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Diamagnetism and orientational order of nematic liquid crystals

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Résumé. — Nous présentons des données expérimentales de l'anisotropie diamagnétique pour treize cristaux liquides dans la phase nématique. L'influence sur la rotation autour de l'axe moléculaire le plus long étant probablement négligeable, les résultats donnent des renseignements directs sur la variation avec la température du facteur S , le paramètre d'ordre d'orientation. Le comportement critique de S , près de la transition de phase isotrope-nématique, peut être décrit à l'aide d'un exposant β égal à 0,25. Nous considérons aussi des méthodes permettant d'obtenir l'anisotropie magnétique moléculaire. En changeant systématiquement la structure des molécules on peut évaluer les contributions des groupes moléculaires distincts. Il apparaît pourtant assez difficile d'obtenir des résultats précis de l'anisotropie magnétique moléculaire. Par conséquent l'échelle absolue de S ne peut être fixée qu'avec une précision de l'ordre de 10 %.

Abstract. — Measurements are presented for the diamagnetic anisotropy of thirteen nematic liquid crystals. As any bias in the rotation around the long molecular axis is most probably small, the results probe accurately the temperature variations of S , the degree of orientational order. The critical behaviour of S near the nematic-isotropic phase transition can be described by an exponent β of the order of 0.25. Procedures are considered to obtain the molecular magnetic anisotropy. By a systematic variation of the structure of the molecules an impression of the contributions of the various molecular groups can be obtained. It turns out to be rather difficult to obtain accurate data for the molecular magnetic anisotropy. As a consequence the absolute scale of S can only be fixed with an accuracy of the order of 10 %.

1. **Introduction.** — In the nematic liquid crystalline phase [1] the elongated molecules are, on the average, aligned with their long axis parallel to a preferred direction in space. This direction can be labelled by a unit vector \mathbf{n} , the director. The molecules translate freely as in the isotropic phase. Around \mathbf{n} there exists uniaxial symmetry while the directions given by \mathbf{n} and $-\mathbf{n}$ are equivalent. Due to this symmetry various physical properties are anisotropic. It is the purpose of this work to investigate the anisotropy of the diamagnetic susceptibility of some nematic liquid crystals, which can be used to describe the degree of orientational order. The critical behaviour of the order parameter near the nematic-isotropic transition at T_{NI} is found to be in agreement with the view that T_{NI} has the properties of a tricritical point. The mesogenic compounds are chosen such that it is also possible to investigate the effect of systematic differences in the molecular constitution on the diamagne-

tic anisotropy. However, it turns out to be rather difficult to obtain accurate estimates for the molecular diamagnetic anisotropy.

The magnetic moment \mathbf{M} (per unit volume) induced by a magnetic field \mathbf{H} in an anisotropic medium is related to the field by

$$M_\alpha = \chi_{\alpha\beta} H_\beta, \quad \alpha, \beta = x, y, z, \quad (1)$$

where $\chi_{\alpha\beta}$ is an element of the magnetic susceptibility tensor χ . In the uniaxial nematic phase we can choose the director \mathbf{n} along the z -axis. Then χ is given by

$$\begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_\parallel \end{pmatrix}, \quad (2)$$

where the subscripts \parallel and \perp refer to the directions parallel and perpendicular to \mathbf{n} , respectively. The average susceptibility is given by

$$\bar{\chi} = \frac{1}{3} \sum_\gamma \chi_{\gamma\gamma} = \frac{1}{3} (\chi_\parallel + 2 \chi_\perp). \quad (3)$$

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The magnetic anisotropy is defined as

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp} = \frac{3}{2}(\chi_{\parallel} - \bar{\chi}). \quad (4)$$

In the isotropic phase we have $\chi_{\alpha\beta} = \chi \delta_{\alpha\beta}$. The mass susceptibility χ^m is related to the volume susceptibilities used so far by $\chi^m = \chi\rho$, ρ being the density. As diamagnetism is independent of temperature we have $\chi^m = \bar{\chi}^m$.

