

Physical Properties of Liquid Crystalline Materials in Relation to Their Applications†

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A short review is given of successively the diamagnetic susceptibility, the refractive index, the dielectric permittivity, the elastic constants and the viscosity coefficients of nematic liquid crystals. Emphasis is on typical results that have been obtained, and the possibilities and problems connected with a molecular interpretation. In particular an attempt is made to distinguish in the macroscopic quantity the influence of the molecular properties involved, of the direct temperature dependence, and of the dependence on the orientational order (indirect temperature dependence).

1 INTRODUCTION

The application of liquid crystals in display devices and as solvents in nuclear magnetic resonance spectroscopy and chromatography, lays down certain requirements for the mesomorphic materials. These can be written as: a certain nematic temperature range, often preferably around room temperature; chemical properties, for example (photo)chemical stability, colour, safety in handling; physical properties, for example birefringence, sign and magnitude of dielectric anisotropy.

In fact the “molecular engineering” to obtain classes of liquid crystal that fulfil these requirements is largely responsible for the success of present-day applications. Many examples can be found in the review by Demus.¹ In this paper we restrict ourselves to the last point: physical properties. In this respect three aspects are important:

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—Molecular properties, e.g., the molecular tensor that gives rise to a certain macroscopic property.

—Direct temperature dependence, for example, the activation energy associated with a viscosity.

—Indirect temperature dependence, in the first place *via* the dependence on the orientational order, but also *via* the density and possibly other factors.

Of these, only the first point is usually accessible to molecular engineering. For that reason it is important to be able to distinguish these various aspects. To do so, one has to consider the processes through which an anisotropic molecular property leads to a macroscopic anisotropy. In general this is only possible if one dares to rely on approximate models to represent the real molecules.

In the following I shall review some properties that are important in present-day applications. After a short summary of the orientational statistics of the molecules, successively the diamagnetic susceptibility, the refractive index, the dielectric permittivity, the elastic constants, and the viscosity coefficients will be considered. Emphasis will be on the type of results that have been obtained and the problems connected with its interpretation. Results of more theoretical discussions will just be stated. For derivations and more details reference is made to my recent book,² on which this review strongly relies.

2 ORIENTATIONAL STATISTICS

Let us consider a nematic sample with a uniform preferred direction given by the director \mathbf{n} , which is taken along the z axis of a laboratory-fixed coordinate system x, y, z . To specify the orientation of a molecule with respect to this system one can introduce a molecule-fixed coordinate system ξ, η, ζ . The ζ axis is along the molecular axis. The orientation of the molecule is completely determined by the three Euler angles α, β and γ ³ (see Figure 1):

α : angle between the y axis and the normal to the z, ζ plane, describing a rotation of the molecule around the director.

β : angle between the z axis and the ζ axis.

γ : angle between the η axis and the normal to the z, ζ plane, describing a rotation of the molecule around its long axis.

Because of the uniaxial symmetry of the nematic phase the angle α does not come into play. The other angles play a crucial role in the discussion. With a physical property, usually a molecular tensor of rank two is associated, whose elements are needed in the laboratory system. This is accomplished through a series of transformations³ through the angles β and γ , and by taking an ensemble average over all possible orientations.

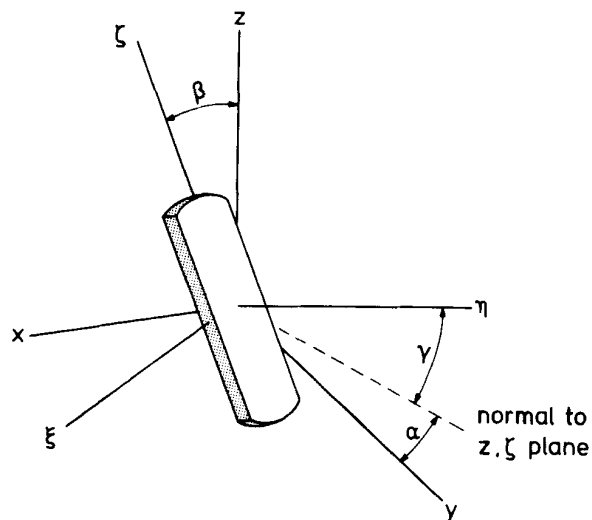


FIGURE 1 Definition of the molecular frame and the three Euler angles.

In the case of real molecules, the first problem is how to define the molecular frame. Usually the relatively rigid aromatic core is considered to be the most relevant part for this choice. For molecules with a *trans*-configuration the axis through the two outer *para*-carbon atoms of the aromatic part is often taken as the ζ axis. If the various benzene rings are coplanar (as for example with azobenzenes), the ξ , ζ plane is identified with this plane. Where such a coplanarity is not present, a plane containing the ζ axis and making equal angles with the planes of the benzene rings can be chosen. In practice, the differences between the various choices that are possible are probably not very important. A second problem is that mesogenic molecules usually contain flexible groups such as, for example, alkyl chains. Moreover, various types of internal rotations are possible. For most of the present discussion we shall assume that, in spite of these considerations, a rigid body can be used to represent a molecule in its "average" conformation. In fact this implies that the time scale of the internal motions is faster than the time scale of the orientational fluctuations. As recently discussed by Emsley *et al.*,⁴ this is not necessarily true. As already pictured in Figure 1, we assume that the molecules possess two mirror planes perpendicular to the ξ and η axis. If the molecules can be assumed to rotate freely around the ζ axis, there is effectively cylindrical symmetry, and the model reduces to that of a rigid rod.

The average orientation of the molecules can be described by an orientational distribution function $f(\beta, \gamma)$, where $f(\beta, \gamma) d\Omega = f(\beta, \gamma) \sin \beta d\beta d\gamma$ is the fraction of molecules with Euler angles between β and $\beta + d\beta$ and γ and

$\gamma + d\gamma$.⁵ The orientational average of a quantity X is then given by

$$\langle X \rangle = \int_0^\pi \sin \beta d\beta \int_0^{2\pi} d\gamma X f(\beta, \gamma). \quad (1)$$

Because \mathbf{n} and $-\mathbf{n}$ are equivalent we have $f(\pi - \beta, \gamma) = f(\beta, \gamma)$. Instead of working with the full distribution function, order parameters are often used. To describe the average orientation of the long molecular axis one considers ξ_z , the projection of a unit vector along the ζ axis on the director, which is used to define an order parameter as:

$$\begin{aligned} \langle P_2 \rangle \equiv S &= \langle \frac{3}{2} \xi_z^2 - \frac{1}{2} \rangle \\ &= \langle \frac{3}{2} \cos^2 \beta - \frac{1}{2} \rangle. \end{aligned} \quad (2)$$

If the distribution of the molecular long axes is random, as in the isotropic phase, we have $\langle \cos^2 \beta \rangle = 1/3$, and $S = 0$. The value $S = 1$ corresponds to the case of perfectly aligned molecules. In practice, S varies from values around 0.3–0.4 at T_{NI} to about 0.8 at much lower temperatures. Hence the deviations from perfect alignment are considerable: $\langle \beta \rangle$ may be as large as 40° ! To specify the average orientation of the molecules further, one must give in addition either $\xi_z^2 = \sin^2 \beta \cos^2 \gamma$ or $\eta_z^2 = \sin^2 \beta \sin^2 \gamma$. It is convenient to take instead

$$\begin{aligned} D &= \frac{3}{2} \langle \xi_z^2 - \eta_z^2 \rangle \\ &= \frac{3}{2} \langle \sin^2 \beta \cos 2\gamma \rangle. \end{aligned} \quad (3)$$

A finite D means that there is a difference in tendency of the two transverse molecular axes to project on the z axis. It does *not* mean that the nematic phase is biaxial. There is no preference for either the ζ axis or the η axis of different molecules to be parallel.

