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Dependence of solute orientational order on the structure and orientational order of the liquid crystal solvent. A deuterium N.M.R. study of *p*-xylene-d_{10} dissolved in a series of 4-*n*-alkyloxy-4'-cyanobiphenyls

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LIQUID CRYSTALS, 1989, VOL. 5, NO. 3, 953–967

Dependence of solute orientational order on the structure and orientational order of the liquid crystal solvent

A deuterium N.M.R. study of p-xylene-d_{10} dissolved in a series of 4-n-alkyloxy-4′-cyanobiphenyls

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The quadrupolar splittings from the ring and methyl deuterons have been used to determine the principal components S_{zz} and $S_{xx} - S_{yy}$ of the second rank orientational ordering matrix for p-xylene dissolved in the first 12 members of the 4-n-alkyloxy-4′-cyanobiphenyls (NOCB). The two order parameters are used to obtain the coefficients a and b in a potential of mean torque

$$U(\beta_2\gamma_2) = -RT\,[ad^2_{00}(\beta_2) + bd^2_{02}(\beta_2)\cos 2\gamma_2]$$

for the solute molecules at infinite dilution in the solvent. The ratio $\lambda_{\text{exp}} = b/2a$, which is a measure of the departure of $U(\beta_2\gamma_2)$ from cylindrical symmetry, is found to vary with temperature for each solute–solvent pair, and to increase as N, the number of chain carbon atoms, increases. The dependences of aRT and bRT on the orientational order of the solvent is explored.

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1. Introduction

There have been many studies of the orientational order of liquid crystals (see e.g. [1]), but the nature of the intermolecular potential that governs this ordering is still not clear. In part this stems from the complex structure of the mesogenic molecules, which are flexible and lacking in symmetry. These particular complicating factors can be avoided by studying rigid molecules, which are not mesogenic, dissolved in a liquid-crystalline phase. The simplest kinds of molecule to study are those with cylindrical symmetry, dissolved in uniaxial mesophases so that their orientational order may be characterized by a single second rank order parameter S_{zz} (often referred to as $\bar{P}_2$), where z is the molecular symmetry axis. The variation of S_{zz} with temperature and the nature of the solvent have been used to test models for the potential of mean torque [2], such as that proposed by Humphries, James and Luckhurst [3], which has the form

$$U(\beta_2) = -\bar{u}_2\bar{C}_{2,0}P_2(\cos\beta_2). \tag{1}$$

The solvent molecules are assumed to be rigid and cylindrically symmetric and to have a second rank order parameter $\bar{C}_{2,0}$, which is denoted by the average of a modified spherical harmonic [4] in order to distinguish clearly between the solute and solvent ordering; the relationship between the order parameters $S_{\alpha\beta}$ and $\bar{C}_{2,m}$ has been discussed by Emsley *et al.* [5]. The coefficient $\bar{u}_2$ is an interaction strength averaged over the solute–solvent molecular separations. It is difficult to test the form of equation (1) because a measurement of S_{zz} can only be used to obtain the product $\bar{u}_2\bar{C}_{2,0}$, and the value of $\bar{C}_{2,0}$ is not usually measured in the experiment. We have shown that this problem can be avoided to some extent by measuring the orientational ordering of a biaxial solute in a liquid crystal with uniaxial phase symmetry [6]. In this case the

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orientational ordering matrix has two non-zero independent elements S_{zz} and $S_{xx} - S_{yy}$, known as the principal components, and choosing a solute with at least C_{2v} symmetry ensures that the principal axes xyz can be located in the solute. The potential of mean torque now depends on the polar angles β_2 and γ_2 of the director in the xyz frame and a general second rank potential can be written as [7],

$$U(\beta_2\gamma_2) = -\varepsilon_{2,0}d^2_{00}(\beta_2) - 2\varepsilon_{2,2}d^2_{02}(\beta_2)\cos 2\gamma_2, \tag{2}$$

where the $d^2_{mn}(\beta)$ are reduced Wigner functions. When the solute concentration is such that solute–solute interactions can be neglected, the coefficients $\varepsilon_{2,0}$ and $\varepsilon_{2,2}$ are related to the solvent orientational order via the molecular field approximation by [6]

$$\varepsilon_{2,0} = \bar{u}_{200}\bar{C}_{2,0} + 2\bar{u}_{220}\bar{C}_{2,2}, \tag{3}$$

$$\varepsilon_{2,2} = \bar{u}_{202}\bar{C}_{2,0} + 2\bar{u}_{222}\bar{C}_{2,2}. \tag{4}$$

The potential also allows for the possible biaxial ordering of the solvent through the terms involving $\bar{C}_{2,2}$, the biaxial order parameter of the mesogen. However, measurements of $\bar{C}_{2,2}$ have found it to be less than 5 per cent of $\bar{C}_{2,0}$ [8], and we expect $\bar{u}_{200} > \bar{u}_{220}$ and $\bar{u}_{202} > \bar{u}_{222}$; the coefficients $\varepsilon_{2,0}$ and $\varepsilon_{2,2}$ are to a good approximation therefore dependent only on $\bar{C}_{2,0}$, so that their ratio

$$\lambda = \varepsilon_{2,2}/\varepsilon_{2,0} \tag{5}$$

is equal to $\bar{u}_{202}/\bar{u}_{200}$, which, at constant volume, should be independent of temperature. The coefficients $\bar{u}_{2mn}$ are dependent on the nature of the intermolecular anisotropic interactions between the solvent and solute. If a single interaction dominates $U(\beta_2\gamma_2)$, and is such that $\bar{u}_{2mn}$ can be factorized as

$$\bar{u}_{2mn} = A_{12}X_1^{(2,m)}X_2^{(2,n)}, \tag{6}$$

where X_1 and X_2 are second rank properties associated with the solvent and solute respectively, then λ will be independent of the nature of the solvent [9].

