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## The order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in nematic p-alkyl-p'-cyano-biphenyls : polarized Raman measurements and the influence of molecular association

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**Résumé.** — Nous présentons des résultats de mesures d'effet Raman polarisé sur une série homologue d'alkylcyanobiphényles fournissant la valeur des paramètres d'ordre  $\langle P_2 \rangle$  et  $\langle P_4 \rangle$ . En fonction de la longueur des chaînes, nous observons une augmentation de  $\langle P_4 \rangle$  commençant aux valeurs basses jusqu'aux valeurs plus hautes correspondant à la théorie de champ moyen de Maier et Saupe. De plus, nous évaluons les facteurs de corrélation décrivant l'association moléculaire antiparallèle en vue de mesures de permittivité. Un modèle qualitatif attribue les valeurs faibles de  $\langle P_4 \rangle$  à cette association. Ceci conduit à une certaine proportion de « dimères » dont l'axe moléculaire n'est plus parallèle à la direction de vibration Raman. Additionnellement on s'attend à ce que les interactions stériques provoquent une absence de parallélisme entre l'axe « long » du dimère et le monomère voisin. Pour certains paramètres particuliers du dimère, la combinaison de ces deux effets peut entraîner un élargissement de  $f(\beta)$  et, par suite, des valeurs de  $\langle P_4 \rangle$  basses ou mêmes négatives.

**Abstract.** — Values for the order parameters  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  from polarized Raman measurements are reported for the homologous series of nematic alkylcyanobiphenyls. With increasing chain length a change of behaviour is observed from « low »  $\langle P_4 \rangle$ -values to higher values corresponding to the Maier-Saupe mean-field theory. In addition, correlation factors describing the anti-parallel molecular association in these compounds have been derived from permittivity measurements. A tentative qualitative model is given in which the low  $\langle P_4 \rangle$ -values are attributed to this association. This leads to a certain proportion of « dimers », for which the long molecular axis is not parallel to the direction of the Raman-vibration anymore. In addition, steric interactions can be expected to lead to non-parallelism of the long axis of a dimer and of a neighbouring monomer. For specific parameters of the dimer, the combination of these two effects can lead to a marked broadening of  $f(\beta)$ , and thus to low or negative values for  $\langle P_4 \rangle$ .

### 1. Introduction.

Nematic liquid crystals [1] are true liquids in the sense that the centres of mass of the molecules have 3-dimensional translational symmetry. They are distinguished from isotropic liquids by an anisotropic orientational distribution function. For a simplified model of rod-like molecules this function can be denoted by  $f(\beta)$ , where  $\beta$  is the angle between the long molecular axis and the preferred direction (director  $\mathbf{n}$ ). Though knowledge of  $f(\beta)$  is of primary importance to test theories of the nematic phase, this is not readily available [2]. In principle,  $f(\beta)$  could be determined from X-ray or neutron scattering methods [3, 4]. However, this requires absolute intensity measurements, which are not easily obtained with sufficient accuracy. Alternatively it is useful to

expand  $f(\beta)$  as

$$f(\beta) = \sum_{l=0}^{\infty} \frac{1}{2} (2l+1) \langle P_{2l} \rangle P_{2l}(\cos \beta), \quad (1)$$

where the coefficients  $\langle P_{2l} \rangle$  are the order parameters. The first three are given by

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

Only the even terms in the Legendre development of  $f(\beta)$  are nonzero, as due to the equivalence of  $\mathbf{n}$  and  $-\mathbf{n}$  one has  $f(\pi - \beta) = f(\beta)$ .

The order-parameter  $\langle P_2 \rangle$  can be measured by usual techniques probing a second order tensor property [5], such as diamagnetic anisotropy, birefringence, nuclear magnetic resonance (NMR) parameters, etc.  $\langle P_2 \rangle$  as well as  $\langle P_4 \rangle$  can be determined from the polarized Raman scattering of uniformly aligned samples, as first pointed out by Jen *et al.* [6]. Although reliable measurements are available for only a few compounds, surprisingly, for some of these compounds, rather low or even negative values for  $\langle P_4 \rangle$  have been reported [6, 7, 8], far below the predictions from the Maier-Saupe mean-field theory. This contrasts with results for  $\langle P_2 \rangle$  in general, and for  $\langle P_4 \rangle$  in some other cases [9, 10], that are in reasonable agreement with the mean-field calculations. The origin of these low values of  $\langle P_4 \rangle$  and its interpretation in terms of the orientational distribution of the molecules still constitutes one of the major problems in our understanding of the nematic liquid crystalline state [11]. 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  $\mathbf{n}$ .