3 MAGNETIC SUSCEPTIBILITY

Although applications of the magnetic susceptibility are not of the utmost importance, we include a short discussion, because the magnetic susceptibility provides a nice simple model example. In the SI system of units the magnetic susceptibility tensor χ of an anisotropic medium is defined in terms of the magnetization \mathbf{M} (per unit volume) and the magnetic induction \mathbf{B} through

$$\mathbf{M}_i = \mu_0^{-1} \chi_{ij} \mathbf{B}_j, \quad i, j = x, y, z \quad (4)$$

where χ_{ij} is an element of χ , and μ_0 is the permeability of free space. Taking

n along the z axis χ is diagonal and takes the form

$$\begin{pmatrix} \chi_{\perp} & 0 & 0 \\ 0 & \chi_{\perp} & 0 \\ 0 & 0 & \chi_{\parallel} \end{pmatrix}.$$

The subscripts \parallel and \perp are used to indicate the components parallel and perpendicular to the director, respectively. The average susceptibility is given by

$$\bar{\chi} = \frac{1}{3} \sum_i \chi_{ii} = \frac{1}{3} (\chi_{\parallel} + 2\chi_{\perp}), \quad (5)$$

while the magnetic anisotropy is defined as

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp} = \frac{3}{2} (\chi_{\parallel} - \bar{\chi}). \quad (6)$$

In addition to the dimensionless volume susceptibility used so far, one can introduce the mass susceptibility $\chi^m = \chi/\rho$ (m^3/kg), where ρ is the density. The molar susceptibility $\chi^M = \chi^m M$, where M is the mass number, refers to a mole of substance. Like most organic substances, liquid crystals are usually diamagnetic. Consequently χ_{\parallel} and χ_{\perp} are small and negative, of the order of 10^{-5} SI units. In SI units χ is a factor of 4π larger than in CGS units; for χ^m and χ^M additional factors of 10^{-3} occur.

Figure 2 shows the magnetic susceptibility of *p*-azoxyanisole (PAA), for which compound the results of various authors agree very well. For *N*-(*p*-methoxybenzilidene)-*p*'-butylaniline (MBBA) there is considerable disagreement amongst the results of different authors, as has already been discussed.^{6c} In the nematic phase, only χ_{\parallel} is measured with the usual methods. As $\bar{\chi}^m$ in the nematic phase equals χ^m measured in the isotropic phase, with Eq. (6) full information on $\Delta\chi$ is available.

In order to discuss a molecular interpretation of χ , let κ be the tensor of the molecular magnetic polarisability. The tensor κ will be diagonal in the molecular frame we have chosen. Transformation to the laboratory coordinate system and averaging over the orientations of the molecules leads⁷ to

$$\langle \kappa \rangle_{\parallel} - \langle \kappa \rangle_{\perp} = [\kappa_{\zeta\zeta} - \frac{1}{2}(\kappa_{\xi\xi} + \kappa_{\eta\eta})]S + \frac{1}{2}[\kappa_{\eta\eta} - \kappa_{\xi\xi}]D. \quad (7)$$

As the diamagnetic moments of the molecules are very small, the interactions between these moments can be ignored. This can be concluded from the fact that the relative diamagnetic permeability $\mu_r = 1 + \chi$ differs only very little from unity. Consequently, the field working on a molecule can be taken as equal to the externally applied field and $\chi_{\parallel} = N\langle \kappa \rangle_{\parallel}$ and $\chi_{\perp} = N\langle \kappa \rangle_{\perp}$, where N is the number of molecules per unit volume. When either $\kappa_{\xi\xi} = \kappa_{\eta\eta}$

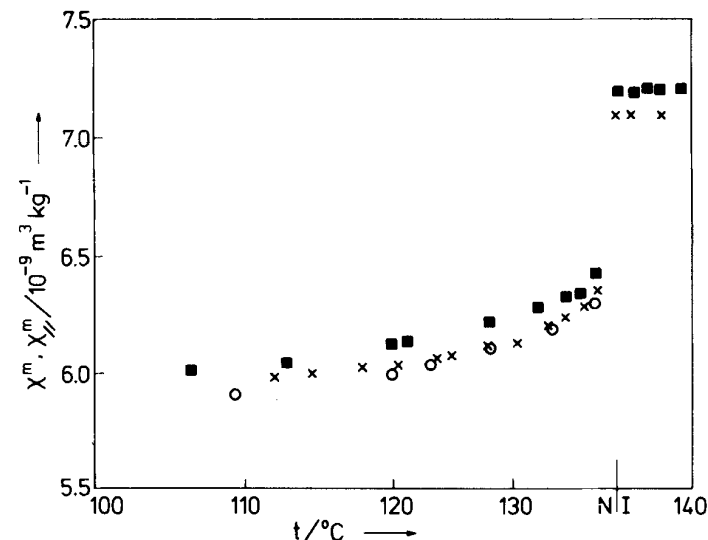


FIGURE 2 Magnetic susceptibility of PAA, ○ Ref. [6a], × Ref. [6b], ■ Ref. [6c].

or $D = 0$, the second term at the right-hand side of Eq. (7) is zero. Taking $\chi_{\perp} = N\kappa_{\xi\xi}$ and $\chi_{\parallel} = \frac{1}{2}N(\kappa_{\xi\xi} + \kappa_{\eta\eta})$ Eq. (7) then can be written as


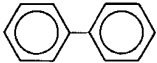

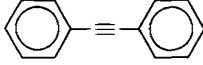
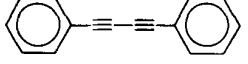
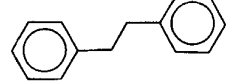
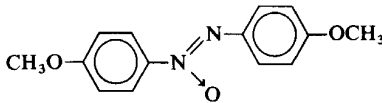
$$\chi_{\parallel} - \chi_{\perp} = (\chi_{\parallel} - \chi_{\perp})S, \quad (8)$$

which is Tvetkov's expression for the order parameter in case of axially symmetric molecules.⁸

A measurement of $\chi_{\parallel} - \chi_{\perp}$ is sufficient to obtain a macroscopic order parameter that distinguishes the nematic from the isotropic phase. To characterize the average degree of orientation of the molecules, we need in principle two parameters, which cannot both be determined from a single experiment. Only if we assume $D = 0$ is the anisotropy of the diamagnetic susceptibility directly proportional to the microscopic order parameter S . Recent nuclear magnetic resonance experiments indicate that D , though rather small, is finite.^{4,9} An upper limit is probably $D \approx S/20$. As at the right-hand side of Eq. (7) both terms between square brackets are of the same order of magnitude, no considerable error is involved when the molecules are taken as axially symmetric. This conclusion is not necessarily true, however, for other physical properties.