Knowledge of the diamagnetic properties of liquid crystals, and especially of the magnetic anisotropy, is important for at least two reasons [2] :

(i) An order parameter $Q_{\alpha\beta}$ can be defined by extracting the anisotropic part of the magnetic susceptibility [3] :

$$Q_{\alpha\beta} = \chi_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \sum_{\gamma} \chi_{\gamma\gamma}. \quad (5)$$

Q is a second-rank tensor, which is real, symmetric, has zero trace, and vanishes in the isotropic phase. The choice of the magnetic tensor for the order parameter is convenient because the molecular diamagnetism is so small that interactions between the molecular magnetic moments can be neglected. Consequently, the internal field can be taken equal to the macroscopic field, which facilitates a molecular interpretation of the $Q_{\alpha\beta}$.

(ii) The response of a liquid crystal to an applied external magnetic field is largely determined by the value of $\Delta\chi$. As an application we mention the effect of a large field on the NI phase transition, a subject that has not been fully explored yet. Another example is provided by the elastic constants K_i ($i = 1, 2, 3$) of a nematic liquid crystal, which are often determined from the field induced deformation of a uniform layer. Then in fact $K_i/\Delta\chi$ is measured and an independent measurement of $\Delta\chi$ is required to obtain values for the elastic constants themselves.

2. Experimental. — The magnetic susceptibilities are measured by the classical Faraday-Curie method : a sample is placed in a magnetic field that has a gradient in the vertical direction, and the force acting on the sample is determined using a sensitive balance [4]. Various authors have applied this method to the nematic phase [5]. Provided $\Delta\chi > 0$ the field causes a uniform orientation of the director and χ_{\parallel} will be measured. As $\bar{\chi}$ can be determined in the isotropic phase, in this way full information on $\Delta\chi$ is obtained.

A Bruker BE15 electromagnet gives a field of about 12 kOe over a gap of 40 mm. Pole caps of the same make are used, especially designed to provide a large region of constant dH^2/dx . A Mettler ME21 electrobalance can measure on three different ranges, 2, 20 or 200 mg, respectively, with an accuracy of 10^{-4} , while allowing a total weight of 6 g. The balance is attached to a column on a vibration-isolated platform. With various micromanipulators the column with balance and sample can be moved to obtain the optimum

position for the sample between the poles of the magnet.

The sample holder is a small cylinder of quartz (outer diameter 5 mm) that contains up to about 0.3 cm³ substance. At the lower end a quartz rod is attached in order to minimize the corrections for the susceptibility of the empty sample holder. Sample and quartz rods are placed in a double cylinder of glass in which a thermostated liquid is circulated. The temperature is measured near the sample in the circulating liquid with a Pt100 resistance thermometer. The temperature stabilization is of the order of 0.1 °C. The measurements are carried out under a He atmosphere. The reference substance chosen is dibutylphthalate, a conveniently non-volatile liquid at room temperature. The total weight of the empty sample holder plus attachments is of the order of 2 g. For about 200 mg substance typically a weight change of the order of 1.5 mg is obtained on application of the field.

3. Results. — In order to test the experimental set up we first measured the susceptibility of dibutylphthalate as a function of temperature. Taking $\chi^m = -0.6290 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ at 20 °C [5c] we found that χ^m varied no more than 0.2 % as a function of temperature. As nematic test substance N4 was chosen (E. Merck, Darmstadt), a mixture of the two isomers of *p*-methoxy-*p'*-butylazoxybenzene (nematic range 18-75 °C). These results for χ_{\parallel} and $\Delta\chi$ are in excellent agreement with those by Haller *et al.* [6] and by de Jeu and Claassen [5i], our relative accuracy being somewhat better.