In this paper results will be given for  $\langle P_4 \rangle$  of the series of *p*-alkyl-*p'*-cyanobiphenyls (*n*CB), that provide in our opinion a possible clue to the anomalous behaviour of  $\langle P_4 \rangle$  described above. With increasing alkyl chain length  $n$ ,  $\langle P_4 \rangle$  shows at low temperatures a change of behaviour from « low » to mean-field behaviour. A tentative qualitative model will be given in which the low values are attributed to a broadened distribution function, which is due to association between the strongly polar molecules. The degree of association is characterized by a correlation factor derived from permittivity measurements.

The plan of the paper is as follows. In section 2 the theory of the depolarized Raman method to determine  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  will be summarized. In addition it is described how correlation factors are derived from the permittivity measurements. Section 3 discusses the experimental methods, and section 4 gives the results. Finally, section 5 contains an attempt to interpret these and other results for  $\langle P_4 \rangle$ , as well as a concluding discussion.

## 2. Theory of the methods.

2.1 POLARIZED RAMAN SCATTERING AND ORDER PARAMETERS. — For an ensemble of molecules the intensity of the scattered Raman light can be written as

$$I_s = \alpha \langle (\mathbf{e}_s \mathbf{R}' \mathbf{e}_i)^2 \rangle \quad (3)$$

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 Refs. [6, 8]). On principal axes  $\mathbf{R}'$  reads

$$\mathbf{R}' = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (4)$$

The  $z$ -axis of  $\mathbf{R}'$  is directed along the axis of symmetry of the molecular bond stretch vibration considered. In the scattering geometry depicted in figure 1 three independent depolarization ratios can be defined, given by

$$\begin{aligned} R_1 &= I_{yz}/I_{zz}, \\ R_2 &= I_{zy}/I_{yy}, \\ R_3 &= I_{yx}/I_{xx}, \end{aligned} \quad (5)$$

where the subscripts of  $I$  refer to the polarization of the scattered and incident light, respectively. A fourth depolarization ratio,  $R_{\text{iso}}$ , can be determined 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 [6, 9]. In these formulae appear five unknown parameters,  $\langle P_2 \rangle$ ,  $\langle P_4 \rangle$ ,  $a$ ,  $b$  and  $\beta'$ , 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 that have been discussed in some detail elsewhere [6, 8]. It is of primary importance that the orientational distribution does not depend on the Euler angle  $\gamma$ . 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  $\beta'$  is small (say  $< 15^\circ$ ) and, moreover  $a$  and  $b$  are small compared with unity [6].

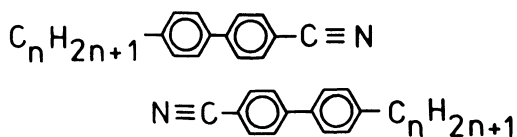
In practice the molecular bond of which the vibration is studied should be located in the aromatic core such that  $\beta'$  is small. When  $\beta'$  is small, an error of the order of  $5^\circ$  has a negligible influence on the results for  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$ . Therefore, it suffices to estimate the value of  $\beta'$  with the help of a molecular model. Hence,  $\beta'$  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  $\langle P_4 \rangle$ .

