The determination of average, anisotropic, solute-solvent interaction strengths for biphenyl, 4-bromobiphenyl, 4-cyanobiphenyl and 4-methoxybiphenyl dissolved in the nematic solvent 4'-cyano-4-methoxybiphenyl

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The determination of average, anisotropic, solute–solvent interaction strengths for biphenyl, 4-bromobiphenyl, 4-cyanobiphenyl and 4-methoxybiphenyl dissolved in the nematic solvent 4'-cyano-4-methoxybiphenyl

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Deuterium NMR spectra have been obtained from samples of biphenyl-d_{10}, 4-bromobiphenyl-d_9, 4-cyanobiphenyl-d_9 and 4-methoxybiphenyl-d_5 dissolved in the nematic solvent 4-methoxy-4'-cyanobiphenyl (1-OCB), and the data used to obtain the two principal, solute order parameters, S_{zz} and $S_{xx} - S_{yy}$. These order parameters are then used to determine the average solute–solvent interaction parameters, $\bar{u}_{200}$ and $\bar{u}_{202}$, in a simple potential of mean torque. This reveals that the changes in the biaxiality, $\lambda = \bar{u}_{202}/\bar{u}_{200}$, on going from biphenyl to 1-OCB by introducing CN and OCH_3 groups are dominated by changes in $\bar{u}_{200}$ whilst $\bar{u}_{202}$ remains essentially unchanged.

1. Introduction

4-methoxy-4'-cyanobiphenyl (1-OCB) is the simplest molecule which forms a nematic phase. Its structure (see figure 1) is such that, although there is internal rotation about three bonds, the minimum energy structures are of equal energy and identical in shape. This means that within the approximation that only the minimum energy structures are appreciably populated, the molecule is effectively rigid. In the absence of any truly rigid nematogens, 1-OCB is therefore the closest in practice to a rigid nematogen. It also has an almost cylindrically symmetric ordering matrix S [1], so that 1-OCB approaches the theoretician's dream of a rigid, cylindrically symmetric nematogen.

The small biaxiality in S is perhaps surprising since the structure departs quite significantly from that of a cylinder. In an attempt to shed some light on the relationship between the molecular structure and the biaxiality in the molecular orientational order we present here the results of a study of the orientational ordering of solutes at a low dilution in 1-OCB of the molecules biphenyl, 4-cyanobiphenyl and 4-methoxybiphenyl, which are fragments of 1-OCB. We also present, for comparison, the orientational order parameters for 4-bromobiphenyl.

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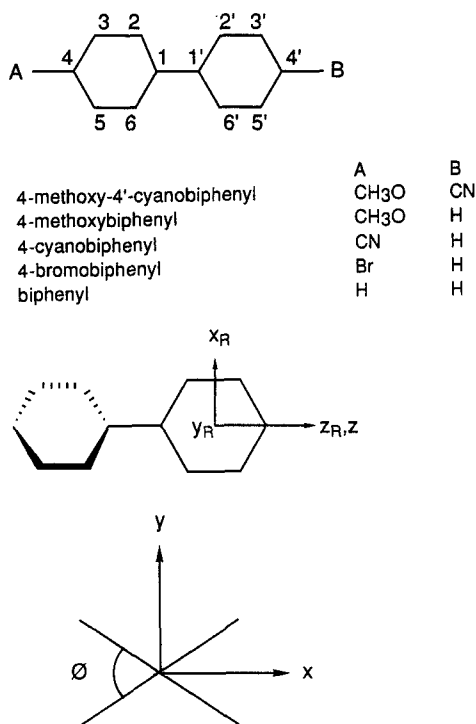
	A	B
4-methoxy-4'-cyanobiphenyl	CH3O	CN
4-methoxybiphenyl	CH3O	H
4-cyanobiphenyl	CN	H
4-bromobiphenyl	Br	H
biphenyl	H	H

Figure 1.   The structures of biphenyl, 4-bromobiphenyl, 4-cyanobiphenyl, 4-methoxybiphenyl
and 4-methoxy-4'-cyanobiphenyl.

2. Experimental

The orientational order parameters were obtained from the quadrupolar splittings
of deuterium nuclei in samples of 2 wt% of biphenyl-d_{10}, 4-cyanobiphenyl-d_9, 4-
bromobiphenyl-d_9 and 4-methoxy-[C^2H_3]-3,5-[^2H]-biphenyl,(4-methoxybiphenyl-
d_5) dissolved in 1-OCB. The sample of biphenyl-d_{10} was obtained from Aldrich
Chemical Company Limited, whilst the other deuteriated samples were synthesized as
follows.

