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A MOLECULAR FIELD THEORY FOR UNIAXIAL NEMATIC LIQUID CRYSTALS FORMED BY NON-CYLINDRICALLY SYMMETRIC MOLECULES

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Most molecular theories of nematic liquid crystals assume that the constituent molecules are cylindrically symmetric. However, although this may be a useful approximation the molecules of real nematogens are of lower symmetry; here we develop a theory for an ensembles of such particles based on a general expansion of the pairwise intermolecular potential together with the molecular field approximation. The dependence of the orientational properties of the uniaxial mesophase on the deviation from molecular cylindrical symmetry is calculated from the series expansion of the pseudo-potential. In these calculation the number of arbitrary parameters in the orientational pseudo-potential is reduced by assuming that the anisotropic intermolecular potential originates solely from dispersion forces. The theoretical predictions for the values of the ordering matrix and the entropy change at the nematic-isotropic, transition are found to be in good agreement with those observed for 4,4′-dimethoxyazoxybenzene. In addition, the theory provides a reasonable account of the temperature dependence of the order parameter at constant volume for this nematogen. The allowance for deviations from molecular cylindrical symmetry appears to remove many of the discrepancies between the Maier–Saupe theory and experiment

1. INTRODUCTION

An essential characteristic of compounds forming liquid crystals is the rod-like shape of their constituent molecules, with an attendant high length to breadth ratio. This common feature has prompted both experimentalists and theoreticians to suppose that the molecules possess cylindrical symmetry;

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an assumption which has many attractions. For example, the ordering matrix, often used to describe the partial alignment in a mesophase, contains just one independent element and this can be determined by a variety of techniques [1]. The assumption of molecular cylindrical symmetry is appealing to a statistical mechanician because the pairwise anisotropic intermolecular potential required in any calculation is particularly simple for such particles [2]. However, the molecules forming liquid crystals are, in fact, lath-like and certainly do not possess the high symmetry which is frequently assumed for them. Indeed, the shapes of real nematogenic molecules cannot be equated with that of a rotation solid such as a cylinder or spheroid.

Two principal components of the ordering matrix are therefore required to describe the orientational order of a uniaxial mesophase composed of lath-like molecules although most investigators are content to assume that one is sufficient. However, Alben *et al.* [3] have estimated the ordering matrix for 4,4′-dimethoxy-azoxybenzene and find the deviation of this matrix from cylindrical symmetry to be significant. Their analysis is open to question [4] and it is regrettable that there have been no further attempts to determine the entire ordering matrix for real nematogens. Fortunately the importance of deviations from cylindrical symmetry may be inferred from unambiguous determinations of the ordering matrix for rod-like molecules, such as 4,4′-dichlorobiphenyl [5], dissolved in a nematic mesophase. In addition these matrices are found to be comparable to that estimated by Alben *et al.* for a pure mesophase.

In unusual contrast to the experimentalists, theoreticians have been more concerned with exploring the consequences of deviations from molecular cylindrical symmetry. Thus Frieser [6] has shown that a system composed of particles with a lower symmetry than D_∞ is capable of existing either as a uniaxial or a biaxial liquid crystal. The possible existence of a biaxial phase has been studied in some detail for a system of hard rectangular plates using a lattice model [7], the Landau approach [8] and the molecular field approximation [9]. These calculations confirm the original prediction of the eventual transition to a biaxial phase although this transition has yet to be discovered. Indeed, all known nematics are uniaxial, so presumably the mesophase freezes before the predicted transition to the biaxial phase can occur. None the less, although deviations from molecular cylindrical symmetry have yet to be evidenced by the observation of a biaxial phase such deviations should influence the order parameters for the liquid crystal in the uniaxial phase. For example, the deviation of the ordering matrix from cylindrical symmetry is clearly determined by the molecular symmetry and the element of the ordering matrix for the long axis will also be influenced by the form of the intermolecular potential. Straley [9] has reported calculations of the ordering matrix for an ensemble

of hard rectangular particles. These calculations are of some interest but they may not be particularly realistic, especially as recent experiments have indicated that dispersion forces may make a dominant contribution to the anisotropic inter-molecular potential [10]. In this paper therefore we shall develop, within the molecular field approximation, a theory for non-cylindrically symmetric particles interacting via a completely general intermolecular potential. We then obtain a series expansion for the orientational pseudo-potential in the uniaxial phase. The expansion coefficients are subsequently determined by assuming that dispersion forces make the only contribution to the anisotropic intermolecular potential. We are then able to investigate the influence of deviations from molecular cylindrical symmetry on the nematic-isotropic transition and the various order parameters. Finally we compare these predictions with the data available for the nematogen 4,4′-dimethoxyazoxybenzene.

2. THE ORIENTATIONAL PSEUDO-POTENTIAL

The orientational pseudo-potential for non-cylindrically symmetric molecules is obtained by following the procedure developed for cylindrically symmetric particles [11]. The starting point is the intermolecular potential for two particles because we assume pairwise additivity of the energy. We then obtain the orientational pseudo-potential for a single particle, as a consequence of its interaction with all the other particles, by taking three averages of the intermolecular potential. The first of these is over all orientations of the intermolecular vector, the second over all orientations of one particle and finally over the intermolecular separation.

