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Solute alignment in liquid crystal solvents

The Saupe ordering matrix for anthracene dissolved in uniaxial liquid crystals

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We have described a theory for $U(\omega)$, the potential of mean torque of rigid solutes at infinite dilution in a uniaxial liquid crystal phase; this may be used to calculate $(S_{xx} - S_{yy})$ and S_{zz}, the principal elements of the Saupe ordering matrix. In its simplest form $U(\omega)$ contains only second-rank terms and the dependence of the biaxiality $(S_{xx} - S_{yy})$ is determined by λ, a parameter which describes the departure of the potential of mean torque from cylindrical symmetry, and is predicted to be temperature independent. If dispersion forces are responsible for the magnitude of the orientational order parameter then λ should be independent of the solvent and depend only on the anisotropy in the electric polarizability of the solute. Indeed, this independence should result for any pair potential which can be factorized into a product of solute and solvent properties. These predictions are tested here by determining values of S_{zz} and $(S_{xx} - S_{yy})$ for anthracene-d_{10} as a solute in several liquid crystal solvents, from the quadrupolar splittings obtained from the deuteron N.M.R. spectra. It is found that λ has a strong dependence on the nature of the solvent, which demonstrates that the solute ordering cannot be determined primarily by dispersion forces, or by a factorizable potential. There is also a weaker temperature dependence of λ observed for each binary mixture, and we show how this might be caused by a dependence of λ on solvent ordering, or by the inclusion of a fourth-rank term in $U(\omega)$.

1. Introduction

The development of a molecular theory for thermotropic liquid crystals is an extremely difficult task. Part of this difficulty results undoubtably from the structural complexity of the molecules which form liquid crystals. Thus although mesogenic compounds, such as the 4-*n*-alkyl-4′-cyanobiphenyls, are composed of rod-like molecules, these are of low symmetry and they are flexible. This complexity has also impeded the experimental investigation of the long range orientational order of a liquid crystal, which is its prime characteristic. However, in recent years N.M.R. spectroscopy in general and deuterium N.M.R. spectroscopy in particular has proved to be a uniquely powerful technique for the determination of the orientational order parameters of the rigid sub-units in a mesogenic molecule [1]. None the less, the complete Saupe ordering matrices for every sub-unit in such a molecule have yet to be measured. One solution to this problem is the synthesis of mesogens with simpler molecular structures, but the choice of these is limited and even then they are liquid crystalline only at high pressures or in a supercooled state at atmospheric pressure [2].

An alternative approach is to study the orientational order of a solute dissolved in a liquid crystal solvent. This has considerable advantages; for example, the solute structure can be chosen to be rigid and with a high degree of symmetry. In consequence the principal elements of the Saupe ordering matrix can be determined using a range of techniques which include N.M.R. spectroscopy [1], optical dichroism [3] and E.S.R. spectroscopy for paramagnetic solutes [4]. In addition the same solute can be used as a probe to investigate the anisotropic intermolecular interactions in different liquid crystal solvents. Alternatively, variations in the structure of the solute may be employed to study the possible contributions to the solute–solvent interactions for a given liquid crystal. Here we report the results obtained from the former approach in which the ordering matrix for anthracene-d_{10} dissolved in a range of liquid crystals has been determined using deuterium N.M.R. spectroscopy. However, before we describe and then discuss our results we shall outline the background to the measurement of the Saupe ordering matrix and its interpretation at the molecular level.

The ordering matrix is defined by

$$S_{ab} = (3\overline{l_a l_b} - \delta_{ab})/2, \tag{1}$$

where l_a is the direction cosine between the director of a uniaxial liquid crystal and an axis a set in the molecule; the bar denotes an ensemble average [5]. There are five independent elements of S because the ordering matrix is symmetric and traceless, but for molecules with C_{2v} symmetry or higher the principal axes may be identified and so this number is reduced to just two. The two independent quantities are best expressed as the major element, S_{zz}, and the biaxiality $(S_{xx} - S_{yy})$ which measures the deviation of S from cylindrical symmetry. The principal axes, xyz, are selected so that $(S_{xx} - S_{yy})$ is positive and $|S_{zz}| > (S_{xx} - S_{yy})$. The determination of the principal components of the ordering matrix therefore requires a technique which is capable of yielding at least two independent pieces of information, provided the principal axes are defined by the molecular symmetry. Deuterium N.M.R. spectroscopy of a deuteriated solute gives a quadrupolar splitting, $\Delta\tilde{\nu}$, for each inequivalent deuteron; this results directly from the alignment of the solute and is related to the principal elements of S by

$$\Delta\tilde{\nu} = (3/2)\,q_{zz}S_{zz} + (1/2)(S_{xx} - S_{yy})(q_{xx} - q_{yy}). \tag{2}$$

Here $q_{\alpha\alpha}$ are the diagonal elements of the quadrupolar interaction tensor in the principal axis system of the ordering matrix, and we assume that contributions to the electric field gradients at each deuteron which stem from the surrounding molecules are negligibly small. Equation (2) applies to a liquid crystal with a positive anisotropy $\Delta\chi\,(= \chi_{\parallel} - \chi_{\perp})$ in the magnetic susceptibility and which is therefore aligned parallel to the magnetic field. The equation can be applied to liquid crystals with $\Delta\chi$ negative by multiplying the observed quadrupolar splittings by -2, since, for such materials, the director is aligned orthogonal to the magnetic field. Provided the solute contains at least two deuterons with significantly different principal axes for their quadrupolar tensors then it is possible to determine both S_{zz} and $(S_{xx} - S_{yy})$ from their quadrupolar splittings.

The measurement of the Saupe ordering matrix is clearly a straightforward task for a solute dissolved in a liquid crystal solvent. However if such experiments are to allow us to explore the anisotropic intermolecular interactions in liquid crystal solutions it is necessary to develop a molecular theory for solute alignment. The principal elements of S are related to the potential of mean torque, $U(\omega)$, governing the solute alignment by

$$S_{aa} = Z^{-1} \int \{(3l_a^2(\omega) - 1)/2\} \exp\{-U(\omega)/kT\}\, d\omega, \tag{3}$$

where Z is the orientational partition function

$$Z = \int \exp\{-U(\omega)/kT\}\, d\omega, \tag{4}$$

and ω denotes the spherical polar angles made by the director in the principal axis system of the solute. One of the earliest attempts to understand solute alignment was made by Nehring and Saupe [6] who proposed that, by analogy with the Maier–Saupe theory of nematics [7], the potential of mean torque is of the form,

$$U(\omega) = -(\varepsilon_{zz} l_z^2 + \varepsilon_{xx} l_x^2 + \varepsilon_{yy} l_y^2). \tag{5}$$

Subsequently we shall find it convenient to use irreducible spherical tensor notation and in this formalism equation (5) becomes

$$U(\omega) = -[\varepsilon_{2,0} C_{2,0}(\omega) + \varepsilon_{2,2}\{C_{2,2}(\omega) + C_{2,-2}(\omega)\}], \tag{6}$$

where $C_{2,m}(\omega)$ is a modified spherical harmonic and $\varepsilon_{2,m}$ is the irreducible spherical tensor form of the cartesian interaction tensor ε_{aa} [8].