The quantity $\chi_{\parallel} - \chi_{\perp}$ can be determined from measurements on a solid single crystal. The only nematogenic compound for which such measurements have been performed is PAA.^{6a} In Table I, the result is compared with that

TABLE I
Molecular diamagnetism¹⁰ of some compounds ($10^{-9} \text{ m}^3 \text{ mol}^{-1}$)

| Compound | χ_{zz} | χ_{yy} | χ_{nn} | $\chi_{\parallel} - \chi_{\perp}$ |
|---|-------------|-------------|-------------|-----------------------------------|
|  | -0.438 | -0.438 | -1.189 | 0.374 |
|  | -0.851 | -0.775 | -2.310 | 0.690 |
|  | -1.216 | -1.107 | -3.409 | 1.042 |
|  | -1.024 | -0.852 | -2.492 | 0.648 |
|  | -1.375 | -0.946 | -2.597 | 0.397 |
|  | -1.141 | -1.141 | -2.542 | 0.701 |
|  | -1.330 | -1.130 | -3.079 | 0.774 |

of biphenyl and with that of other substances related to some classes of liquid crystals.

Diamagnetism is due to changes in the precession of the electrons around the nuclei under the influence of a magnetic field. This leads to an induced magnetic moment that counteracts the field from which it originates, and hence to a negative sign of χ . As atomic susceptibilities are isotropic, one would expect little anisotropy of the susceptibility in the case of molecules as well. However, in aromatic systems, a strong anisotropy is observed.¹¹ Qualitatively this can be attributed to the fact that the π -electrons in a benzene ring are delocalized and form a "ring-current". Consequently, when the magnetic field is perpendicular to the plane of the ring, a large counteracting induced moment can be expected (compare χ_{nn} in Table I). According to Eq. (8) we may then expect in nematic liquid crystals a positive anisotropy of the susceptibility that is proportional to the number of aromatic rings. This proportionality was in fact observed by Tsvetkov and Sosnovsky,^{12a} and is once more illustrated in Figure 3 for some more recently synthesised compounds.^{2, 12b} For a compound with two benzene rings, $\Delta\chi^m$ is of the order $10^{-9} \text{ m}^3/\text{kg}$. For each benzene ring that is replaced by a cyclohexane ring,

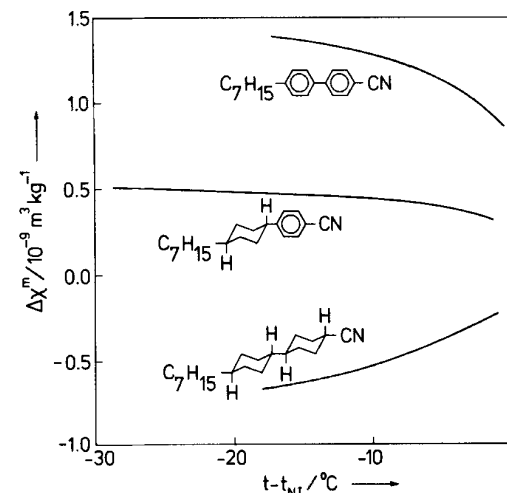
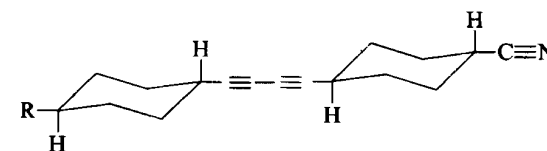


FIGURE 3 Magnetic anisotropy of some nematogenic compounds with different numbers of benzene rings.

the anisotropy of the susceptibility drops. When no aromatic ring is left, $\Delta\chi^m$ has become negative. This is due to the negative anisotropy of the $\text{C}\equiv\text{N}$ bond.¹³ From Table I, we see that an analogous effect is observed for other triple bonds, in particular for the $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ bridge. Qualitatively this effect can be attributed to ring currents perpendicular to the long axis, which are possible in the case of triple bonds. Combining this information, we can expect nematic liquid crystals with a relatively large negative anisotropy for compounds like



which have not yet been synthesised.

4 REFRACTIVE INDEX

A uniaxial (liquid) crystal has two principal refractive indices, n_o and n_e . In the case of a nematic (but not for a chiral nematic) liquid crystal, the optical axis is given by the director, and we have $n_o = n_{\perp}$ and $n_e = n_{\parallel}$. The birefringence is given by $\Delta n = n_e - n_o = n_{\parallel} - n_{\perp}$. In practice, we find $n_{\parallel} > n_{\perp}$;

Δn is therefore positive and varies from values close to zero to about 0.4. More formally, we note that the refractive index is related to the response of matter to an electric field. On application of a field E , an electric polarization P is induced given by

$$P = \varepsilon_0(\varepsilon - \mathbf{I})E, \quad (9)$$

where ε_0 is the permittivity of free space, ε the relative permittivity tensor, and \mathbf{I} the unit tensor. Again taking the director along the z axis, ε will be diagonal. In general ε will depend on the frequency of the applied field. In this section, we are interested in the optical frequency range, where

$$\varepsilon_{ii} = \eta_i^2, \quad i = x, y, z, \quad (10)$$

n_i being the refractive index along the i direction. Furthermore, we have $n_{\parallel} = n_z$ and $n_{\perp} = [\frac{1}{2}(n_x^2 + n_y^2)]^{1/2}$. In Figure 4 we give some results for the refractive indices of PAA at various wavelengths. In the nematic phase, both refractive indices show normal dispersion (n decreases with increasing λ), which is, however, much larger for n_{\parallel} than for n_{\perp} . Figure 5 gives some results for Δn for the series of p,p' -dialkoxyazoxybenzenes. Within the homologous series, there is a pronounced alternation of Δn . For some other recent results we refer to Ref. [15].

In order to give a molecular interpretation of the refractive index, we have to consider the polarizability tensor α , associated with a molecule. This gives

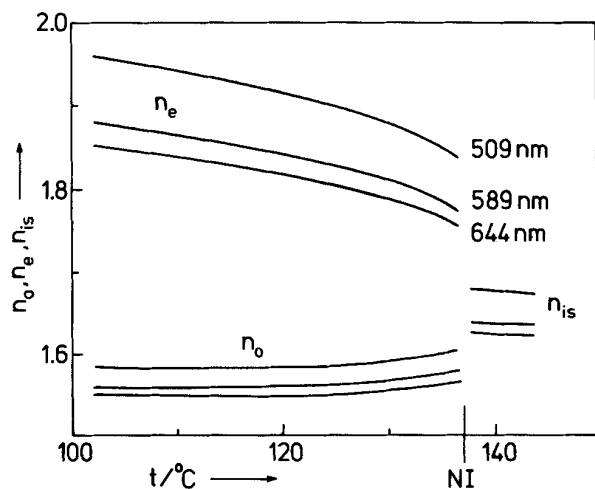


FIGURE 4 Refractive indices of PAA at various wavelengths.^{14a}

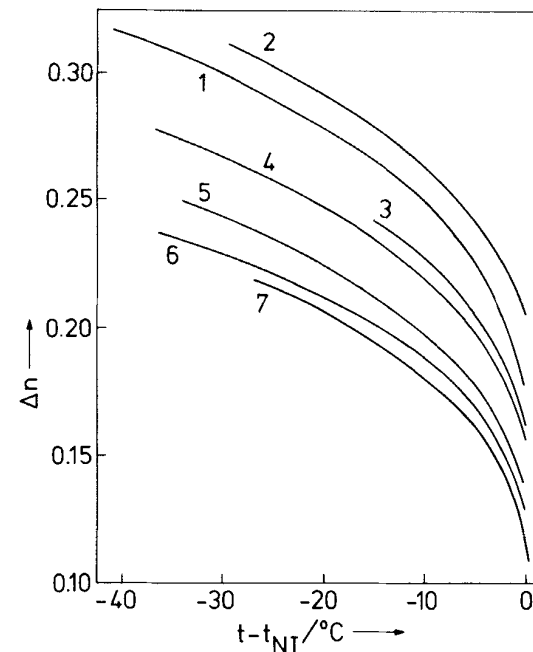


FIGURE 5 Birefringences of members of the series of p,p' -dialkoxyazoxybenzenes;^{14b} the number of carbon atoms in the alkoxy chain is indicated.