Experimental biaxiality parameters $\lambda_{\text{exp}} = b/2a$, where $b = 2\varepsilon_{2,2}/RT$ and $a = \varepsilon_{2,0}/RT$ can be obtained for any particular solute–solvent pair at each temperature in a liquid-crystalline phase from measured values of the solute order parameters. Thus

$$S_{zz} = 2\pi Z^{-1}\int_0^\pi d^2_{00}(\beta_2)I_0(bd^2_{02}(\beta_2))\exp[ad^2_{00}(\beta_2)]\sin\beta_2\, d\beta_2 \tag{7}$$

and

$$S_{xx} - S_{yy} = (24)^{1/2}\pi Z^{-1}\int_0^\pi d^2_{02}(\beta_2)I_1(bd^2_{02}(\beta_2))\exp[ad^2_{00}(\beta_2)]\sin\beta_2\, d\beta_2, \tag{8}$$

where $I_n(bd^2_{02}(\beta_2))$ are nth-order Bessel functions, and the orientational partition function is

$$Z = 2\pi\int_0^\pi I_0(bd^2_{02}(\beta_2))\exp[ad^2_{00}(\beta_2)]\sin\beta_2\, d\beta_2. \tag{9}$$

Studies made of the biaxial ordering of *p*-dinitrobenzene [6], and of anthracene [9], have revealed that λ_{exp} is temperature dependent, which may stem in part from the pressure rather than the volume being constant in the experiments. However, a study of the density dependence of the biaxial ordering of anthracene in the liquid crystal 4-(*trans*-4-*n*-heptylcyclohexyl)benzonitrile (PCH7) suggests that such an effect, although important, is not the only source of the temperature dependence of λ_{exp} [10].

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It was also found that λ_{exp} is strongly dependent on the nature of the solvent, which shows that a single second rank interaction that obeys equation (6) cannot be the dominant contribution to $U(\beta_2\gamma_2)$.

The temperature and solvent dependences of λ_{exp} demonstrate that some of the assumptions that lead to the predictions of the independence of λ on temperature and solvent are incorrect. These assumptions are as follows:

(i) the potential of mean torque is second rank (see equation (2));
(ii) the interaction parameters depend on the solvent ordering according to equations (3) and (4);
(iii) the biaxial order parameter $\bar{C}_{2,2}$ is negligible;
(iv) the solvent non-rigidity can be neglected;
(v) the interaction obeys equation (6).

Assumptions (iii)–(v) are probably stronger than (i) and (ii). Higher rank terms may be important if anisotropic repulsive forces make a major contribution to $U(\beta_2\gamma_2)$, as suggested by Barker *et al.* [11], and hence (i) may be incorrect, especially far below the transition, when the ordering is high. The validity of assumption (ii) rests on the approximation made in deriving $U(\beta_2\gamma_2)$ that the solvent–solute intermolecular vector $\mathbf{r}_{\mathrm{ss}}$, has no orientational preference. This also leads to the prediction that electrostatic interactions cannot affect the magnitudes of the $\bar{u}_{2mn}$. However, Patey *et al.* [12] have presented evidence for a contribution to these coefficients from an interaction between the electric quadrupole moment of the solute with an average electric field gradient from the solvent molecules, thus bringing into question the validity of (ii). In addition, the intermolecular vectors $\mathbf{r}_{\mathrm{ss}}$ may also have a non-uniform distribution if the solute sees the solvent molecules as heterogeneous, for example, being attracted to the aromatic rings more than to the alkyl chains.

To investigate this possibility, we present here the results of a study of the ordering of a single solute, *p*-xylene, in a homologous series of liquid crystals, the 4-*n*-alkyloxy-4′-cyanobiphenyls (*N*OCB). These molecules comprise an aromatic core plus an alkyl chain, as shown in figure 1, and if the solute interacts to differing extents with these two molecular regions then we expect this to be reflected in a correlation between λ_{exp} and chain length. These liquid crystals have the added advantage for this study that

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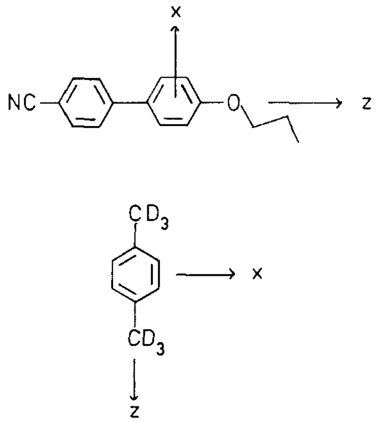

Figure 1. Molecular structures of the 4-*n*-alkyloxy-4′-cyanobiphenyl liquid crystals, and *p*-xylene, showing the reference axes referred to in the text.

their orientational order has been characterized for the first eight members of the series [13], so that it will be possible to test the validity of equations (3) and (4).

The order parameters for the solute were determined by recording the deuterium N.M.R. spectra of *p*-xylene-d_{10}, and using their relationship to the quadrupolar splittings $\Delta\tilde{\nu}_i$ for the ring and methyl deuterons. The solute was chosen because it gives a well-resolved deuterium spectrum and is available commercially. The hindered internal rotation of the CD_3 groups about the *para* axis is between conformers of identical shape, so that the molecule can be described by a single ordering matrix, whose principal axes are fixed by the effective molecular symmetry.

2. Experimental

The liquid crystal samples were obtained from BDH Ltd., except for the deuteriated sample of 4OCB, which was available from a previous investigation of the orientational order of *N*OCB mesogens [13]. The sample of *p*-xylene-d_{10} was purchased from the Aldrich Chemical Company Ltd. Approximately 1 per cent by weight of *p*-xylene was dissolved in the *N*OCB solvents, and the deuterium spectra recorded at 30·7 MHz on a Bruker CXP 200 spectrometer. Figure 2 shows a typical spectrum of *p*-xylene in one of the solvents ($N = 6$). The spectra were recorded at ambient pressure, except when 2OCB was the solvent. In this case a stable nematic phase could not be sustained in the supercooled state at one atmosphere pressure. A stable phase was obtained by increasing the pressure to 1·5 kbar with the equipment described previously [14].

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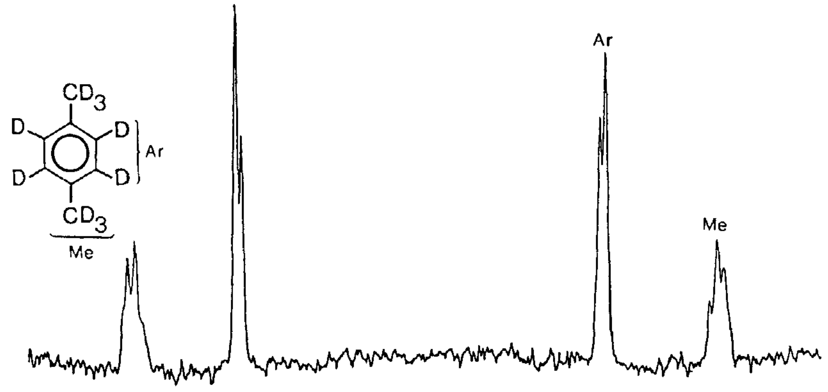

Figure 2. Deuterium N.M.R. spectrum at 30·7 MHz of *p*-xylene-d_{10} dissolved in 4-*n*-hexyloxy-4′-cyanobiphenyl in the nematic phase. The full spectral width is 23 kHz.