The second-rank interaction tensor $\boldsymbol{\varepsilon}$ depends on a variety of factors including temperature, the solvent order and the solute concentration. One further advantage of N.M.R. spectroscopy is that the solute concentration can be made so small that $\boldsymbol{\varepsilon}$ is determined by solute–solvent interactions alone and does not involve solute–solute interactions. Even so the development of expressions for the interaction tensor in the potential of mean torque for the solute presents a serious challenge. There have been several attempts at this development, each based on the molecular field approximation but differing in the symmetries assumed for the solute and the solvent. The latest of these developments has been given by Emsley *et al.* [9]; they have derived a general expression for the potential of mean torque for a biaxial solute in a solvent of rigid biaxial particles at the infinite dilution limit. According to this theory the components of the second-rank interaction tensor are

$$\varepsilon_{2,0} = -(\bar{u}_{200}\bar{C}_{2,0} + 2\bar{u}_{220}\bar{C}_{2,2}), \tag{7}$$

$$\varepsilon_{2,2} = -2(\bar{u}_{202}\bar{C}_{2,0} + 2\bar{u}_{222}\bar{C}_{2,2}). \tag{8}$$

Here the solvent ordering tensor $\bar{C}_{2,m}$ is expressed in irreducible form; $\bar{C}_{2,0}$ is equivalent to the major order parameter while $\bar{C}_{2,2}$ describes the biaxiality in the Saupe ordering matrix for the solvent.

The averaged coefficients, $\bar{u}_{2mn}$, are related to the anisotropic solute–solvent interactions and expressions for them can be derived from a formal expansion of the intermolecular pair potential [9]. In such an expansion the distance dependent coefficients are not necessarily associated with particular intermolecular forces and they may contain contributions from several. For the second-rank averaged coefficients $\bar{u}_{2mn}$ the first subscript denotes the rank of the interaction, the second is a component associated with the solvent and the third with the solute. Thus for a uniaxial solvent and a biaxial solute only $\bar{u}_{200}$ and $\bar{u}_{202}$ are non-zero, while for uniaxial solute and solvent only $\bar{u}_{200}$ survives. The relative magnitudes of these interaction coefficients depend, *inter alia*, on the extent of the departure of the particles, both solute and solvent, from cylindrical symmetry. For a typical mesogenic solvent we expect

$$\bar{u}_{200} > \bar{u}_{220} \quad \text{and} \quad \bar{u}_{202} > \bar{u}_{222} \tag{9}$$

since the molecules approximate closely to cylindrical symmetry; this need not be the case for the solute where the relative magnitudes of $\bar{u}_{2m0}$ and $\bar{u}_{2m2}$ can vary significantly with the molecular structure.

The biaxial order parameter for the solvent is small in comparison with the major order parameter; typically $\bar{C}_{2,2}/\bar{C}_{2,0}$ is about 0·05 [1, 10]. This, taken together with the inequalities in equation (9), allows us to approximate the components of the interaction tensor in equations (7) and (8) by

$$\varepsilon_{2,0} = -\bar{u}_{200}\bar{C}_{2,0} \tag{10}$$

and

$$\varepsilon_{2,2} = -2\bar{u}_{202}\bar{C}_{2,0}. \tag{11}$$

The ratio, λ, of these coefficients is then given by

$$\begin{aligned}\lambda &= \varepsilon_{2,2}/2\varepsilon_{2,0},\\ &= \bar{u}_{202}/\bar{u}_{200},\end{aligned} \tag{12}$$

and so is predicted to be independent of the solvent order but not necessarily the nature of the solvent since the coefficients themselves are determined by the solute–solvent interactions. However if these interactions are dominated by dispersion forces then λ is indeed independent of the solvent. This situation obtains because the coefficients are related to the polarizabilities, $\alpha_1^{(2,m)}$ and $\alpha_2^{(2,n)}$, of the solvent and solute, respectively [11]

$$\bar{u}_{2mn} = B_{12}\alpha_1^{(2,m)}\alpha_2^{(2,n)}, \tag{13}$$

and so λ depends on the solute properties alone

$$\lambda = \alpha_2^{(2,2)}/\alpha_2^{(2,0)}. \tag{14}$$

Indeed λ should be independent of the solvent for any molecular interaction which may be factorized into a product of solute and solvent properties.

These predictions have been tested by measuring the Saupe ordering matrix for 1,4-dinitrobenzene dissolved in the mesogens 4,4′-di-*n*-heptyl-azoxybenzene (HAB), Merck Phase 5 which is a mixture of 4,4′-di-*n*-alkyloxyazoxybenzenes, and E5 which is a mixture of 4-*n*-alkyl-4′-cyanobiphenyls and 4-*n*-alkyl-4″-cyanoterphenyls [9]. The biaxiality parameter λ was found to exhibit a strong solvent dependence and so clearly demonstrated that dispersion forces do not make the dominant contribution to the anisotropic solute–solvent interactions and that the pair potential cannot be factorized as has been supposed [3, 12]. In addition λ was observed to decrease slightly with increasing temperature which is not in accord with the general theory of solute alignment. Both of these results might be specific to the particular solute, which possesses at least one property not allowed for in the theory. Thus 1,4-dinitrobenzene is not rigid; the nitro groups must rotate about the para-axis and they may not be coplanar with the phenyl ring or even with each other in the ground state conformation. The solute is also small in comparison with the liquid crystal solvent and is strongly polar; in consequence it may interact specifically with parts of the solvent molecule.

Such specific interactions are not included in the theory and so we have extended our studies of solute ordering by using anthracene. This is certainly rigid, it is larger

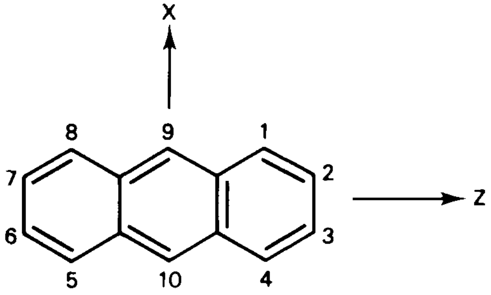


Figure 1. Atomic labelling and location of the symmetry axes for anthracene. The y axis is normal to the molecular plane.

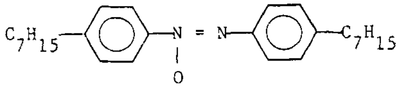
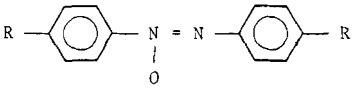
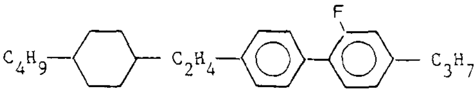
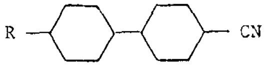
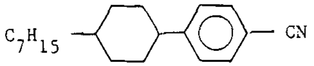
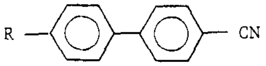
than 1,4-dinitrobenzene and is considerably less polar. The choice of anthracene has other advantages; its structure (cf. figure 1) has been characterized by X-ray diffraction and the quadrupolar interaction tensors for the deuterons in anthracene-d_{10} have been determined from a single crystal study [13]. Such information is needed when we come to extract the principal elements of the Saupe ordering matrix from the observed quadrupolar splittings.

The solvents used in our study are shown in table 1; they represent a range of chemical types and, most importantly, have wide mesomorphic ranges which result in a large variation in the orientational order of both solvent and solute. Phase 5 and HAB were studied with 1,4-dinitrobenzene as solute; E9 is a very similar mixture to E5, which was the other solvent used with 1,4-dinitrobenzene. The three additional solvents employed with anthracene differ from the others in containing saturated ring systems and so may interact with anthracene in a different way to the solvents containing purely aromatic cores.

