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THE RELATIONSHIP BETWEEN THE SECOND AND FOURTH RANK ORDER PARAMETERS FOR LIQUID CRYSTALS COMPOSED OF NON-RIGID MOLECULES

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Abstract: The values of the fourth rank order parameter $\overline{P}_4$ determined by Raman scattering experiments are invariably lower than those predicted by the Maier-Saupe theory of nematic liquid crystals. However this theory is only applicable to rigid particles whereas the nematogenic molecules studied contain flexible alkyl chains. We have estimated the influence of the alkyl chain on $\overline{P}_4$ with the aid of a model which accounts successfully for the variation of the second rank order parameter $\overline{P}_2$ along the chain. It is found that the values of $\overline{P}_2$ and $\overline{P}_4$ calculated for the CN direction in the 4-n-alkyl-4'-cyanobiphenyls are indistinguishable from those predicted by the Maier-Saupe theory. It would appear therefore that the low values observed for $\overline{P}_4$ cannot be attributed to the non-rigidity of the alkyl chain.

The prime feature of a liquid crystal is its long range orientational order. This may be characterized

experimentally by determining certain single molecule orientational order parameters which for rigid, cylindrically symmetric particles would be the averages of the even Legendre polynomials, $P_L(\cos\beta)$. Here β is the angle between the molecular symmetry axis and the director. A wide variety of techniques is able to provide the second rank order parameter $\overline{P}_2$ and so theory has tended to concentrate on predicting the temperature variation of $\overline{P}_2$. It is considerably more difficult to devise experiments which are able to yield the higher rank order parameters. These quantities are, however, of importance because they provide a more searching test of theory. The development of the Raman scattering experiment to determine the fourth rank order parameter $\overline{P}_4$ promised therefore to be of particular value.[1] Indeed the discovery by early experiments[1] of negative values of $\overline{P}_4$ was especially intriguing because no theory of nematics appeared able to explain this result. More recently Raman studies of 4-n-pentyl-4'-cyanobiphenyl have also given negative results for $\overline{P}_4$ associated with the CN bond.[2] In contrast $\overline{P}_4$ determined for 4-n-heptyl-4'-cyanobiphenyl is positive[3] although considerably lower than that predicted by the Maier-Saupe theory.[4] Knowledge of $\overline{P}_2$ and $\overline{P}_4$ is important because it enables us to test the form of the singlet orientational distribution function $f(\beta)$ which is predicted by this theory to be

$$f(\beta) = \exp\{\varepsilon P_2(\cos\beta)\}/Z \quad ; \tag{1}$$

the normalization constant Z is

$$Z = \int \exp\{\varepsilon P_2(\cos\beta)\}\sin\beta d\beta \quad . \tag{2}$$

The parameter ε depends on the orientational order but the form of this dependence does not affect the unique relation-

ship between $\bar{P}_2$ and $\bar{P}_4$ which is shown in the figure together with some typical experimental results. These include values found for trans-4-n-heptyl-(4'-cyanophenyl)-cyclohexane[5] which are in reasonably close agreement with theory in contrast to the results for the other nematogens.

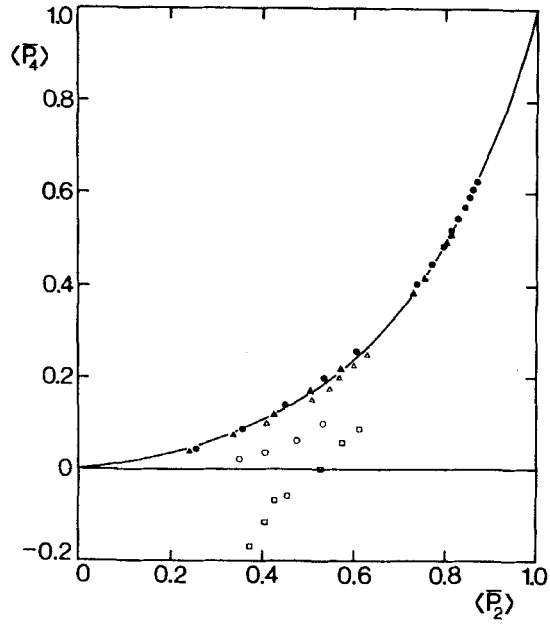


FIGURE The dependence of the fourth rank order parameter $\langle\bar{P}_4\rangle$ on the second rank $\langle\bar{P}_2\rangle$ observed for 4-n-pentyl-4'-cyanobiphenyl (□), 4-n-heptyl-4'-cyanobiphenyl (○) and trans-4-n-heptyl-(4'-cyanophenyl)-cyclohexane (△). The dependence predicted by the Maier-Saupe theory is shown as the solid line while that by the theory for flexible molecules is indicated as (●) for model 4-n-heptyl-4'-cyanobiphenyl and as (▲) for the n-octyl homologue.

