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Order parameters of a nematic liquid crystal with low optical anisotropy as determined by depolarized Raman scattering

L. G. P. Dalmolen, E. Egberts and W. H. de Jeu

Solid State Physics Laboratory, University of Groningen, Melkweg 1, 9718 EP Groningen, The Netherlands

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Résumé. — On a mesuré en diffusion Raman polarisée les paramètres d'ordre $\langle P_2 \rangle$ et $\langle P_4 \rangle$ de composés nématiques partiellement hydrogénés. Ainsi que dans le cas des composés avec une grande biréfringence, $\langle P_4 \rangle$ est beaucoup plus petit que la prédiction théorique. Par ailleurs on a utilisé l'effet Raman résonant pour une sonde colorée dissoute dans le composé nématique. Les paramètres d'ordre de la sonde ne représentent pas l'ordre orientational de l'hôte.

Abstract. — Depolarized Raman measurements are reported for the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of a partially hydrogenated nematic compound. Similar to the situation observed for some nematic compounds of large birefringence the value of $\langle P_4 \rangle$ is anomalously low compared with theoretical predictions. Furthermore, resonant Raman measurements are reported for coloured probe molecules dissolved in the nematic compound. The order parameters of the probe are not typical for the ordering of the host-material.

1. Introduction.

Nematic liquid crystals are true liquids in the sense that there exists no long range positional ordering of the molecules. In addition, the molecules possess a unique axis, which is, on average, oriented along a preferred direction, the director \mathbf{n} . The number of molecules making an angle between β and $\beta + d\beta$ with the director is given by

$$N(\beta) = f(\beta) 2 \pi \sin \beta d\beta.$$

The orientational distribution function $f(\beta)$ is difficult to determine completely, but the first few coefficients of an expansion in Legendre polynomials of $f(\beta)$ are accessible by experiment. Because of the equivalence of \mathbf{n} and $-\mathbf{n}$ the odd coefficients are zero. The first non-zero ones are then

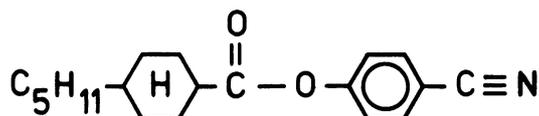
$$\begin{aligned} \langle P_0 \rangle &= 1 \\ \langle P_2 \rangle &= \frac{1}{2} \langle 3 \cos^2 \beta - 1 \rangle \\ \langle P_4 \rangle &= \frac{1}{8} \langle 35 \cos^4 \beta - 30 \cos^2 \beta + 3 \rangle. \end{aligned}$$

$\langle P_2 \rangle \equiv S$, the well-known Saupe order parameter can be determined by common techniques probing any second-rank tensor property like the diamagnetic anisotropy ($\Delta\chi$), or the birefringence (Δn) [1]. $\langle P_4 \rangle$ as well as $\langle P_2 \rangle$ can be determined by depolarized Raman scattering on uniformly aligned samples, as

pointed out by Jen *et al.* [2]. The experimental values for $\langle P_2 \rangle$ are always in reasonable agreement with predictions from mean-field and related theories describing the orientational ordering in liquid crystals. However, for several compounds $\langle P_4 \rangle$ has been reported to be much lower than the theoretically predicted values; in some cases even negative values have been given [2-4].

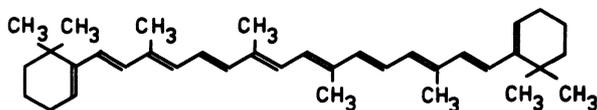
In principle, low values of $\langle P_4 \rangle$ indicate that either the distribution function is broadened, or, for a sufficiently low $\langle P_4 \rangle$, is even not peaked at $\beta = 0$. Such a behaviour is in conflict with the usual picture of nematic liquid crystals, as the latter case means that the molecules are locally tilted with respect to the macroscopic preferred direction \mathbf{n} . Therefore, it is of primary importance to check the assumptions that have been made to evaluate the experimental data.