3. Results and discussion

The peaks in the deuterium spectra are assigned on the basis of their relative intensities. The large doublet separations give the quadrupolar splittings $\Delta\tilde{\nu}_{Ar}$ and $\Delta\tilde{\nu}_{Me}$, from which the principal order parameters S_{zz} and $S_{xx} - S_{yy}$ are obtained; the axes xyz are shown in figure 1. Thus

$$\Delta\tilde{\nu}_{Ar} = \tfrac{3}{4}q_{CD}^{Ar}\,[S_{zz}(3\cos^2\theta - 1) + (S_{xx} - S_{yy})\sin^2\theta] \tag{10}$$

and

$$\Delta\tilde{\nu}_{Me} = \tfrac{3}{4}q_{CD}^{Me}S_{zz}\,(3\cos^2\alpha - 1); \tag{11}$$

the asymmetry parameters for the quadrupolar tensors of aromatic and methyl deuterons are assumed to be zero. The quadrupolar coupling constants are assigned the values $q_{CD}^{Ar} = 186$ kHz and $q_{CD}^{Me} = 168$ kHz [15]. θ is the angle that the C–D bonds in the aromatic ring make with z, and which we assume to be 60°, the value for a benzene ring with all bond angles equal to 120°. α is the angle between the C–D bonds in the CD_3 group and z; we assume this to be 70·5°, which is that for a tetrahedral geometry. The sign of S_{zz} for a molecule of this shape is expected to be positive, and this determines $\Delta\tilde{\nu}_{Me}$ to be negative. The fine structure on the peaks in figure 2 stems from dipolar coupling $\tilde{D}_{DD}$ to nearest neighbour deuterons. For the aromatic deuterons the sign of $\tilde{D}_{DD}$ is determined by that of S_{zz}, which makes $\tilde{D}_{DD}$ negative. The relative intensities of the four lines resolved in the spectrum for the aromatic deuterons then determine $\Delta\tilde{\nu}_{Ar}$ to be positive [16].

The errors in S_{zz} and $S_{xx} - S_{yy}$ stemming from errors in the measurement of the quadrupolar splittings are of the order of $\pm 0{\cdot}5$ per cent and ± 1 per cent, respectively. There are much larger errors possible in the order parameters, which are caused by the need to assume values for θ and α. The magnitude of these systematic errors is difficult to assess. Changes in α and θ by $\pm 1°$ produce changes in S_{zz} and $S_{xx} - S_{yy}$ on average of the order of ± 7 per cent. However, the systematic errors affect the data for different solvents and temperatures to almost the same extent, and therefore their presence does not affect the large, general trends that are observed.

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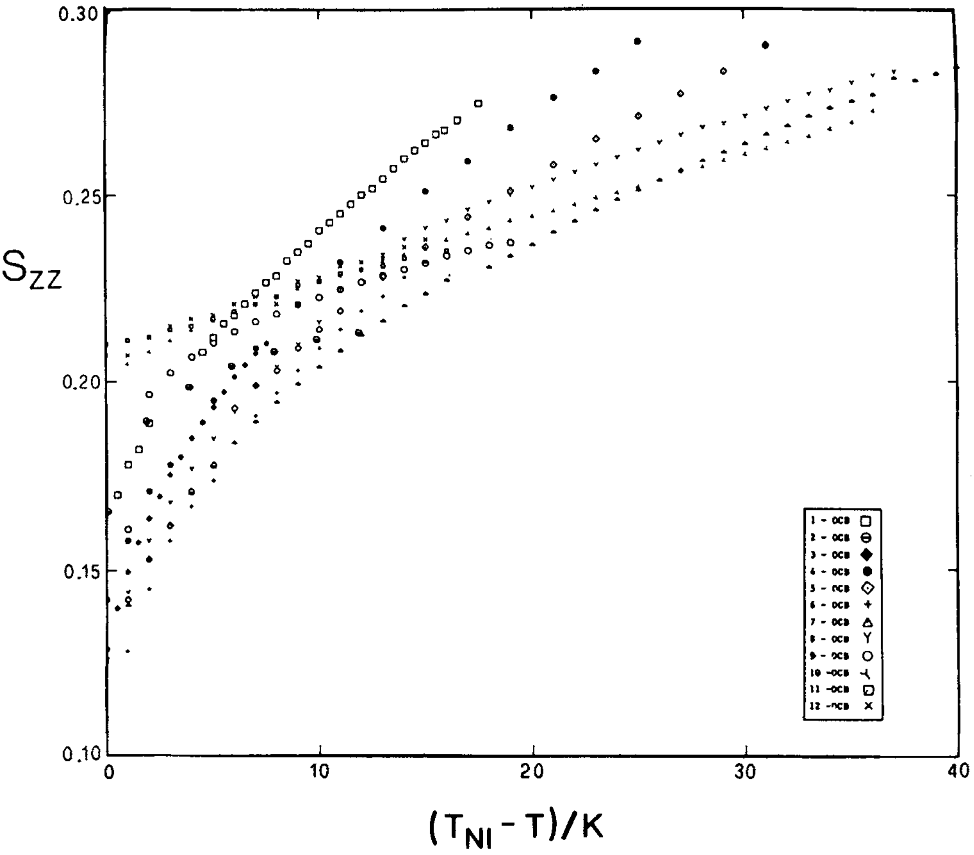

Figure 3. Dependence of S_{zz} on the shifted temperature $T_{NI} - T$ for p-xylene-d_{10} dissolved in the NOCB liquid crystals.

The values of S_{zz} and $S_{xx} - S_{yy}$ determined from the quadrupolar splittings are shown in figures 3 and 4 as functions of the shifted temperature $T_{NI} - T$ for all the mixtures studied. The solutions display a biphasic region, and so T_{NI} has been taken as the highest temperature at which a sample is wholly nematic. Clearly, there are major changes in the orientational ordering of *p*-xylene as the solvent is changed. The most obvious differences are between those solvents that have only a smectic A phase ($N > 9$) and those that are only nematic ($N < 8$), with 8OCB and 9OCB showing behaviour characteristic of both. The dependence of both S_{zz} and $S_{xx} - S_{yy}$ on chain length varies to some extent with the shifted temperature $T_{NI} - T$, as shown in figures 5 and 6.