In figures 1 and 2 results for $\Delta\chi$ are given for *p*, *p'*-alkylcyano substituted compounds including different ring systems. In figure 3 results for compounds with different bridging groups. Using a non-linear least-square routine the data were fitted to the following equation [7] :

$$\Delta\chi^m = \Delta\chi_0^m(1 - yT/T_{NI})^z. \quad (6)$$

The values for the three coefficients in this equation are given for the various substances in table I, together

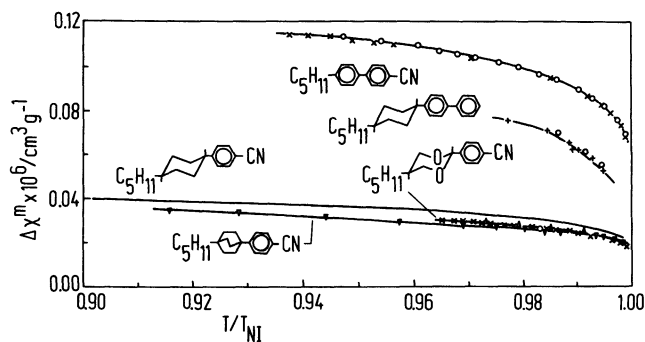


Fig. 1. — Magnetic anisotropies of some *p*-pentyl substituted compounds. Different symbols refer to separate measurements.

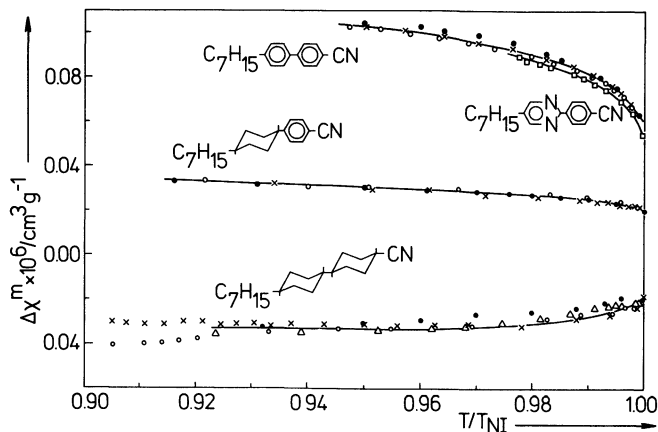


Fig. 2. — Magnetic anisotropies of some *p*-heptyl-*p*'-cyano substituted compounds (● from Ref. [9]).

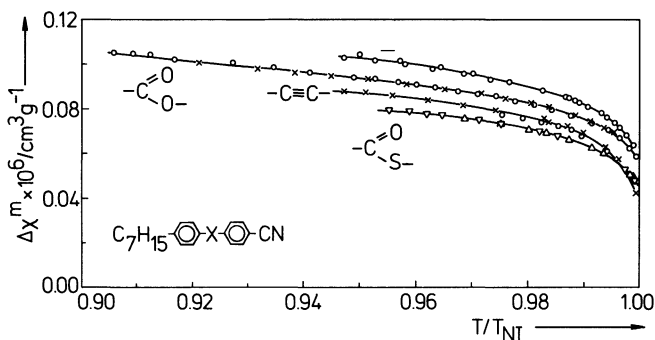


Fig. 3. — Magnetic anisotropy of some compounds with different bridging groups.

with the NI transition temperatures. The quality of the fit is illustrated in figure 4 for a typical case. To compare the influence of the molecular structure, in table I not only $\Delta\chi_0^m$ is given but also $\Delta\chi_0^M = \Delta\chi_0^m M$, where M is the mass number.

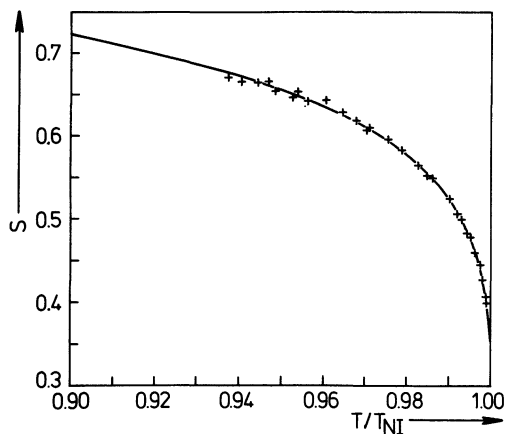


Fig. 4. — Experimental data and theoretically fitted curve according to equation (13) for 5 CB (no. 1).