In this paper, we focus the attention mainly on the problem of the importance of a proper treatment of the internal field corrections due to the macroscopic optical anisotropy. This problem can be studied on compounds with a relatively low birefringence (Δn), for which, consequently, the local field correction should be smaller than for the usual aromatic compounds with a relatively large optical anisotropy. We used the *eq-4-(n-pentyl)-cyclohexane-*eq-4'** carboxylic ester or *p*-cyanophenol, a so called Demus ester (to be indicated as 5D) for this study. This compound



shows a relatively low Δn of about 0.07.

In addition, measurements were done on a colored probe molecule, β -carotene,



dissolved in small quantity in the liquid crystal. Choosing the frequency of the incident light near that of one of the electronic transitions of the probe, resonant Raman scattering can be used to determine $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of the probe. Such a method was recently proposed by Nakajima [5]. The combination of the two methods provides an answer to the question whether the order parameters of the probe are in some way typical for those of the nematic host, i.e. if the probe method is generally applicable to determine the order parameters of a liquid crystal.

2. Theory.

For the theory of the depolarized method for the determination of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ we refer to reference 2, and only a short summary will be given.

For an ensemble of molecules the intensity of the scattered Raman light can be written as

$$I_s = \alpha \langle (\mathbf{e}_s \mathbf{R}' \mathbf{e}_i)^2 \rangle$$

where \mathbf{e}_s and \mathbf{e}_i are unit vectors denoting the direction of polarization of the scattered and incident light, respectively. \mathbf{R}' is the effective or « dressed » molecular Raman tensor (see discussion). On principal axes \mathbf{R}' reads

$$\mathbf{R}' = \begin{pmatrix} a & & \\ & b & \\ & & 1 \end{pmatrix}.$$

The z-axis of \mathbf{R}' lies along the axis of symmetry of the molecular bond stretch vibration considered, which is practically the same as the bond axis. The depolarization ratio is defined as the ratio of the intensity of the scattered light with its polarization parallel and perpendicular to the polarization of the incident light, respectively. In the scattering geometry depicted in figure 1 three independent depolarization ratios can be defined, depending on the orientation of the director of the sample with respect to the polarization of the incident light. These depolarization ratios are given by

$$\begin{aligned} R_1 &= I_{yz}/I_{zz}, \\ R_2 &= I_{zy}/I_{yy}, \\ R_3 &= I_{yx}/I_{xx}, \end{aligned}$$

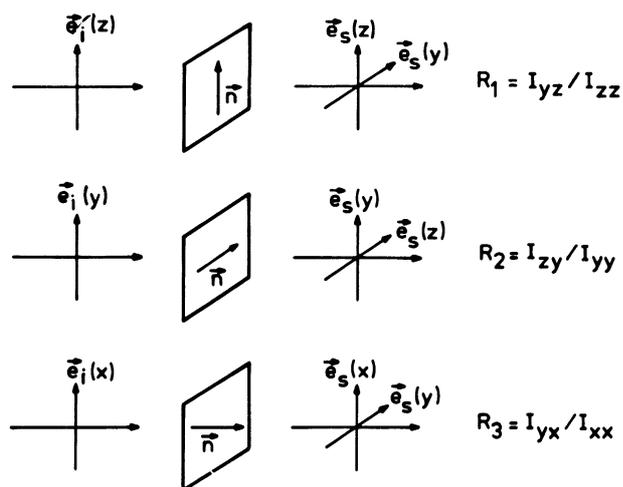


Fig. 1. — Definition of the different scattering geometries. \mathbf{e}_i and \mathbf{e}_s indicate the direction of polarization of the incident and scattered light. The director \mathbf{n} is taken along \hat{Z} .

where the subscripts of I refer to the polarization of the scattered and incident light, respectively. A fourth depolarization ratio, R_{iso} , can be determined in the isotropic phase ($R_{iso} \equiv R_1$ in the isotropic phase). Formulae giving the relation between the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ and the depolarization ratios can be found in references 2, 6. In these formulae appear five unknown parameters, $\langle P_2 \rangle$, $\langle P_4 \rangle$, a , b and β_0 , the angle between the long molecular axis and the principal axis of the normal mode of vibration. These formulae are only valid under certain restrictions :

(i) The orientational distribution is supposed not to depend on the Euler angle γ . This is correct if the influence of the « flatness » order parameter D is small. The latter is always the case if the molecular vibration is chosen such that β_0 is small (say $< 15^\circ$) and, moreover, a and b are small compared to 1 [2].