According to theory, there are two factors contributing to these changes in S_{zz} and $S_{xx} - S_{yy}$ as N and temperature are changed: the magnitudes of the coefficients $\bar{u}_{2mn}$ and the orientational order parameters $\bar{C}_{2,0}$ and $\bar{C}_{2,2}$ of the solvents, as shown in equations (3) and (4). In order to separate these two effects, we have determined λ_{exp}, *aRT* and *bRT* from each pair of order parameters. In figure 7 we show the temperature and chain length dependences of λ_{exp}; clearly, both of these factors have large effects on the biaxiality of the potential of mean torque for *p*-xylene in a liquid-crystalline environment. The solvent dependence of λ_{exp} is perphaps the most striking feature, and this is shown more clearly in figure 8, where we give the dependence on chain length at three values of $T_{NI} - T$. The variation of λ_{exp} with N means that

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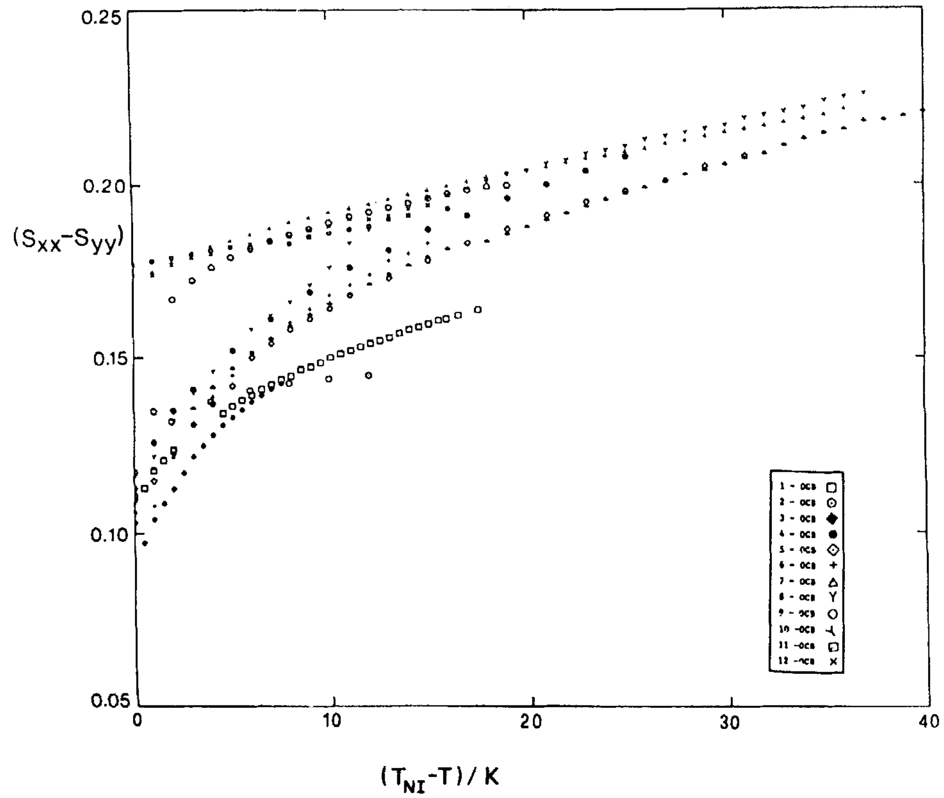

Figure 4. Dependence of $S_{xx} - S_{yy}$ on the shifted temperature $T_{NI} - T$ for *p*-xylene-d$_{10}$ dissolved in the *N*OCB liquid crystals.

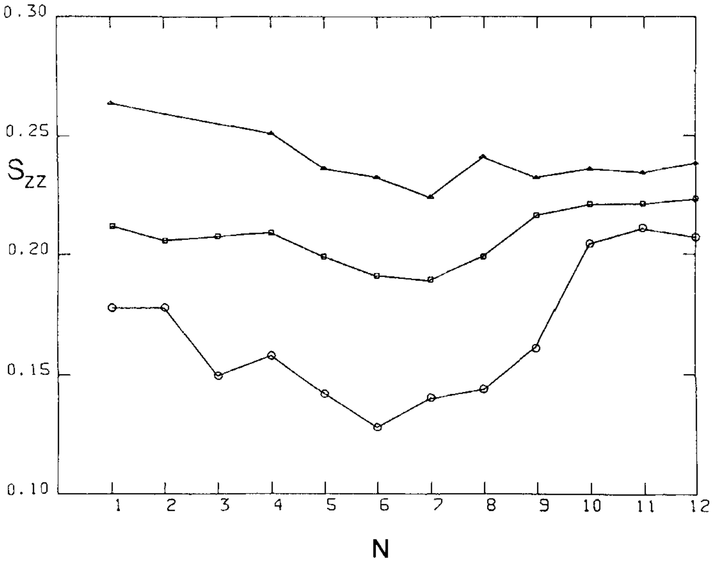

Figure 5. Variation of S_{zz} with chain length N at $T_{NI} - T$ of 1 K (○), 7 K (□) and 15 K (△).

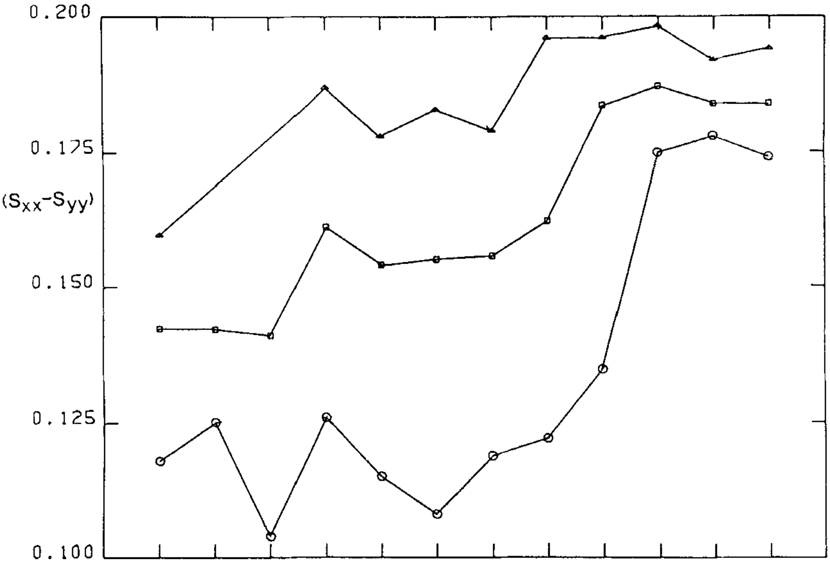

Figure 6. Variation of $S_{xx} - S_{yy}$ with chain length N at $T_{NI} - T$ of 1 K (○), 7 K (□) and 15 K (△).