4-Bromobiphenyl-d_9

4-Bromobiphenyl-d_9 was obtained by exchange with C_6D_6 catalysed by ethyl
aluminium dichloride [2]. Benzene-d_6 (10 ml) and a 1M solution of ethyl aluminium
dichloride in hexane (2 ml) (Aldrich Chemical Company Limited) were added under
nitrogen to 4-bromobiphenyl (2·25 g, 0·01 mol). The solution was heated under reflux
for 1 h using a condenser fitted with a calcium chloride guard tube, after which the heat
was removed, the flask opened to the air and the contents allowed to cool to room
temperature. The reaction was quenched by the addition of D_2O until the yellow
colour in the organic layer disappeared. The organic layer was separated, dried with
magnesium sulphate and the deuteriated benzene recovered by distillation. The
residue, deuteriated 4-bromobiphenyl, was recrystallized from ethanol. A mass
spectrum and proton NMR showed the level of deuteriation to be 85 per cent.
Repeating the procedure raised this to 95 per cent.

4-Cyanobiphenyl-d₉

Copper (I) cyanide (0·7 g, 0·008 mol) was added to a solution of 4-bromobiphenyl-d₉ (1·18 g, 0·005 mol) in *N*-methyl-2-pyrrolidone (25 ml) and the mixture heated under reflux for 4 h. The reaction mixture was allowed to cool to 80°C, and an aqueous solution of ferric chloride (1·5 g in 5 ml of H₂O) and hydrochloric acid (2 ml) added. The mixture was maintained at 80°C for 30 min and then left to cool overnight. The reaction mixture was added to water (200 ml) and the organic components extracted with dichloromethane (3 × 100 ml), washed with water (3 × 100 ml) and dried with anhydrous calcium chloride. The solvent was removed by vacuum distillation, and the crude product purified by passing it through a column of alumina and silica gel with dichloromethane as eluent. After evaporating the solvent, the pale yellow crystals were recrystallized from ethanol to give white crystals (mp 82–84°C, lit. 85–87°C).

4-methoxy-[C²H₃]-3,5-[²H]-biphenyl

4-Methoxybiphenyl-d₅ was prepared by methoxylation of 4-hydroxybiphenyl-3,5-d₂, which was obtained by dissolving 4-hydroxybiphenyl (2 g, 0·012 mol) in hot toluene (20 ml) and DCl in D₂O (100 ml of 37 wt% DCl) and heating under reflux for 24 h. On cooling, the hydroxybiphenyl was extracted from the aqueous layer with toluene (3 × 20 ml), and the combined organic phases washed with water until the washings ceased to be acidic, and then dried with anhydrous sodium sulphate. The dry toluene solution was filtered hot, the solvent removed and the crude product recrystallized from toluene. The purified 4-hydroxybiphenyl-d₂ (0·9 g, 0·005 mol) was dissolved in acetone (50 ml), methyl iodide-d₃ (1·4 g, 0·01 mol) and anhydrous potassium carbonate (3·1 g, 0·022 mol) were added and the mixture heated under reflux for 6 h and then filtered. The solid was washed with hot acetone and the filtrate was evaporated to dryness to yield the crude product, which was recrystallized from methanol to give off-white crystals (mp 87–89°C, lit. 89–90°C). The NMR spectrum showed an approximately 90 per cent incorporation of deuterium in the 3,5-positions.

NMR spectra

Samples containing approximately 2 wt% of each solute in 1-OCB were prepared and their deuterium spectra obtained at 30·7 MHz on a Bruker MSL 200 spectrometer. The solvent has a monotropic nematic phase with $T_{NI} = 358·5$ K, whilst it melts at 380 K. Supercooling was achieved by maintaining the sample at 390 K for several hours before cooling to the nematic phase.

3. Analysis of the spectra

Figure 2 shows an example of the complete deuterium spectrum of a sample of biphenyl-d₁₀ dissolved in 1-OCB. The pair of lines with the largest splitting stem from the 4,4′-deuterons, and the intense group near the centre are from the remaining eight deuterons. The centre group is shown on an expanded scale in figure 3. The spectrum is consistent with approximately equal quadrupolar splittings for the deuterons at positions 2, 3, 5, 6, 2′, 3′, 5′ and 6′. The fine structure is a result of the only resolvable dipolar coupling being $D_{23} = D_{56} = D_{2'3'} = D_{5'6'}$, and the relative intensities of the lines show that the dipolar coupling has an opposite sign (negative) to the quadrupolar splitting (positive).