2. Experimental and spectral analysis

Anthracene-d_{10} was obtained from the Aldrich Chemical Company and approximately 1 per cent w/w solutions prepared in the six liquid crystal solvents shown in table 1. For E9 as solvent we also made measurements on a 0·5 per cent w/w solution as a check that the 1 per cent solutions are sufficiently dilute that the variation of $(S_{xx} - S_{yy})$ with S_{zz} is independent of the solute concentration. The deuteron spectra were recorded at 30·7 MHz on a Bruker CXP200 spectrometer; a typical spectrum is shown in figure 2. The outer pair of lines is unambiguously assigned to the deuterons at positions 2, 3, 6 and 7 on the grounds of their smaller relative intensity. The central group of lines originate from the remaining six deuterons and are shown on an expanded scale as the middle trace in figure 2. The complex structure on these inner bands is caused by dipolar couplings between the deuterons and also because the four symmetrically equivalent deuterons at positions 1, 4, 5 and 8 have a different quadrupolar splitting from those at positions 9 and 10. A full analysis of the spectrum of an oriented sample containing ten interacting deuterons is not practicable. However, it was found to be possible to reproduce the spectral envelope with good precision by simulating the spectrum as caused by deuterons 1, 2, 7, 8, 9 and 3, 4, 5, 6 10 as two identical but non-interacting groups. This result is perhaps surprising since the dipolar couplings $\tilde{D}_{23} = \tilde{D}_{67}$ are not small. None the less any errors introduced by this approximate analysis are certainly not expected to invalidate the main conclusions reached on the relative signs and magnitudes of the quadrupolar splittings. The results

Table 1. The liquid crystals used as solvents for anthracene.

	Abbreviation	Composition	Structure
(1)	HAB	4,4′-di-*n*-heptylazoxy benzene (T_{CS_A} = 307 K; T_{S_AN} = 326·5 K; T_{NI} = 344·5 K)	
(2)	Phase 5	Eutectic mixture of: 4-butyl, 4′-methoxy-azoxybenzene 4-methoxy, 4′-butyl-azoxybenzene 4-ethyl, 4′-methoxy-azoxybenzene 4-methoxy, 4′-ethyl-azoxybenzene (T_{CN} = 268 K; T_{NI} = 348 K)	$R = C_4H_9$, $R' = OCH_3$ $R = CH_3O$, $R' = C_4H_9$ $R = C_2H_5$, $R' = OCH_3$ $R = CH_3O$, $R' = C_2H_5$ 
(3)	14, 3	1-(4-trans butyl-cyclohexyl) 2-(2′-fluoro, 4′-propyl, 4-biphenyl)ethane (T_{CN} = 297·5 K, T_{NI} = 376 K)	
(4)	ZLI 1167	Eutectic mixture of: 4-trans cyano, 4′-trans propyl bicyclohexyl 4-trans cyano, 4′-trans pentyl bicyclohexyl 4-trans cyano, 4′-trans heptyl bicyclohexyl (T_{CS_A} = 298 K; T_{S_AN} = 305 K; T_{NI} = 356 K)	$R = C_3H_7$ $R = C_5H_{11}$ $R = C_7H_{15}$ 
(5)	PCH 7	4-cyano (4′-trans heptyl-cyclohexyl) benzene (T_{CN} = 303 K, T_{NI} = 330·5 K)	
(6)	E9	Mixture of: 15 per cent 4-propyl, 4′-cyano-biphenyl 38 per cent 4-pentyl, 4′-cyano-biphenyl 38 per cent 4-heptyl, 4′-cyano-biphenyl 9 per cent 4-pentyl, 4″-cyano-*p*-terphenyl (T_{CN} = 280 K; T_{NI} = 355·5 K)	$R = C_3H_7$ $R = C_5H_{11}$ $R = C_7H_{15}$ $R = C_5H_{11}Ph$ 

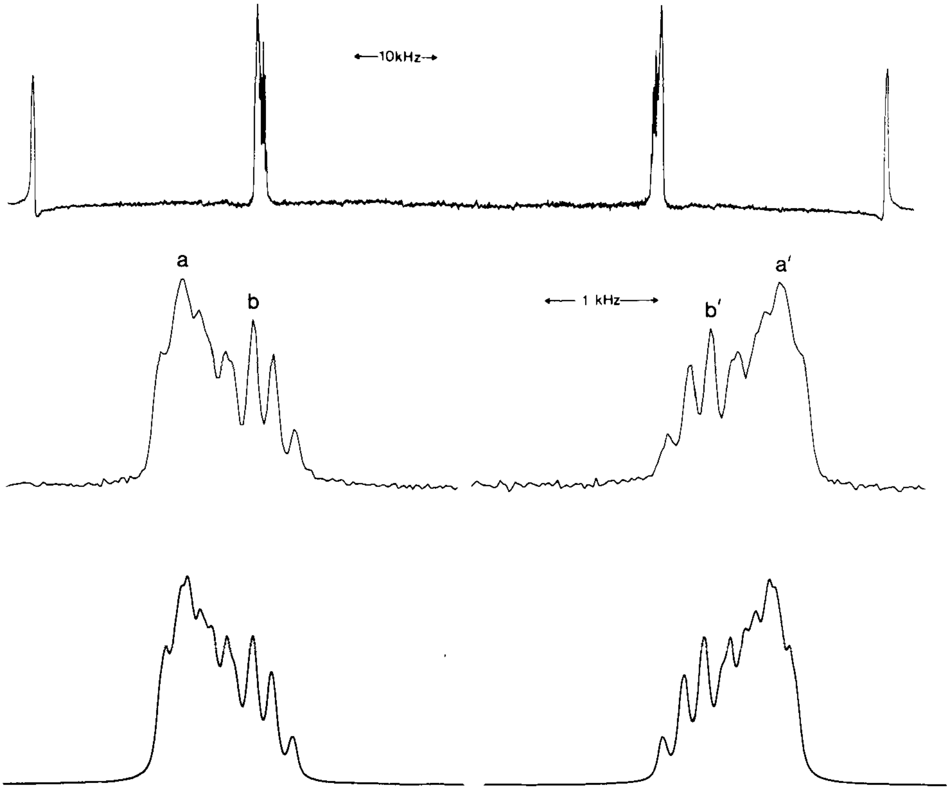


Figure 2. 30·7 MHz N.M.R. spectrum of deuterons in anthracene-d_{10} dissolved in HAB at $T_{NI} - T = 23$ K. The top trace is the complete spectrum, whilst the middle trace shows an expansion of the inner groups of lines. The points *a*, *a′* and *b*, *b′* give the positions from which values of $\Delta\tilde{\nu}_1$ and $\Delta\tilde{\nu}_9$ may be measured. The bottom trace is a spectrum calculated for the deuterons 1, 4, 5, 8, 9 and 10 with the parameters given in table 2.

Table 2. Dipolar couplings and quadrupolar splitting obtained by analysis of the deuteron spectrum of anthracene-d_{10} dissolved in HAB at $T_{NI} - T = 23$ K.

$\Delta\tilde{\nu}_1 = \Delta\tilde{\nu}_4 = \Delta\tilde{\nu}_5 = \Delta\tilde{\nu}_8$	−49 230 Hz
$\Delta\tilde{\nu}_2 = \Delta\tilde{\nu}_3 = \Delta\tilde{\nu}_6 = \Delta\tilde{\nu}_7$	104 000 Hz
$\Delta\tilde{\nu}_9 = \Delta\tilde{\nu}_{10}$	−48 070 Hz
$\tilde{D}_{12} = \tilde{D}_{78} = \tilde{D}_{34} = \tilde{D}_{56}$	−64 Hz
$\tilde{D}_{19} = \tilde{D}_{89} = \tilde{D}_{4,10} = \tilde{D}_{5,10}$	−105 Hz
$\tilde{D}_{18} = \tilde{D}_{45}$	−13 Hz
$\tilde{D}_{17} = \tilde{D}_{28} = \tilde{D}_{35} = \tilde{D}_{46}$	−6 Hz

obtained by an iterative analysis of the spectrum of the HAB solution recorded at $T_{NI} - T = 23$ K are given in table 2, and the bottom trace in figure 2 shows a simulation of the peaks from deuterons 1, 4, 5, 8, 9 and 10. This analysis reveals that $\Delta\tilde{\nu}_1$ can be obtained directly from the separation of peaks *a* and *a′* whilst the separation of peaks *b* and *b′* gives $\Delta\tilde{\nu}_9$, both to a precision of approximately 50 Hz.