$U(\beta_2\gamma_2)$ cannot be determined by a single interaction obeying equation (6), and in this respect p-xylene behaves like the other solutes for which values of λ_{exp} have been determined [6, 9]. The values of λ_{exp} increase with chain length, and are considerably greater for the smectic A phase. This is exemplified by the temperature dependences of λ_{exp} for 8OCB and 9OCB, which show a marked increase as the transition to the smectic A phase is approached (see figure 7). The temperature dependences of λ_{exp}

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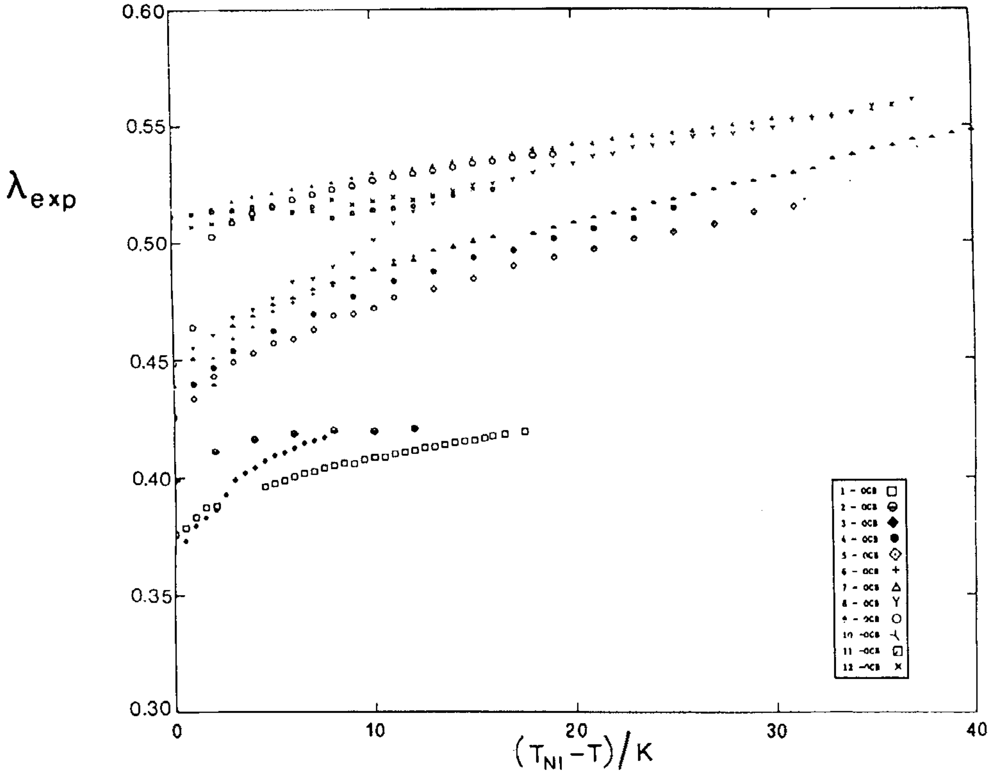

Figure 7. Temperature dependence of λ_{exp} for p-xylene-d_{10} dissolved in the NOCB series.

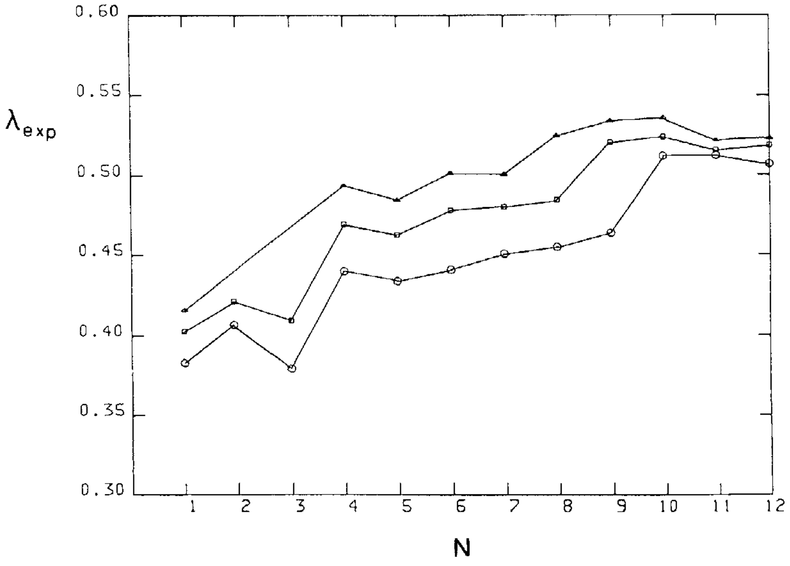

Figure 8. Variation of λ_{exp} for p-xylene-d_{10} with the chain length of the NOCB solvent, at 1 K (○), 7 K (□) and 15 K (△).