We begin with the intermolecular potential which, for particles of general shape, we expand in a product basis of Wigner rotation matrices [12] as

$$U_{12} = \sum u_{L_1L_2m_1m_2n_1n_2}(r_{12})\mathscr{D}_{m_1,n_1}{}^{(L_1)}(\Omega_{1-R})\mathscr{D}_{m_2,n_2}{}^{(L_2)}(\Omega_{2-R}), \qquad (1)$$

where r_{12} is the separation between molecules 1 and 2 [13]. The orientation of molecule i in a coordinate system containing the intermolecular vector as the z axis is denoted by Ω_{i-R}. The energy U_{12} is clearly invariant under rotation of the coordinate system about this z axis and so we restrict the summation to those terms with m_1 equal to $-m_2$ [13]:

$$U_{12} = \sum u_{L_1L_2mn_1n_2}(r_{12})\mathscr{D}_{m,n_1}{}^{(L_1)}(\Omega_{1-R})\mathscr{D}_{-m,n_2}{}^{(L_2)}(\Omega_{2-R}); \qquad (2)$$

both here and elsewhere redundant subscripts on the coefficient $u(r_{12})$ will be suppressed. It is convenient to define the molecular orientation in terms of a common coordinate system and so we transform the potential U_{12} to a laboratory frame. The choice of this coordinate system is determined by the symmetry of the liquid crystal phase and for a uniaxial mesophase we

shall take the laboratory z axis to be parallel to the symmetry axis of the mesophase. This corresponds to the preferred orientation of the molecular long axis and is often referred to as the director. The transformation of U_{12} is carried out by performing the rotation from the intermolecular vector to the molecule in two steps using the relationship

$$\mathscr{D}_{m,n}^{(L)}(\Omega_{1-R}) = \sum_q \mathscr{D}_{q,\,m}^{(L)^*}(\Omega_{R-L})\mathscr{D}_{q,\,n}^{(L)}(\Omega_{1-L}). \tag{3}$$

Here the subscript $R-L$ denotes the rotation from the laboratory to the intermolecular frame while $1-L$ indicates that from the laboratory to the molecule coordinate system. The intermolecular potential becomes

$$U_{12} = \sum u_{L_1L_2mn_1n_2}(r_{12})\mathscr{D}_{q_1,\,n_1}^{(L_1)}(\Omega_{1-L})\mathscr{D}_{q_2,\,n_2}^{(L_2)}(\Omega_{2-L})\mathscr{D}_{q_1,\,m}^{(L_1)^*}(\Omega_{R-L}) \times \mathscr{D}_{q_2,-m}^{(L_2)^*}(\Omega_{R-L}), \tag{4}$$

and we may now take the average over the orientation of the intermolecular vector. If the distribution function for the intermolecular vector is orientation independent then we may take advantage of the orthogonality of the rotation matrices to evaluate the ensemble average $\overline{\mathscr{D}_{q_1,m}^{(L_1)^*}(\Omega_{R-L})\mathscr{D}_{q_2,-m}^{(L_2)^*}(\Omega_{R-L})}$ as

$$\overline{\mathscr{D}_{q_1,m}^{(L_1)^*}(\Omega_{R-L})\mathscr{D}_{q_2,-m}^{(L_2)^*}(\Omega_{R-L})} = (-1)^{q_2+m}\delta_{q_1,-q_2}\delta_{L_1,L_2}/(2L_1+1). \tag{5}$$

This assumption appears to imply a spherically symmetric pair distribution function in the mesophase but is in fact demanded by the factorization of the total partition function for the ensemble implicit in this analysis [14,15]. The partially averaged potential may then be written as

$$U_{12} = \sum \frac{(-1)^{q+m}}{(2L+1)} u_{Lmn_1n_2}(r_{12})\mathscr{D}_{q,\,n_1}^{(L)}(\Omega_{1-L})\mathscr{D}_{-q,\,n_2}^{(L)}(\Omega_{2-L}). \tag{6}$$

The next stage is to average over the orientations adopted by particle 2 and so we require $\overline{\mathscr{D}_{-q,\,n_2}^{(L)}}$. Within the molecular field approximation this average is taken to be independent of the orientation of molecule 1 and is to be identified with the normal ensemble average. Since we are only concerned with a uniaxial mesophase the average $\overline{\mathscr{D}_{-q,\,n_2}^{(L)}}$ will vanish unless q is zero and L is even. The potential is now reduced to

$$U_{12} = \sum{}' \frac{(-1)^m}{(2L+1)} u_{Lmn_1n_2}(r_{12})\overline{\mathscr{D}_{0,\,n_2}^{(L)}}\mathscr{D}_{0,\,n_1}^{(L)}(\Omega_{1-L}); \tag{7}$$

where the prime denotes a summation restricted to even values of L greater than zero. The scalar contribution to the potential is ignored because we are only concerned with the orientational properties of the

mesophase. The final average is over all intermolecular separations and gives the orientational pseudo-potential, for molecule 1, as

$$U_1 = \sum{}' \frac{(-1)^m}{(2L+1)} \bar{u}_{Lmn_1n_2} \overline{\mathscr{D}_{0,n_2}{}^{(L)}} \mathscr{D}_{0,n_1}{}^{(L)}(\Omega_{1-L}). \tag{8}$$

The expansion coefficients are defined by

$$\bar{u}_{Lmn_1n_2} = \frac{\int u_{Lmn_1n_2}(r_{12}) \exp\{-U_0(\mathbf{r}_1 \ldots \mathbf{r}_N)/kT\} d\mathbf{r}_1 \ldots d\mathbf{r}_N}{\int \exp\{-U_0(\mathbf{r}_1 \ldots \mathbf{r}_N)/kT\} d\mathbf{r}_1 \ldots d\mathbf{r}_N}, \tag{9}$$

where $U_0(\mathbf{r}_1 \ldots \mathbf{r}_N)$ is the scalar potential of the N molecules in the ensemble [14, 15].