The spectral envelope from peaks 1, 4, 5, 8, 9 and 10 does not change on varying either the solvent or the temperature so it was possible to obtain $\Delta\tilde{\nu}_1$ and $\Delta\tilde{\nu}_9$ from each spectrum without recourse to an iterative fit. Spectra for each sample were recorded over a wide temperature range and the results are contained in six tables comprising 8 pages which have been deposited with the British Library Lending Division; copies of this Supplementary Publication may be obtained from the British Library by using the procedure described at the end of this issue and quoting the number SUP 16501.

The analysis of the dipolar structure shown in figure 2 requires $\tilde{D}_{19}$ to be the same sign as both $\Delta\tilde{\nu}_1$ and $\Delta\tilde{\nu}_9$; in addition we can establish the sign of $\tilde{D}_{19}$ in the following way. The dipolar coupling $\tilde{D}_{19}$ is given by

$$\tilde{D}_{19} = -\gamma_D^2 h S_{zz}/4\pi^2 r_{19}^3, \tag{15}$$

where γ_D is the gyromagnetic ratio of the deuteron and r_{19} is the internuclear separation. At the lowest reduced temperatures $|S_{zz}|$ is observed to be greater than one-half and S_{zz} must therefore be positive, making $\tilde{D}_{19}$, $\Delta\tilde{\nu}_1$ and $\Delta\tilde{\nu}_9$ negative.

3. Results and discussion

To obtain the order parameters S_{zz} and $(S_{xx} - S_{yy})$ from the quadrupolar splittings with the aid of equation (2) it is necessary to relate q_{zz} and $(q_{xx} - q_{yy})$ to the components of $\mathbf{q}$ in its principal frame of reference. The principal axes (*abc*) of the quadrupolar interaction tensor of a deuteron in anthracene are such that to a good approximation *a* lies along the appropriate C–D bond and *c* is normal to the ring plane. These axes are chosen so that $|q_{aa}| > |q_{cc}| > |q_{bb}|$ and the asymmetry parameter $\eta = (q_{bb} - q_{cc})/q_{aa}$ is positive. Thus, for a deuteron at the *i*th site where the C–D bond has direction cosines $l^i_{\alpha a}$, $l^i_{\alpha b}$, $l^i_{\alpha c}$ with axis α (x, y or z)

$$q^i_{\alpha\alpha} = q^i_{aa}[(3l^{i2}_{\alpha a} - 1)/2 + \eta^i(l^{i2}_{\alpha b} - l^{i2}_{\alpha c})/2]. \tag{16}$$

Substituting equation (16) into equation (2) and noting that for anthracene both y and c are normal to the ring plane we obtain

$$\Delta\tilde{\nu}_i = \tfrac{3}{2}q^i_{aa}[S_{zz}\{(3l^{i2}_{za} - 1)/2 + \eta^i l^{i2}_{zb}/2\} + (S_{xx} - S_{yy})(l^{i2}_{xa} + \tfrac{1}{3}\eta(l^{i2}_{xb} + 1))/2]. \tag{17}$$

The bonds C–D (9) and C–D (10) are necessarily parallel to x so that for these the geometrical factors in equation (17) are known with certainty. The bonds to deuterons at position 2, 3, 6 and 7 are taken to make an angle of 29·5° to z; this value is obtained by assuming that these bond directions bisect the CCC bond angle at their attached carbon atoms, the value of which is available from an X-ray study [14]. To calculate S_{zz} and $(S_{xx} - S_{yy})$ from the quadrupolar splittings $\Delta\tilde{\nu}_2$ and $\Delta\tilde{\nu}_9$ it is necesary to know the values of q_{aa} and η at these positions. We take $q_{aa} = 181$ kHz and $\eta = 0{\cdot}064$ which are the values found for all deuterons in solid anthracene [12]. We note, however, that our spectra show that $\Delta\tilde{\nu}_1 \neq \Delta\tilde{\nu}_9$ which could result because the C–D bonds (or more correctly, the principal axes of the quadrupolar tensors) are not parallel, or because $q^{(1)}_{aa} \neq q^{(9)}_{aa}$; differences in $\eta^{(1)}$ and $\eta^{(9)}$ will also contribute to a difference in the quadrupolar splittings but this effect is expected to be negligible. We can eliminate the geometrical factor as the sole cause of the difference between $\Delta\tilde{\nu}_1$ and $\Delta\tilde{\nu}_9$; the bond C–D(9) must be parallel to x and rotating C–D(1) either towards z or $-z$ about y serves to decrease $|\Delta\tilde{\nu}_1|$ relative to $|\Delta\tilde{\nu}_9|$, whereas the opposite magnitudes are observed. Attributing the difference between $\Delta\tilde{\nu}_1$ and $\Delta\tilde{\nu}_9$ $(\Delta\tilde{\nu}_1 - \Delta\tilde{\nu}_9)$ entirely to the difference in the quadrupolar coupling constants $q^{(1)}_{aa}$ and $q^{(9)}_{aa}$ gives this as 4·4 ± 0·1 kHz, which is reasonable in view of the variations observed in this quantity for different aromatic compounds [15]. The inequality in $q^{(1)}_{aa}$ and $q^{(9)}_{aa}$ contrasts with the conclusion drawn by

Ellis and Bjorkstam [13] from their study on solid anthracene that the $q_{aa}^{(i)}$ are equal at all positions in anthracene, however, the large line widths in the deuteron spectra of solid anthracene could mask the small difference in splittings which we observe for liquid-crystalline solutions with their narrower line widths. The values of $q_{aa}^{(2)}$ and $q_{aa}^{(9)}$, which we need to extract S_{zz} and $(S_{xx} - S_{yy})$ from the observed quadrupolar splittings, could also differ by an amount similar to $|q_{aa}^{(1)} - q_{aa}^{(9)}|$. Accordingly in using a single value of q_{aa} for positions 2 and 9 we should recognize that this will introduce an uncertainty of approximately ±3 per cent into calculations of the order parameters. We note that this is a systematic error and does not affect the precision with which order parameters at different temperatures or in different solvents can be compared. The errors arising from the precision in measuring the quadrupolar splittings are much smaller; they are 0·5 per cent in S_{zz} and 3 per cent in $(S_{xx} - S_{yy})$.

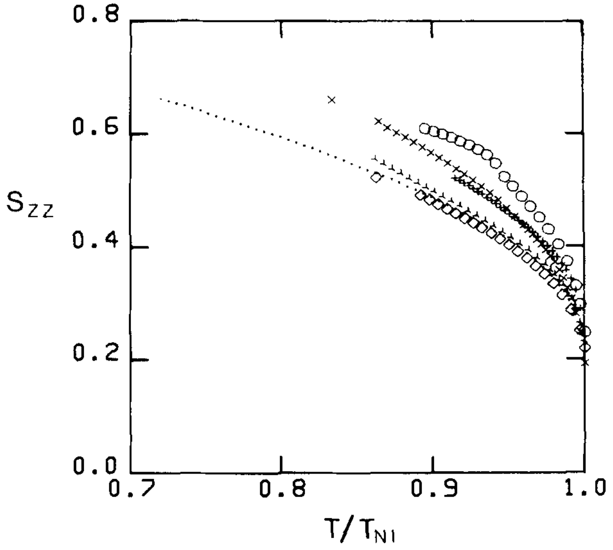


Figure 3. The variation of the major order parameter S_{zz} with the reduced temperature, T/T_{NI}, for anthracene-d_{10} dissolved in HAB (○), E9 (×), PCH 7 (+), ZLI 1167 (⅄), I 4,3 (·) and Phase 5 (◇).