2.2 PERMITTIVITY AND CORRELATION. — It is well known that *para*-cyano substituted compounds show strongly anti-parallel dipole association. Formally, this can be described as a monomer-dimer equilibrium



where the dimers  $D$  in the case of the *n*CB-series can

be visualized as



Evidence for this behaviour stems from the observation that when a smectic phase is formed, a layer spacing is observed that indeed corresponds to the length of the dimer, i.e. approximately twice the length of the aliphatic end groups plus the length of the aromatic core [12]. In addition the dielectric permittivity does not show the usual behaviour  $\epsilon \sim \mu^2/kT$  [13, 14]. Instead  $\mu$  must be interpreted as an effective dipole moment, with  $\mu_{\text{eff}}^2(T) = g(T) \mu^2$ . Here  $\epsilon$  stands either for the isotropic permittivity or for the average permittivity in the liquid crystalline phases, while  $g < 1$  gives the amount of antiparallel correlation. For the purpose of this paper we do not want to go into a discussion of the problems around the interpretation of the anisotropic permittivity of nematics, in particular in relation to the internal field [15]. We choose to consider either the average or the isotropic  $\epsilon$  and to apply the Kirkwood-Fröhlich formalism to obtain  $g$  via [15]

$$\frac{Ng\mu^2}{9kT} = \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} \quad (7)$$

Here  $N$  is the number of molecules and  $\epsilon_\infty$  the permittivity at high frequencies. This means that the anisotropy of the permittivity of the nematic medium is taken into account, but subsequently averaged out by integrating over the orientational order of the molecules. Anisotropies are disregarded in all other aspects, just as usually done for an isotropic liquid, even if it consists of anisotropic molecules. Though the absolute values of  $g$  thus obtained will not be very reliable, we can expect that trends will be reasonably well reproduced. Various alternatives to calculate  $g$  have been compared by Dunmur and Miller [16].

To describe the equilibrium (6) we introduce the number of monomers  $n_M$  and the number of dimers  $n_D$ . The total number of particles  $n = n_M + n_D$  changes with the molar dimer and monomer fractions  $x_D$  and  $x_M = 1 - x_D$ , respectively. Note that the total number of molecules  $N = n_M + 2n_D$  is constant. Taking  $\mu_M^2 = \mu^2$  and  $\mu_D^2 = 0$  it follows that

$$\mu_{\text{eff}}^2 = g\mu^2 = n_M \mu^2 / N \quad (8)$$

Thus one finds  $g = n_M/N$ , or for the dimer fraction

$$x_D = (1 - g)/(1 + g) \quad (9)$$

Equations (7) and (9) allow us to calculate  $x_D$  from the experimental data. Equation (9) differs from the

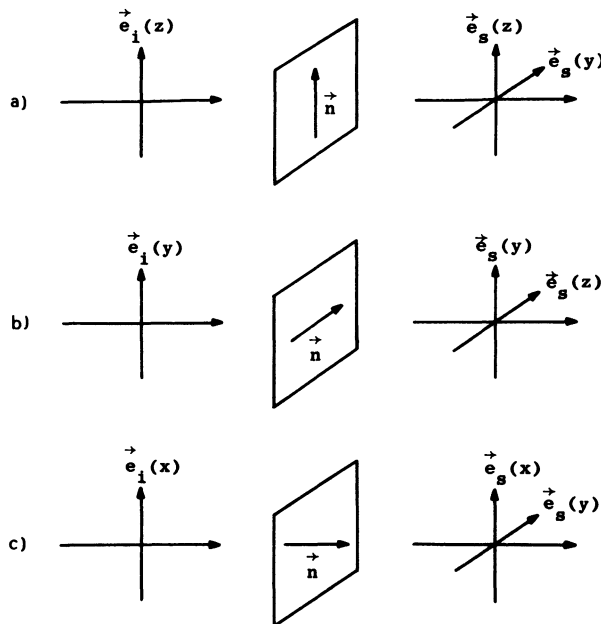


Fig. 1. — Definition of the different scattering geometries.  $e_i$  and  $e_s$  indicate the direction of polarization of the incident and scattered light. The director  $n$  is taken along  $z$ .

formula used in reference [17] to calculate the association in some liquid nitriles, because the latter authors use incorrectly  $g = n_M/n$ .