The pseudo-potential is conveniently written as

$$U(\beta\gamma) = \sum{}' c_{Lqp} \overline{\mathscr{D}_{0,p}{}^{(L)}} \mathscr{D}_{0,q}{}^{(L)}(\beta\gamma), \tag{10}$$

where

$$c_{Lqp} = \sum_m (-1)^m \bar{u}_{Lmqp}/(2L+1);$$

the Euler angles (β, γ) define the orientation of the director in the molecular coordinate system.

We have three checks on this form of the pseudo-potential. The first occurs for an ensemble of cylindrically symmetric molecules for then the summation in equation (2) for the pairwise intermolecular potential is restricted to terms for which both n_1 and n_2 are zero. With these restrictions the pseudo-potential, given in equation (10), reduces to

$$U(\beta) = \sum{}' c_{L00} \bar{P}_L P_L(\cos\beta), \tag{11}$$

in complete agreement with the result derived by Humphries *et al.* [11]. The second particular case is an infinitely dilute solution of molecules of arbitrary shape in a liquid of cylindrically symmetric particles. The orientational pseudo-potential for the non-cylindrically symmetric molecule in such a system is obtained formally from equation (10) by setting p equal to zero and yields

$$U(\beta\gamma) = \sum{}' c_{Lq0} \bar{P}_L \mathscr{D}_{0,q}{}^{(L)}(\beta\gamma), \tag{12}$$

in accord with the result obtained by Humphries and Luckhurst [16]. Finally, if the summation in equation (10) is restricted to terms with L equal to 2, then the pseudo-potential is identical in form to that proposed by Straley on the basis of symmetry arguments [9].

We conclude this section by considering the symmetry properties of the coefficients c_{Lqp}. For identical particles the permutation symmetry of the pairwise intermolecular potential ensures that [13]

$$u_{L_1L_2mn_1n_2}(r_{12}) = (-1)^{L_1+L_2}u_{L_2L_1-mn_2n_1}(r_{12}), \tag{13}$$

and so

$$c_{Lqp} = c_{Lpq}. \tag{14}$$

The pair potential must also be real and this requires that

$$u_{L_1L_2mn_1n_2}(r_{12}) = (-1)^{n_1+n_2}u_{L_1L_2-m-n_1-n_2}(r_{12})^*; \tag{15}$$

consequently

$$c_{Lqp} = (-1)^{q+p}c_{L-q-p}.^* \tag{16}$$

3. PARAMETERIZATION

One of our major objectives is to investigate the influence of deviations from molecular cylindrical symmetry on various orientational order parameters for a uniaxial nematic mesophase. We therefore seek to minimize the number of variables in the calculation while maintaining the essential physics. As a first approximation we shall consider only those terms with L equal to 2 in the expansion of the pseudo-potential. We expect the neglect of terms higher than quadratic to be a realistic approximation since similar assumptions for cylindrically symmetric particles have led to results in reasonable agreement with experiment [11,17]. We can reduce the number of expansion coefficients still further by appealing to some specific model for the interactions or by imposing symmetry restrictions on the molecules. For example, if we follow Straley [9] and take the particles to be hard rectangular parallelopipeds, then the coefficients $c_{2_{qp}}$ are independent of the sign of either p or q and zero if either of these subscripts is odd. In fact

$$c_{200} = \{-2B(W^2 + L^2) - 2W(L^2 + B^2) + L(W^2 + B^2) + 8WBL\}/3, \tag{17}$$

$$c_{220} = (L^2 - BW)(B - W)/\sqrt{6}, \tag{18}$$

and

$$c_{222} = -L(W - B)^2/2, \tag{19}$$

where L is the length, B the breadth and W the width of the particle. This particular parametrization is only approximate [9] and in addition anisotropic repulsive forces are probably not dominant in determining the behavior of real liquid crystals. We have therefore derived expressions for the $c_{2_{qp}}$ for molecules interacting via dispersion forces and, as we show in the Appendix, these coefficients again vanish if either p or q is odd and are also independent of the sign of p or q.

It is possible to place similar restrictions on the expansion coefficients c_{Lqp}, without appealing to specific forms of the intermolecular interactions, by using more formal arguments based on the molecular symmetry and its influence on the pair potential. For example, if each molecule has a center of symmetry then [13]

$$\begin{aligned} u_{L_1L_2mn_1n_2}(r_{12}) &= (-1)^{L_1-n_1}u_{L_1L_2m-n_1n_2}(r_{12}) = (-1)^{L_2-n_2}u_{L_1L_2mn_1-n_2}(r_{12}) \\ &= (-1)^{L_1+L_2-n_1-n_2}u_{L_1L_2m-n_1-n_2}(r_{12}); \end{aligned} \tag{20}$$