The deuterium spectra of 4-bromo and 4-cyanobiphenyl-d₉ are very similar, and figure 4 shows an example of the complete spectrum of 4-cyanobiphenyl-d₉ at T_{NI}-T of 9 K. The outer pair of lines are from the single deuteron at position 4′, whilst the rest of
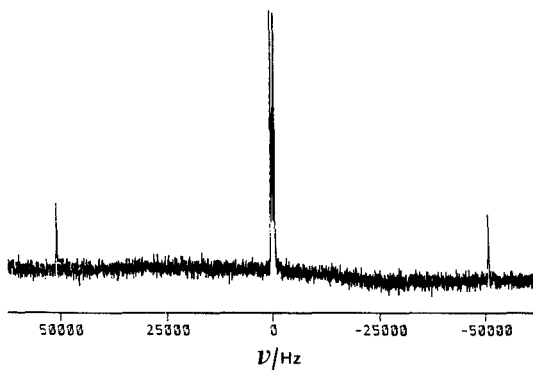
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Figure 2. 30·7 MHz spectrum of the deuterons in a sample of biphenyl-d_{10} dissolved in 1-OCB at $T_{NI} - T = 1\cdot1°C$.
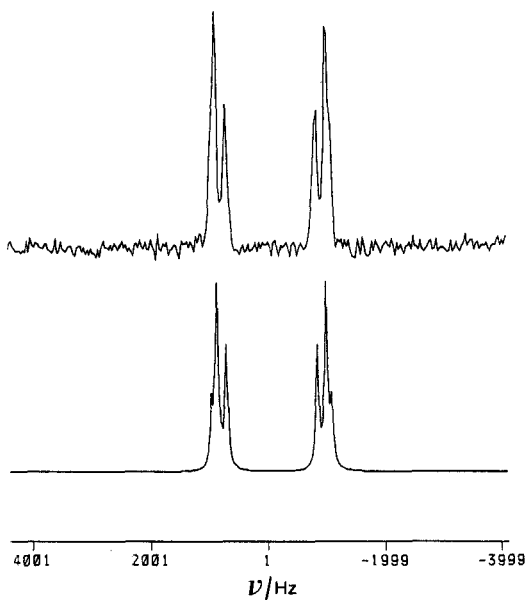

Figure 3. Expansion of the central group of peaks in figure 2 (top), compared with a simulated spectrum (bottom) for the eight deuterons at positions 2, 3, 5, 6, 2′, 3′, 5′, and 6′. The simulation has an equal quadrupole splitting Δv for all eight deuterons, and the only non-zero dipolar coupling is $D = D_{23} = D_{56} = D_{2'3'} = D_{5'6'}$. The sign of Δv is opposite to that of D.

