Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Multiple contributions to potentials of mean torque for solutes dissolved in liquid crystal solvents. A comparison of the orientational ordering of anthracene and anthraquinone as solutes in nematic solvents

J. W. Emsley[a]; S. K. Heeks[a]; T. J. Horne[a]; M. H. Howells[a]; A. Moon[a]; W. E. Palke[ab]; S. U. Patel[a]; G. N. Shilstone[a]; A. Smith[a]
[a] Department of Chemistry, University of Southampton, Southampton, England [b] Department of Chemistry, University of California Santa Barbara, Santa Barbara, California, U.S.A.

To cite this Article Emsley, J. W. , Heeks, S. K. , Horne, T. J. , Howells, M. H. , Moon, A. , Palke, W. E. , Patel, S. U. , Shilstone, G. N. and Smith, A.(1991) 'Multiple contributions to potentials of mean torque for solutes dissolved in liquid crystal solvents. A comparison of the orientational ordering of anthracene and anthraquinone as solutes in nematic solvents', Liquid Crystals, 9: 5, 649 — 660

To link to this Article: DOI: 10.1080/02678299108030379
URL: http://dx.doi.org/10.1080/02678299108030379

LIQUID CRYSTALS, 1991, VOL. 9, NO. 5, 649–660

Multiple contributions to potentials of mean torque for solutes dissolved in liquid crystal solvents

A comparison of the orientational ordering of anthracene and anthraquinone as solutes in nematic solvents

by J. W. EMSLEY*, S. K. HEEKS, T. J. HORNE, M. H. HOWELLS,
A. MOON, W. E. PALKE†, S. U. PATEL,
G. N. SHILSTONE and A. SMITH
Department of Chemistry, University of Southampton,
Southampton SO9 5NH, England

(*Received 19 October 1990; accepted 26 January 1991*)

The two principal orientational order parameters of anthracene and anthraquinone as solutes in several liquid crystal solvents have been obtained via deuterium NMR spectra. The ordering of anthraquinone is much more solvent dependent than that of anthracene, and possible explanations of this behaviour are examined. In particular, the possibility that electrostatic as well as dispersive and repulsion forces could contribute to a mean field potential is explored. It is concluded that the most probable cause of the large differences in orientational ordering of these two molecules in some solvents, but not in others, is a dependence on both solute and solvent of order parameters $\bar{C}^{+}_{4,0}$ and $\bar{C}^{+}_{2,0}$ for the distribution of solute–solvent intermolecular vectors.

1. Introduction

The orientational ordering of rigid solutes in liquid crystal solvents depends strongly on the nature of the solvent. In particular, studies of biaxial solutes, which have two non-zero order parameters, S_{zz} and $S_{xx}-S_{yy}$, have revealed the solvent dependence in a uniquely clear way via the biaxiality parameter λ, as discussed in the preceding paper [1]. This measure of the biaxiality in the potential of mean torque, $U(\beta_2, \gamma_2)$, which when truncated at second rank terms has the form [2, 3]

$$U(\beta_2,\gamma_2) = -\varepsilon_{2,0}C_{2,0}(\beta_2,\gamma_2) - 2\varepsilon_{2,2}C_{2,2}(\beta_2,\gamma_2), \tag{1}$$

has $\lambda = \varepsilon_{2,2}/\varepsilon_{2,0}$. Here the $C_{2,m}(\beta_2,\gamma_2)$ are modified spherical harmonics, with β_2 and γ_2 the polar angles made by the mesophase director in the principal molecular frame xyz fixed in the solute molecules. Within the molecular field approximation the coefficients $\varepsilon_{2,m}$ are given by

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

and

$$\varepsilon_{2,2} = \bar{u}_{202}\bar{C}_{2,0} + 2\bar{u}_{222}\bar{C}_{2,2}; \tag{3}$$

---

* Author for correspondence.

† Permanent address: Department of Chemistry, University of California Santa Barbara, Santa Barbara, California, U.S.A.

the $\bar{C}_{2,m}$ are order parameters of the solvent molecules, and the coefficients $\bar{u}_{2mn}$ may be sums of contributions from dispersion, $\bar{u}^{\mathrm{d}}_{2mn}$, electrostatic, $\bar{u}^{\mathrm{e}}_{2mn}$, and repulsion, $\bar{u}^{\mathrm{r}}_{2mn}$, interactions. Thus,

$$\bar{u}_{2mn} = \bar{u}^{\mathrm{d}}_{2mn} + \bar{u}^{\mathrm{e}}_{2mn} + \bar{u}^{\mathrm{r}}_{2mn}. \tag{4}$$

The solvent order parameters have the relative order of magnitudes $\bar{C}_{2,2} \ll \bar{C}_{2,0}$, so that equations (2) and (3) can be simplified to

$$\varepsilon_{2,0} = \bar{u}_{200}\bar{C}_{2,0}, \tag{5}$$

and

$$\varepsilon_{2,2} = \bar{u}_{202}\bar{C}_{2,0}, \tag{6}$$

so that

$$\lambda = \bar{u}_{202}/\bar{u}_{200}. \tag{7}$$

The contributions to $\bar{u}_{20n}$ from either electrostatic or dispersion interactions can be written in the form [1]

$$\bar{u}_{20n} = BA^{(1)}_{2,0}A^{(2)}_{2,n}, \tag{8}$$

with B dependent on the type of interaction, but independent of n. $A^{(1)}_{2,0}$ and $A^{(2)}_{2,n}$ are components of either the electric polarizability or the electric quadrupole moments of solvent (molecule 1), or solute (molecule 2). This means that if either dispersion or electrostatic terms dominate $U(\beta_2, \gamma_2)$, then λ should be independent of the solvent.