rise to a macroscopic polarization

$$P = N\langle \alpha \cdot E_i \rangle, \quad (11)$$

which can be equated to Eq. (9). E_i is the internal field, the average field that acts on a molecule, which is equal to the macroscopic field plus the average field of the induced dipoles of the surrounding particles. In general, one expects E_i to depend both on the properties and the orientation of the molecule at which the internal field is considered, and on the dielectric tensor of the macroscopic sample. For that reason E_i has to be included in the averaging procedure over all possible orientations. Without going into details, we remark that the effect of the internal field can be incorporated^{2,16} in an effective or "dressed" polarizability α^* . This conclusion is not founded theoretically, but based on an experimental proportionality between $\Delta\varepsilon = n_{\parallel}^2 - n_{\perp}^2$ and $\Delta\chi^m$. From this proportionality one can conclude that the internal field depends on molecular properties only, and thus can be incorporated in the polarizability tensor. In order to calculate molecular electronic polarizabilities from the refractive indices one has to rely on models for the

internal field. As there are hardly any independent polarizability data available, these models cannot be tested sufficiently. Only checks on internal consistency are possible.¹⁶

Reasonable estimates of the electronic polarizabilities of a molecule can often be obtained from the addition of tabulated bond polarizability data.¹⁷ Unfortunately, this method does not work very well for conjugated systems, where the polarizability can be much larger than the value obtained from such a summation. For example, using the polarizabilities of benzene and of the $-\text{N}=\text{N}-$ group, one calculates¹⁸ for azobenzene

$$\alpha_l = 28, \quad \alpha_t = 21 \quad (10^{-40} \text{ Fm}^2).$$

From measurements of the Kerr effect for azobenzene, it has been estimated that

$$\alpha_l = 38, \quad \alpha_t = 22 \quad (10^{-40} \text{ Fm}^2).$$

Apart from the uncertainties in the interpretation, it is evident that the conjugation in the longitudinal direction has led to a strong increase in the value of α_l . From the polarizabilities of a C—C and C—H bond one can calculate for an alkyl chain in a planar all-trans "zig-zag" conformation increments of α_l and α_t after addition of a methylene group. These results are given in Table II. As we see, addition of a methylene group leads to an increase of $\alpha_l - \alpha_t$ when starting from an even number of chain atoms, whereas starting from an odd number of chain atoms one expects a small decrease. This explains qualitatively the alternation of Δn that is observed on increasing the chain length in a homologous series (Figure 5). This alternation is parallel to the well-known alternation of T_{NI} .

Dispersion forces are often assumed to play an important role in determining nematic behaviour. As far as the anisotropy of the dispersion forces plays a role, a proportionality between T_{NI} and $(\alpha_l - \alpha_t)^2$ can be expected. More probably the isotropic part of the dispersion forces in combination with the anisotropic excluded volume is important.⁵ Then $\bar{\alpha} = \frac{1}{3}(\alpha_l + 2\alpha_t)$ is expected to be relevant. In Table III we compare some results for Δn , $\bar{n} = \frac{1}{3}(n_{\parallel} + 2n_{\perp})$ and T_{NI} for various substances. Assuming that the density and the order parameter at $(T_{\text{NI}} - 10)^\circ\text{C}$ are not significantly different for the various substances, Δn and \bar{n} are rough measures of $\alpha_l - \alpha_t$ and $\bar{\alpha}$, respectively. Examples 1–3 show that when an alkyl is substituted for an alkoxy group, Δn , \bar{n} and T_{NI} decrease. This is to be expected, because an oxygen atom possesses lone pairs of electrons that can easily become involved in the conjugated system. The decrease in α_l and thus in $\alpha_l - \alpha_t$ and $\bar{\alpha}$ when an oxygen is replaced by a CH_2 group is in this case accompanied by a decrease in T_{NI} . Phenyl benzoates (no. 5) have a much less rigid bridging group than that in the other examples, and this leads to relatively small conjugative interactions.

TABLE II
Increments in longitudinal and transverse polarizability for an alkyl group in the planar "zig-zag" conformation (10^{-40} Fm^2)

| $C_m \rightarrow C_{m+1}$ | $\delta\alpha_l$ | $\delta\alpha_t$ | $\delta(\alpha_l - \alpha_t)$ |
|---------------------------|------------------|------------------|-------------------------------|
| odd \rightarrow even | 1.86 | 2.14 | -0.28 |
| even \rightarrow odd | 2.59 | 1.76 | +0.83 |

Accordingly, Δn and \bar{n} are also smaller. In this case, however, T_{NI} is still relatively high. Finally, in examples 6–8, the benzene rings (which are rather polarizable along the plane of the ring, because of the delocalized π -electrons) are replaced by much less polarizable cyclohexane rings. As expected, both the birefringence and the refractive indices themselves decrease strongly. Nevertheless, an increase of T_{NI} is observed. These examples show that though the refractive indices can be roughly correlated with the presence of polarizable groups in the molecules, no simple relation with T_{NI} can be expected. Evidently in the last three examples, other factors than the dispersion forces between individual molecules (probably related to the larger excluded volume of associated pairs of molecules) are important in determining T_{NI} .

5 DIELECTRIC PERMITTIVITY

The relative permittivity tensor was already introduced in Eq. (9), where only the optical frequency range was considered. In this section we are interested in the (quasi-)static values. In a material consisting of non-polar molecules, there is only an induced polarization, which consists of two parts: the electronic polarization (which is also present at optical frequencies) and the ionic polarization. In materials with polar molecules, there is in addition the orientation polarization, due to the tendency of the permanent dipole moments to orientate themselves parallel to the field. In solids, where the permittivity will usually be anisotropic, the permanent dipole moments generally have a relatively fixed orientation and the contribution from the orientation polarization is less important. In liquid crystals, we have the complicated situation of an anisotropic permittivity in combination with liquid-like behaviour. Hence in the case of polar molecules, there is an important contribution to the anisotropic permittivity from the orientation polarization.