In figures 3 and 4 we show the temperature dependences of S_{zz} and $(S_{xx} - S_{yy})$ for anthracene in the six solvents. The magnitude of S_{zz} increases with decreasing reduced temperature, T/T_{NI}, for all the solvents, as expected. There is an enhancement in S_{zz} as the smectic A phase is entered for the solution of anthracene in HAB, which again is to be anticipated. There is, however, no obvious correlation between the relative magnitudes of S_{zz} for anthracene in different solvents at the same reduced temperature. For example, HAB and Phase V both have azoxybenzene cores and yet anthracene is most ordered in HAB and least in Phase V. However, anthracene is similarly ordered in E9 and PCH7 both of which have benzonitrile groups but differ in that PCH7 contains a cyclohexyl group. Figure 4 gives the variation of $(S_{xx} - S_{yy})$ with T/T_{NI}; the observed curves exhibit the increase and then the decrease predicted by theory [9, 11] as the reduced temperature is lowered. At all temperatures and in all the solvents studied we find $|S_{zz}| > |S_{yy}| > |S_{xx}|$, with S_{xx} and S_{yy} both negative. This correlates with the anisotropy in both the shape and the electric polarizability of anthracene and hence is consistent with either steric or dispersion forces being

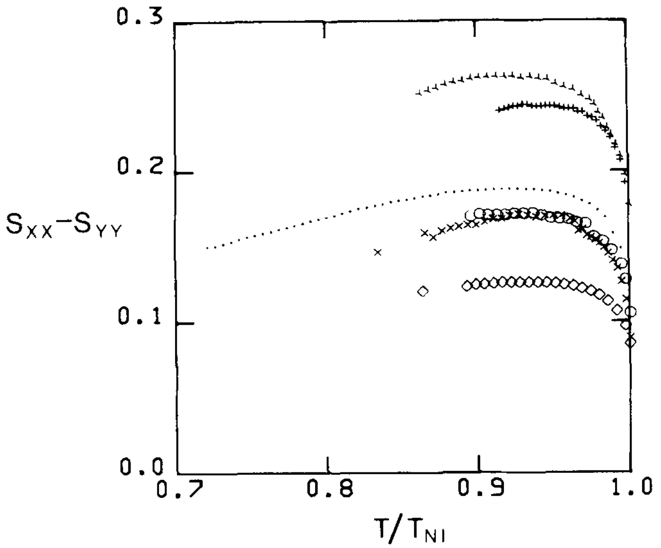


Figure 4. The variation of the biaxiality ($S_{xx} - S_{yy}$) with the reduced temperature, T/T_{NI}, for anthracene-d_{10} dissolved in HAB (o), E9 (×), PCH 7 (+), ZLI 1167 (λ), I 4,3 (·) and Phase 5 (◇).

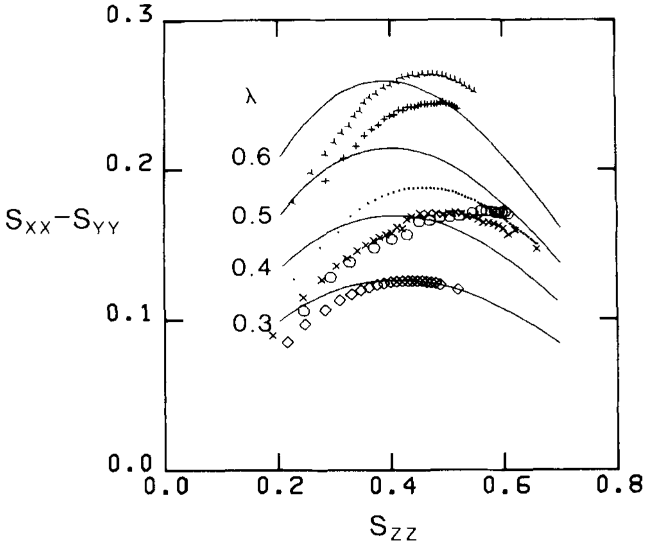


Figure 5. The variation of the biaxility ($S_{xx} - S_{yy}$) with the major order parameter S_{zz} for anthracene-d_{10} in HAB (o), E9 (×), PCH 7 (+), ZLI 1167 (λ), I 4,3 (·) and Phase 5 (◇). The continuous curves are those calculated for the λ values shown.

important ordering mechanisms for anthracene. There is no obvious correlation of the magnitudes of ($S_{xx} - S_{yy}$) at a given T/T_{NI} with the structure of the solvent. The data in figures 3 and 4 are combined in figure 5 to give the variation of the biaxiality ($S_{xx} - S_{yy}$) with the major order parameter, S_{zz}. This presentation of the data shows more clearly the influence of the solvent on the deviation from cylindrical symmetry of the potential of mean torque for the solute. The continuous curves shown in figure 5 were calculated from equations (3), (6), (10), (11) and (12) using the values of λ indicated beside the curves.

In general, the biaxiality parameter λ will be independent of the nature of the solvent provided that a single interaction dominates $U(\omega)$ and that the averaged coefficients $\bar{u}_{2mn}$ can be factorized according to

$$\bar{u}_{2mn} = A_{12} X_1^{(2,m)} X_2^{(2,n)}, \tag{18}$$

where X_1 and X_2 are second-rank properties associated with the solvent and solute respectively. This factorization is exact for dispersion forces, as noted earlier, and so the data in figure 5 clearly show that this interaction cannot be the sole contribution to the potential of mean torque for anthracene in all the solvents studied here. The same conclusion can be reached for the electrostatic interaction between permanent quadrupole moments on solvent and solute molecules; this has been proposed by Patey *et al.* [16] as the dominant contribution to the potential of mean torque for some small solute molecules in various liquid-crystalline solvents. It can be shown [17] that such an interaction does yield coefficients $\bar{u}_{2mn}$ which obey equation (18), although we note that the contribution of electrostatic forces to $U(\omega)$ vanish within the normal approximations used by Emsley *et al.* [9] to develop the potential of mean torque for biaxial solutes. The factorization of $\bar{u}_{2mn}$ given by equation (18) is not necessarily valid for repulsion forces, although such a division into solute and solvent contributions has been suggested by van der Meer and Vertogen [18]. It is not possible, therefore, to exclude with any certainty that repulsion forces dominate the potential of mean torque for anthracene in the solvents we have studied. It is more probable, however, that the solvent dependence of λ shown in figure 5 is a consequence of a contribution to $U(\omega)$ of more than one kind of force.

This conclusion contrasts with that reached by Sackmann *et al.* [3] who included anthracene in their study of solute alignment in mixtures of cholesteryl esters; they concluded that the solute ordering was determined by the dispersion interaction alone. These authors predicted the order parameter S_{zz} for a number of solutes by assuming the potential of mean torque to result from the dispersion interaction. They used the data for anthracene as a means of calibrating the strength of the interaction and found good agreement between theory and experiment for several other aromatic hydrocarbons. For anthracene they measured S_{zz} to be 0·33 and $S_{xx} - S_{yy}$ as 0·13 at 30°C. These two values can be used to determine an effective biaxiality parameter, λ_{eff}. To do this we combine equation (3) with equations (6), (10) and (11) to give

$$S_{zz} = 2\pi Z^{-1} \int_0^\pi d^2_{00}(\beta)\, I_0\{b d^2_{02}(\beta)\} \exp\{a d^2_{00}(\beta)\} \sin\beta\, d\beta, \tag{19}$$

and

$$S_{xx} - S_{yy} = \sqrt{24}\pi\, Z^{-1} \int_0^\pi d^2_{02}(\beta)\, I_1\{b d^2_{02}(\beta)\} \exp\{a d^2_{00}(\beta)\} \sin\beta\, d\beta, \tag{20}$$

where $d^2_{00}(\beta)$ and $d^2_{02}(\beta)$ are reduced Wigner rotation matrices and β and γ are Euler angles defining the director in the molecular principal axis system. The $I_n\{b d^2_{02}(\beta)\}$ are nth order modified Bessel functions, and a and b are the scaled parameters

$$a = \varepsilon_{2,0}/kT, \tag{21}$$

$$b = \varepsilon_{2,2}/kT, \tag{22}$$

hence $\lambda = b/2a$. Inverting equations (19) and (20) gives a and b, and hence λ_{eff} from a pair of order parameters at a given temperature. For the values of S_{zz} and $S_{xx} - S_{yy}$ determined by Sackmann *et al.* [3] for anthracene we obtain λ_{eff} to be 0·35. If λ_{eff} results from the dispersion forces and hence is determined by the polarizability of the solute through [11],

$$\begin{aligned} \lambda &= \alpha_2^{(2,2)}/\alpha_2^{(2,0)} \\ &= (\alpha_{xx} - \alpha_{yy})/\surd 6(\alpha_{zz} - \bar{\alpha}), \end{aligned} \tag{23}$$

where α_{xx}, α_{yy} and α_{zz} are the principal components of the electric polarizability tensor of anthracene, and $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$.