The same argument cannot be applied with equal certainty to the contribution of repulsion to the solute–solvent interaction, since the molecular mean field approximations are invalid for such a short-range force. It is possible, therefore, that the observed solvent dependence of solute ordering simply reflects the complex dependence of the repulsion forces on molecular structure, but there is as yet no unambiguous evidence to support this view. We shall concentrate our attention, therefore, on the contributions to $U(\beta_2, \gamma_2)$ from the dispersion and electrostatic interactions, whilst not losing sight of the possible importance of repulsion.

The clearest evidence for the importance of the electrostatic contribution to $U(\beta_2, \gamma_2)$ is provided by studies [4–7] of the orientational ordering of molecular hydrogen dissolved in the solvents EBBA and ZLI 1132, whose structures are given in table 1. It was concluded from these studies that $\varepsilon^{\mathrm{e}}_{2,0}$, the contribution to $\varepsilon_{2,0}$ from the

Table 1. Liquid crystal solvents.

No.	Abbreviation	Composition
1	4O.2	*N*-(4-*n*-Butyloxybenzylidene)-4′-ethylaniline
2	EBBA	*N*-(4-Ethoxybenzylidene)-4′-*n*-butylaniline
3	PAA	4,4′-Dimethoxyazoxybenzene
4	Phase 5	Mixture of 4-*n*-alkyloxy-4′-*n*-alkyl and 4-*n*-alkyl-4′*n*-alkyloxyazoxybenzenes
5	1-OCB	4-Methoxy-4′-cyanobiphenyl
6	ZLI 2585	Mixture of 4-*axial*-cyano-4-*eq*-*n*-alkyl-4′-*n*-alkylbicyclohexyl
7	E9 or E63	Mixture of 4-*n*-alkyl-4′-cyanobiphenyls
8	ZLI 1132	Mixture of 4-cyano-(4′-*trans*-*n*-alkylcyclohexyl)-benzenes and 4-cyano-(4′-*trans*-*n*-pentylcyclohexyl)-biphenyl
9	PCH7	4-Cyano-(4′-*trans*-*n*-heptylcyclohexyl)-benzene
10	FCHB	3-Fluoro, 4-cyano-phenyl-*n*-heptylbenzoate
11	CCH3	4-*trans*-(4-*trans*-*n*-Propylcyclohexyl)cyclohexylcarbonitrile
12	ZLI 1167	Mixture of CCH3, CCH5, and CCH7

Table 2. Components of the polarizability, $\alpha_{2,m}$ and quadrupole moment, $Q_{2,m}$, tensors in the principle frame of $\boldsymbol{\alpha}$ for anthracene and anthraquinone and some of the liquid crystal solvents.

Compound	$\alpha_{2,0}/\text{Å}^3$	$\alpha_{2,2}/\text{Å}^3$	$Q_{2,0}/\text{C m}^2 \times 10^{40}$	$Q_{2,2}/\text{C m}^2 \times 10^{40}$
Anthracene	40	6	−3	23
Anthraquinone	42	7	33	−20
EBBA	37	9	−20	30
PAA	26	11	−10	17
1-OCB	44	11	−120	17
PCH7	45	6	−170	3
ZLI 2585†	50	2	−13	−7
FCHB	51	10	−177	0
CCH3	33	2	−147	−7

† The component of the mixture with a pentyl chain.

electrostatic interactions, can be expressed as an interaction between the quadrupole moment, $Q_{zz}^{(2)}$, of the hydrogen molecule and F_{ZZ}, the component along the director of an average electric field gradient of the solvent molecules, thus

$$\varepsilon_{2,0}^{\mathrm{e}} = -\tfrac{1}{2} F_{ZZ} Q_{zz}^{(2)}. \tag{9}$$

The experimental results were used to obtain values for F_{ZZ}, and this was found to be negative for EBBA, positive for ZLI 1132, and zero at approximately 300 K in a mixed solvent containing 55 wt% of EBBA and 45 wt% of ZLI 1132. The value of F_{ZZ} has been assumed to be a property only of the solvent molecules, so that the mixed solvent can be used in studies of other solutes as one in which the electrostatic contributions to the potential of mean torque are zero.

In the molecular field theory developed by Emsley *et al.* [1] the coefficients $\bar{u}_{2mn}^{\mathrm{e}}$ are given by

$$\bar{u}_{2mn}^{\mathrm{e}} = A^{QQ} \overline{r_{12}^{-5}} Q_{2,m}^{(1)} Q_{2,n}^{(2)} \bar{C}_{4,0}^{+}, \tag{10}$$

so that

$$F_{ZZ} \propto \overline{r_{12}^{-5}} Q_{2,0}^{(1)} \bar{C}_{4,0}^{+} \bar{C}_{2,0}. \tag{11}$$

The product $\overline{r_{12}^{-5}} \bar{C}_{2,0}$ is positive for both EBBA and ZLI 1132, so that the change in sign of F_{ZZ} is caused by a change in sign of either, or both of $Q_{2,0}^{(1)}$ and $\bar{C}_{4,0}^{+}$.