In the nematic phase with \mathbf{n} parallel to the z axis, the principal elements of $\boldsymbol{\varepsilon}$ are $\varepsilon_{\parallel} = \varepsilon_{zz}$ and $\varepsilon_{\perp} = \frac{1}{2}(\varepsilon_{xx} + \varepsilon_{yy})$. In Figure 6 we give experimental results for ε_{\parallel} and ε_{\perp} for the nematic phase of a non-polar compound for which $\Delta\varepsilon > 0$. In the case of polar compounds rather large values of $|\Delta\varepsilon|$ can be

TABLE III

Birefringence, average refractive index, (at $t_{NI} - t = 10^\circ\text{C}$ and 589 nm) and clearing point for some nematogenic compounds

| No. | Substance | Δn | \bar{n} | $t_{NI}(^\circ\text{C})$ | Reference |
|-----|-----------|------------|-----------|--------------------------|-----------|
| 1 | | 0.26 | 1.65 | 135 | [14] |
| 2 | | 0.21 | 1.60 | 76 | [19] |
| 3 | | 0.18 | 1.60 | 32 | [20] |
| 4 | | 0.19 | 1.61 | 47 | [21] |
| 5 | | 0.13 | 1.54 | 77 | [22] |
| 6 | | 0.16 | 1.58 | 42 | [23] |
| 7 | | 0.09 | 1.51 | 57 | [23] |
| 8 | | 0.05 | 1.47 | 83 | [23] |

obtained, depending on the magnitude of the total dipole moment μ and the long molecular axis (see Figure 7). A description of the permittivity of liquid crystals must show how the macroscopically observed anisotropy arises from the anisotropies of the various molecular quantities, taking account of the imperfect orientational order. However, for polar molecules, specific interactions between the dipole moments may occur. In that case, there is

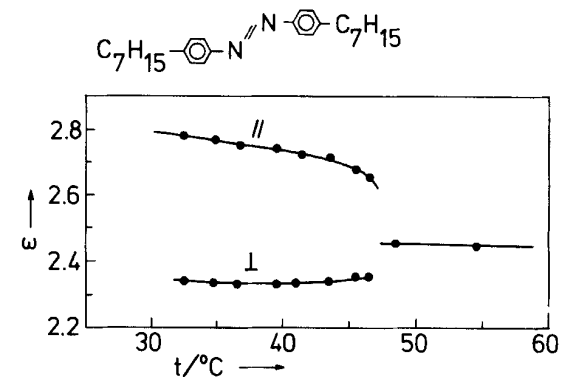


FIGURE 6 Dielectric permittivities of the non-polar compound *p,p'*-diheptylazobenzene.²⁴

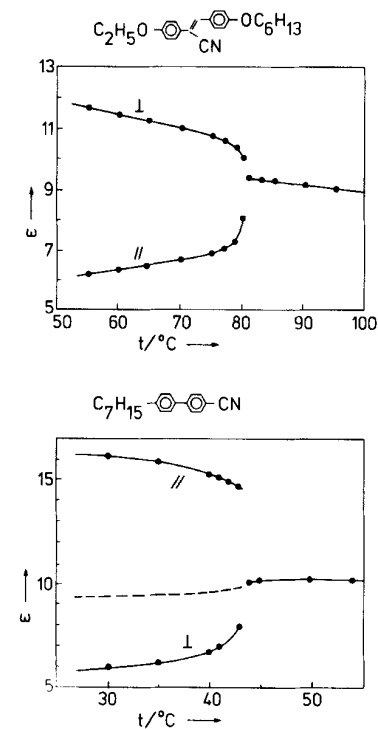


FIGURE 7 Dielectric permittivities of some compounds with (a) a large negative dielectric anisotropy,²⁵ and (b) a large positive dielectric anisotropy.²⁶

usually not enough independent information on the molecular properties to test conclusively the various possible approaches.

In the case of polar molecules, the orientation polarization must be added to Eq. (11):

$$\mathbf{P} = N(\langle \boldsymbol{\alpha} \cdot \mathbf{E}_i \rangle + \langle \bar{\boldsymbol{\mu}} \rangle), \quad (12)$$

where $\bar{\boldsymbol{\mu}}$ is the average value of the dipole moment in the presence of the electric field, and the brackets indicate the average over the orientations of all molecules. Combination of Eq. (9) with Eq. (12) leads to

$$(\mathbf{e} - \mathbf{I}) \cdot \mathbf{E} = (N/\epsilon_0)(\langle \boldsymbol{\alpha} \cdot \mathbf{E}_i \rangle + \langle \bar{\boldsymbol{\mu}} \rangle) \quad (13)$$

Maier and Meier²⁷ have evaluated this expression in the case of nematic liquid crystals, following closely Onsager's theory of the isotropic phase. The result for $\bar{\epsilon}$ and $\Delta\epsilon$ is:

$$\bar{\epsilon} = 1 + \left(\frac{NhF}{\epsilon_0} \right) \left(\bar{\alpha} + \frac{F\mu^2}{3k_B T} \right). \quad (14a)$$

$$\Delta\epsilon = \left(\frac{NhF}{\epsilon_0} \right) \left[\alpha_{\parallel} - \alpha_{\perp} - F \left(\frac{\mu^2}{2k_B T} \right) (1 - 3 \cos^2 \varphi) \right] S. \quad (14b)$$

Here $h = 3\epsilon/(2\epsilon + 1)$ is the cavity field factor, F the so-called reaction field factor, k_B Boltzmann's constant, and φ the angle between the direction of the dipole moment and the long molecular axis. Maier and Meier's equations account satisfactorily for many essential features of the permittivity of nematic liquid crystals with polar molecules. This is best illustrated using Eq. (14b) for $\Delta\epsilon$. If $3 \cos^2 \varphi = 1$ ($\varphi \approx 55^\circ$), the dipole moment contributes equally to ϵ_{\parallel} and ϵ_{\perp} . Then $\Delta\epsilon$ is determined by the (positive) anisotropy of the polarizability. The dipole contribution to $\Delta\epsilon$ is positive for $\varphi < 55^\circ$ and negative for $\varphi > 55^\circ$. In the latter case, whether $\Delta\epsilon$ itself becomes negative depends on the relative magnitude of the two contributions. The contribution of the induced polarization to $\Delta\epsilon$ varies with temperature like S ; the temperature dependence of the orientation polarization varies with S/T . The temperature dependence of the other factors is weak. For practical applications one is mainly interested in large values of $|\Delta\epsilon|$. Then the dipole contribution dominates, and we have

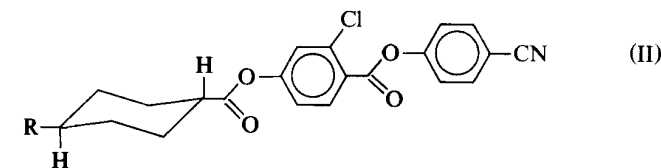
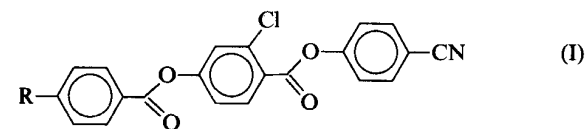
$$\begin{aligned} \bar{\epsilon} &\sim \frac{\mu^2}{T}, \\ \Delta\epsilon &\sim \frac{\mu^2 S}{T}. \end{aligned} \quad (15)$$

In the case of Figure 7b, the experimentally observed temperature dependence

of $\bar{\epsilon}$ is not in agreement with Eq. (15). As we see $\bar{\epsilon}$ decreases with decreasing temperature. This means that μ is not a constant. These data give direct evidence for anti-parallel dipole association, leading to an effective dipole moment that decreases with decreasing temperature, where the association becomes stronger.^{26,28} It seems likely that the liquid crystalline behaviour of the compounds 6–8 in Table III is directly related to the occurrence of these associated entities. Then these must have an anisotropic excluded volume more favourable for nematic behaviour than in the case of a single molecule.

Other types of dipole correlation occur in smectic phases. In these phases, the interaction of a dipole moment with the dipoles of surrounding molecules works out differently from that in the nematic phase, owing to the non-isotropic distribution of the centres of mass. For dipoles situated in the central part of the molecules, the distance between the dipoles of molecules in different smectic layers is much greater than the distance between neighbouring dipoles in the same layer. For the dipole components along the director, this leads to an increased anti-parallel correlation (see Figure 8). Consequently, the effective moment in this direction is reduced, leading to a decrease of ϵ_{\parallel} . An increase of ϵ_{\perp} can be similarly explained.²⁹ Because the average value of a dipole $\boldsymbol{\mu}$ in an electric field is proportional to μ^2 , rotation of the molecules around a long or short axis does not affect this result. When the nematic-smectic A transition is almost second-order, large effects due to pre-transitional smectic order may already be present in the nematic phase.