consequently

$$c_{Lqp} = (-1)^q c_{L-qp} = (-1)^p c_{Lq-p} = (-1)^{q+p} c_{L-q-p'} \tag{21}$$

but for this to be compatible with equation (16) the coefficients must be real. Further, if the molecules also possess a plane of symmetry orthogonal to their z axes, then

$$\begin{aligned} u_{L_1L_2mn_1n_2}(r_{12}) &= (-1)^{L_1}u_{L_1L_2m-n_1n_2}(r_{12}) = (-1)^{L_2}u_{L_1L_2mn_1-n_2}(r_{12}) \\ &= (-1)^{L_1+L_2}u_{L_1L_2m-n_1-n_2}(r_{12}), \end{aligned} \tag{22}$$

and so

$$c_{Lqp} = (-1)^L c_{L-qp} = (-1)^L c_{Lq-p} = c_{L-q-p}. \tag{23}$$

However, equations (21) and (23) can only be consistent if both p and q are restricted to even values; in addition the coefficients are independent of the sign of p and q.

Given these general restrictions on the coefficients c_{Lqp} we may write the pseudo-potential as

$$\begin{aligned} U(\beta\gamma) = \sum_{\substack{L,\,|p|,\,|q| \\ \text{(even)}}} & c_{Lqp}\{\overline{\mathscr{D}_{0,\,p^{(L)}}} + \overline{\mathscr{D}_{0,\,-p^{(L)}}}\}\{\mathscr{D}_{0,\,q}{}^{(L)}(\beta\gamma) + \mathscr{D}_{0,\,-q}{}^{(L)}(\beta\gamma)\}/ \\ & (1+\delta_{0,\,q})(1+\delta_{0p}). \end{aligned} \tag{24}$$

If we now limit the summation to those terms with L equal to 2 we have

$$\begin{aligned} U(\beta\gamma) = &\{c_{200}\,\overline{d_{0,\,0}{}^{(2)}} + 2c_{220}\,\overline{d_{02}{}^{(2)}\,\cos 2\gamma}\}\,d_{0,\,0}{}^{(2)}(\beta) \\ &+ 2\{c_{200}\,\overline{d_{0,0}{}^{(2)}} + 2c_{222}\,\overline{d_{02}{}^{(2)}\cos 2\gamma}\}\,d_{0,\,2}{}^{(2)}(\beta)\cos\,2\gamma, \end{aligned} \tag{25}$$

where $d_{m,n}{}^{(2)}(\beta)$ is a reduced Wigner rotation matrix [12]. The second-rank order parameters $\overline{d_{0,\,0}{}^{(2)}}$ and $\overline{d_{0,\,2}{}^{(2)}\cos 2\gamma}$ occurring in this expression are directly related to the principal elements of the ordering matrix by

$$S_{zz} = \overline{d_{0,\,0}{}^{(2)}} \tag{26}$$

and

$$S_{xx} - S_{yy} = \sqrt{(6)}\overline{d_{0,2}{}^{(2)}\cos 2\gamma}. \tag{27}$$

We see therefore that the order parameter $\overline{d_{0,2}{}^{(2)}\cos 2\gamma}$ reflects the deviation of the ordering matrix from cylindrical symmetry†. For calculations it is convenient to write the pseudo-potential as

$$U(\beta\gamma) = -kT\{a\ d_{0,0}{}^{(2)}(\beta) + b\ d_{0,2}{}^{(2)}(\beta)\ \cos\ 2\gamma\}, \tag{28}$$

where

$$a = -\{c_{200}\,\overline{d_{0,0}{}^{(2)}} + 2c_{220}\,\overline{d_{0,2}{}^{(2)}\cos\ 2\gamma}\}/kT \tag{29}$$

and

$$b = -\{2c_{220}\,\overline{d_{0,0}{}^{(2)}} + 4c_{222}\,\overline{d_{0,2}{}^{(2)}\cos\ 2\gamma}\}/kT. \tag{30}$$

The partition function for this single particle potential is then

$$\begin{aligned} Z(a,b) &= \int_0^{2\pi}\int_0^{\pi} \exp\{a\ d_{0,0}{}^{(2)}(\beta) + b\ d_{0,2}{}^{(2)}(\beta)\cos\ 2\gamma\}\sin\ \beta\, d\beta\, d\gamma, \\ &= 2\pi \int_0^{\pi} I_0\{b\ d_{0,2}{}^{(2)}(\beta)\}\exp\{a\ d_{0,0}{}^{(2)}(\beta)\}\sin\ \beta\, d\beta, \end{aligned} \tag{31}$$

where $I_n(x)$ is an nth-order modified Bessel function. The orientational molar potential energy U is just one-half the total average energy $\overline{U}$ [11],

$$U = -(RT/2)(a\,\overline{d_{0,0}{}^{(2)}} + b\,\overline{d_{0,2}{}^{(2)}\cos\ 2\gamma}, \tag{32}$$

the molar entropy S is

$$S = -R(a\,\overline{d_{0,0}{}^{(2)}} + b\ \overline{d_{0,2}{}^{(2)}\cos\ 2\gamma}) + R\ln\ Z(a,b), \tag{33}$$

and so the orientational molar Helmholtz function is

$$A_m = -(RT/2)(a\,\overline{d_{0,0}{}^{(2)}} + b\overline{d_{0,2}{}^{(2)}\cos\ 2\gamma}) - RT\ln\ Z(a,b). \tag{34}$$

This free energy will be a minimum provided the consistency equations for the order parameters