(ii) The molecular bond stretch vibration considered should be located in the rigid aromatic core of the molecule. Thus, the ordering of the bond axis, which is actually determined, is typical for the ordering of the whole molecule, which is not true if it is located in the flexible alkyl chain (see discussion).

(iii) The local field tensor (\mathbf{K}^c) and \mathbf{R} , the molecular Raman tensor, should commute in order to justify the use of a constant « dressed » tensor \mathbf{R}' throughout the nematic and isotropic temperature range. As \mathbf{K}^c diagonalizes in the molecular frame, \mathbf{R} should do the same. This means again, that β_0 should be small (say $< 15^\circ$).

Combining these restrictions, one should choose the molecular bond to be located in the aromatic core such that β_0 is small. When β_0 is small, an error of the order of 5° has a negligible influence on the results for $\langle P_2 \rangle$ and $\langle P_4 \rangle$. Therefore, it suffices to estimate the value of β_0 with help of a space filling molecular model. Hence, β_0 being determined in this

manner, there remain four unknown parameters. As four independent measurements of the depolarization ratios are available, it is now possible to calculate $\langle P_2 \rangle$ and $\langle P_4 \rangle$. In principle, a and b can be calculated too, but these parameters are extremely sensitive to possible experimental errors in the input parameters [6], which is fortunately not true for $\langle P_2 \rangle$ and $\langle P_4 \rangle$. Therefore, values of a and b will not be presented in this paper.

The theory of the resonant Raman measurements is essentially a simplification of the general case. In the resonant case, according to reference 5, the Raman tensor reduces to

$$\mathbf{R}' = \begin{pmatrix} 0 & & \\ & 0 & \\ & & 1 \end{pmatrix}.$$

By introducing $a = b = 0$ in the formulas for the general case, the formulas for the resonant case are found. It is noted that R_{iso} as well as R_3 necessarily equal $1/3$ (the latter only provided β_0 is small). Hence, two unknown variables are left, and the measurement of R_1 and R_2 suffices to determine $\langle P_2 \rangle$ and $\langle P_4 \rangle$. As $R_{\text{iso}} = 1/3$ for all compounds, this provides us with a perfect opportunity to check the calibration of the experimental set-up. Furthermore, because R_{iso} is not needed to determine the order parameters, the results will not be influenced by any possible difference between the internal field in the nematic and isotropic phase, respectively.

3. Experimental.

5D was obtained from Hoffmann-La Roche (Basle, Switzerland) and used without further purification. It has a nematic range from 47.5-79.5 °C. The depolarization ratios belonging to the different scattering orientations of the sample are clarified in figure 1. A newly built oven permitted to place the sample close to the collection optics; this led to an improvement of the signal-to-noise-ratio of about four compared to our previous measurements [6]. In fact, this made the experiment possible as, quite generally, the intensity of the scattered light is smaller for less polarizable compounds like the present one. Nevertheless, relatively thick samples had to be used for intensity considerations. As is well known, multiple scattering due to thermal director fluctuations causes the depolarization ratios to depend on the thickness of the sample. Up to about 100 μm this effect is linear in the sample thickness [2]. Therefore, all measurements were performed on samples of 100 μm and 50 μm , and the measured depolarization ratios were extrapolated to zero thickness. As a check, R_1 was also measured on a 25 μm sample (non-resonant case). In the resonant case, R_{iso} was determined to check the alignment of the set-up. The value obtained was 0.32 ± 0.02 , which is in perfect agreement with the theoretical value of $1/3$.

The laser was normally run at about 100 mW at the 5 145 Å line. In the resonant case we had to lower the intensity to 2 mW to prevent overheating of the sample. The effective absorption of the green laser light by β -carotene also limits the concentration that can be used. At too high concentrations the incident light is not transmitted anymore through the whole sample, and the order parameters correspond mainly to the upper part of the sample [7]. The optimum concentration was determined such that the intensity of the scattered light still depends linearly on the sample thickness (for 100 μm and 50 μm). A concentration of about 0.1 % by weight proved to be suitable. The resonant enhancement of the intensity of the scattered Raman light of β -carotene was so large, that, even for this low concentration, the Raman light of 5D itself disappeared completely in the background of the β -carotene spectrum! The measurements were performed on the 1515 cm^{-1} symmetric stretch vibration [5] of the central $\dots\text{C}=\text{C}-\text{C}=\text{C}-\text{C}\dots$ core of the β -carotene. β_0 is estimated to be zero in this case.