To investigate further the relative importance of the dispersion, electrostatic and repulsion interactions in determining the orientational ordering of rigid solutes in liquid crystal solvents we have chosen to study the biaxial molecules anthracene and anthraquinone, whose structures are shown in figure 1. These molecules have similar shapes, and we expect, therefore, that they will have similar values of $\bar{u}_{2mn}^{\mathrm{d}}$ and $\bar{u}_{2mn}^{\mathrm{r}}$, since these are probably determined mainly by shape. At the very least, it is expected that $\bar{u}_{2mn}^{\mathrm{d}}$ and $\bar{u}_{2mn}^{\mathrm{r}}$ will have the same sign for both solutes in each solvent. The charge distributions in the two solutes are, however, quite different, and hence the values of $\bar{u}_{2mn}^{\mathrm{e}}$ are expected to differ considerably. These solutes also have the advantage that their order parameters can be accurately and easily determined by deuterium NMR.

In choosing the solvents we were guided initially by the suggestion by Burnell and his co-workers [4] that EBBA and ZLI 1132 (also known as TCN 1132) produce electric field gradients of opposite signs at some solutes. We have included solvents

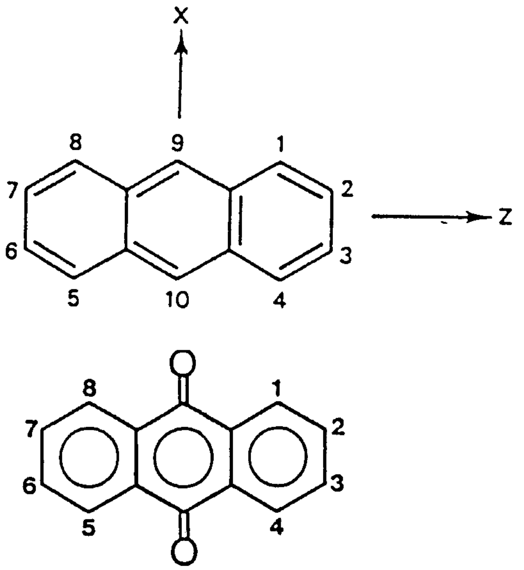

Figure 1. Anthracene (top) and anthraquinone (bottom). The principal axes *xyz* are the same for both molecules.

which are of the same structural type as these two solvents, and others which have quite different shapes and charge distributions. The complete list of solvents is given in table 1.

2. Experimental

The solutes were studied as 1 per cent solutions by weight in the solvents listed in table 1. In the cases of EBBA, PAA, and CCH3, the solvent contained about 5 per cent of deuteriated molecules. The sample of anthracene-d_{10} was purchased from the Aldrich Chemical Company. The sample of anthraquinone-d_8 was synthesized from anthracene-d_{10} by the method described by Underwood and Walsh [8] and was found to be 98 per cent deuteriated.

The deuterium spectrum of a sample of anthracene dissolved in a liquid crystal solvent has been described previously [9]. That of anthraquinone-d_8 presents a problem of peak assignment, which was solved for the spectrum of a sample dissolved in E63 as solvent by comparing the spectra obtained from the d_8 with that from a sample of 1-[^{2}H]-anthraquinone dissolved in the same solvent. The sample of 1-[^{2}H]-anthraquinone was synthesized from 1-aminoanthraquinone by a method described in Vogel [10].

3. Results and discussion

Deuterium spectra were recorded for each sample over the complete nematic range for each solvent. The quadrupolar splittings, $\Delta\nu_i$, for anthracene and anthraquinone were used to obtain the two principal order parameters S_{zz} and $S_{xx}-S_{yy}$ from the equation

$$\Delta\nu_i = 3q_{\mathrm{CD}}\{S_{zz}(3l_{zai}^2 - 1 + \eta l_{zbi}^2) + (S_{xx}-S_{yy})(l_{xai}^2 + \eta(l_{xbi}^2 + 1)/3)\}/4, \qquad (12)$$

where l_{zai} is the direction cosine for the ith C–D bond with respect to the z axis (see figure 1). The deuterium quadrupolar coupling constant, q_{CD}, and the asymmetry parameter, η, are assumed to be independent of molecular site, and were assigned values of 181 kHz and 0·064 for anthracene, values measured from deuterium spectra of anthracene single crystals [11], and 185 kHz and 0·03 for anthraquinone, which are average values observed for aromatic deuterons [12]. Note that uncertainty in these values of q_{CD} and η for anthraquinone introduces systematic errors in the values derived for S_{zz} and $S_{xx}-S_{yy}$ of about 5 per cent and 10 per cent respectively, but does not affect our general conclusions. Equation (12) is valid for liquid-crystalline samples with a positive anisotropy of the magnetic susceptibility, $\Delta\chi$, which is the case for all the solvents in table 1, except **6**, **11** and **12**. For these solvents $\Delta\nu$ must be multiplied by -2 to allow for the perpendicular alignment of the director by the magnetic field.

Figures 2 and 3 show S_{zz} and λ_{exp} values at a constant value of $T_{NI}-T$ of 1°C for all the mixtures studied, and the striking feature is the large variation in S_{zz} for anthraquinone. The ordering of the points along the abscissa in these two figures is that which produces a gradual increase in the value of $\Delta S_{zz}=S_{zz}$(anthracene) $-S_{zz}$(anthraquinone). It is clear that anthraquinone ordering is much more strongly solvent dependent than that of anthracene and we shall now explore possible reasons for this variation in ordering of these two solutes. Note that EBBA produces an S_{zz} value for anthraquinone almost a half of that when ZLI 1132 is the solvent, whilst the S_{zz} value for anthracene is practically identical for these two solvents. This fits in with the idea that these two solvents can produce very different electrostatic contributions to the potential of mean torque. The solvents used include 4O.2, which differs in structure from EBBA only in the reversed positions of the ethyl and n-butyl chains (EBBA is 2O.4). It is not surprising, therefore, that the order parameters for the two solutes in these solvents are very similar. ZLI 1132 is a mixed solvent, one of the components being PCH7, and as expected the order parameters are almost identical.