### 3. Experimental.

The compounds of the  $n$ CB-series were obtained from BDH (Poole, U.K.), and used without further purification [18]. The transition temperatures as measured with a Mettler FP52 hot stage under a polarization microscope are given in table I. The depolarization ratios were measured with a Spex Ramalog system, which has been described in detail in reference [9]. There one can also find details of the sample preparation and a discussion of some of the experimental precautions that are essential to obtain reliable results. The measurements were performed on the  $\text{C}\equiv\text{N}$  stretch vibration, which is for all compounds found at  $2225 \pm 2 \text{ cm}^{-1}$ . To correct for the effect of director fluctuations, the measurements were carried out on samples of 50 and 25  $\mu\text{m}$ ,

Table I. — Transition temperature ( $^\circ\text{C}$ ) and depolarization ratio  $R_{\text{iso}}$  in the isotropic phase of the  $n$ CB series.

	K	S <sub>A</sub>	N	I	$R_{\text{iso}}$
5CB	. 22	—	. 34.6	. 0.275	
6CB	. 15	—	. 29.7	. 0.272	
7CB	. 28	—	. 41.7	. 0.275	
8CB	. 21	. 32.6	. 39.4	. 0.270	
9CB	. 42	. 46.9	. 48.8	. 0.275	

respectively, and extrapolated to zero thickness. The laser was run at 100 mW at the 514.5 nm line.

The permittivities were measured at 1 kHz and 1.5 V with a General Radio type 1673 automatic bridge. The liquid crystal was confined to a display-like cell consisting of two glass plates with evaporated gold electrodes kept at a distance of 100  $\mu\text{m}$  or 190  $\mu\text{m}$  with mylar spacers. Each cell was used only once and calibrated using the known permittivities of benzene and chlorobenzene, giving an empty capacitance of the order of 10-15 pF. The cell was placed in an oven and stabilized to within 0.1 K. A magnetic field was used to align the nematic, in order to determine both  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$ . Various values of the field up to 1 T were used and the resulting permittivities were extrapolated to infinite field.

#### 4. Results.

We shall refrain from giving all details of the experimental depolarization ratios, which can be found in reference [19]. In relation to the reliability of the results we quote in Table I values for  $R_{\text{iso}}$ . The result for 5CB is in good agreement with the values 0.262 and 0.267 given in references [7] and [10], respectively. As  $R_{\text{iso}}$  depends only on the coefficients  $a$  and  $b$  of the Raman tensor (Eq. (4)) one does not expect much variation along the  $n\text{CB}$  series. This is indeed the case. The values of  $R_{\text{iso}}$  differ rather much from those given in reference [20]. In figure 2 the results are given for  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  of the various members of the  $n\text{CB}$  series. For  $n = 7$  and  $n = 8$  these results can be compared with data from reference [21], where rather lower  $\langle P_4 \rangle$ -values are reported. In the absence of sufficient experimental details we can only speculate on the reasons for this discrepancy. As a further check the  $\langle P_2 \rangle$ -values have been compared with results for  $\Delta\chi$ . As shown in figure 3 for 5CB, the temperature dependence of both quantities is in good agreement. This is also true for the other members of the series [19]. In addition for 5CB  $\langle P_2 \rangle$  from Raman and from NMR measurements are found to agree very well (Fig. 3).

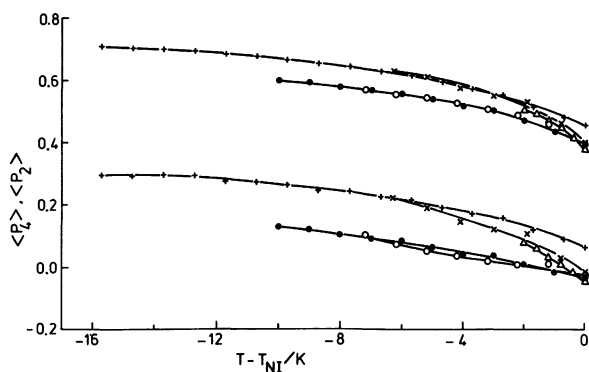


Fig. 2. — Results for  $\langle P_2 \rangle$  (upper curves) and  $\langle P_4 \rangle$  (lower curves) of the  $n\text{CB}$  series;  $\bullet$   $n = 5$ ,  $\circ$   $n = 6$ ,  $+$   $n = 7$ ,  $\times$   $n = 8$ ,  $\Delta$   $n = 9$ .