The measurements on the pure compound 5D were performed on the 2227 cm^{-1} cyano stretch vibration and the 1597 cm^{-1} symmetric stretch-vibration of the phenyl ring [8]. The axes of these vibrations do not lie perfectly along the molecular axis, but make an angle $\beta_0 = 7^\circ \pm 2$ with this long axis. This angle was estimated from a space filling model of 5D.

To evaluate the results, values of the birefringence are required to calculate C_n [2]. The ordinary index of refraction was determined using an Abbe refractometer (Zeiss model B), the birefringence by interference measurements.

4. Experimental results.

Data for the birefringence are given in figure 2. The measured depolarization ratios of 5D are depicted in figure 3. The birefringence of the β -carotene mixture was found to differ only very slightly from the pure compound 5D. The values of R_{iso} for the 2227 cm^{-1} and the 1597 cm^{-1} line, respectively, were found to be

$$R_{\text{iso}}(2227) = 0.235 \pm 0.05$$

$$R_{\text{iso}}(1597) = 0.515 \pm 0.05.$$

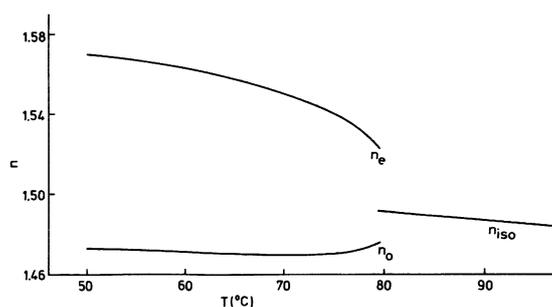


Fig. 2. — Refractive indices of 5D at 589 nm.