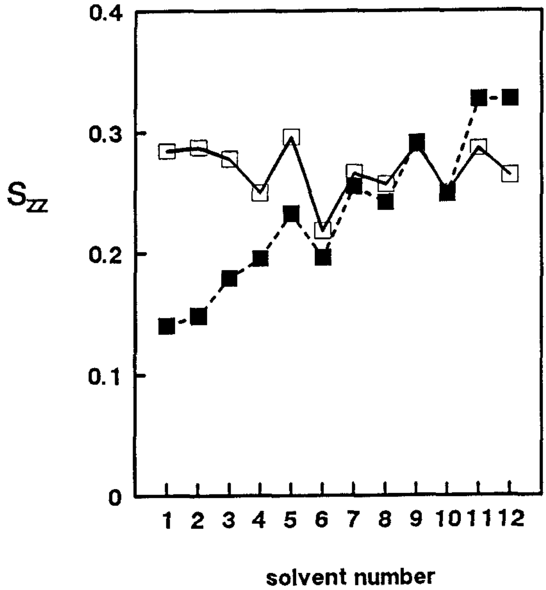

Figure 2. S_{zz} at $T_{NI}-T=1$°C for anthracene (□) and anthraquinone (■) as solutes in the solvents listed in table 1.

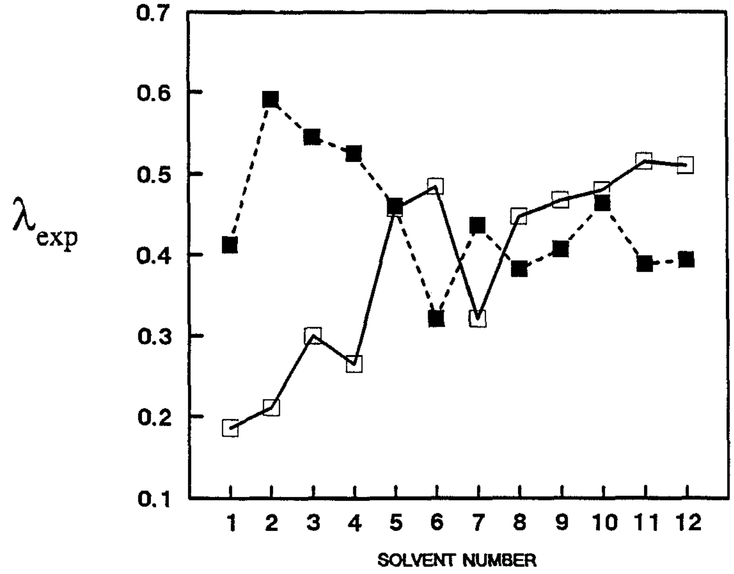

Figure 3. λ_{exp} at $T_{NI}-T=1°C$ for anthracene (□) and anthraquinone (■) as solutes in the solvents listed in table 1.

To make any further progress we shall first use the observed order parameters to derive experimental values for the interaction coefficients $\varepsilon_{2,0}$ and $\varepsilon_{2,2}$ from the equations

$$S_{zz}=Z^{-1}\int C_{2,0}(\beta_2,\gamma_2)\exp\{-U(\beta_2,\gamma_2)/kT\}\sin\beta_2\,d\beta_2\,d\gamma_2, \tag{13}$$

and

$$S_{xx}-S_{yy}=\sqrt{6}Z^{-1}\int C_{2,2}(\beta_2,\gamma_2)\exp\{-U(\beta_2,\gamma_2)/kT\}\sin\beta_2\,d\beta_2\,d\gamma_2, \tag{14}$$

where

$$Z=\int\exp\{-U(\beta_2,\gamma_2)/kT\}\sin\beta_2\,d\beta_2\,d\gamma_2.$$

The ratio

$$\lambda_{exp}=\varepsilon_{2,2}^{exp}/\varepsilon_{2,0}^{exp}$$

is found to vary with temperature for each of the solutes in all the solvents in a way similar to that observed for other solutes in nematic solvents, that is λ_{exp} always decreases as T_{NI} is approached. The variation of λ_{exp} with solvent at constant shifted temperature of 1°C is shown in figure 3. The values of λ_{exp} for both solutes change dramatically with solvent, and the difference

$$\Delta\lambda_{exp}=\lambda_{exp}(\text{anthracene})-\lambda_{exp}(\text{anthraquinone}) \tag{15}$$

is largest for those solvents for which ΔS_{zz} is largest.

