.51      | -0.56      | 0.29            | 0.113           |
| MBBA     | 0.947      | -0.617     | -0.330     | 0.011           | 0.095           |

In order to investigate the influence of the OH-chain of OHMBBA we have collected in table VII our experimental data for the viscous properties of OHMBBA as well as the viscous data of MBBA obtained from literature [21, 22]. Apparently the data of MBBA differ significantly from those of OHMBBA for $|\alpha_3/\alpha_2|$. To our opinion, however, this rather large difference cannot be explained completely in terms of equation (14). An explanation in terms of dipolar interaction due to the polarized OH-chain seems to be more relevant.

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