the deuterons produce the group close to the centre, which are shown on an expanded scale in figure 5. It was not possible to resolve a sufficient number of quadrupolar lines in order to obtain a complete analysis of this spectrum, but a good, approximate analysis was achieved by fixing $D_{2'3} = D_{23'} = -5\,Hz$, $D_{33'} = -2\,Hz$, $D_{22'} = -37\,Hz$, which are based on the inter-proton dipolar couplings in 1-OCB with the same order parameter for the 4,4′-axis. The four quadrupolar splittings and $D_{23} = D_{2'3'}$ were then varied to obtain the best agreement with the experimental line positions. The observed
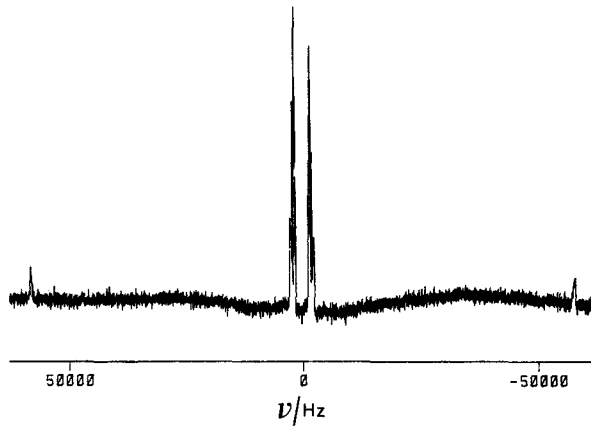
Figure 4. 30·7 MHz spectrum of the deuterons in a sample of 4-cyanobiphenyl-d$_9$ dissolved in 1-OCB at $T_{NI} - T = 9°C$.
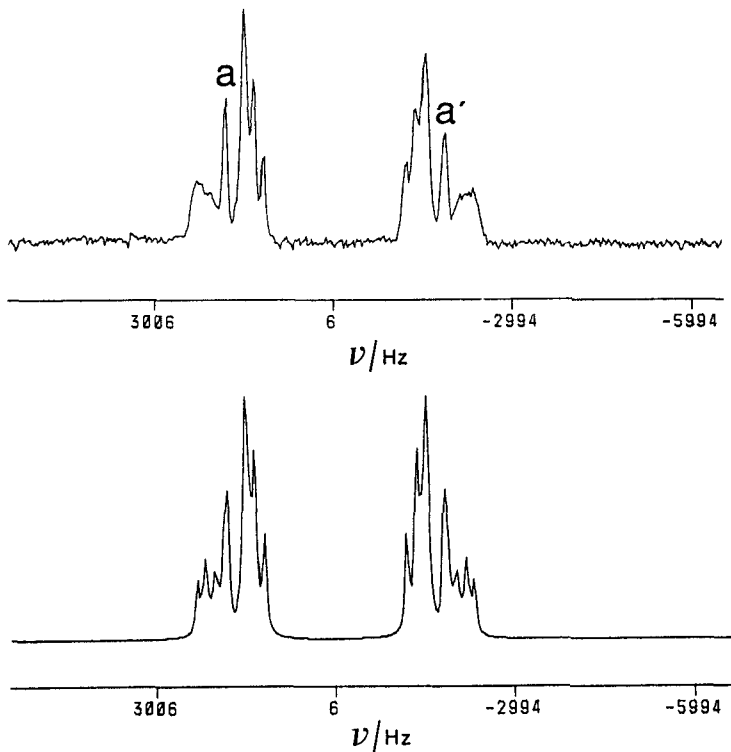

Figure 5. Expansion of the central group of peaks in figure 4 (top) and a simulated spectrum with the parameters in table 1 (underneath).

Table 1. Quadrupolar splittings $\Delta \nu_i$ and dipolar couplings D_{ij} obtained by an analysis of the deuterium spectrum of 4-cyanobiphenyl-d$_9$ dissolved in 1-OCB.

i	$\Delta \nu / \text{Hz}$
2	-4216 ± 15
3	-2748 ± 8
2'	-3156 ± 30
3'	-3254 ± 28
4'	-111053 ± 30

i, j	D_{ij} / Hz
2, 3	-81 ± 3
2', 3	-5†
3, 3'	-2†
2, 2'	-37
2, 3'	-5†
2', 3'	-81 ± 3

† Fixed.

and calculated spectra are shown in figure 5, and the values of the quadrupolar splittings are given in table 1. The variation of $\Delta \nu_i$ with the site could be a consequence of differences in the quadrupolar tensors q_i, or changes in θ^i_{CDz}, the angle which the ith C–D bond makes with the z axis. Thus,

$$\Delta \nu_i = 3q^i_{\text{CD}}[S^R_{zz}\{3\cos^2\theta^i_{\text{CDz}} - 1)\} + (S^R_{xx} - S^R_{yy})\sin^2\theta^i_{\text{CDz}}]/4, \qquad (1)$$

where q^i_{CD} is the deuterium quadrupolar coupling at the ith site, and the asymmetry, η, in the q tensor has been set to zero; values of η for deuterons in benzene rings are approximately 0·05, but using a non-zero value here for η is not justified in view of the uncertainties in the values of θ^i_{CDz}. We wish to use the quadrupolar splittings to obtain the two order parameters, S^R_{zz} and $S^R_{yy} - S^R_{yy}$, which refer to axes x_R, y_R, z_R fixed in the plane of one of the benzene rings. The value of q^i_{CD} was taken to be 186 kHz by comparison with values obtained for deuterons in aromatic compounds [3], and the benzene rings were assumed to be regular hexagons. Thus for both 4-cyano- and 4-bromobiphenyl, $\Delta \nu_{4'}$ gives S^R_{zz} with an uncertainty determined by that of q^i_{CD}, which is no more than ± 3 per cent. The separation between the peaks marked a and a' in figure 5 was taken as a convenient measure of an average value for $\Delta \nu$ for deuterons in positions 2, 3, 5, 6, 2', 3', 5' and 6', and together with an average value of θ_{CDz} of 60° for these positions gives $S^R_{xx} - S^R_{yy}$ with a systematic error which is probably less than 15 per cent.