Can the large variations in ΔS_{zz} and $\Delta\lambda_{\mathrm{exp}}$ be caused by changes with solvent of the relative magnitudes $\bar{u}^{\mathrm{e}}_{2mn}$, $\bar{u}^{\mathrm{d}}_{2mn}$ and $\bar{u}^{\mathrm{r}}_{2mn}$? To explore this possibility we examine first the dependence on solvent ordering of $\varepsilon^{\mathrm{exp}}_{2,0}$ and $\varepsilon^{\mathrm{exp}}_{2,2}$. If the solute–solvent vectors have a spherical distribution then the $\bar{u}^{\mathrm{e}}_{2mn}$ vanish [1], and the coefficients $\varepsilon^{\mathrm{exp}}_{2,n}$ should depend linearly on $\bar{C}_{2,0}$, provided that equations (5) and (6) hold, since the ratios $\bar{u}^{\mathrm{d}}_{2mn}/\bar{u}^{\mathrm{r}}_{2mn}$ in the same solvent should not have a strong temperature dependence. However, if the r_{12} are not distributed spherically then $\bar{u}^{\mathrm{e}}_{20n}$ will have a temperature dependence dominated by $\bar{C}^{+}_{4,0}\bar{C}_{2,0}$, that of $\bar{u}^{\mathrm{d}}_{20n}$ (and probably $\bar{u}^{\mathrm{r}}_{20n}$) will depend on $\bar{C}^{+}_{4,0}\bar{C}_{2,0}$ and $\bar{C}^{+}_{2,0}\bar{C}_{2,0}$. The magnitude of $\bar{C}^{+}_{4,0}$ and $\bar{C}^{+}_{2,0}$ are zero in the isotropic phase, and in the nematic phase they can have values between $-0{\cdot}43$ and $1{\cdot}0$ ($\bar{C}^{+}_{4,0}$) and $-0{\cdot}5$ and $1{\cdot}0$ ($\bar{C}^{+}_{2,0}$). The temperature dependences of the products with $\bar{C}_{2,0}$ are difficult to predict, but might be expected to deviate from that of $\bar{C}_{2,0}$ alone. It is more probable, therefore, that the dependence of the $\varepsilon_{2,n}$ on $\bar{C}_{2,0}$ will be non-linear when the distribution of the r_{12} is non-spherical, and linear when it is spherical.

Values of $\bar{C}_{2,0}$ have been measured for 1-OCB, which can be regarded as an effectively rigid molecule because the 24 conformations generated by rotations about the bonds between minimum energy structures are of equal energy and shape [13]. Adding a small amount of a solute is not expected to change the values of $\bar{C}_{2,0}$ at constant shifted temperature, and so we have used the values of $\bar{C}_{2,0}$ measured by Emsley *et al.* [13]. In the case of CCH3 as solvent we incorporated 5 per cent of solvent molecules deuteriated in the cyanylated cyclohexane ring, and obtained $\bar{C}_{2,0}$ by measuring the larger of the two quadrupolar splittings, the smaller being obscured by partial overlap with the resonances from deuterons in the anthraquinone. The order parameters $\bar{C}_{2,0}$ were obtained by using their relationship with $\Delta\nu_{\mathrm{CCH3}}$ noted by Dong *et al.* [14]. A similar method was used to monitor solvent ordering in PAA and EBBA. For EBBA the deuterons are in the two positions ortho to the nitrogen substituent in the *n*-butylated ring, whilst for PAA the molecule is fully deuteriated, but we take only the largest quadrupolar splitting, which is from deuterons in one of the rings, to be a measure of orientational order. If the solvent molecules really were rigid and cylindrically symmetric then $\Delta\nu_{\mathrm{EBBA}}$ and $\Delta\nu_{\mathrm{PAA}}$ would each depend linearly on $\bar{C}_{2,0}$, but this linearity could be destroyed by non-rigidity and lower symmetry of the real mesogens. In practice, $\Delta\nu$ for ring deuterons in a number of mesogens have only small deviations from a linear dependence on $\bar{C}_{2,0}$ and hence can be used to give a good approximation to the solvent order [13, 15–19].

The results of plotting $\varepsilon_{2,n}$ against solvent order are shown in figures 4–7. Both $\varepsilon_{2,0}$ and $\varepsilon_{2,2}$ for each of the solutes are linearly dependent on $\bar{C}_{2,0}$ with 1-OCB and PAA as solvent, and therefore for these solute–solvent pairs these plots do not provide any additional evidence about the relative importance of the three terms in equation (4). The only evidence for the importance of the different possible contributions to the potential of mean torque for the two solutes in 1-OCB and PAA comes from the relative magnitudes of the slopes of the solid lines in figures 4 and 5, which mirror the values of ΔS_{zz} for the two solutes.

Significant deviations from linearity are observed for the dependence of $\varepsilon_{2,2}$ on $\Delta\nu_{\mathrm{EBBA}}$, as shown in figure 6, and for both $\varepsilon_{2,0}$ and $\varepsilon_{2,2}$ against $\bar{C}_{2,0}$ for CCH3 (see figure 7). For these solute–solvent pairs, therefore, equations (1), (5) and (6), together with temperature independent coefficients $\bar{u}_{2mn}$, do not provide an adequate description of the potential of mean torque. A temperature dependence of $\bar{u}_{2mn}$ could arise if there is a non-spherical distribution of the r_{12}, and hence a possible contribution to $U(\beta_2, \gamma_2)$ from the quadrupole–quadrupole interaction. We should note, however, that there are

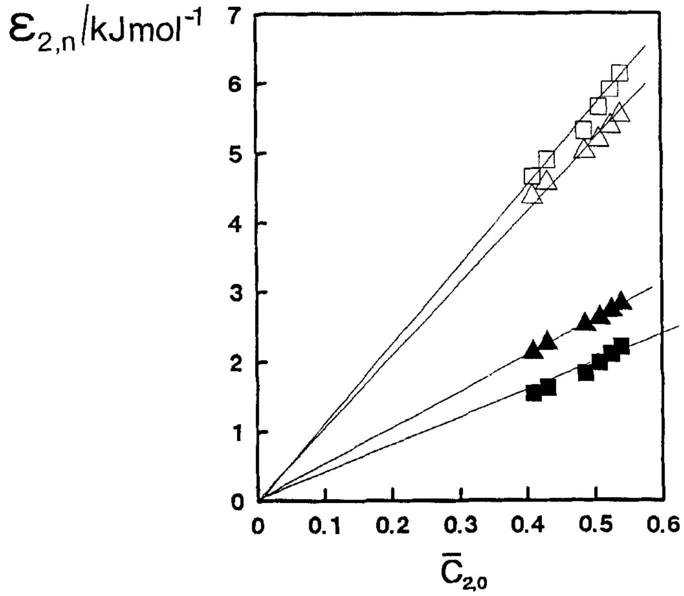

Figure 4. The dependence on the solvent order parameter $\bar{C}_{2,0}$ of the interaction coefficients $\varepsilon_{2,0}$ (open symbols) and $\varepsilon_{2,2}$ (filled symbols) for anthracene (□, ■) and anthraquinone (△, ▲) dissolved in 1-OCB. The straight lines drawn through the origin and passing closest to each set of points are to demonstrate the linearity of the plots.