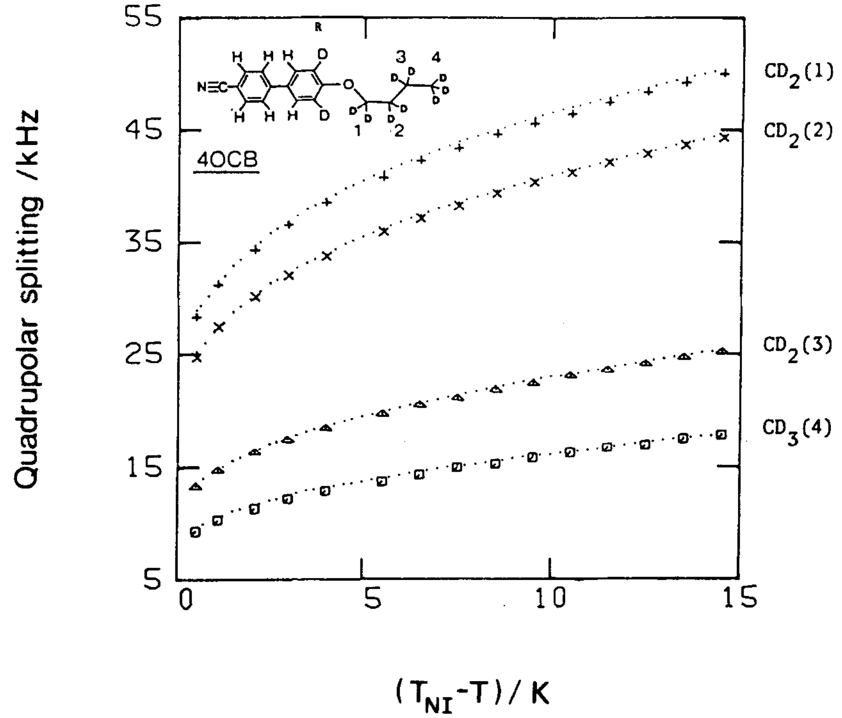

Figure 9. Temperature variation of the quadrupolar splittings $\Delta\tilde{\nu}$ for the chain deuterons in pure 4OCB-d_{11} (dotted lines) compared with those in a sample containing 4OCB + 1 per cent (wt) 4OCB-d_{11} + 2 per cent (wt) p-xylene-d_{10} (symbols).

for those mixtures that exist only in the nematic phase are all similar in that the increase with $T_{NI} - T$ is at first rapid and then reduces to being almost linear, and of similar slope to that of those solutions that exist only in smectic A phases.

To proceed further, we need to compare the values of aRT and bRT with the order parameters $\bar{C}_{2,m}$ for the solvent. It is possible to obtain estimates of $\bar{C}_{2,m}$ for the pure solvents, which we shall assume can be used for the ordering of the solvent when contaminated with a small amount of p-xylene-d_{10}. To test this assumption, a sample was prepared containing 2 per cent of p-xylene-d_{10}, 4OCB + 1 per cent 4OCB-d_{11}, and the quadrupolar splittings of both solute and solvent measured as functions of temperature. The quadrupolar splittings of the chain deuterons in this mixture are compared with those obtained on a pure sample of 4OCB-d_{11} [13] in figure 9. The two sets of quadrupolar splittings agree at all positions and temperatures within experimental error (which is essentially determined by the precision with which $T_{NI} - T$ can be measured). This result is strong evidence that the values of $\bar{C}_{2,m}$ obtained for the pure solvents can be used for the samples containing p-xylene.

Equations (3) and (4) assume the solvent molecules to be rigid, whereas in reality all have some internal motions, and they do not therefore have a single second rank ordering matrix [17]. We shall, however, explore the consequences of assuming that their orientational order can be described by single values of $\bar{C}_{2,0}$ and $\bar{C}_{2,2}$. In the case of 1OCB this involves only the assumption that the molecule exists in the lowest energy forms (the RIS approximation [18]), all of which have the same shape and hence the same orientational ordering matrices. Values of $\bar{C}_{2,m}$ have been measured

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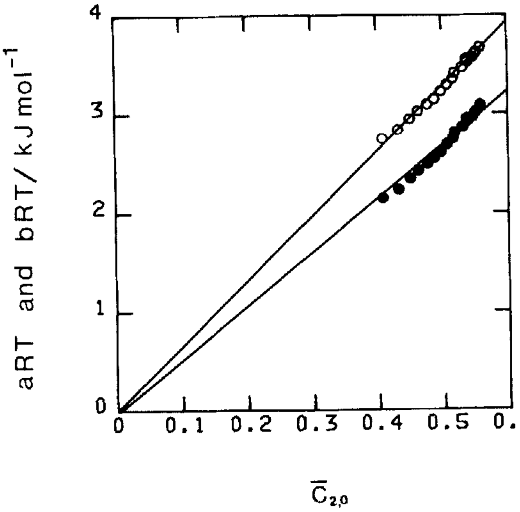

Figure 10. The dependence of the interaction parameters aRT (○) and bRT (●) for p-xylene-d$_{10}$ on the order parameter $\bar{C}_{2,0}$ of the solvent 1OCB. The lines are the result of fitting the data to the linear relationships of equations (12) and (13).

for 1OCB [19], and in figure 10 we show plots of aRT and bRT for p-xylene-d$_{10}$ against $\bar{C}_{2,0}$ for this solvent. There is a linear dependence of aRT on $\bar{C}_{2,0}$, passing through the origin, within the precision of the measurements, so that the importance of the term $\bar{u}_{220}\bar{C}_{2,2}$ in equation (3) cannot be determined; it is probably negligible in magnitude, rather than indistinguishable from the term $\bar{u}_{200}\bar{C}_{2,0}$, because in the range studied $\bar{C}_{2,2}$ is not linearly dependent on $\bar{C}_{2,0}$. The continuous line in figure 10 is a least-squares fit of the data to

$$aRT = -\bar{u}_{200}\bar{C}_{2,0}, \tag{12}$$

to give $\bar{u}_{200}$ as 6·54 ± 0·06 kJ mol^{-1}. The dependence of bRT on $\bar{C}_{2,0}$ for 1OCB is linear over the range studied, but the straight line fitted to the points does not pass through the origin, as demanded by equation (4) since $\bar{C}_{2,2}$ must vanish when $\bar{C}_{2,0}$ is zero. Fitting bRT to equation (4) gives $\bar{u}_{202}$ as 2·91 ± 0·04 and $\bar{u}_{222} = -1{\cdot}9 \pm 0{\cdot}3$ kJ mol^{-1}. One should note, however, that these values have been obtained with the assumption that the $\bar{u}_{2mn}$ are independent of temperature, and this may not be true for conditions of constant pressure rather than constant volume [10].