Compound 8 is different from the others in that it has a negative magnetic anisotropy [8, 9]. In such a case no uniform director pattern is obtained on application of the field. The director is confined to lie perpendicular to \mathbf{H} , and χ_{\perp} is measured in the nematic phase. In principle this non-uniformity of \mathbf{n} should not influence the accuracy of the measurements. Nevertheless the reproducibility is in this particular case considerably less than for the other compounds.

In figure 2 for the compounds 6, 7 and 8 also results for $\Delta\chi$ from Schäd *et al.* [9] are given, that are obtained using a different method in which the combined effect of an electric and a magnetic field on a uniform nematic layer is compared. The agreement is excellent for 6 and 7 and — taking account of the limited reproducibility in this case — also for 8. Both our and Schäd's results for 1 and 6 differ about 7 percent from those of Sherrell and Crellin [10].

4. Discussion. — First we shall discuss a molecular interpretation of the magnetic susceptibility χ and its anisotropic part \mathbf{Q} . Let ξ, η, ζ be the axes of a molecule-fixed coordinate system, and κ the tensor of the molecular magnetic polarizability. Because of the uniaxial symmetry around \mathbf{n} (taken along the z -axis) and due to the fact that \mathbf{Q} is traceless, it is sufficient to consider only one element of \mathbf{Q} , for which we choose Q_{zz} . Thus we find :

$$Q_{zz} = \frac{2}{3}(\chi_{\parallel} - \chi_{\perp}) = \frac{2}{3} N \sum_{ij} \kappa_{ij} S_{ij}, \quad i, j = \xi, \eta, \zeta, \tag{7}$$

where N is the number of molecules per unit volume, and the generalized order parameter S_{ij} has been introduced [11]. If we denote the z -component of a unit vector along the ξ, η or ζ -axis by i_z , we can write

$$S_{ij} = \frac{1}{2}(3 i_z j_z - \delta_{ij}), \quad i, j = \xi, \eta, \zeta. \tag{8}$$

In fact all the information about \mathbf{Q} is contained in $\Delta\chi$. We shall now choose the coordinate system ξ, η, ζ such that S_{ij} is diagonal. As \mathbf{S} has zero trace there are two independent order parameters. Taking the ζ -axis as the long molecular axis we choose $S = S_{\xi\xi}$ and $D = S_{\xi\xi} - S_{\eta\eta}$. Then equation (7) reduces to [2, 12] :

$$\begin{aligned} (\chi_{\parallel} - \chi_{\perp})/N &= \\ &= [\kappa_{\zeta\zeta} - \frac{1}{2}(\kappa_{\xi\xi} + \kappa_{\eta\eta})] S + \frac{1}{2}(\kappa_{\xi\xi} - \kappa_{\eta\eta}) D. \end{aligned} \tag{9}$$

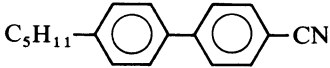
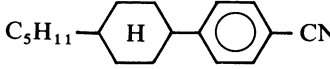
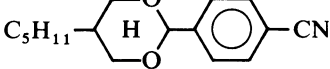
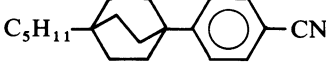
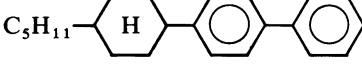
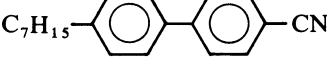
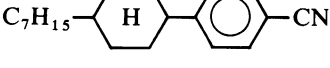
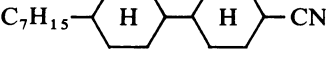
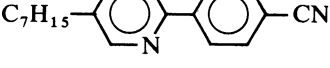
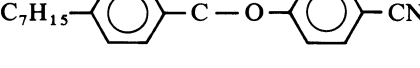
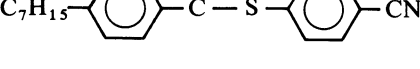
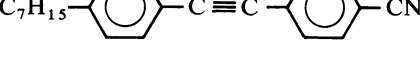
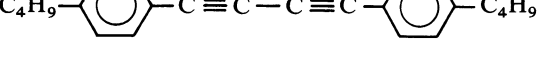
Here S is the usual order parameter given by ,