We conclude that, in principle, reasonable estimates of the dielectric anisotropy of a certain nematogenic compound can be obtained from the addition of group moments of the various polar groups. Correlation effects as described above may, however, alter these results considerably in practice. A further uncertainty is due to the amount of conjugation. As an extreme example of these effects we consider the following two molecules:³⁰



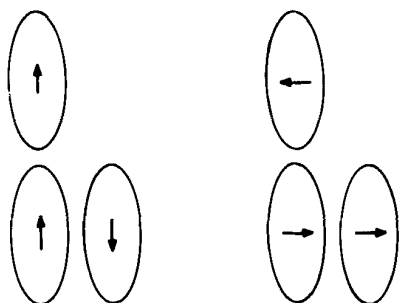


FIGURE 8 Dipole correlation between neighbouring molecules.

Compound (I) has a very large dielectric anisotropy of the order of 30 ($\epsilon_{\parallel} \approx 35$, $\epsilon_{\perp} = 7$). Compound (II) has $\epsilon_{\parallel} \approx 20$ and $\epsilon_{\perp} \approx 7$, in spite of the fact that there is hardly any difference in group moments.

6 ELASTIC CONSTANTS

As is well known, the bulk elastic properties associated with curvature of the director \mathbf{n} of a nematic liquid crystal can be described by three elastic constants. These constants are associated with the restoring torques opposing splay (K_1), twist (K_2) and bend (K_3) of the director pattern. The elastic distortion free energy density is given by:

$$F_d = \frac{1}{2}[K_1(\nabla \cdot \mathbf{n})^2 + K_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3(\mathbf{n} \cdot \nabla \mathbf{n})^2]. \quad (16)$$

In spite of the importance of the elastic constants for the various electro-optic effects, it is only during the last few years that systematic studies of the relation between molecular structure and elastic constants have been made.³¹⁻³⁶ The ratio K_3/K_1 has been found to vary considerably, in contrast to the results for K_2/K_1 . For the nematogenic compounds studied up to now one has:

$$0.5 < \frac{K_3}{K_1} < 4.0,$$

$$0.5 < \frac{K_2}{K_1} < 1.2.$$

However, it should be said that the range of compounds studied is much smaller in the latter case. Reliable measurement of K_2 are still scarce. Most studies of elastic constants have been made using the technique of the Frédericks transition. However, many of the older results are not very trustworthy, because the crucial role of the anchoring conditions was not fully

appreciated.^{6c} Data for the individual elastic constants of some selected compounds can be found in Ref. [2].

Intuitively one would expect relations between the elastic constants and the molecular dimensions, as we shall illustrate using a greatly simplified model. We shall take the molecules as rigid and cylindrically symmetric so that they can be represented by rods of length L and width W . Moreover, we assume ideal order ($S = 1$). Let the distance between the centres of neighbouring molecules in the direction of \mathbf{n} be denoted by z_0 , and perpendicular to \mathbf{n} by x_0 or y_0 . For a close-packed nematic liquid we then can take approximately

$$\frac{z_0}{x_0} = \frac{z_0}{y_0} \approx \frac{L}{W}. \quad (17)$$

Introducing a distortion of \mathbf{n} , neighbouring molecules will have slightly different preferred directions making an angle θ with each other. The elastic distortion free energy density then will be given by $\frac{1}{2}K_1(\theta/W)^2$ for a splay distortion, by $\frac{1}{2}K_2(\theta/W)^2$ for a twist distortion, and by $\frac{1}{2}K_3(\theta/L)^2$ in the bend configuration. (Note that the elastic constants have the dimensions of energy/length). Thus we find

$$K_1 : K_2 : K_3 = 1 : 1 : \left(\frac{L}{W}\right)^2. \quad (18)$$

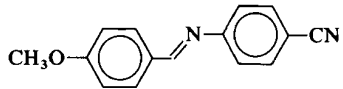
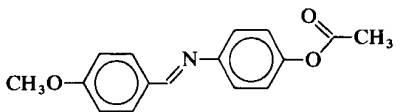
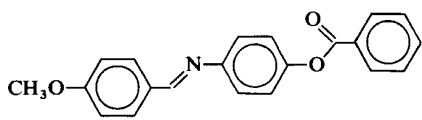
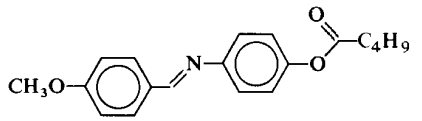
Results analogous to Eq. (18) have been derived by various authors in a more sophisticated and sometimes better acceptable way.³⁷⁻³⁹ The weakness of these lattice models lies in the assumption of a particular configuration of the molecules. However, the results of a more general calculation of the elastic constants by Priest^{40a} confirm the dependence of K_3/K_1 on L/W , albeit in a more complicated form.

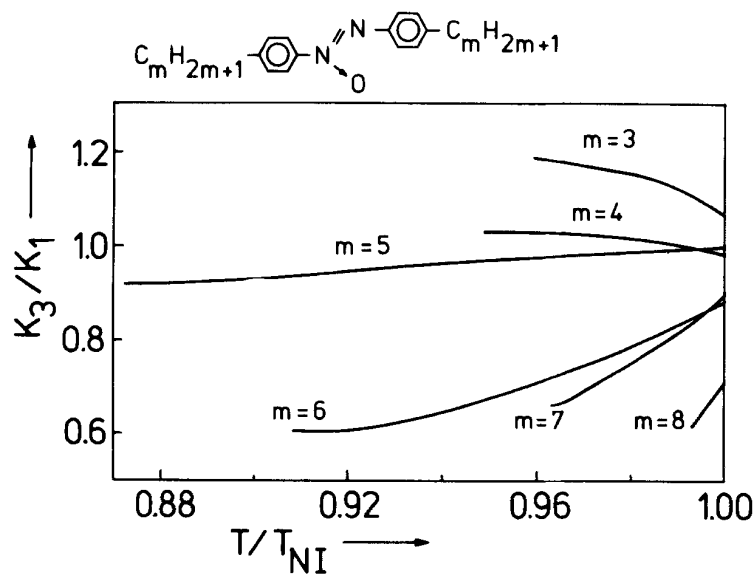
Leenhouts³⁴ observed that, in the case of some relatively rigid molecules, the ratio K_3/K_1 indeed increases if the molecular length is increased, as is illustrated in nos. 1-3 of Table IV. PAA, although different in its bridging group from the other compounds, fits in with the general trend. Furthermore, if for MBBA the width is increased by adding an *ortho*-hydroxyl group, K_3/K_1 decreases^{34a,41} from 1.35 to 1.06 (at $T/T_{N1} = 0.96$). These experiments are at least qualitatively in agreement with the theoretical ideas discussed above. Recently it has been observed that replacement of a benzene ring by a cyclohexane ring or a bicyclo-octane ring of about the same size, does lead³⁶ to an increase in K_3/K_1 , in contrast to the results just quoted. However, this particular case concerns molecules with a *p*-CN group, and differences in association may be involved.