The orientational ordering of the other NOCB molecules, even with the RIS approximation, requires an ordering tensor $\bar{C}^n_{2,m}$ for each of the n conformations adopted by the molecule. The $\bar{C}^n_{2,m}$ may be determined for reference frames fixed in any rigid sub-unit of the molecule, and averages of the $\bar{C}^n_{2,m}$ over n determined to yield a single ordering tensor from which to estimate the $\bar{C}_{2,m}$ in equations (3) and (4). However, the values obtained for the $\bar{C}_{2,m}$ depend on the location of the reference frame, and there is no reason for choosing any particular rigid part of the molecule for this frame. The most important factors in determining $U(\beta_2\gamma_2)$ are the probable, strong, anisotropic interactions between the aromatic solute and the aromatic core units, $N{\equiv}C{-}C_6H_4{-}C_6H_4{-}O$, of the solvent; we shall therefore explore the relationships between aRT and bRT and $\bar{C}^a_{2,0}$, determined with the reference frame shown in figure 1. The values of $\bar{C}^a_{2,0}$ are those determined by Counsell *et al.* [13] for N = 3, 4, 6 and 8, and by Heeks [20] for 5OCB, in each case by comparing experimental

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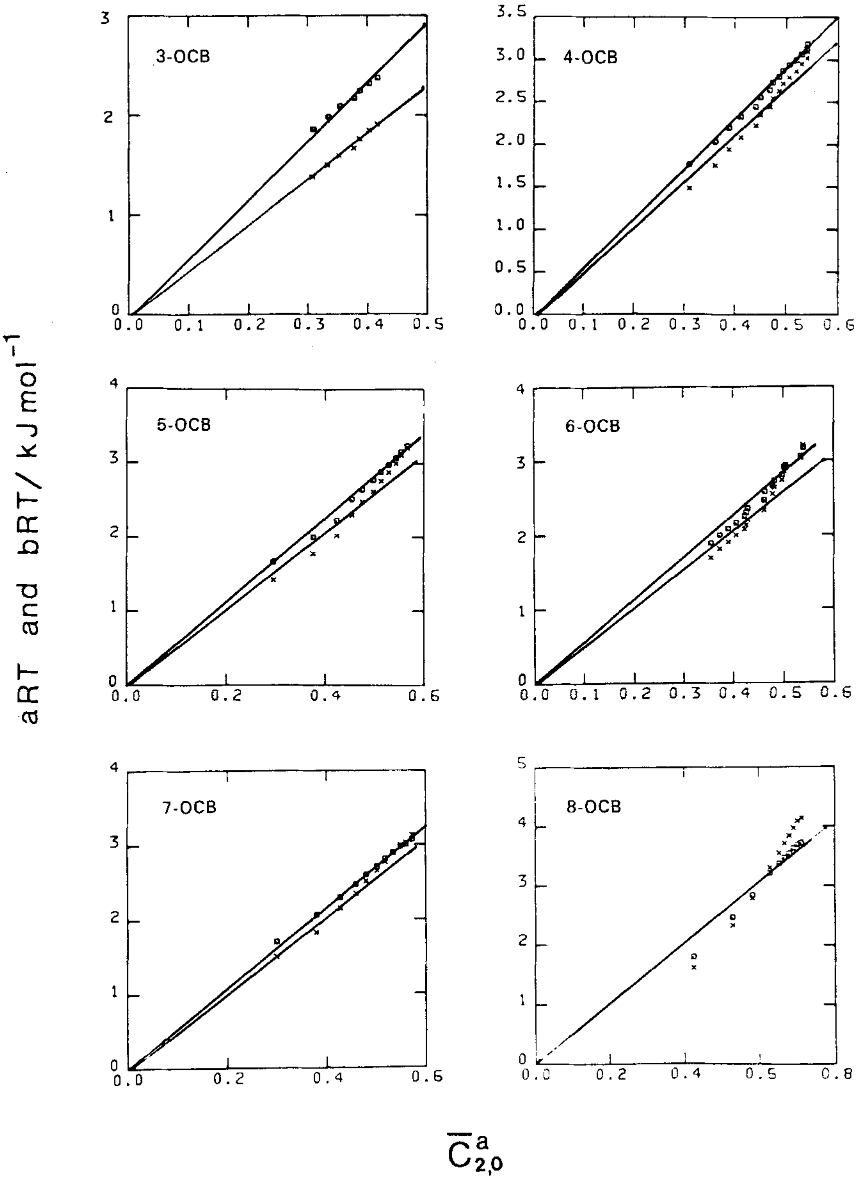

Figure 11. The dependence on $\bar{C}^{a}_{2,0}$, the order parameter for the core fragment of the *N*OCB molecules, of the interaction parameters *aRT* (□) and *bRT* (×) for the solute *p*-xylene-d_{10}. The lines are the result of fitting the data to equations (12) and (13). In the case of 8OCB the two lines are virtually coincident.

deuterium quadrupolar splittings with values calculated with the theoretical model proposed by Emsley, Luckhurst and Stockley [21]. The values of $\bar{C}^{a}_{2,0}$ for 7OCB were obtained by calculation with a potential of mean torque derived from the data of Counsell *et al.* [13]. We have not included the values of *aRT* and *bRT* for 2OCB in our comparison because these were obtained at high pressure, and strictly should be compared with values of $\bar{C}^{a}_{2,0}$ at the same pressure; these are not available.

Figure 11 shows the result of fitting the aRT data to equation (12) for $N = 3, 4, 5, 6$ and 7, and clearly in these cases the linear relationship is a good approximation. The values obtained for $\bar{u}_{200}$ are given in the table, and show an overall decrease as N increases, with an alternation in magnitude for adjacent members of the series. The dependence of bRT on $\bar{C}^{a}_{2,0}$ for $N = 3$ is linear within experimental error, passing through the origin, and the slope gives $\bar{u}_{202}$ as 2·96 ± 0·03 kJ mol^{-1}. Considerable departures from linearity are observed for the plots of bRT against $\bar{C}^{a}_{2,0}$ for the other compounds ($N = 4, \ldots, 8$), but an estimate of the relative values of $\bar{u}_{202}$ can be obtained by fitting the data to

$$bRT = -2\bar{u}_{202}\bar{C}^{a}_{2,0}, \tag{13}$$

giving the results shown in the table. Again there is a trend to lower values as N increases.

Estimates of interaction coefficients $\bar{u}_{200}$ and $\bar{u}_{202}$ for *p*-xylene dissolved in the *N*OCB solvents obtained from the slopes of the dependences of aRT and bRT on $\bar{C}^{a}_{2,0}$.