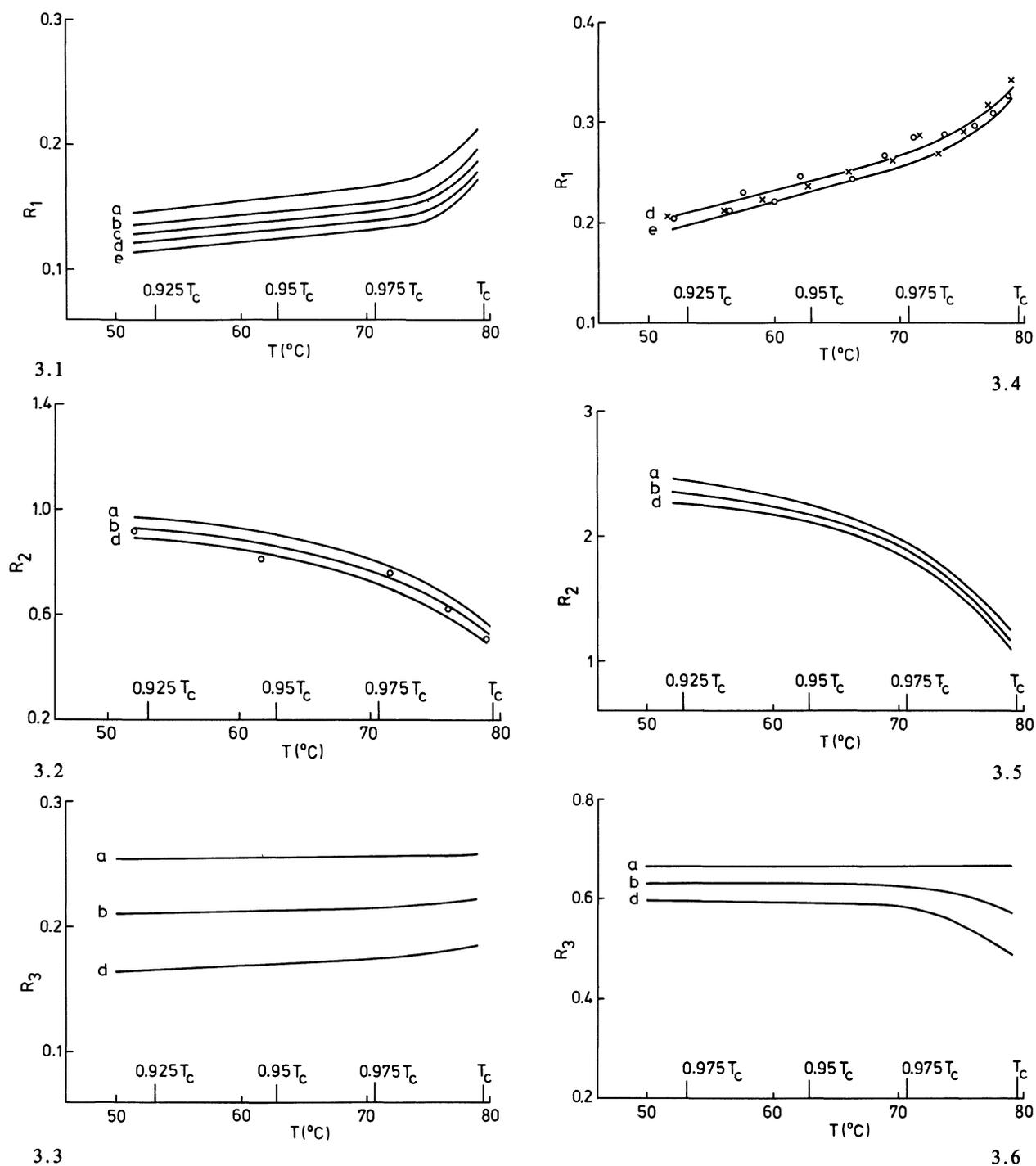


Fig. 3. — Depolarization ratios of 5D for the $C \equiv N$ stretch vibration (3.1, 3.2, 3.3) and the benzene ring symmetric stretch vibration (3.4, 3.5, 3.6), 3.a : 100 μm , 3.b : 50 μm , 3.c : 25 μm , 3.d : extrapolation to zero thickness, 3.e : R_1/C_n .

The order parameters obtained from both the « normal » and the « resonant » measurements are given in figures 4 and 5, respectively. In figure 4 the values of $\langle P_2 \rangle$ obtained from Δn are given for comparison, using an isotropic internal field (Vuks' approximation) [1]. The absolute values are adjusted assuming $\langle P_2 \rangle = 1$ at zero temperature. The agreement with $\langle P_2 \rangle$ as obtained by the Raman experiment is good. The values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of pure 5D from the 2227 cm^{-1} and 1597 cm^{-1} band agree within the

experimental error. $\langle P_4 \rangle$ appears to be lower than the value predicted by mean-field theory, while the value of $\langle P_2 \rangle$ agrees reasonably well with the mean field value, as can be seen in figure 6.

The order parameters of β -carotene obtained from the resonant Raman measurements are substantially higher than the order parameters of the pure compound. However, the values of both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ at the nematic to isotropic transition temperature are higher than expected from theory.

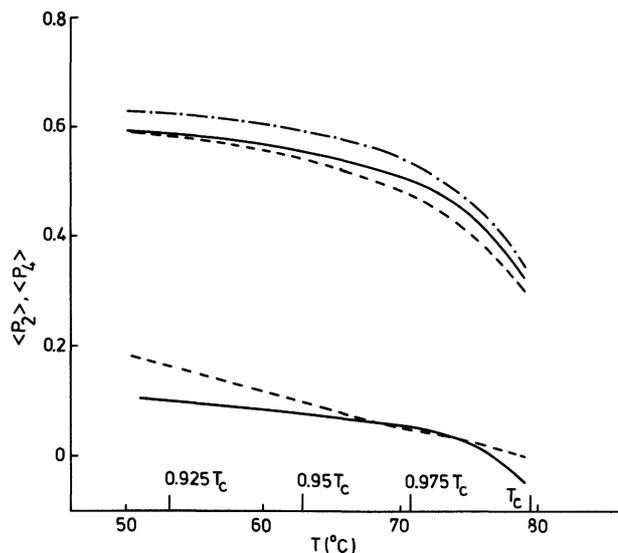


Fig. 4. — $\langle P_2 \rangle$ (upper curves) and $\langle P_4 \rangle$ (lower curves) vs. temperature. — C≡N stretch, ----- benzene stretch, -.-.-. $\langle P_2 \rangle$ from Δn .