† Other order parameters have been introduced to measure the deviation of the ordering matrix from cylindrical symmetry although they only differ by simple numerical factors; thus Alben *et al.* [3] use the symbol D to denote $\sqrt{(6)}\overline{d_{0,2}{}^{(2)}\cos 2\gamma}$ while Straley [9] has chosen U which is equivalent to $\sqrt{(8/3)}\overline{d_{0,2}{}^{(2)}\cos 2\gamma}$.

$$\overline{d_{0,0}{}^{(2)}} = \int_0^{2\pi}\int_0^{\pi} d_{0,0}{}^{(2)}(\beta)\exp\{a\,d_{0,0}{}^{(2)}(\beta) + b\,d_{0,2}{}^{(2)}(\beta)\cos 2\gamma)\}$$
$$\times \sin\beta\, d\beta\, d\gamma / Z(a,b)$$
$$= 2\pi \int_0^{\pi} d_{0,0}{}^{(2)}(\beta) I_0\{b\,d_{0,2}{}^{(2)}(\beta)\}\exp\{a\,d_{0,0}{}^{(2)}(\beta)\}\sin\beta\, d\beta / Z(a,b) \quad (35)$$

and

$$\overline{d_{0,2}{}^{(2)}\cos 2\gamma} = \int_0^{2\pi}\int_0^{\pi} d_{0,2}{}^{(2)}(\beta)\cos 2\gamma \exp\{a\,d_{0,0}{}^{(2)}(\beta) + b\,d_{0,2}{}^{(2)}(\beta)\cos 2\gamma\}$$
$$\times \sin\beta\, d\beta\, d\gamma / Z(a,b)$$
$$= 2\int_0^{\pi} d_{0,2}{}^{(2)}(\beta) I_1\{b\,d_{0,2}{}^{(2)}(\beta)\}\exp\{a\,d_{0,0}{}^{(2)}(\beta)\}$$
$$\times \sin\beta\, d\beta / Z(a,b) \quad (36)$$

are satisfied.

The two consistency equations may be solved in a variety of ways. For example, we might first fix the three variables c_{200}/kT, c_{220}/kT and c_{222}/kT and then evaluate the integrals in equations (35) and (36) for trial values of the order parameters $\overline{d_{0,0}{}^{(2)}}$ and $\overline{d_{0,2}{}^{(2)}\cos 2\gamma}$. The trial value would then be varied, using a non-linear least squares fitting routine [11], until the consistency conditions are satisfied. An alternative, and often more convenient approach, is to tabulate the order parameters and thermodynamic functions for a range of values of the variables a and b. The ratios c_{220}/c_{200} and c_{222}/c_{200} of the expansion coefficients may then be extracted from the variables with the aid of equations (29) and (30). This exercise is particularly straightforward when the particles interact via dispersion forces because the ratio c_{222}/c_{200} is just $(c_{220}/c_{200})^2$, as we may see from equation (A12). Equations (29) and (30) now become

$$a = -\alpha\{\overline{d_{0,0}{}^{(2)}} + 2\lambda\overline{d_{0,2}{}^{(2)}\cos 2\gamma}\}, \quad (37)$$

and

$$b = 2\lambda a, \quad (38)$$

where

$$\alpha = -c_{200}/kT; \quad (39)$$

and λ is the ratio c_{220}/c_{200}.

We may therefore fix the parameter λ, which is a measure of the deviation from cylindrical symmetry, at the start of the calculation and from the results, tabulated simply as a function of α, obtain the behaviour of the ensemble as the temperature is varied. In the next section we shall describe the results of such calculations and compare these theoretical predictions with experiment. For this final section we shall denote the order $\overline{d_{0,0}{}^{(2)}}$ by the more usual $\bar{P}_2$ and the secondary parameter $\overline{d_{0,2}{}^{(2)}\cos 2\lambda}$ by $\overline{\mathscr{D}_{0,2}{}^{(2)}}$.

4. PREDICTIONS AND REALITY

The first stage in the calculation is the identification of the transition from the isotropic phase to the uniaxial nematic phase. This may be accomplished for a given molecular symmetry by determining the value of α at which the orientational Helmholtz function vanishes, provided of course there is no volume change at the transition. The value, α_K is then related to the transition temperature T_K by

$$\alpha_K = -c_{200}/kT_K. \tag{40}$$

The results of such calculations are listed in the table for a range of λ values including $\lambda = 0$ which corresponds to the Maier-Saupe limit for cylindrically symmetric particles. We can see immediately that increasing the deviation from cylindrical symmetry decreases α_K and so increases the nematic-isotropic transition temperature for constant c_{200}. At first sight this trend is somewhat surprising although it is in accord with calculations based on a quite different model [9]. To appreciate the origin of this effect it is important to realize that varying λ while holding c_{200} fixed corresponds to keeping the component α'_{zz} of the traceless polarizability tensor constant, increasing α'_{xx} by a given amount and decreasing α'_{yy} by the same amount. Under these conditions the orientational energy of a pair of particles, with parallel principal coordinate systems, becomes more negative as the deviation from cylindrical symmetry increases. It is this stabilization of the parallel configuration which is responsible for the increased range of the nematic mesophase.