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle, \tag{10}$$

where θ is the (z, ζ) angle. Furthermore

$$D = \frac{3}{2} \langle \sin^2 \theta \cos 2\Psi \rangle, \tag{11}$$

Table I. — *Clearing temperatures and fitting parameters of equation (6) for the compounds used.*

No.	Compound	T_{NI} (°C)	$\Delta\chi_0^m \times 10^6$ (cm ³ g ⁻¹)	$\Delta\chi_0^M \times 10^6$ (cm ³ mol ⁻¹)	y	z
<u>1</u>		34.5	0.170	42.3	0.999 5	0.141
<u>2</u>		55.0	0.059	15.0	0.998 7	0.165
<u>3</u>		48.0	0.053	14.0	0.998 8	0.174
<u>4</u>		100.0	0.062	17.5	0.989 0	0.252
<u>5</u>		93.3	0.155	47.3	0.999 7	0.184
<u>6</u>		41.9	0.158	43.8	0.999 2	0.146
<u>7</u>		56.8	0.047	13.3	0.995 2	0.145
<u>8</u>		83.5	- 0.045	- 13.0	0.999 6	0.114
<u>9</u>		50.6	0.162	45.5	0.999 2	0.159
<u>10</u>		56.0	0.151	48.5	0.997 8	0.160
<u>11</u>		92.4	0.127	42.7	0.999 3	0.150
<u>12</u>		67.5	0.144	43.3	0.999 9	0.164
<u>13</u>		100.3	0.124	38.9	0.995 4	0.181

where Ψ is the Euler angle specifying the rotation around the ζ -axis. D measures the difference in tendency of the two transverse molecular axes to project on the z -axis. If the molecules can be taken as effectively axially symmetric, $D = 0$. With

$$\chi_1^M = N_A \kappa_{\zeta\zeta} \quad \text{and} \quad \chi_t^M = \frac{1}{2} N_A (\kappa_{\xi\xi} + \kappa_{\eta\eta}),$$

N_A being Avogadro's number, we then derive from equation (9) Tsvetkov's expression for the order parameter S [13, 14] :

$$S = \Delta\chi^M / (\chi_1^M - \chi_t^M). \quad (12)$$

In order to decide whether $D = 0$ is a good approximation we have to rely on other methods, in particular nuclear magnetic resonance. For 5CB (compound 1) Emsley *et al.* [15] could measure the value of D and found it to be rather small (≈ 0.02). This is consistent with other results which seem to indicate for some different compounds

$$D = 0.03 \pm 0.03.$$

As the coefficients in front of S and D in equation (9) can be of the same order of magnitude [2], assuming $D = 0$ could introduce errors of maximum, say, 5%.

From equation (12) we see that $\Delta\chi^m$ as depicted in figures 1-3 is directly proportional to S . To fix the absolute value of S we have to know $\chi_1 - \chi_t$. In principle such data can be obtained from measurements of the susceptibility in the solid state. Unfortunately, only very few results are available that are of interest in connection with liquid crystals [2]. Various people have tried extrapolation procedures to obtain an estimate for $\chi_1 - \chi_t$ [6, 7, 16]. In equation (6) $\Delta\chi_0$ is the maximum anisotropy at $T = 0$, and can be considered as an approximation to $\chi_1 - \chi_t$. However, $T = 0$ is rather far from the limited temperature range where the constants in equation (6) are determined. Accepting nevertheless this procedure we find

$$S = \Delta\chi^m / \Delta\chi_0^m = (1 - yT/T_{NI})^z, \quad (13)$$

with coefficients y and z given in table I. Typical errors are a few units of the last decimal.