Again rather different results have been obtained when flexible alkyl chains are present. This can be illustrated dramatically when in no. 3 of Table IV the terminal benzene ring is replaced by a C_4H_9 group. In spite of the fact

TABLE IV

Ratio K_3/K_1 for some compounds^{34b,41} with a different length/width ratio ($T/T_{NI} = 0.96$)

| No. | Compound | K_3/K_1 |
|-----|---|-----------|
| 1 |  | 1.9 |
| 2 |  | 2.1 |
| 3 |  | 2.4 |
| 4 |  | 1.3 |

FIGURE 9 Ratio K_3/K_1 for the series of p,p' -dialkylazoxybenzenes.³¹

that L/W hardly changes, K_3/K_1 drops from 2.4 to 1.3. This is in agreement with earlier results for homologous series, where if the length of the alkyl chain is increased, the ratio K_3/K_1 is found to *decrease*. In this way rather low values of K_3/K_1 (even smaller than unity) can be obtained (see Figure 9). This effect has been attributed to differences in short-range order.^{31,42} Compared with more rigid molecules, the alkyl chains hinder a sliding of the molecules along each other. This means that neighbouring molecules have an enhanced preference to be with their aromatic cores close to each other. This modifies the treatment leading to Eq. (18), leading to smaller K_3/K_1 ratios.⁴²

As we see from Figure 9, the ratio K_3/K_1 varies with temperature. Often it is assumed that $K_i \sim S^2$ ($i = 1, 2, 3$), where $S \equiv \langle P_2 \rangle$ is the nematic order parameter. However, such a proportionality would lead to ratios of elastic constants independent of the temperature, and therefore cannot be generally valid. In fact it has been shown theoretically, that only when the intermolecular interaction is restricted to the lowest order terms, one finds $K_i \sim S^2$. Moreover, in that case $K_1 = K_3$ is predicted.^{40,43} More precisely, one can write:^{40a}

$$\begin{aligned} \frac{K_1}{\bar{K}} &= 1 + \Delta - 3\Delta' \frac{\bar{P}_4}{\bar{P}_2}, \\ \frac{K_2}{\bar{K}} &= 1 - 2\Delta - \Delta' \frac{\bar{P}_4}{\bar{P}_2}, \\ \frac{K_3}{\bar{K}} &= 1 + \Delta + 4\Delta' \frac{\bar{P}_4}{\bar{P}_2}. \end{aligned} \quad (19)$$

where

$$\bar{K} = \frac{1}{3}(K_1 + K_2 + K_3) \sim \langle P_2 \rangle^2, \quad (20)$$

and

$$\langle P_4 \rangle = \frac{1}{8} \langle 35 \cos^4 \beta - 30 \cos^2 \beta + 3 \rangle. \quad (21)$$

The proportionality between \bar{K} and $\langle P_2 \rangle^2$ has been verified experimentally.⁴¹ The quantities Δ and Δ' are constants depending on molecular properties. In order to calculate them, further assumptions have to be made. Representing the molecules by spherocylinders, interacting *via* hard core repulsions, qualitatively again $K_3/K_1 \sim L/W$ is predicted.

From Figure 9, we see that these predictions are in excellent agreement with experiment. If $K_1 \approx K_3$ the ratio K_3/K_1 is almost independent of temperature. With increasing temperature S decreases, and the errors due to disregarding higher order terms become smaller. Indeed, the temperature dependence of K_3/K_1 in the case $K_3/K_1 \geq 1$ is such that with increasing temperature the values of K_1 and K_3 approach each other.

In theoretical studies of curvature elasticity, the approximation $K_1 = K_2 = K_3$ is often made. From the experimental results we note that this one-constant approximation bears little relation to physical reality. On the other hand, in Figure 9 we see that for $m = 4$ and $m = 5$ we have $K_1 \approx K_3$. Then a two-constant approximation can be used, which may result in a considerable simplification of the equations of the continuum theory.

For various electro-optic applications of nematic liquid crystals one is interested in sharp thresholds. This property is largely determined by ratios of elastic constants, for which now some general rules can be given. High values of K_3/K_1 are obtained with relatively rigid molecules with a high L/W ratio. Low values of K_3/K_1 are found when long alkyl chains are incorporated in the molecular structure. The ratio K_2/K_1 seems to vary not much, and a high value of K_3/K_2 (important for the cholesteric-nematic transition) must be obtained *via* compounds with a high K_3/K_1 .

7 VISCOSITY COEFFICIENTS

Experimental studies on the viscosities of liquid crystals that can be interpreted in a quantitative way are scarce, in spite of the fact that the viscosities are important for the dynamic behaviour of devices based on the various electro-optic effects. This is due to the fact that the situation is rather complicated when the state of alignment is considered. In the first place, the flow depends on the angles the director makes with the flow direction and with the velocity gradient. Secondly, the translational motions will disturb the alignment and cause the director to rotate. Hence the state of alignment must be controlled (for example by an external field) and/or be measured. As nematics are turbid, optical measurements of the alignment are restricted to thin samples, and conventional viscometric equipment (based on capillaries, falling spheres, rotating cylinders, etc.) is of little use.

As an example we consider simple shear flow. Let the flow be along the z axis between two parallel plates normal to the x axis. If we assume that the orientation of \mathbf{n} is fixed by external forces, this situation defines the three Miesowicz viscosities (Figure 10a, b, c):

η_1 : \mathbf{n} parallel to velocity gradient,

η_2 : \mathbf{n} parallel to flow direction,

η_3 : \mathbf{n} normal to shear plane.

In the original paper by Miesowicz⁴⁴ on PAA, the definitions of η_1 and η_2 are interchanged; we have retained here the notation of Helfrich.⁴⁵ In the literature, the notation η_a, η_b, η_c can also be found, with $\eta_a = \eta_3, \eta_b = \eta_2$ and $\eta_c = \eta_1$. Apart from two possible shears depicted in Figure 10 (a) and (b)

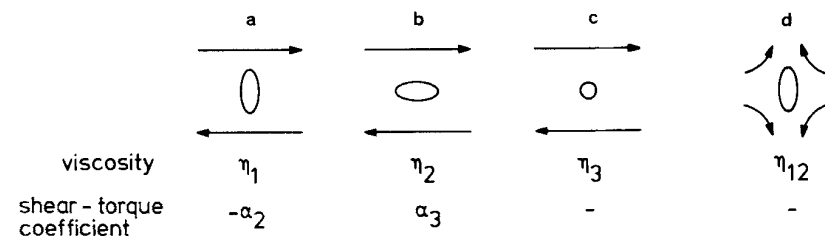


FIGURE 10 The viscosity coefficients of a nematic liquid crystal.

that are antisymmetric in x and z , a stretch type of deformation is also possible that is symmetric in these coordinates (n_{12} , see Figure 10 (d)). In a shear experiment, the maximum contribution from n_{12} is found when the director is in the shear plane at an angle of 45° with both the flow direction and the velocity gradient. In that case

$$\eta_{45^\circ} = \frac{1}{2}(\eta_1 + \eta_2) + \frac{1}{4}\eta_{12}. \quad (22)$$

For PAA and MBBA, η_{12} is much smaller than the other viscosities, which is, however, not true in general.^{46b} For a survey of other methods of measuring viscosities and further references, we refer to Ref. [2].