The polarizabilities have been determined from measurements of the Kerr effect [19]; they are

$$\alpha_{xx} = 26{\cdot}0\,\text{Å}^3, \quad \alpha_{yy} = 12{\cdot}0\,\text{Å}^3, \quad \alpha_{zz} = 40{\cdot}2\,\text{Å}^3,$$

and hence λ is predicted to be 0·41, in the middle of the range of values found for λ_{eff} for anthracene in the solvents used in this work, and significantly greater than the value of λ_{eff} calculated from the data of Sackmann *et al.* [3]. This confirms our previous conclusion that anisotropic dispersion forces cannot make the dominant contribution to the potential of mean torque for anthracene dissolved in a variety of nematics.

There are differences in the relative behaviour of the biaxiality $(S_{xx} - S_{yy})$ found for anthracene and for 1,4-dinitrobenzene. Thus for the two solvents HAB and Phase 5, the only solvents common to both studies, the λ_{eff} values have relative magnitudes λ_{eff} (Phase 5) < λ_{eff} HAB for anthracene but this order is reversed and the difference is larger for 1,4-dinitrobenzene. We do not have a simple explanation for this variation in λ_{eff} but it does illustrate the sensitivity of this parameter to the nature of solute–solvent interactions.

A closer comparison of the experimental data shown in figure 5 with theoretical curves corresponding to fixed values of λ shows that the general shape of the experimental and theoretical curves are in good agreement, although there are significant deviations between experiment and theory. Thus, the maximum in $(S_{xx} - S_{yy})$ occurs at a higher value of S_{zz} for the experimental compared with the theoretical curves. To quantify this discrepancy we show in figure 6 values of λ_{eff} for anthracene which have been obtained from pairs of values of S_{zz} and $S_{xx} - S_{yy}$ at each temperature.

The increase of λ_{eff} with decreasing T/T_{NI} for all the solvents studied parallels the behaviour found for 1,4-dinitrobenzene and suggests a common origin for the phenomenon. Thus, the potential of mean torque $U(\omega)$ must be more complex than we have assumed. The inclusion of only second-rank terms in equation (6) may be an inadequate representation of the orientational dependence of $U(\omega)$, and in addition the linear dependence of the interaction tensor components $\varepsilon_{2,m}$ on the solvent order parameters, $\bar{C}_{2,m}$, of equations (7) and (8) may be a bad approximation.

We now explore each of these possibilities. Our data does not indicate a dependence of λ_{eff} on the flexibility or the biaxial character of the solvent molecules and so we shall retain the approximation that the solvent molecules can be regarded as being rigid and cylindrically symmetric.

We consider first the consequences of expanding $\varepsilon_{2,0}$ and $\varepsilon_{2,2}$ as power series in $\bar{C}_{2,0}$ as proposed for pure nematics [20, 21]

$$\varepsilon_{2,0} = -\{a_1\bar{C}_{2,0} + a_2\bar{C}_{2,0}^2 + \ldots\}, \tag{24}$$

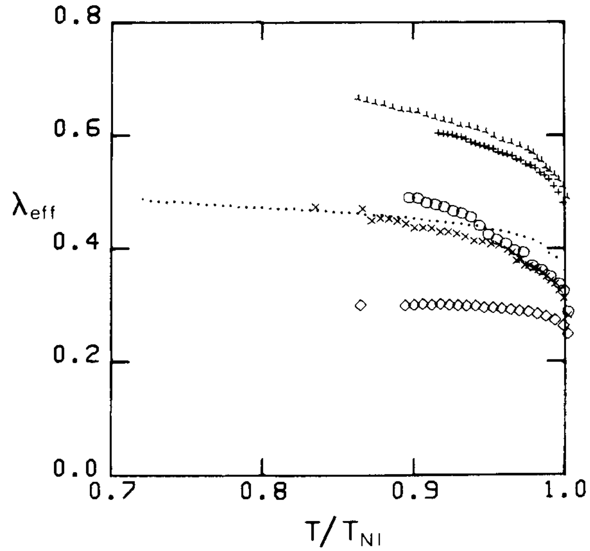


Figure 6. The dependence of λ_{eff} on the reduced temperature, T/T_{NI}, for anthracene-d_{10} in HAB (○), E9 (×), PCH7 (+), ZLI 1167 (⅄), I 4,3 (·) and Phase 5 (◇).

and

$$\varepsilon_{2,2} = -2\{b_1\bar{C}_{2,0} + b_2\bar{C}^2_{2,0} + \ldots\}. \tag{25}$$

Thus λ may now be written as

$$\lambda = \lambda_0(1 + d_1\bar{C}_{2,0} + d_2\bar{C}^2_{2,0} + \ldots) \tag{26}$$

where a_1, b_1, d_1 are temperature independent coefficients. We do not have a direct measure of $\bar{C}_{2,0}$ for the solvent in any of the mixtures which we have studied. However, we expect $a_2 \ll a_1$ and $b_2 \ll b_1$ so that from equations (21), (22), (24) and (25) we see that $\bar{C}_{2,0}$ is proportional to both akT and bkT. In figure 7, therefore, we show the dependence of λ_{eff} on akT, and we note that for all the mixtures studied there is a significant departure from linearity. We have fitted the experimental points by the method of least squares to a quadratic dependence of λ_{eff} on akT and extrapolated the curves, as shown in figure 7, to give the values of λ_0 listed in table 3. Note that we have excluded the data for the nematic phase of HAB as solvent from figure 7 since these are practically superimposable on those obtained for E9, and the data for the smectic phase of HAB has too small a range for a fit to a quadratic to be meaningful. The

Table 3. Values of λ_0, A and B obtained by fitting λ_{eff} to the equation $\lambda_{\mathrm{eff}} = \lambda_0 + A(akT) + B(akT)^2$.