In figure 5 the results for S of 5CB (no. 1) from equation (13) are compared with those from other methods like nuclear magnetic resonance and depolarized Raman scattering. The Raman results from Miyano [18] have been recalculated, leaving out the relatively inaccurate results for the depolarization ratio R_3 , and combining the data of both the CC- and the CN-band for the other ratio's [19]. We have hesitated to include in figure 5 also values for S from birefringence measurements, as these not only suffer from similar uncertainties in fixing the absolute scale for S as discussed here for $\Delta\chi$, but also from uncertainties concerning the internal field [2]. Finally

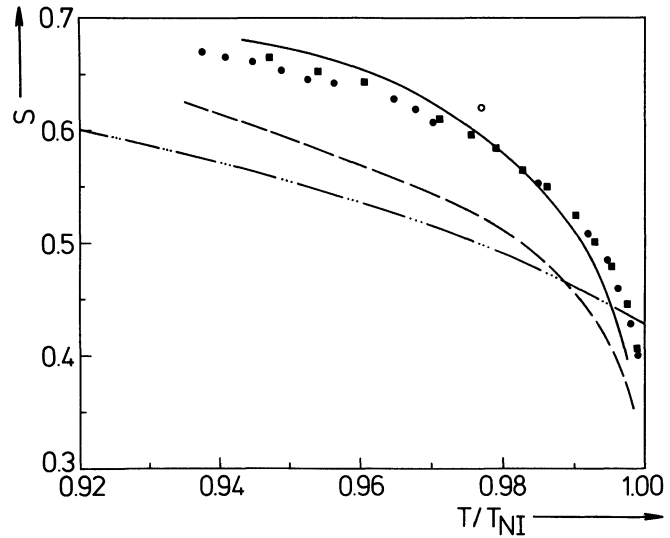


Fig. 5. — Order parameters for 5 CB (no. 1) : ● ■ magnetic susceptibility (this work); — depolarized Raman scattering (Ref. [18], recalculated as indicated in text); ○ nuclear magnetic resonance (Ref. [15]); — — — birefringence (Ref. [20]); ····· mean-field theory.

the data from Horn [20] have been included. Results for S from some other authors [21] are rather far below those depicted in figure 5. As we see the agreement between the magnetic susceptibility and the Raman measurements is better than one could expect. The difference with the NMR result is well within the error limits, while the birefringence results are somewhat different. This is not only a question of scaling. As discussed by Bunning *et al.* [22] the ratio $\Delta\chi / (n_{\parallel}^2 - n_{\perp}^2)$ varies for 5 CB over the nematic temperature range about 10%. If both were proportional to S this ratio should be constant. For several other nematogens, however, the agreement between optical and magnetic data is much better [5i, 16d]. Finally we have included in figure 5 the results of Maier and Saupe's mean-field theory [17], for which a fit to equation (13) over a typical nematic temperature range gives $y = 0.98$ and $z = 0.22$. The temperature variation of S close to T_{NI} is experimentally somewhat stronger than predicted by simple mean-field theory, as reflected in the relatively high values of y (see Table I).

In this paper equation (6) is used as an empirical fitting formula to the experimental data for $\Delta\chi$ over the entire nematic temperature range. The anisotropy $\Delta\chi$ extrapolates to zero at a temperature T_{NI}/y , slightly above T_{NI} . However, T_{NI}/y should not be identified with T^{\dagger} , the temperature of maximum superheating of the nematic phase, where a second-order phase transition would occur if a first-order one did not intervene at T_{NI} [1, 23]. To study the critical behaviour of the order parameter a fit has to be made according to

$$S - S_c = A(1 - T/T^{\dagger})^{\beta}, \quad (14)$$

where S_c is a constant that gives the value of S at T^\dagger . The importance of including S_c can be demonstrated on the mean-field theory of Maier and Saupe [17]. A fit of the numerical results for S to equation (13) gives an exponent $z = 0.22$; only with equation (14) the correct mean-field exponent $\beta = 0.5$ is obtained. Though in our measurements of $\Delta\chi$ the temperature was not controlled to the extent required for a study of critical exponents, we attempted to fit the data to equation (14). For the compounds studied values for β in the range 0.25 ± 0.1 were found, certainly excluding mean-field behaviour. Keyes [24] has argued that due to diverging biaxial fluctuations the critical behaviour around T_{NI} should be that of a tricritical point, in which case $\beta = 0.25$. Though a better temperature control, especially close to T_{NI} , is required to exclude other possibilities, our results seem to support the idea of tricritical behaviour at T_{NI} .