The improvement in agreement between theory and experiment is at first sight encouraging but may be quite misleading for the distribution function is appropriate for rigid particles whereas the nematogenic molecules studied possess flexible alkyl chains. It is important therefore to see how the presence of the alkyl chain might influence the relationship between $\overline{P}_2$ and $\overline{P}_4$. We may attempt to estimate this with the aid of a theory developed to explain the variation in the second rank order parameters determined, using deuterium NMR, for the methylene groups in the alkyl chain.[6] Here we extend the theory to calculate the fourth rank ordering tensor averaged over the conformational states adopted by the chain. We begin with a brief description of the theory.

The probability of finding a molecule in a conformation n and with the director at an orientation ω with respect to a reference frame set in the molecule is $f(n,\omega)$. It is assumed that the statistical weight of a conformational state, p_n, is independent of the molecular orientation and so we may write

$$f(n,\omega) = p_n f_n(\omega) \quad . \tag{3}$$

Here $f_n(\omega)$ is the singlet orientational distribution function for conformer n and may be used to define the potential of mean torque $U_n(\omega)$ experienced by this conformer as

$$f_n(\omega) = \exp\{-U_n(\omega)/kT\}/Q_n \quad , \tag{4}$$

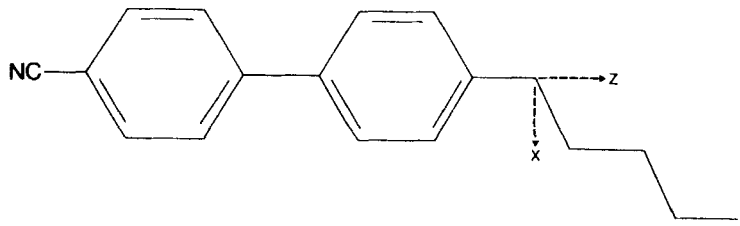
where the normalization is

$$Q_n = \int \exp\{-U_n(\omega)/kT\} d\omega \quad . \tag{5}$$

One of the essential elements of the theory is to approximate $U_n(\omega)$ by

$$U_n(\omega) = \sum_m (-)^m \varepsilon^n_{2,m} C_{2,-m}(\omega) \quad , \tag{6}$$

where $C_{2,m}(\omega)$ is a modified spherical harmonic. Further the interaction tensor $\varepsilon^n_{2,m}$ for the conformer n is assumed to be made up of bond or group contributions. For example, for a molecule such as a 4-n-alkyl-4'-cyanobiphenyl the basic units are taken to be a C-C segment in the chain and the aromatic core which includes both the cyano group and the first methylene group. In addition the interaction tensors are assumed to be cylindrically symmetric so that in the reference frame:



the total interaction tensor is

$$\varepsilon^n_{2,m} = X_c \delta_{om} + X_c \sum_i C_{2,m}(\omega^n_i) \quad . \tag{7}$$

Here X_c and X_a are the interaction tensors for the chain and core segments respectively while ω^n_i denotes the orientation of the ith C-C bond in the reference frame for conformation n. The total tensor is then diagonalized and

in the principal frame for $\varepsilon^n_{2,m}$ the components of the ordering tensor $\bar{C}^n_{L,p}$ will vanish unless both L and p are even; in addition $\bar{C}^n_{L,p}$ is equal to $\bar{C}^n_{L,-p}$. The non-zero components for conformation n are

$$\bar{C}^n_{L,p} = 2\pi Q_n^{-1} \int_o^\pi d^L_{o,p}(\beta) I_{p/2}\{b_n d^2_{o,2}(\beta)\} \times \exp\{a_n P_2(\cos\beta)\} \sin\beta d\beta \quad , \qquad (8)$$