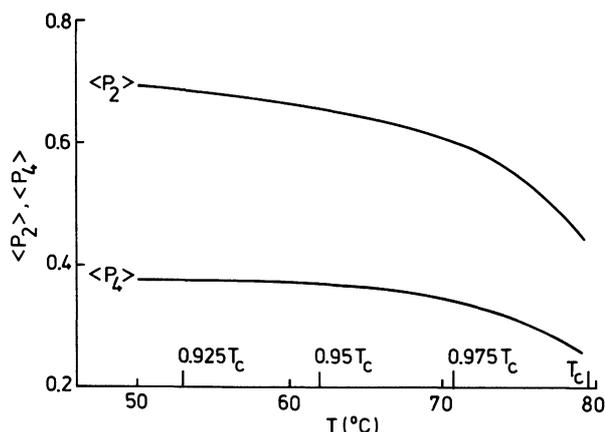


Fig. 5. — $\langle P_2 \rangle$ (upper curve) and $\langle P_4 \rangle$ (lower curve) vs. temperature of β -carotene in 5D.

5. Discussion.

5.1 THE LOCAL FIELD CORRECTION. — As discussed elsewhere [6], the total anisotropic part of the local field correction consists of two parts :

(i) The anisotropy of the molecular shape, which is directly connected with that of the local environment of the molecule. This part is called the « microscopic » part.

(ii) The anisotropy of the medium (Δn). This part, which is due to the long range effects, is called the « macroscopic » part.

The first part is not expected to be temperature dependent, even when going from the nematic to the isotropic phase, because of the strong correlations

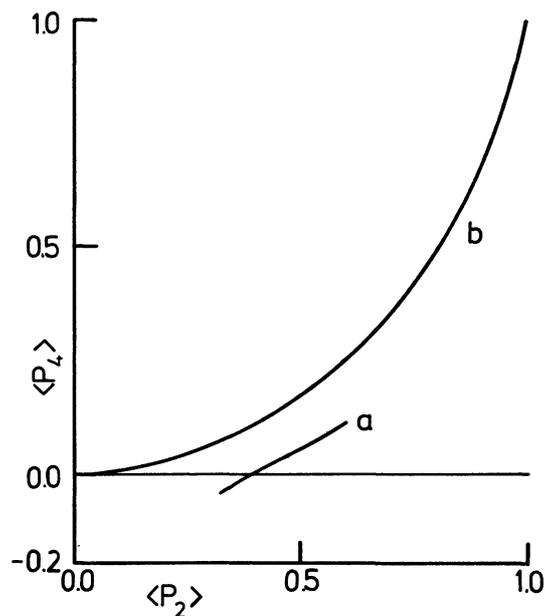


Fig. 6. — Curves of $\langle P_4 \rangle$ vs. $\langle P_2 \rangle$, a : results for 5D (C≡N vibration), b : as obtained from the mean field theory.

between neighbouring molecules. Therefore, this part can be incorporated together with the isotropic part of the local field correction into the molecular Raman polarizability tensor \mathbf{R} , leading to an effective or « dressed » polarizability tensor \mathbf{R}' [2]. The second part is temperature dependent *via* $\Delta n(T)$, and in principle should be taken into account. In the isotropic phase it will be zero. Several arguments have been given that this part is still small in the nematic phase [6, 9].

Seeliger *et al.* [10] also performed depolarized Raman measurements on compounds with a low Δn , for which, consequently, a small macroscopic local field correction can be expected. These compounds, taken from the alkyl-cyanophenylcyclohexane (nPCH) series, show a mean field like behaviour of both $\langle P_2 \rangle$ and $\langle P_4 \rangle$. This led then to the conclusion that, in spite of previous assumptions, a proper treatment of the local-field correction is of primary importance. Our measurements on 5D show that low values of $\langle P_4 \rangle$ can be found also in compounds with a low Δn , in contradiction to Seeliger's assumption. The reverse also appears to be true, as is demonstrated by the measurements on some tolanes [6]. These compounds possess a fairly high value of Δn and, nevertheless, show a mean field like behaviour of $\langle P_4 \rangle$.