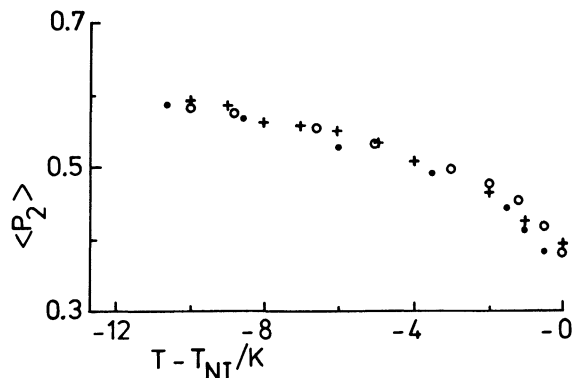


Fig. 3. —  $\langle P_2 \rangle$  from Raman (+), NMR ( $\bullet$ , Ref. [22]), and  $\Delta\chi$  ( $\circ$ ) measurements for 5CB. The  $\Delta\chi$  data are scaled to the Raman data at the lower end of the temperature scale.

In figure 4 the results for the relative dielectric permittivity  $\epsilon/\epsilon_0$  are given. In order to see any variation in the association, the measurements have been extended to fairly high temperatures. As far as such data are available in the literature [23] they are in good agreement with the results shown in figure 4. The dimer fraction derived from these data is shown in figure 5, using equations (7) and (9), values for  $\epsilon_{\infty}$  from refractive indices of reference [24], and densities from reference [25].

#### 5. Discussion.

The order parameters  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  of the  $n\text{CB}$ -series as given in figure 2 show in the first place an even-odd variation with  $n$ . This is quite common in homologous series and generally attributed to some preference of the alkyl chains for the all-*trans* conformation. As a consequence the odd members have relatively high and the even members have relatively

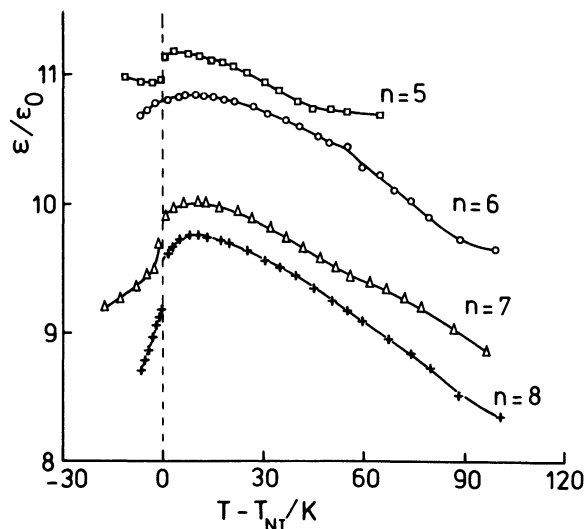


Fig. 4. — Isotropic relative permittivity and mean relative permittivity in the nematic phase of the  $n\text{CB}$  series.

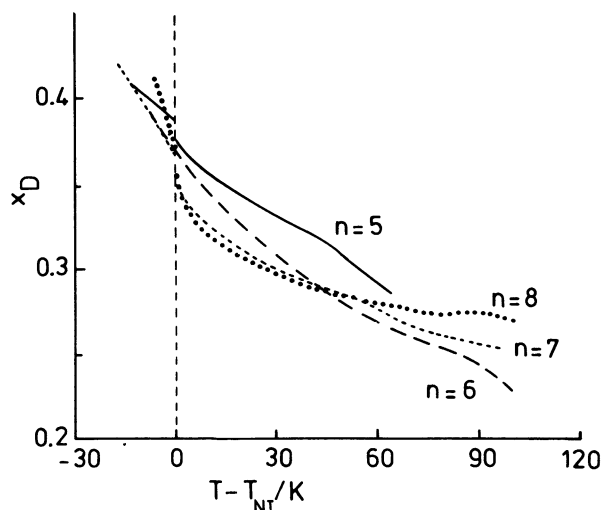


Fig. 5. — Dimer fractions of the *n*CB series as calculated from figure 4 using equations (7) and (9).

low order parameters. More importantly (for the present discussion) the lower members of the series (5CB, 6CB) show over the whole nematic range the anomalous behaviour of a low  $\langle P_4 \rangle$ -value. In contrast to this, at temperatures well below the nematic-isotropic transition  $T_{NI}$ , the higher homologues approach  $\langle P_4 \rangle$ -values rather close to what is expected from the Maier-Saupe mean-field theory. We shall attempt to interpret this change of behaviour in terms of the monomer-dimer model of equation (6), incorporating thus the anti-parallel dipole association of these types of compounds.