Solvent	λ_0	A	B
ZLI 1167	0·3205 ± 0·0010	0·3487 ± 0·0006	−0·0800 ± 0·0002
PCH 7	0·2977 ± 0·0006	0·3432 ± 0·0004	−0·0792 ± 0·0001
I4, 3	0·2336 ± 0·0007	0·2689 ± 0·0004	−0·0703 ± 0·0001
HAB (nematic phase only)	0·180 ± 0·006	0·2265 ± 0·0047	−0·0196 ± 0·0017
E9	0·1758 ± 0·0003	0·2695 ± 0·0002	−0·0527 ± 0·00005
Phase 5	0·1278 ± 0·0007	0·3394 ± 0·0006	−0·1658 ± 0·0003

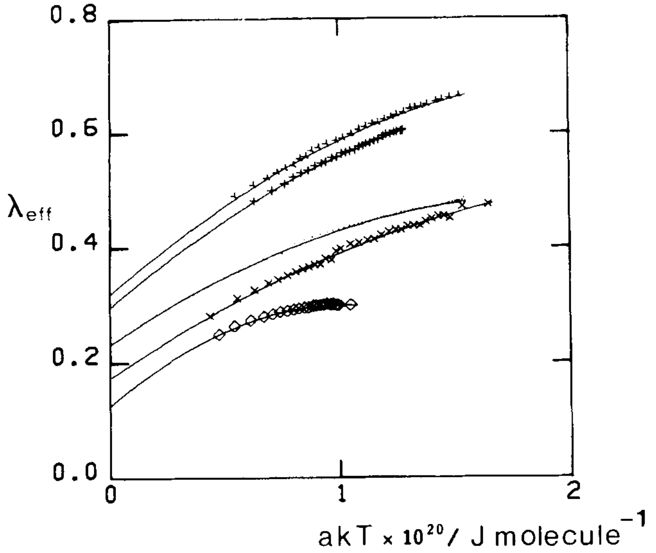


Figure 7. The variation of λ_{eff} with akT for anthracene-d_{10} dissolved in HAB (○), E9 (×), PCH7 (+), ZLI 1167 (⅄), I 4,3 (·) and Phase 5 (◇).

values of λ_0 for the different mixtures still have very different magnitudes, as do the values of λ_{eff} obtained from the order parameters of anthracene close to T_{NI} for the nematogenic mixture, and hence the strong solvent dependence of the biaxial ordering of anthracene does not vanish when we allow for a possible dependence of λ on the solvent order.

The variation of λ_{eff} with temperature could also result because the expansion of the potential of mean torque in equation (6) contains only second rank terms. More generally, for a solute at low concentration

$$U(\omega) = -\sum_{L,m,n} \bar{u}_{Lmn}\bar{C}_{L,m}C^{*}_{L,n}(\omega), \tag{27}$$

where L for a phase with $D_{\infty h}$ symmetry must be even and m,n take values L, $L-1, \ldots, -L+1, -L$ [9]. Equation (27) is appropriate only when the solvent and solute molecules are rigid, and although we may always restrict our choice of solute to such a case the solvent molecules are almost invariably non-rigid and lacking in symmetry. However, to simplify the form of $U(\omega)$ we shall assume that the solvent molecules are both rigid and cylindrically symmetric; this restricts m to being zero. Anthracene has D_{2h} symmetry and using the molecular symmetry axes to define the frame of reference for the solute restricts n to being even and $\bar{u}_{L0n}$ to equal $\bar{u}_{L0-n}$, thus

$$U(\omega) = 2\sum_{\substack{L\\ \text{even}}}\sum_{\substack{|n|\\ \text{even}}} \bar{u}_{L0n}\bar{C}_{L,0}d^{L}_{0n}(\beta)\cos n\gamma/(1+\delta_{0n}). \tag{28}$$

Equation (28) reduces to equation (6) (using equations (10) and (11) to express the interaction coefficients in terms of the solvent order parameters) when L is restricted to 2.

To investigate the influence of the fourth-rank terms we require the order parameters $\bar{C}_{2,0}$ and $\bar{C}_{4,0}$, but as these are not available experimentally for the solvents which we have studied we shall adopt a purely theoretical approach to determine their magnitude. To do this we assume that for the solvent molecules the potential of mean torque $U(\beta)$ is of the Maier–Saupe form, that is of second rank, and hence

$$U(\beta) \;=\; -\bar{u}_{20}\bar{C}_{2,0}C_{2,0}(\beta), \tag{29}$$

where β is now the angle between the assumed symmetry axis of the solvent molecules and the director. This potential is chosen because of its simplicity which results in the interaction parameter $\bar{u}_{20}$ being directly related to the nematic–isotropic transition temperature [12, 22]

$$\bar{u}_{20} \;=\; kT_{\mathrm{NI}}/0{\cdot}2202. \tag{30}$$

Despite the simplicity of $U(\beta)$ it leads to predictions of the orientational order which are reasonably close to experimental results [21]. The solvent order parameters are given by

$$\bar{C}_{L,0} \;=\; Z^{-1}\int_0^{\pi} C_{L,0}(\beta)\exp\{-U(\beta)/kT\}\sin\beta\, d\beta, \tag{31}$$

where the orientational partition function for the solvent is

$$Z \;=\; \int_0^{\pi} \exp\{-U(\beta)/kT\}\sin\beta\, d\beta. \tag{32}$$

Even with these simplifying assumptions concerning the orientational order of the solvent molecules the introduction of fourth-rank terms into the potential of mean torque for a molecule with the symmetry of anthracene requires three extra interaction parameters, $\bar{u}_{404}$, $\bar{u}_{402}$ and $\bar{u}_{400}$. We expect these to have the relative magnitudes $\bar{u}_{400} > \bar{u}_{402} > \bar{u}_{404}$ and so to reduce the number of variables we retain only the largest term in order to produce a potential of mean torque with which to explore the effect of introducing some fourth-rank character. We write this potential as

$$U(\beta\gamma) \;=\; -kT\{ad^2_{00}(\beta) \;+\; bd^2_{02}(\beta)\cos 2\gamma \;+\; cd^4_{00}(\beta)\}, \tag{33}$$

with

$$c \;=\; -\bar{u}_{400}\bar{C}_{4,0}/kT. \tag{34}$$

However we note that there is still only one term in the potential, namely $bd^2_{02}(\beta)\cos 2\gamma$, which will produce a non-zero biaxiality in the solute ordering. The fourth-rank term will change the variation of $(S_{xx} - S_{yy})$ with S_{zz} by an amount which depends on the magnitude of δ ($\equiv \bar{u}_{400}/\bar{u}_{200}$). To explore the effect that inclusion of the dominant fourth-rank term in $U(\beta\gamma)$ has on the dependence of solute biaxiality on the major order parameter requires that we have a reasonable estimate of δ. Recent computer simulation studies [23] suggest that c/a is approximately $-0{\cdot}1$ for a single component model nematogen comprising axially symmetric, rigid particles interacting through a continuous potential. Since $\bar{C}_{4,0}/\bar{C}_{2,0}$ calculated from the Maier–Saupe potential is 0·3 to 0·5 for the range of reduced temperatures used in our experiments, this suggests values for δ in the region of $-0{\cdot}2$ to $-0{\cdot}4$. We have investigated the effect of varying δ over the range 0·4 to $-0{\cdot}4$, the positive values being included to explore more fully the influence of δ on the order parameters. The value of λ we take to be 0·3, which is close to that found for λ_{eff} for anthracene in Phase 5. It remains to obtain an estimate for $\bar{u}_{200}$ in order to calculate solute order parameters using the potential of mean torque given by equation (33). For fixed values of λ and δ the value of $\bar{u}_{200}$ determines S_{zz}^{NI}, the value of S_{zz} at the nematic–isotropic transition temperature. If the solute–solvent interactions, which are dominated by $\bar{u}_{200}$, are comparable to the solvent–solvent interactions, whose strength is dictated by $\bar{u}_{20}$, then $\bar{u}_{200}/\bar{u}_{20}$ would be

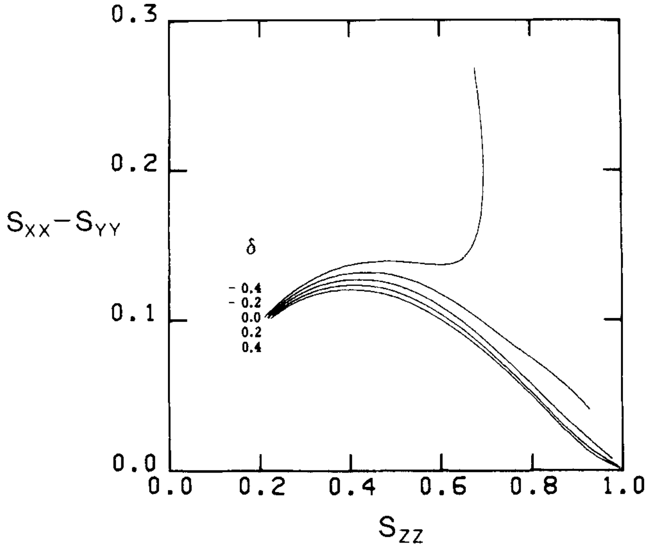


Figure 8. The calculated variation of $(S_{xx} - S_{yy})$ with S_{zz} obtained with the inclusion of the dominant fourth-rank term in the potential of mean torque, the strength of this new term is proportional to δ (see text). The biaxiality parameter λ is held constant at 0·3 and $\bar{u}_{200}/\bar{u}_{20}$ at 0·5.