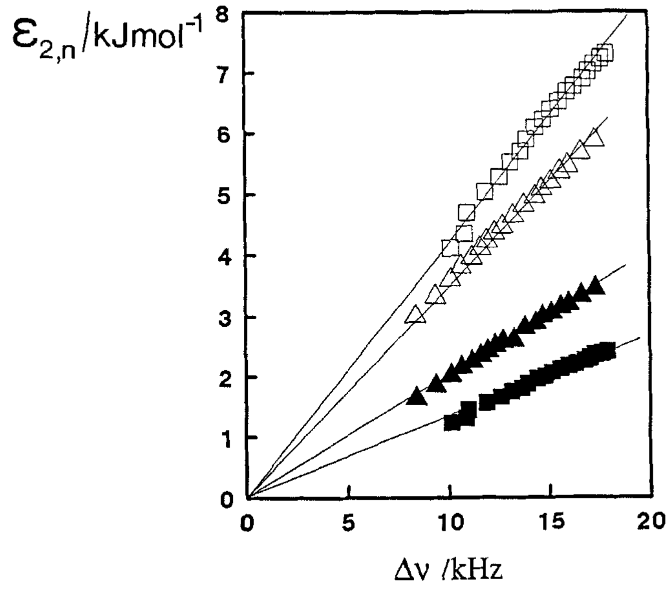

Figure 5. The dependence of the solvent order, as measured by Δν, the quadrupolar splitting of deuterons, in PAA of the interaction coefficients $\varepsilon_{2,0}$ (open symbols) and $\varepsilon_{2,2}$ (filled symbols) for anthracene (□, ■) and anthraquinone (△, ▲). The straight lines drawn through the origin and passing closest to each set of points are to demonstrate the linearity of the plots.

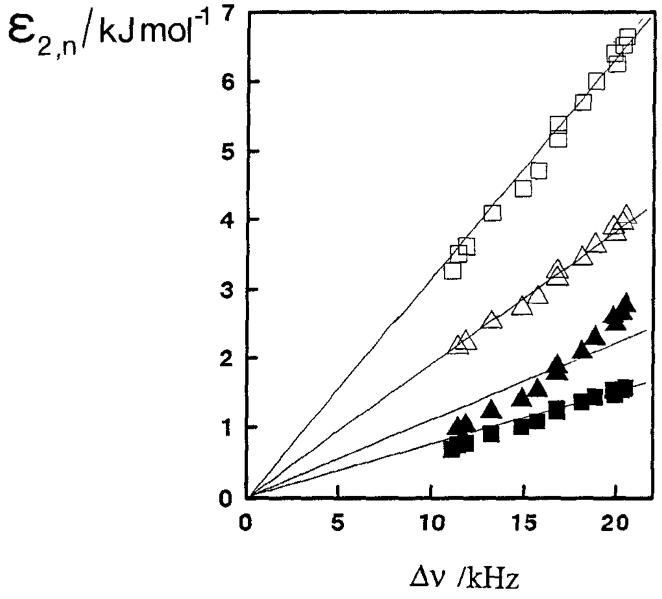

Figure 6. The dependence on the solvent order, as measured by $\Delta\nu$, the quadrupolar splittings of deuterons, in EBBA, of the interaction coefficients $\varepsilon_{2,0}$ (open symbols) and $\varepsilon_{2,2}$ (filled symbols) for anthracene (□, ■) and anthraquinone (△, ▲) dissolved in 1-OCB. The straight lines drawn through the origin and passing closest to each set of points are to demonstrate the linearity of the plots.

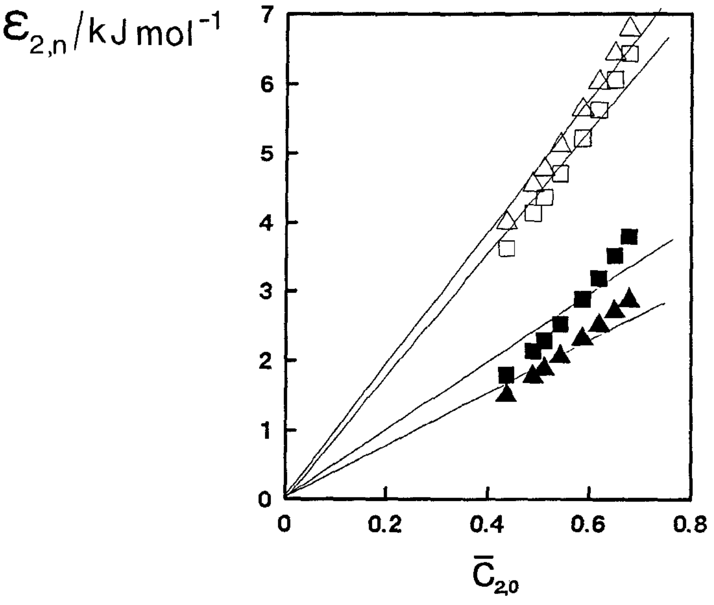

Figure 7. The dependence on the solvent order parameter $\bar{C}_{2,0}$ of the interaction coefficients $\varepsilon_{2,0}$ (open symbols) and $\varepsilon_{2,2}$ (filled symbols) for anthracene (□, ■) and anthraquinone (△, ▲) dissolved in CCH3. The straight lines drawn through the origin and passing closest to each set of points are to demonstrate the linearity of the plots.

other possible causes of a non-linear dependence of the $\varepsilon_{2,n}$ on $\bar{C}_{2,0}$, such as the importance of higher rank terms in the potential of mean torque, and the neglect of the flexibility of the solvent molecules.