The anti-parallel association into dimers will influence the measured order parameters by two effects :

(i) There will be an angle  $\beta_0$  between the long axis of the dimer and monomer units. This is illustrated at the left-hand-side of figure 6 for a model of a dimer

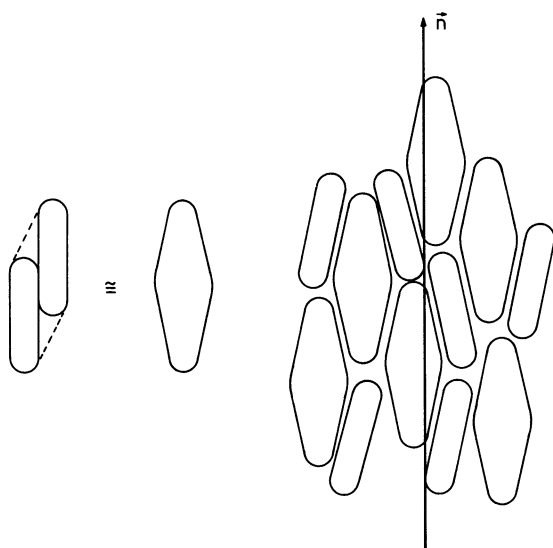


Fig. 6. — Local orientation of monomers and dimers illustrating the angle between the respective long axes.

as two overlapping cylinders representing the monomers. A more realistic model would be to take two lath-like monomers, and combine them to a dimer. In that case it seems reasonable for the purpose of a qualitative discussion to assume both the monomer and the dimer units to be effectively uniaxial. The effect to be discussed is in principle independent of the type of model for the molecules. Now for the monomers any angle  $\beta'_M$  between the long axis and the direction of the cyano-stretch vibration will be small, and can be disregarded. This is not necessarily so for the corresponding angle  $\beta'_D$  in the dimer unit, which then equals  $\beta_0$ . This leads to a broadening of  $f(\beta)$  and the ratio  $\langle P_4 \rangle / \langle P_2 \rangle$  will be lowered. From the orthogonality of the Legendre polynomials it follows that the effect is given by

$$\langle P_L(\cos \beta) \rangle_{\text{exp}} = P_L(\cos \beta'_D) \langle P_L(\cos \beta) \rangle, \quad L = 2, 4, \dots \quad (10)$$

(ii) By definition the long axes of the monomer and dimer units are, on average, parallel to  $\mathbf{n}$ . However, on a microscopic level, steric repulsions between the differently shaped species will lead to tilting of the long axes of a dimer and a neighbouring monomer. From the simple picture of figure 6 one would expect the relative angle to be equal to  $\beta'_D$ . This effect will broaden  $f(\beta)$  of the mixture, and thus lead to a decrease of  $\langle P_4 \rangle$ . In principle, one can simulate this effect by considering a mean-field type distribution of the form

$$f(\beta) = Z^{-1} \exp \{ -UP_2[\cos(\beta - \beta'_D)] \langle P_2 \rangle / k_B T \}, \quad (11)$$

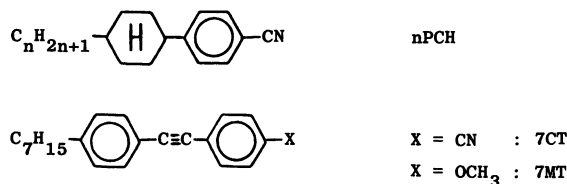
where  $U$  gives the strength of the potential and  $Z$  is a normalization constant. The results for  $\langle P_4 \rangle$  as a function of the parameter  $\beta'_D$  is very similar to that of equation (10).