We conclude that low values of $\langle P_4 \rangle$ most probably do not arise from erroneous local field corrections. The important microscopic part of the correction is incorporated into the dressed Raman tensor. The macroscopic part of the correction is too small to have a significant influence on the value of the order parameters as obtained by experiment.

5.2 MOLECULAR FLEXIBILITY AND MOLECULAR ASSOCIATION. — Two other possibilities have been considered to explain the anomalously low values of $\langle P_4 \rangle$.

(i) Molecular association, due to strongly dipolar end groups as e.g. the CN group [6].

(ii) Molecular flexibility, especially due to the alkyl-chain [2-4].

The usual theoretical models assume rigid molecules, which is not correct. Luckhurst [11] pointed out that, theoretically, any influence of the alkyl-chain flexibility should be small or absent. Measurements on the compounds of a homologous series offer an opportunity to check whether this is true. Increasing the alkyl-chain length increases the number of *gauche-trans* conformations of the alkyl-chain. However, the influence of the alkyl-chain length on the order parameters is of a complicated nature. The chain-length does not only affect the number of possible *gauche-trans* conformations, but in the case of strongly polar compounds, also the degree of molecular association. This effect can be studied by dielectric permittivity measurements. Anti-parallel molecular association leads to an effective reduction of the dipolar moment of the end-group ($C \equiv N$), which then gives a value of both $\Delta\epsilon$ and $\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$ lower than expected from the dipole moment of a free molecule. Furthermore, one observes an increase with temperature of ϵ in the isotropic phase and $\bar{\epsilon}$ in the nematic phase, because the molecular complexes dissociate with increasing temperature.

The dielectric permittivity of the first four nematic homologues of the *p*-alkyl-*p'*-cyanobiphenyl (*n*CB) series and of 7PCH were determined by Parneix [12, 13]. Schad [14] determined $\Delta\epsilon$ of 3, 5 and 7PCH. A decreasing value of $\bar{\epsilon}$ is observed with increasing chain-length, indicating an increasing degree of molecular association, as well in the *n*CB as in the *n*PCH series. The low values of $\bar{\epsilon}$ of all these compounds indicate a high degree of molecular association.

Experimentally, the order parameters of two homologous series have been studied by Raman measurements [3, 10]. For the *n*PCH-series $\langle P_4 \rangle$ is found to be independent of the alkyl-chain length for $n = 3, 5$ and 7 . Prasad *et al.* [3] performed measurements on the *n*CB series. They found a trend of decreasing $\langle P_4 \rangle$ with increasing chain-length. However, they did not make any correction for the effect of the sample-thickness, while this leads to important differences [6]. Furthermore, we were unable to reproduce the reported values of R_{iso} of the different compounds. Therefore, we remeasured the order-parameters of the *n*CB series. In a future paper we will report

that in fact in this series $\langle P_4 \rangle$ increases with increasing chain-length. According to the permittivity measurements this could be related to an increasing degree of molecular association.

5.3 THE RESONANT RAMAN MEASUREMENTS. — The order parameters of β -carotene do not agree with those of the pure host material 5D. In general, there seems to be little reason that in any other host-material the ordering of β -carotene as a probe is typical for the ordering of the pure host. The fact that the ordering of a coloured probe can be higher than the degree of molecular ordering of the host is well known from experiments. It is advantageously used in the so-called « guest-host » displays, that are manufactured commercially nowadays. In conclusion, in general one should be very careful to consider the order parameters of a guest-material to be typical for the order parameters of the host.

6. General conclusions.

(1) The anomalously low values of $\langle P_4 \rangle$ reported for several compounds cannot be ascribed to incorrect local-field corrections in the evaluation of the experimental results.

(2) Any possible influence of molecular association on $\langle P_4 \rangle$ remains to be clarified. Preliminary results on the *n*CB series indicate that probably the order parameters vary due to an influence of the alkyl-chain length on the molecular association.

(3) Any direct influence of the molecular flexibility of the molecular ordering is possibly small. However, measurements on a homologous series of molecules with a small dipole moment are needed to draw a final conclusion.

(4) The order parameters of a coloured probe, determined by resonant Raman scattering are not typical for the order parameters of the host in which the probe is dissolved.

Acknowledgments.

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