To pursue the importance of electrostatic contributions to the solute–solvent potential of mean torque further we note that $\bar{u}^{\mathrm{e}}_{2mn}$ depends on $Q^{(1)}_{2,0}Q^{(2)}_{2,n}\bar{C}^{+}_{4,0}$. We have no easy way of determining $\bar{C}^{+}_{4,0}$, but it is possible to estimate values of the components of the quadrupole tensor.

The quadrupole tensors for the molecules studied here have not been determined experimentally, and we have therefore resorted to estimating their values by the method proposed by Gierke *et al.* [20]. This calculates the quadrupole moments from atomic dipoles, which have been determined to fit the known electric moments of certain model compounds. The accuracy of the predicted quadrupole tensors is difficult to assess since the liquid crystal molecules in particular are much larger than any model compounds used to fix the values of the atomic dipoles. It is, however, the best model available. For the solvent molecules the components of the quadrupole tensors are required in the frame which diagonalizes the total interaction tensor for the solvent–solvent interactions. We do not know the location of these principal axes for the solvent molecules, and so we have assumed that they coincide with the principal axes of the polarizability tensor, $\alpha^{(1)}$. To estimate the components of the polarizability tensors for the solvent molecules we have used the method described by Applequist *et al.* [21]. This method goes beyond the simple bond or group additivity schemes, such as those of Le Fevre and his collaborators [22], and includes additional contributions which depend on interactions between induced dipoles and local fields from other induced dipoles in the same molecule. Experimental values exist for the components $\alpha_{2,n}$ for anthracene [23], but not for anthraquinone. For the latter molecule, and indeed for anthracene, the method of Applequist *et al.* breaks down, and we have therefore estimated the components $\alpha_{2,n}$ for anthraquinone by subtracting from the components for anthracene the polarizabilities for aromatic C–H bonds and adding polarizabilities for C=O bonds, as suggested by Le Fevre [22].

It could be argued that steric, rather than dispersive forces, dominate the solvent–solvent potential, and it has been suggested [24] that in this case the principal axes for the solvent–solvent interaction should be close to those of the moment of inertia tensor, **I**. In fact, **I** and $\boldsymbol{\alpha}$ for the solvent molecules have virtually the same principal axes, so it is a good approximation to use, for convenience, those of $\boldsymbol{\alpha}$. To calculate the components of **I** and $\boldsymbol{\alpha}$ requires that we choose a geometry and conformation for the solvent molecules. We have used standard bond lengths and angles, and constrained the conformation to being that with lowest energy, although we have explored the effect of changing the conformation in the case of EBBA and PAA. The tensors **Q**, **I**, and $\boldsymbol{\alpha}$ were calculated for selected solvents from table 1, and in table 2 we show values of the components of **Q** and $\boldsymbol{\alpha}$ in the principal frame of the latter.

The simplest expression for relating $\bar{u}_{2mn}$ to the values of the tensor components of the polarizability and quadrupolar tensors is

$$\bar{u}_{2mn} \propto \alpha^{(1)}_{2,m}\alpha^{(2)}_{2,n} + \mathrm{x}Q^{(1)}_{2,m}Q^{(2)}_{2,n}, \tag{15}$$

where x is a constant independent of m, n, solvent or solute, which implies that $\bar{C}^{+}_{4,0}$, $\bar{C}^{+}_{2,0}$ and the averages over the solute–solvent separations are similarily independent of these factors. It is interesting to see if the data for anthracene and anthraquinone are consistent with such a simple expression. To explore this possibility we consider the data for the solvents EBBA and CCH3, which are representative of the range of behaviour shown in figures 2 and 3. To reproduce the values of ΔS_{zz} for EBBA requires x to be about 13. With this value of x the values predicted for λ are $-0{\cdot}2$ (anthracene) and 0·9 (anthraquinone), compared with observed values of 0·2 and 0·6, respectively, at $T_{\mathrm{NI}}-T=1°\mathrm{C}$, so that the predicted values are in the correct order. However, the application of equation (15) to the data for CCH3 gives predictions which are the reverse of those observed. Thus, S_{zz} is actually predicted to be large and negative for anthraquinone in CCH3, and the values predicted for λ are very different from those observed (predicted -2, observed 0·5 for anthracene; predicted $-0{\cdot}8$, observed 0·4 for anthraquinone). Note that although the magnitudes of the predicted values of S_{zz} and λ depend on the accuracy of the calculated $Q_{2,m}^{(1)}$ and $Q_{2,n}^{(2)}$, the observed changes in ΔS_{zz} and $\Delta\lambda$ with solvent are inconsistent with any fixed values of these tensor components, and it is clear that equation (15) does not hold for the data in all solvents for anthracene and anthraquinone. This is probably because the distribution of the solute–solvent vectors changes dramatically with the nature of both solute and solvent.