If we lift the restriction that the orientation of the director is fixed, then, in addition, the motion of the director comes into play. This part of the hydrodynamics illustrates the unique properties of nematic liquid crystals that have no isotropic counterpart. Experiments show that a pure rotation of the director does not necessarily involve motion of the fluid. From the symmetry of the situation, as depicted in Figure 10, we see that in case (a) and (b) a torque can be exerted on the director due to the shear. The corresponding shear-torque coefficients, that have the dimension of a viscosity, are denoted by $-\alpha_2$ and α_3 . (In Helfrich's notation $-\alpha_2 = \kappa_1$ and $\alpha_3 = \kappa_2$). No torque is possible in the situation of Figure 10 (c) and (d). As a result, there is in the shear-plane a situation of vanishing shear-induced torque when the director makes an angle θ_0 with the flow direction, with

$$\tan^2 \theta_0 = \frac{\alpha_3}{\alpha_2}. \quad (23)$$

This situation is illustrated in Figure 11. Of the six coefficients introduced so far, only five are independent. There exists a relation between shear and shear-torque in the configurations of Figures 10(a) and (b):

$$\eta_1 + \alpha_2 = \eta_2 - \alpha_3. \quad (24)$$

A more formal treatment of the hydrodynamics of nematics has been given

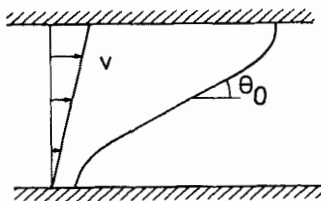


FIGURE 11 Flow alignment in a shear experiment with a nematic fluid with homeotropic boundary conditions.

by Ericksen and Leslie⁴⁷ in terms of six coefficients $\alpha_1 \dots \alpha_6$, that can easily be related to the ones used here. In many problems α_2 and α_3 appear in combinations, written as:

$$\begin{aligned}\gamma_1 &= \alpha_3 - \alpha_2, \\ \gamma_2 &= \alpha_3 + \alpha_2.\end{aligned}\quad (25)$$

In Figure 12, the three Miesowicz viscosities of MBBA are given. As is well known, the viscosity of an isotropic liquid varies approximately as

$$\eta_{is} = \eta_0 \exp\left(\frac{E}{k_B T}\right), \quad (26)$$

where $E > 0$ is an activation energy for diffusion and η_0 is a constant. From Figure 12, we see that in the case of MBBA, the translational viscosities η_2

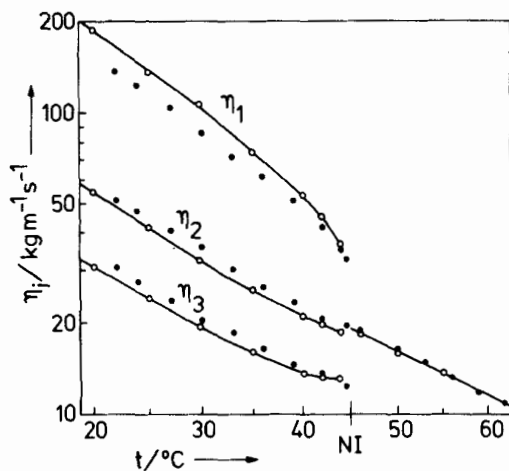


FIGURE 12 Miesowicz viscosities for MBBA; ● Ref. [46a], ○ Ref. [48]; the temperature scale is linear in $1/T$.

and η_3 , to a first approximation, have the same temperature dependence as η_{is} ($E \approx 0.3$ eV). Especially close to T_{NI} there are deviations, however. As this is the region where S varies strongly, a more complicated formula depending also on S must be involved. The temperature range, and thus the variation of S , is too limited to allow one to decide on the actual functional dependence, but the suggestion of Imura and Okano⁴⁹ that

$$\frac{(\eta_2 - \eta_{is})}{S} = \text{constant} \quad (27)$$

can be excluded. Here η_{is} is understood to be the isotropic viscosity extrapolated to the relevant temperature in the nematic phase. Recently, Schneider and coworkers observed that the scaled viscosity $\eta_i/\bar{\eta}$ ($i = 1, 2, 3$), where $\bar{\eta} = \frac{1}{3}(\eta_1 + \eta_2 + \eta_3)$ is very similar for various nematic substances.^{46b}

With respect to the rotational viscosities, γ_1 and γ_2 , somewhat more information is available. From the published data for γ_1 and for the anisotropy of the magnetic susceptibility of both MBBA and N4 (the mixture of the two isomers of *p*-methoxy-*p'*-butylazoxybenzene, E. Merck, Darmstadt), one finds that a plot of $\ln(\gamma_1/\Delta\chi^m)$ against $1/T$ gives a straight line (see Figure 13). Assuming, as before, rotational symmetry around the molecular long axis, we have $\Delta\chi^m \sim S$, leading to

$$\gamma_1 \sim S \exp\left(\frac{E'}{k_B T}\right). \quad (28)$$

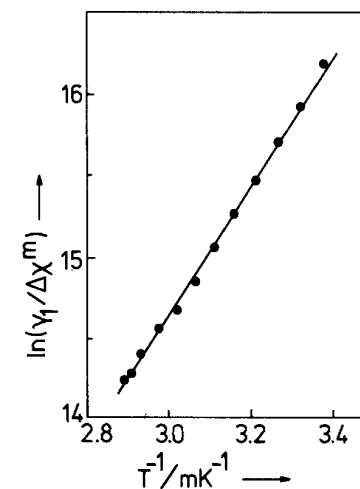


FIGURE 13 Rotational viscosity $\gamma_1/\Delta\chi^m$ versus $1/T$ for N4.⁵⁰

Other functional dependences can clearly be ruled out. For MBBA⁵¹ one has $E' \approx 0.5$ eV, which is rather higher than the activation energy associated with η_{is} . Various authors^{49,52,53} have given theoretical discussions of the temperature dependence of the viscosity coefficients, but no theory with two activation energies has yet been developed. We conclude that there is ample room for new theoretical approaches.

Helfrich⁴⁵ has given a molecular theory of flow alignment in nematic liquid crystals. It is based on the rod-like shape of the molecules, which are considered as ellipsoids of revolution. The most important result of the calculations is

$$\frac{\alpha_3}{\alpha_2} = \left(\frac{b}{a}\right)^2, \quad (29)$$

where a and b are the long and the short axes of the ellipsoid, respectively. For PAA and MBBA the ratio a/b is of the order of 5, giving $\alpha_3/\alpha_2 \approx 0.04$. This is in excellent agreement with the experimental results (see Tables 7.1 and 7.2 of Ref. [2]).

We conclude that still little is known about the detailed behaviour of the viscosities of liquid crystals. There is a need for both accurate and complete data and for new theoretical approaches. For applications, one is often only interested in the differences in order of magnitude of the viscosities of various classes of compounds. Then a flow experiment in which the orientation of the director is not controlled may suffice. In that case, an effective viscosity is observed that depends on the flow alignment angle. Far from T_{NI} one often finds that θ_0 is small and approximately η_2 is measured. However, if T_{NI} is approached, θ_0 may increase.⁵⁴ Then a value in between η_2 and η_1 will be measured. An increase of θ_0 can explain the increase in the effective viscosity that is often observed near T_{NI} . Some cases have been observed where α_3 changes sign as a function of temperature.^{54,55} Then there is no longer a real solution to Eq. (23). No flow alignment can occur and the director tumbles in a way that depends on the pre-tumbling velocity field in the sample. It is clear that great care must be taken to interpret data when the state of alignment is not controlled or monitored.

Acknowledgements

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