close to unity. In consequence, S_{zz}^{NI} for both solute and solvent would be approximately equal, and in the Maier–Saupe theory would have the value of 0·429. Figure 3 shows that anthracene dissolved in all solvents has S_{zz}^{NI} close to 0·2, which implies that $\bar{u}_{200}/\bar{u}_{20}$ should be significantly less than unity, and so we have chosen 0·5 as a reasonable value; from equation (30) this serves to fix $\bar{u}_{200}$. Figure 8 shows the predicted dependence of $(S_{xx} - S_{yy})$ on S_{zz} for $\bar{u}_{200}/\bar{u}_{20}$ equal to 0·5, λ equal to 0·3 and values for δ of 0·4, 0·2, 0·0, −0·2 and −0·4. A positive δ increases the tendency of the solute to align with the director along z relative to x or y and shifts the maximum in the curve towards smaller S_{zz}. A negative δ has precisely the opposite effect and, as seen in figure 8 for $\delta = -0{\cdot}4$, this can result in a dramatic change in the shape of the curve with the predicted S_{zz} reaching a maximum value. However, when δ is negative and not greater in magnitude than 0·4, the calculated shape of the $(S_{xx} - S_{yy})$ versus S_{zz} curve is closer to those observed experimentally. This is shown in figure 9 where we compare calculations of $(S_{xx} - S_{yy})$ and S_{zz} obtained with $\delta = 0$ and $-0{\cdot}4$ with experimental values of anthracene in Phase 5. The value of $\lambda = 0{\cdot}3$ combined with $\delta = 0$ gives a close fit to the experimental data for anthracene in Phase 5 at the lowest reduced temperature, whereas with $\delta = -0{\cdot}4$ a better fit to the data at this temperature is obtained by reducing λ to 0·273. The inclusion of a negative δ clearly improves the agreement between theory and experiment, and could explain, in part, the temperature dependence of the λ_{eff} values obtained directly from experimental data and which refer to a potential of mean torque with $\delta = 0$. To demonstrate that a negative δ will produce a λ_{eff} which varies with reduced temperature we show in figure 10 values of λ_{eff} obtained from points on the theoretical curves shown in figure 9, and we compare these with the values obtained for anthracene in Phase 5. Making δ more negative will increase the rate of change of λ_{eff} with reduced temperature, but it will also have the the effect of reducing the maximum value which S_{zz} can achieve (see figure 8). We have not observed, for any of the solvents studied, the attainment of a maximum value of

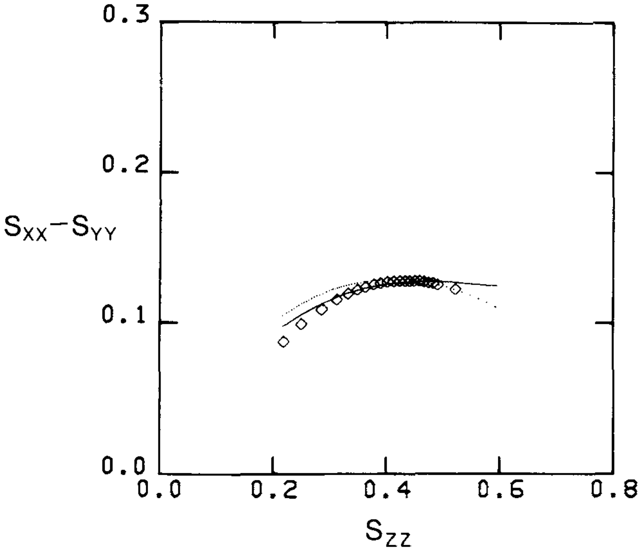


Figure 9. The calculated values of the biaxiality $(S_{xx} - S_{yy})$ and the major order parameter, S_{zz}, obtained with $\lambda = 0{\cdot}3$ and $\delta = 0$ (– – –) and with $\lambda = 0{\cdot}273$ and $\delta = -0{\cdot}4$ (——). The experimental values for anthracene-d_{10} in Phase 5 (◇) are shown for comparison.

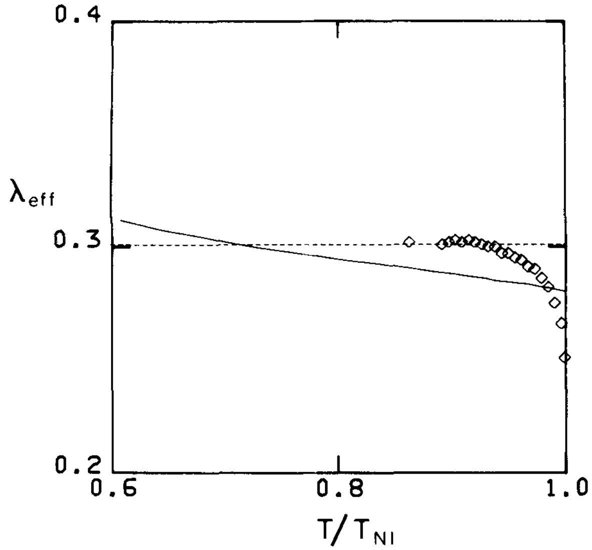


Figure 10. λ_{eff} derived from the calculated values of $(S_{xx} - S_{yy})$ and S_{zz} shown in figure 9 and obtained with values of the relative fourth-rank interaction parameter δ of zero (– – –) and $-0{\cdot}4$ (——); λ_{eff} determined from the experimental data for anthracene-d_{10} in Phase 5 (◇) are shown for comparison.

S_{zz} which then remains almost constant whilst $(S_{xx} - S_{yy})$ continues to increase. The order parameters S_{zz} were calculated for a similar range to those observed experimentally, as shown in figure 9. However, in figure 10 we see that these calculated values of S_{zz} correspond to a very much wider temperature range than that for the experimental data. This results from the well-known discrepancy between the temperature dependence of the order parameter S_{zz} predicted by the Maier–Saupe potential and that observed experimentally. This discrepancy is thought to originate mainly from the neglect of the effect on $\bar{u}_{20}$ of changes in density with temperature for systems under constant pressure [24]. Figure 10, therefore, is useful only in showing that inclusion of the fourth-rank term does lead to the correct qualitative temperature variation of λ_{eff}, that is increasing as T/T_{NI} decreases.

Inclusion of all three fourth-rank terms into the potential of mean torque for the solute could produce still larger changes in the shape of the $(S_{xx} - S_{yy})$ versus S_{zz} curves, but at the expense of introducing four adjustable parameters into the theory. Before attempting such calculations it would be prudent to consider other factors which may contribute to the observed temperature dependent values of λ_{eff}. In particular we note that the data for anthracene were obtained from samples at constant pressure, and hence include the effect of changing density with temperature, whilst the potential of mean torque for the solute refers to constant density.

The coefficients $\bar{u}_{2mn}$ in the potential of mean torque are expected to depend on the average separations of solute and solvent molecules and therefore to be dependent on density [22]. An investigation into the magnitude of the density dependence of λ_{eff} for anthracene-d_{10} dissolved in a nematic solvent is currently in progress using the temperature and pressure dependence of the deuteron quadrupolar splittings.

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