where $a_n = -\varepsilon^n_{2,o}/kT$ and $b_n = -2\varepsilon^n_{2,2}/kT$. In general the principal axes for the ordering tensor will not correspond to the direction for which the order parameter has been measured. For example, the Raman scattering experiment is often used to determine $\bar{P}_2$ and $\bar{P}_4$ along the -CN direction[1] and so we must transform from the principal axes to the axis of interest; this gives

$$\bar{P}^n_L = \sum_p \bar{C}^n_{L,p} C^*_{L,p}(\omega^n) \quad , \qquad (9)$$

where ω^n is the orientation of the relevant axis in the principal frame.

The order parameters determined by the Raman experiment are not for individual conformers but are averages over all conformations and so we need to calculate

$$\langle \bar{P}_L \rangle = \sum_n p_n \bar{P}^n_L \quad . \qquad (10)$$

The statistical weight p_n is given by

$$p_n = Q_n \exp\{-U_n/kT\} / \sum_n Q_n \exp\{-U_n/kT\} \qquad (11)$$

and differs from its value in the isotropic phase because

the potential of mean torque, via Q_n, tends to favour the more elongated conformations. According to the rotameric state model[7] the conformational energy U_n is

$$U_n = N_g E_{tg} + N_{g\pm g\mp} E_{g\pm g\mp} \quad , \tag{12}$$

where N_g is the number of gauche linkages and E_{tg} is the energy of a gauche link with respect to a trans. The term $N_{g\pm g\mp} E_{g\pm g\mp}$ where $N_{g\pm g\mp}$ is the number of $g\pm g\mp$ arrangements in a conformer is included in an attempt to allow for the fact that the rotational potential about a bond does depend on the conformation of the remainder of the chain.

This completes our outline of the theory needed to calculate the order parameters $\langle\bar{P}_2\rangle$ and $\langle\bar{P}_4\rangle$ for a particular axis set in a non-rigid molecule such as a 4-n-alkyl-4'-cyanobiphenyl. Values for the parameters required in these calculations have been obtained by fitting $\bar{P}_2$ observed for the C-D bond directions along the alkyl chains in deuteriated 4-n-pentyl- and 4-n-octyl-4'-cyanobiphenyls.[6] Using these values as a guide we have set $X_c^*/X_a^* = 0.35$, $E_{tg}^* = 1.0$ and $E_{g\pm g\mp}^* = 4.0$ where the star indicates that the quantity is divided by kT. The ratio X_c^*/X_a^* is slightly larger than that found previously (0.30) but we wish to enhance the influence of the chain on the order parameters. The core interaction parameter X_a^* changes with temperature primarily because it depends on the orientational order which varies markedly with temperature.[8] In contrast the ratio X_c^*/X_a^* is predicted to be independent of temperature[8] while the variation of E_{tg}^* and $E_{g\pm g\mp}^*$ is expected to be minimal. Accordingly pairs of values for the order parameters $\langle\bar{P}_2\rangle$ and $\langle\bar{P}_4\rangle$ for the z axis of the

aromatic core were determined by varying X_a^* alone.

The results of these calculations are shown in the figure for model n-heptyl (●) and n-octyl (▲) cyanobiphenyl. The most striking feature of these results is that they are almost identical to the predictions of the Maier-Saupe theory for rigid particles. Closer inspection reveals that the values calculated for $\langle \overline{P}_4 \rangle$ at a given $\langle \overline{P}_2 \rangle$ are slightly higher than those obtained from the Maier-Saupe theory with the deviation for the n-heptyl homologue being greater than for the n-octyl. An essentially similar behaviour was also observed for both the n-pentyl and n-hexyl homologues. We are forced to conclude therefore that the deviation of the Raman values for the second and fourth rank order parameters from the Maier-Saupe predictions cannot be attributed to the effect of the flexible chain. In view of the success of the theory in predicting the second rank order parameters it is tempting to suppose that the discrepancy between theory and experiment stems from the Raman determination of $\langle \overline{P}_4 \rangle$. This conclusion would be in accord with estimates of $\langle \overline{P}_4 \rangle$ obtained from X-ray[9] and neutron[10] scattering experiments as well as electron resonance studies.[11]

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