The values of several order parameters, at the transition temperature, are also given in the table. The parameter $\bar{P}_2^{(K)}$ is seen to decrease with

λ	α_K	$\bar{P}_2{}^{(K)}$	$\overline{\mathscr{D}_{0,2}{}^{(2)}}$(K)	$\bar{P}_4{}^{(K)}$	$S^{(K)}/R$
0	4.541	0.429	0	0.120	0.417
0.1	4.505	0.408	0.017	0.109	0.384
0.2	4.386	0.341	0.035	0.075	0.275
0.3	4.160	0.207	0.041	0.029	0.112

The order parameters and entropy at the nematic-isotropic transition.

increasing λ, a behavior which might appear to be incompatible with the greater tendency for parallel molecular alignment. However, in the limit that the components α'_{zz} and α'_{xx} of the traceless polarizability tensor become identical, as for a disc-like particle, it is the y axis which will tend to be parallel to the director. Consequently the z axis will tend to be orthogonal to the director and $\bar{P}_2$ will be small or even negative ; the order parameter $\bar{P}_2$ must therefore decrease with increasing deviation from cylindrical symmetry so as to approach this limit. Similar arguments hold for the higher-order parameter $\bar{P}_4$ and the calculated values given in the table confirm the decrease in $\bar{P}_2^{(K)}$ as λ is increased. In contrast the order parameter $\overline{\mathscr{D}_{0,2}{}^{(2)}}(\mathrm{K})$ which reflects the deviation from cylindrical symmetry, shows the expected increase with increasing λ. Finally, the entropy change at the order-disorder transition, also listed in the table, decreases with increasing λ, in accord with the decrease in $\bar{P}_2^{(K)}$.

The temperature dependence of the order parameters $\bar{P}_2$ and $\bar{P}_4$ for the long molecular axis is shown in Figure 1 for several values of λ. The results are plotted as a function of the reduced variable $(\alpha/\alpha_K)^{-1}$ which is identical to the reduced temperature T/T_K provided the coefficients $c_{2_{qp}}$ are themselves independent of temperature. The lines labeled $\lambda = 0$ correspond to the Maier–Saupe limit and the effect of introducing deviations from cylindrical symmetry is to lower these curves as well as changing their slopes. The order parameter $\bar{P}_4$ is found to be positive for all reasonable values of λ and so deviations from cylindrical symmetry cannot be invoked

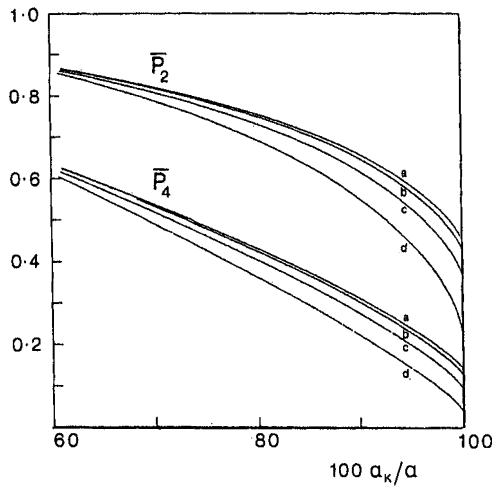

FIGURE 1 The dependence of the order parameters $\bar{P}_2$ and $\bar{P}_4$ on the reduced variable α/α_K for λ equal to (*a*) 0, (*b*) 0.1, (*c*) 0.2, and (*d*) 0.3.

as an explanation for the negative values of $\bar{P}_4$ determined for 4-n-butyloxybenzylidene-4′-cyanoaniline dissolved in 4-methoxybenzylidene-4′-n-butylaniline [18]. The secondary order parameter $\mathscr{D}_{0,2}^{(2)}$ is plotted as function of $\bar{P}_2$ in Figure 2 for various λ values. These results exhibit an unusual behaviour, for the order parameter $\mathscr{D}_{0,2}^{(2)}$ is observed to increase with increasing $\bar{P}_2$ pass through a maximum and then decrease, going finally to zero when the z axis is completely ordered.

We now turn to a detailed comparison of these predictions with experiment. The most direct evidence for the influence of deviations from molecular cylindrical symmetry on the behaviour of the mesophase is the observation of the secondary order parameter $\mathscr{D}_{0,2}^{(2)}$ because this is identically zero for cylindrically symmetric particles. Of course the other order parameters will also depart from their Maier–Saupe values but similar deviations may also be observed for cylindrically symmetric particles if quadratic and quartic terms are retained in the pseudo-potential given by Equation (11) [11,19]. Unfortunately the only attempt to determine $\mathscr{D}_{0,2}^{(2)}$ for a pure nematogen was when Alben *et al.* [3] showed how the nuclear magnetic resonance experiments performed by Rowell *et al.* [20] on partially deuterated samples of 4,4′-dimethoxy-azoxybenzene might be interpreted to yield $\mathscr{D}_{0,2}^{(2)}$ as well as $\bar{P}_2$. Although these experiments were performed throughout the nematic range the analysis was restricted to a single temperature [3]. We have therefore applied an analogous procedure to all of the data obtained by Rowell *et al.* [20] and found the values of $\bar{P}_2$ and $\mathscr{D}_{0,2}^{(2)}$ plotted in Figure 2. The results are reasonably well accounted for by the curve obtained with λ equal to 0.2, especially as the