The values of ΔS_{zz} and $\Delta\lambda_{\mathrm{exp}}$ can be rationalized by the model of Patey *et al.* [5], which explains the magnitudes of the $\bar{u}_{2mn}^{\mathrm{e}}$ in terms of an electric field gradient, F_{ZZ}, experienced by the solute. Thus, for EBBA F_{ZZ} has to be large and negative for anthraquinone, and its value for anthracene in the same solvent has not to be very different, so that large values are predicted for ΔS_{zz} and $\Delta\lambda$. For CCH3, for example, F_{ZZ} has to be small, and possibly of opposite sign for the two solutes, so that ΔS_{zz} and $\Delta\lambda$ are much smaller, and of opposite sign. These changes in the sign and magnitude of F_{ZZ} must be caused by changes in $\bar{C}_{4,0}^{+}$. We have not attempted a detailed analysis with this model, since to do so requires having a good model for predicting both $\bar{u}_{2mn}^{\mathrm{d}}$ and $\bar{u}_{2mn}^{\mathrm{r}}$, and this is not a straightforward procedure within the molecular field approximation.

4. Conclusion

The most important conclusion reached by this study of the orientational ordering of anthracene and anthraquinone in a range of liquid crystal solvents is that the large changes observed in ΔS_{zz} and to a lesser extent in $\Delta\lambda_{\mathrm{exp}}$, are probably caused by changes in the solute–solvent order parameters $\bar{C}_{4,0}^{+}$ and $\bar{C}_{2,0}^{+}$. When these order parameters are non-zero there is the possibility of a contribution to the potential of mean torque of a quadrupole–quadrupole term, but the form of the dispersion interaction also changes, and probably, too, the steric repulsion term. The potential of mean torque in this case becomes very complicated and its usefulness is considerably diminished. Thus, it is not possible to extract values of the solute–solvent order parameters $\bar{C}_{J,M}^{+}$ from the data since they occur as products with components of quadrupole or polarizability tensors and averages over the solute–solvent separations. In other words, analyses based on molecular mean fields cannot reveal how the solute and solvent molecules interact. To gain any further information requires that the experimental data be compared with simulations of the intermolecular interactions using a detailed site–site potential.

References

[1] Emsley, J. W., Palke, W. E., and Shilstone, G. N., 1991, *Liq. Crystals*, **9**, 643.

[2] Luckhurst, G. R., Zannoni, C., Nordio, P. L., and Segre, U., 1975, *Molec. Phys.*, **30**, 1345.

[3] Emsley, J. W., Hashim, R., Luckhurst, G. R., Rumbles, G. N., and Viloria, F. R., 1983, *Molec. Phys.*, **49**, 1321.

[4] Burnell, E. E., De Lange, C. A., and Snijders, J. G., 1982, *Phys. Rev.* A, **25**, 2339.

[5] Patey, G. N., Burnell, E. E., Snijders, J. G., and de Lange, C. A., 1983, *Chem. Phys. Lett.*, **99**, 271.

[6] Barker, P. B., van der Est, A. J., Burnell, E. E., Patey, G. N., and de Lange, C. A., 1984, *Chem. Phys. Lett.*, **107**, 426.

[7] van der Est, A. J., Burnell, E. E., and Lounila, J., 1988, *J. chem. Soc. Faraday Trans. II*, **84**, 1095.

[8] Underwood, H. W., and Walsh, W. L., 1936, *J. Am. chem. Soc.*, **58**, 646.

[9] Emsley, J. W., Hashim, R., Luckhurst, G. R., and Shilstone, G. N., 1986, *Liq. Crystals*, **1**, 437.

[10] Vogel, A. I., 1957, *Practical Organic Chemistry*, 3rd edition (Longmans).

[11] Ellis, D. M., and Bjorkstam, J. L., 1967, *J. chem. Phys.*, **46**, 4460.

[12] Emsley, J. W., and Longeri, M., 1981, *Molec. Phys.*, **42**, 315.

[13] Emsley, J. W., Horne, T. J., Zimmermann, H., Celebre, G., and Longeri, M., 1990, *Liq. Crystals*, **7**, 1.

[14] Dong, R. Y., Emsley, J. W., and Hamilton, K., 1989, *Liq. Crystals*, **5**, 1019.

[15] Emsley, J. W., Khoo, S. K., and Luckhurst, G. R., 1979, *Molec. Phys.*, **37**, 959.

[16] Counsell, C. J. R., Emsley, J. W., Heaton, N. J., and Luckhurst, G. R., 1985, *Molec. Phys.*, **54**, 847.

[17] Catalano, D., Forte, C., Veracini, C. A., Emsley, J. W., and Shilstone, G. N., 1987, *Liq. Crystals*, **2**, 345.

[18] Counsell, C. J. R., Emsley, J. W., Luckhurst, G. R., and Sachdev, H. S., 1988, *Molec. Phys.*, **63**, 33.

[19] Emsley, J. W., Heaton, N. J., Luckhurst, G. R., and Shilstone, G. N., 1988, *Molec. Phys.*, **64**, 377.

[20] Gierke, T. D., Tigelaar, H. L., and Flygare, W. H., 1972, *J. Am. chem. Soc.*, **94**, 330.

[21] Applequist, J., Carl, J. R., and Fung, K.-K., 1972, *J. Am. chem. Soc.*, **94**, 2952.

[22] Le Fevre, R. J. W., 1969, *J. Proc. R. Soc. N.S.W.*, **95**, 1.

[23] Kuball, H. G., and Lob, R., 1969, *Z. phys. Chem.*, **63**, 251.

[24] Samulski, E. T., and Dong, R. Y., 1982, *J. chem. Phys.*, **77**, 5090.