Finally we come to a discussion of the molecular factors influencing $\Delta\chi$. A well known fact is that benzene has a relatively large value of $\Delta\chi$ arising from the high absolute value of the susceptibility perpendicular to the plane of the benzene ring [25]. Qualitatively this can be attributed to the fact that the π -electrons in an aromatic ring are delocalized and form a « ring-current ». Consequently most of the anisotropy of $\Delta\chi$ in liquid crystals arises from the benzene rings. This is illustrated in figures 1-3, where the results form groups of very similar values, which groups depend only on the number of benzene rings. Introduction of foreign atoms in the rings has a rather limited influence. However, it should be realized that a small difference in the slope $d(\Delta\chi)/dT$ leads to a relatively large difference in $\Delta\chi_0$. Some examples are shown in table II. There is a relatively large difference between $\Delta\chi_0$ of 3 and 4, while the value of $\Delta\chi$ at $T/T_{NI} = 0.98$ is very similar. If the difference in $\Delta\chi_0$ is real and not due to the uncertainties in the extrapolation to $T = 0$, it means that 4 has an overall lower order parameter.

Table II. — Values of $\Delta\chi_0^M$ and of $\Delta\chi^M$ at $T/T_{NI} = 0.98$ for some of the compounds.

No. compound	$\Delta\chi_0^M \times 10^6$ ($\text{cm}^3 \text{mol}^{-1}$)	$\Delta\chi^M \times 10^6$ ($\text{cm}^3 \text{mol}^{-1}$) ($T/T_{NI} = 0.98$)
<u>2</u>	15.0 ± 0.1	7.90 ± 0.05
<u>3</u>	14.0 ± 0.1	7.36 ± 0.05
<u>4</u>	17.5 ± 0.1	7.31 ± 0.05

Table III. — Anisotropy contribution to the molar susceptibility of various groups according to two theoretical schemes by Flygare [26], and as determined from experiments.

	$\Delta\chi_0^M \times 10^6$ ($\text{cm}^3 \text{mol}^{-1}$)			
	Theoretical		Experimental	
	atom	bond	solid	nematic
—C≡C—	— 5.0	— 7.2	— 3.5	— 0.5
—C≡N	— 7.8	— 10.1		— 5.0
—CH ₃	— 3.1			— 4.8
—C≡C—C≡C—	— 10.0	— 14.4	— 23.5	— 4.4

Looking into somewhat more detail at the results one would like to correlate the value of $\Delta\chi_0$ with the anisotropy of various molecular groups. Such an approach has been advocated by Flygare [26]. Some results are given in table III. The column indicated by *solid* refers to contributions as calculated from solid state measurements [2, 25]; the results in the column labelled *nematic* are calculated by combining the $\Delta\chi_0$ values from table I. As we see the results are not very encouraging. Neither the crystalline nor the liquid crystal data for $\Delta\chi_0^M$ of various groups agree very well with the calculated ones. Though triple bonds along the long molecular axis certainly seem to contribute to a negative $\Delta\chi$, there is much reason to mistrust the large negative contribution to $\Delta\chi_0^M$ from the —C≡C—C≡C— group, which has been reported from solid state measurements.

In experiments $\Delta\chi$ is often used as a measure for the order parameters S . As far as equation (12) is valid (no biased rotation around the long molecular axis) this is correct for the relative variation of S with temperature. It is rather difficult to estimate the absolute scale of S with some accuracy. It seems that one has to be satisfied with an absolute accuracy of the order of, say, 10 %. For order parameters from measurements of the birefringence this conclusion is valid *a fortiori* because of the additional uncertainties associated with the internal field.

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