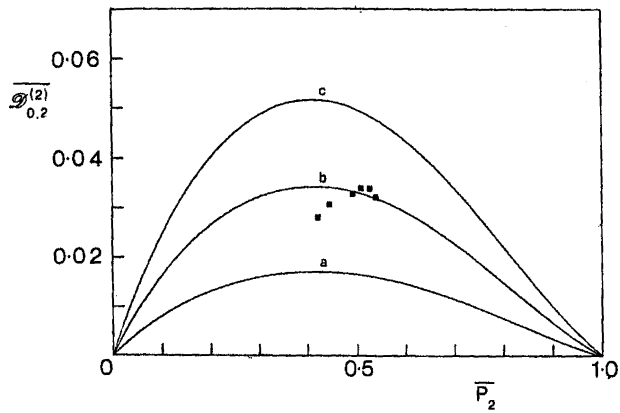

FIGURE 2 The variation of the secondary order parameter $\overline{\mathscr{D}_{0,2}^{(2)}}$ with the order parameter $\bar{P}_2$ calculated for λ equal to (*a*) 0.1, (*b*) 0.2 and (*c*) 0.3.

values of $\overline{\mathscr{D}_{0,2}^{(2)}}$ are particularly sensitive to the fine details of the geometry assumed for the nematogen. Given a λ of 0.2 we predict the entropy of transition $S^{(K)}/R$ to be 0.27, in surprisingly good agreement with the observed value of 0.28, although this does appear to subject to some experimental uncertainty [21]. This prediction is a considerable improvement on the Maier–Saupe value for $S^{(K)}/R$ of 0.42. The order parameter $\bar{P}_2$ at the transition point may also be calculated for this particular λ and we find 0.34, in good agreement with the observed value of about 0.36. This prediction should be contrasted with the Maier–Saupe value of 0.43. The higher parameter $\bar{P}_4$ is predicted to be 0.08 at the order-disorder transition but as yet there are no determinations of this quantity although it is available from light scattering experiments [22].

As a final test of the theory we compare the predicted temperature dependence of the order parameter $\bar{P}_2$ with the observed dependence. This comparison is not straightforward because the measurements are almost always made at constant pressure and as a consequence the volume will also change as the temperature is varied. The pair distribution function employed in evaluating the average $\overline{r_{12}^{-6}}$ will then be temperature dependent and so the coefficients c_{2qp} occurring in the theory will change with temperature. It is possible to allow for this variation by assuming a simple volume dependence of the form

$$c_{2qp} = c_{2qp}^{0}/V^{\gamma},$$

where the c_{2qp}^{0} is temperature independent [11]. However, even though the temperature dependence of the volume is known, such an assumption introduces an additional variable γ into the calculation. This problem can be avoided if the order parameter is measured at constant volume, for then the coefficients c_{Lqp} should, to a good approximation, be independent of temperature. Such measurements are available for 4,4′-dimethoxyazoxybenzene [23] and the order parameter $\bar{P}_2$ is plotted as a function of the reduced temperature in Figure 3. The solid line also shown in the figure was obtained from the theory with λ set equal to 0.2. The agreement with experiment is reasonable although the slope of the theoretical curve is greater than that observed.

The theory based on deviations from cylindrical symmetry and treated within the molecular field approximation would appear to provide an acceptable account of the orientational properities of the nematogen 4,4′-dimethoxyazoxybenzene. However it is important to recall that the same properties have been interpreted, with comparable success, by the pseudo-potential, for cylindrically symmetric particles, given by equation (11) with L restricted to 2 and 4 [11]. The order parameter $\overline{P_2}^{(K)}$ is predicted to be 0.36, the entropy change $S^{(K)}/R$ at the transition is calculated to be 0.32

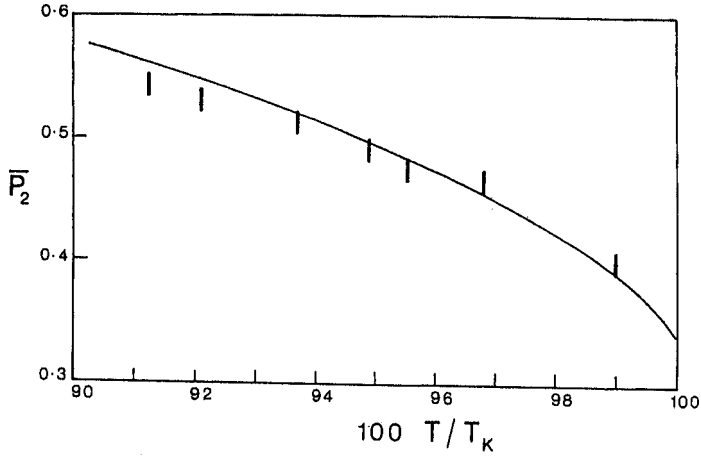

FIGURE 3 The temperature dependence of $\bar{P}_2$ observed for 4,4′-dimethoxyazoxybenzene at constant volume; the curve is calculated with λ equal to 0.2.

and the temperature dependence of the order parameter $\overline{P}_2$ at constant volume is in complete accord with experiment [24]. Of course the theory fails to predict the order parameter $\mathscr{D}_{0,2}^{(2)}$ since for cylindrically symmetric particles this must be zero. On present evidence it is hard to distinguish between the two theories although it may be significant that the parameter $\overline{P_2}^{(K)}$ is usually less than the Maier–Saupe limit [25] which is a natural result of deviations from molecular cylindrical symmetry. Clearly future experimental studies of the orientational order in nematics should concentrate on the secondary order parameter $\mathscr{D}_{0,2}^{(2)}$. In the event that this is shown, unambiguously, to be non-zero, then the appropriate terms must be included in the pseudo-potential. However, such observations may not exclude the retention of the quartic terms in the expansion. Indeed when $\overline{P_2}^{(K)}$ exceeds the Maier–Saupe value of 0.43, as it does for 4,4′-diethoxyazoxybenzene [25], then quartic terms will have to be retained because such an effect cannot be accounted for simply in terms of the pseudo-potential for non-cylindrically symmetric molecules when this is restricted to quadratic terms. We shall not attempt calculations with the extended potential here because the available experimental evidence does not warrant such an extension.