Obviously both effects discussed depend on the dimer concentration  $x_D$  and on the value of the angle  $\beta'_D$ . Effect (i) can be expected to be proportional to  $x_D$ . In a sense it is trivial, and provided reliable absolute values for  $\beta'_D$  and  $x_D$  could be obtained, it would be possible to calculate its effect exactly. Introduction of an angle  $\beta'$  has already been considered by Miyano [7] for 5CB, however without a physical mechanism being proposed. Effect (ii) is essentially related to the presence of a mixture of monomers and dimers, and thus will be absent both for  $x_D = 0$  and  $x_D = 1$ . Hence its temperature dependence will be complicated, with a maximum effect probably around  $x_D \approx 0.5$ . For small dimer concentrations both effects cooperate to decrease  $\langle P_4 \rangle$ , for higher concentrations the important influence is shifted from (ii) towards (i), and the final trend is not *a priori* clear. From figure 5 we note that at temperatures well below  $T_{NI}$  for all homologues  $x_D \approx 0.4$ . Hence to explain the trend of  $\langle P_4 \rangle$  along the series we have to consider in the first place the influence of the angle  $\beta'_D$ .

From equation (10) the determining quantity is  $P_4(\cos \beta'_D)$ . As is easily seen  $P_4(\cos \beta'_D)$  changes sign at  $30.5^\circ$ , and in the region between  $20^\circ$  and  $30^\circ$  the variation of  $P_4(\cos \beta'_D)$  with  $\beta'_D$  is strong. Using space-filling molecular models we have estimated  $\beta'_D$  for the  $n$ CB series, taking fully overlapping aromatic cores, as required by the layer spacings observed in the cases where a smectic phase occurs [12]. The results given in table II indicate a decrease of  $\beta'_D$  with increasing chain length, as expected. Though the absolute values of  $\beta'_D$  thus obtained may not be very reliable, this trend is expected to be correct. As we see,  $\beta'_D$  is in the region where  $P_4(\cos \beta'_D)$  is rather sensitive to changes in  $\beta'_D$ . Hence this variation can in principle explain the trend of increasing  $\langle P_4 \rangle_{\text{exp}}$  along the series. This is shown in figure 7, where the  $\beta'_D$ -values needed are in fact slightly larger than the  $\beta'_D$ -values of table II. In this figure two odd members of the series have been compared, as otherwise the usual even-odd variation mentioned at the beginning of this section would obscure the effect looked for. This even-odd effect causes  $\langle P_4 \rangle$  not to change smoothly parallel to the variation of  $\beta'_D$  with  $n$ . This illustrates the qualitative nature of the model. To do better one should remove the assumption that  $\beta'_M \approx 0$  independent of, for example, the length and conformational freedom of the alkyl chain. In the light of these simplifications we feel that the agreement is satisfactory.

With the ideas given, several more seemingly conflicting results for  $\langle P_4 \rangle$  can be explained. If in the  $n$ CB's one benzene ring is replaced by a cyclohexane ring, one gets the so-called phenylcyclohexanes ( $n$ PCH). The cyclohexane ring does not possess  $\pi$ -electrons, and the delocalization of the dipole will be restricted to the aromatic part. In combination with the fact that cyclohexane is bulkier than benzene one expects now the overlap of two monomers to be restricted to the cyanobenzene part of the molecules.

Table II. — Angle  $\beta'_D$  (see text) and dimer fraction  $x_D$  at  $T = T_{NI} - 5$  K for the  $n$ CB series, the  $n$ PCH series, and two tolanes. The latter compounds have the following structures :



Compound	$\beta'_D$	$x_D$	Compound	$\beta'_D$	$x_D$
5CB	$25^\circ$	0.4	3PCH	$10^\circ$	0.4
6CB	$23.5^\circ$	0.4	5PCH	$10^\circ$	0.4
7CB	$22^\circ$	0.4	7PCH	$9^\circ$	0.4
8CB	$21^\circ$	0.4	7CT	$7^\circ$	0.35
9CB	$20^\circ$	0.4	7MT	—	0.1