N	$\bar{u}_{200}$/kJ mol^{-1}	$\bar{u}_{202}$/kJ mol^{-1}
1	6·54 ± 0·06	2·91 ± 0·04
3	5·83 ± 0·12	2·96 ± 0·03
4	6·23 ± 0·34	2·98 ± 0·17
5	6·03 ± 0·34	2·83 ± 0·18
6	5·55 ± 0·16	2·66 ± 0·17
7	5·43 ± 0·03	2·64 ± 0·11
8	5·01 ± 0·20	2·61 ± 0·27

A possible explanation of the tendency of aRT and bRT to decrease as N increases is that the solute–solvent interactions differ, depending upon whether the solute is interacting with the aromatic core or the alkyl chain. Thus the two interaction parameters can be written as the weighted averages

$$aRT = x\bar{u}^{a}_{200}\bar{C}^{a}_{2,0} + (1 - x)\bar{u}^{c}_{200}\bar{C}^{c}_{2,0} \tag{14}$$

and

$$bRT = 2[x\bar{u}^{a}_{202}\bar{C}^{a}_{2,0} + (1 - x)\bar{u}^{c}_{202}\bar{C}^{c}_{2,0}], \tag{15}$$

by neglecting terms involving the solvent biaxial order parameter. Here x is the probability that the solvent interacts with a core, and $\bar{u}^{a}_{200}$, $\bar{u}^{c}_{200}$, $\bar{u}^{a}_{202}$ and $\bar{u}^{c}_{202}$ are parameters measuring the strengths of the interactions between the solute and the core and chain regions of the solvent averaged over the solute–solvent separations. The core is a well-defined rigid group and there is no problem in obtaining $\bar{C}^{a}_{2,0}$, as discussed already. However, $\bar{C}^{c}_{2,0}$ is introduced into equations (14) and (15) in an attempt to simplify a complex problem, to which there is no unique solution, of how to represent the ordering of a flexible body by a single parameter. The observation that aRT, and to a lesser extent bRT, are approximately linearly dependent on $\bar{C}^{a}_{2,0}$ means that $\bar{C}^{c}_{2,0}$ is probably a constant fraction of $\bar{C}^{a}_{2,0}$. This, for example, is the case to a good approximation when $\bar{C}^{c}_{2,0}$ is equated to the average order parameter S_{CC} introduced by Counsell *et al.* [13], and defined as

$$S_{\mathrm{CC}} = S_{\mathrm{OC}} + \sum_{j=2}^{N} S^{j}_{\mathrm{CC}}, \tag{16}$$

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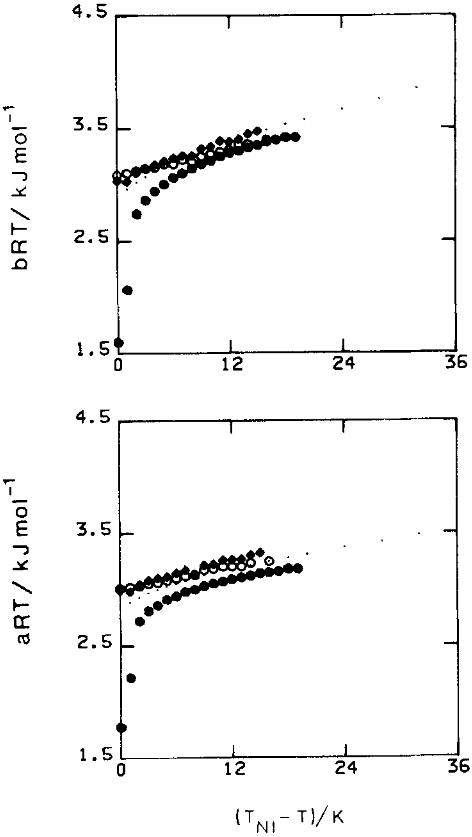

Figure 12. Dependence of aRT and bRT on shifted temperature for p-xylene-d_{10} dissolved in 9OCB (●), 10OCB (•), 11OCB (○) and 12OCB (◆).

where S_{OC} is the calculated, conformationally averaged order parameter for the O–C$_1$ bond, and S^j_{CC} is the similar quantity for the C_{j-1}–C_j bond. Writing

$$\bar{C}^c_{2,0} = r\bar{C}^a_{2,0} \tag{17}$$

gives

$$aRT = (x\bar{u}^a_{200} + r(1 - x)\bar{u}^c_{200})\bar{C}^a_{2,0} \tag{18}$$

and

$$bRT = 2(x\bar{u}^a_{202} + r(1 - x)\bar{u}^c_{202})\bar{C}^a_{2,0}. \tag{19}$$

The value of x may depend on the number of carbons in the chain for two reasons: increasing the chain length both dilutes the cores relative to the chains and leads to more conformations being allowed. The effects on x of these two factors are difficult to separate and are both probably important. If the dilution factor is the most important influence on x, then an increase in x as N increases is expected, which, coupled with the tendency of $\bar{u}_{200}$ and $\bar{u}_{202}$ to decrease as N increases, implies $\bar{u}^a_{200} > \bar{u}^c_{200}$ and $\bar{u}^a_{202} > \bar{u}^c_{202}$.

Estimates of $\bar{C}^a_{2,m}$ for $N > 8$ are not available, and so we can compare only the temperature dependences of aRT and bRT, as shown in figure 12. An increase in both aRT and bRT as the smectic A phase is entered is apparent for 9OCB (and also for

8OCB, not shown in figure 12), and then the values for both interaction parameters are practically independent of chain length in the smectic A phase, suggesting equal values of $\bar{C}^{a}_{2,0}$ for compounds in the smectic A phase at identical shifted temperatures. This in turn suggests constant values for $\bar{u}_{200}$. The tendency for $\bar{u}_{200}$ for the interaction of *p*-xylene with *N*OCB molecules to decrease with chain length in the nematic phase, followed by an increase to a value almost independent of chain length in the smectic A phase, can be rationalized as follows. Suppose that in the nematic phase the *p*-xylene molecules have an almost equal affinity for the aromatic core and segments of the aliphatic chains of the *N*OCB molecules, so that x depends only on the volume fraction of the core relative to the chain. The effect of increasing N in this case will be to decrease x, and hence to change $\bar{u}_{200}$. In the smectic A phase, however, there is a change in the packing of the solvent molecules, which now tend to form into layers. This in turn could increase the affinity of the *p*-xylene molecules for the core of the solvent molecules, so that the decrease in x as N increases is reduced, and as a consequence the interaction parameters $\bar{u}_{200}$ have their dependence on N decreased.

4. Conclusion

This investigation demonstrates the advantages of studying the orientational order of biaxial rather than uniaxial solutes in that the temperature and solvent dependences of λ_{exp}, aRT and bRT give a greater insight into the nature of the potential of mean torque than do studies of the single order parameter of cylindrically symmetric solutes. In addition, it is clearly a major advantage to use solvents whose orientational order is known, so that the separate effects on the solute order parameters of the strength of the solute–solvent interaction and the ordering of the solvent molecules can be assessed. The *N*OCB series is the only one for which good estimates for the ordering of the molecules are available for the first eight members, over wide ranges of $T_{\mathrm{NI}}-T$, and as such it will be an advantage to use these solvents in more studies of the type described here, but with different solutes.

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