APPENDIX

Here we derive expressions for the expansion coefficients $u_{L_1L_2mn_1n_2}(r_{12})$ when the molecules interact via dispersion forces. Our starting point is the

dispersion interaction energy for a pair of molecules in their electronic ground states [26],

$$U_{12} = d_{12} A_{\alpha\delta} B_{\alpha\delta}, \tag{A1}$$

where the tensor convention of summation over repeated Greek subscripts is adopted. The proportionality constant d_{12} is given by

$$d_{12} = -\epsilon_1 \epsilon_2 / (\epsilon_1 + \epsilon_2), \tag{A2}$$

where ϵ_i is an energy parameter often identified with an ionization potential. The tensors $\mathbf{A}$ and $\mathbf{B}$ are defined in terms of the polarizability tensors $\boldsymbol{\alpha}_1$ and $\boldsymbol{\alpha}_2$, for the two molecules, by

$$A_{\alpha\delta} = \nabla_\alpha \nabla_\beta (1/r_{12}) \alpha_{2_{\beta\delta}} \tag{A3}$$

and

$$B_{\alpha\delta} = \alpha_{1_{\alpha\gamma}} \nabla_\gamma \nabla_\delta (1/r_{12}). \tag{A4}$$

The scalar product in equation (A1) may also be written in irreducible spherical tensor form [12] as

$$U_{12} = d_{12} \sum_{L,\, m} A^{(L,\, m)} B^{(L,\, m)^*}, \tag{A5}$$

where L may only take values 0, 1 and 2 because A and B are second-rank tensors. The irreducible components $A^{(L,\, m)}$ are constructed from the tensors $\mathbf{T}$ and $\boldsymbol{\alpha}$ according to the prescription

$$A^{(L,\, m)} = (-1)^{L+1} \sum_{\substack{L_1 L_2 \\ q}} \{(2L_1 + 1)(2L_2 + 1)\}^{1/2} W(L_2 1 L_2 1;\ 1L)$$
$$\times C(L_2 L_1 L;\ m - q, q) \times T^{(L_1, q)} \alpha_2^{(L_2, m-q)}, \tag{A6}$$

where $W(abcd;\, ef)$ and $C(abc;\, de)$ are Racah and Clebsch–Gordan coefficients respectively [12]. The values of L_1 and q may be restricted by working in a coordinate system containing the intermolecular vector as z axis; in this case the only non-vanishing component is

$$T^{(2,\,0)} = \sqrt{\tfrac{3}{2}}\, T_{zz} = \sqrt{6}/{r_{12}}^3. \tag{A7}$$

The same restriction hold for $B^{(L,\, m)}$ and so

$$U_{12} = \sum_{\substack{L_1 L_2 \\ m}} u_{L_1 L_2 m}(r_{12}) \alpha_1^{(L_1, m)^*} \alpha_2^{(L_2, m)}, \tag{A8}$$

where

$$u_{L_1L_2m}(r_{12}) = \frac{30}{r_{12}^6} d_{12}\{(2L_1+1)(2L_2+1)\}^{1/2} \times \sum_L W(L_2121;\ 1L)W(21L_11;\ 1L) \times C(L_22L;\ m0)C(2L_1L;\ 0m). \quad \text{(A9)}$$

Transforming the polarizability tensors to their respective molecular coordinate systems gives the dispersion energy as

$$U_{12} = \sum\{(-1)^{m-n_1-n_2} u_{L_1L_2m}(r_{12})\alpha_1^{(L_1,n_1)^*}\alpha_2^{(L_2,n_2)^*}\}\mathscr{D}^{(L_1)}_{m,n_1}(\Omega_{1-R}) \times \mathscr{D}^{(L_2)}_{-m,n_2}(\Omega_{2-R}). \quad \text{(A10)}$$

This result has the same form as the general expansion of the pairwise inter-molecular potential given in equation (2) and allows us to identify the coefficients in that expansion as

$$u_{L_1L_2mn_1n_2}(r_{12}) = (-1)^{m-n_1-n_2} u_{L_1L_2m}(r_{12})\alpha_1^{(L_1,n_1)^*}\alpha_2^{(L_2,n_2)^*}; \quad \text{(A11)}$$

of course L_1 and L_2 may only take values 0 or 2 because the polarizability $\boldsymbol{\alpha}$ is a symmetric second-rank tensor. Consequently the surviving coefficients c_{Lqp} are found to be

$$c_{2qp} = d_{12}\alpha^{(2,q)}\alpha^{(2,p)}/5\overline{r_{12}^6}, \quad \text{(A12)}$$

after evaluating the vector coupling coefficients.

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