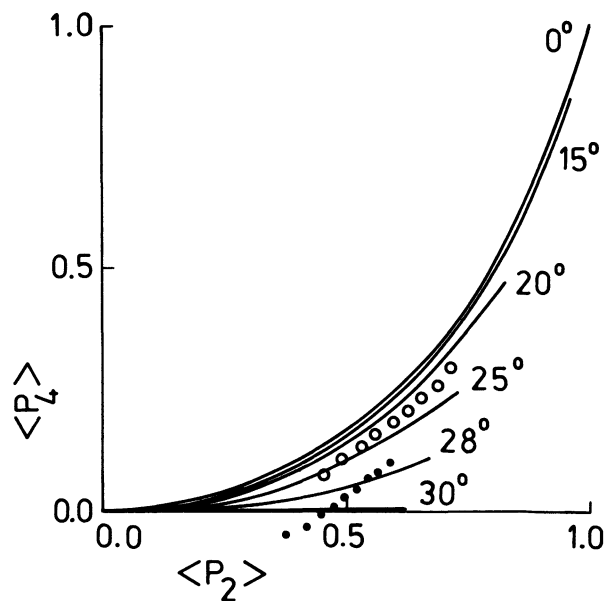


Fig. 7. —  $\langle P_4 \rangle$  versus  $\langle P_2 \rangle$  as predicted by the model for various values of  $\beta'_D$  (Eq. (10));  $\circ$  7CB,  $\bullet$  5CB.

This leads to much smaller values of  $\beta'_D$  as given in table II, and to normal (mean-field) values of  $\langle P_4 \rangle$ . These compounds have been studied extensively by Seeliger *et al.* [10], and indeed mean-field like  $\langle P_4 \rangle$ -values have been observed. The important difference in  $\langle P_4 \rangle$  of the very similar molecules 5CB and 5PCH thus finds a natural explanation [26]. A similar situation as for the  $n$ PCH's is found in the cyanotolanes (7CT, Table II), as the acetylenic triple bond hinders further delocalization of the  $\pi$ -electron system. This explains the at first sight somewhat puzzling result [9] that 7CT has the same type of mean-field behaviour of  $\langle P_4 \rangle$  as 7MT, where in the absence of a CN-group this is expected anyhow.

Though qualitatively several experimental observations seem to fit in nicely with the model described, it is somewhat unsatisfactorily that this cannot be made more quantitative. This is due to the fact that the two effects (i) and (ii) on  $\langle P_4 \rangle$  cannot easily be separated, while moreover more realistic models of the semi-flexible molecules are not tractable. In an attempt to obtain a firmer basis for the model molecular dynamics calculations have been carried out for 5CB [27]. The system consisted of 64 molecules, while periodic boundary conditions were applied. The molecules were simulated by combination of the appropriate atoms, and using specific potentials to describe bond angles, dihedral angles, etc. Lennard-Jones and Coulomb forces were used to describe all other interactions, including intermolecular ones. In this way the molecules are treated rather realistically with internal degrees of freedom. In particular two runs have been compared : one without charges on the atoms, and one in which Coulomb interactions were included from charges calculated to give the correct dipole

moment. Analysis of the orientational distribution showed that «switching on» the charges (and thus allowing for possible anti-parallel dipole correlation) indeed leads for 5CB to a broadening of the distribution function and to a decrease of  $\langle P_4 \rangle$ . Though this does not prove any actual mechanism, it gives some support for the basic ingredient of the model given here.

In conclusion we have given some evidence that the anomalously low values observed for  $\langle P_4 \rangle$  in some nematics might be related to molecular association («dimerization»). For the dimers this leads to an angle  $\beta'_D$  between the long molecular axis of the complex and the direction of the CN-bond. In the mixture of monomers and dimers steric interactions tend to broaden the orientational distribution function  $f(\beta)$ . The two effects cannot be separated and both can lead to a reduction of the effective  $\langle P_4 \rangle$  measured. The decisive factor is the value of the angle  $\beta'_D$ , which

depends on the amount of overlap. Reasonable variations of this overlap explain qualitatively the trend in the experimental results, provided the usual even-odd variation of the order parameters is taken into account as a background. In the picture given negative values of  $\langle P_4 \rangle$  are not more special than small positive ones.

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