Figure 6 shows a typical spectrum of the deuterons in 4-methoxy-d$_3$-biphenyl-d$_2$ dissolved in 1-OCB. This comprises a pair of lines from the methyl deuterons, with a separation $\Delta \nu_{\text{Me}}$, overlapping with four lines from the ring deuterons from a combination of a quadrupolar splitting, $\Delta \nu_{\text{Ar}}$, and a dipolar coupling D_{HD} between the deuteron at position 3 and the proton at position 2. The values of $\Delta \nu_{\text{Ar}}$, $\Delta \nu_{\text{Me}}$ and D_{HD} were obtained by recording spectra with the inversion-recovery sequence 180°–τ–90° with τ adjusted to annul the signals from either the methyl or aromatic deuterons; this is easily achieved since the relaxation rates for these two types of deuteron are very different. The value of D_{HD} was used to obtain S^R_{zz} from

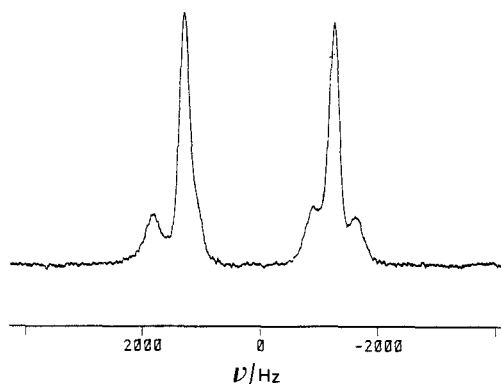$$D_{\text{HD}} = -\gamma_H\gamma_D S^R_{zz}/4\pi^2 r^3_{\text{HD}}. \qquad (2)$$

Figure 6. 30·7 MHz spectrum of deuterons in a sample of 4-methoxy-[^{2}H$_3$]-3,5-[^{2}H]biphenyl dissolved in 1-OCB at $T_{NJ} - T = 1·0$ K.

The factor $\gamma_H \gamma_D / 4\pi^2 r_{HD}^3$ was obtained for pure 1-OCB as 1108 ± 18 Hz by comparing values of D_{HD} with S_{zz}^R determined from D_{HH}, which was obtained by analysis of the proton-{deuterium} spectrum [1]. The quadrupolar splitting $\Delta\nu_{Ar}$ was then used to obtain $S_{xx}^R - S_{yy}^R$ from equation (1) with θ_{CD_z} as $59·7°$, which was also determined from the analysis of data on pure 1-OCB. The methyl quadrupolar splitting was used to obtain S_{xz}^R from

$$\Delta\nu_{Me} = 3q_{Me}\{S_{zz}^R(3\cos^2\theta_{OC} - 1) + (S_{xx}^R - S_{yy}^R)\sin^2\theta_{OC} + 2S_{xz}^R\sin 2\theta_{OC}\}(3\cos^2\alpha - 1)/8. \quad (3)$$

Here α is the angle between the O–C(CD$_3$) bond and the C–D bonds in the methyl group, whilst θ_{OC} is the angle this bond makes with z^R. These angles were again assumed to take the values found for 1-OCB of $\alpha = 70·5°$ and $\theta_{OC} = 55·6°$. The value of q_{Me} was taken to be 168 kHz.

4. Results and discussion

The quadrupolar splittings for biphenyl-d$_{10}$, 4-bromobiphenyl-d$_9$ and 4-cyanobiphenyl-d$_9$ were used with equation (1) to obtain S_{zz}^R and $S_{xx}^R - S_{yy}^R$. The axes $x_R y_R z_R$ are not principal axes for the solute order matrices. The principal axes x, y, z, for biphenyl are such that $z \equiv z_R$ and y is normal to the plane bisecting the two rings, so that x and x_R are at an angle of $\phi/2$, where ϕ is the angle of twist of the two rings. The relationship between $S_{xx} - S_{yy}$ and $S_{xx}^R - S_{yy}^R$ is therefore

$$S_{xx} - S_{yy} = (S_{xx}^R - S_{yy}^R)/\cos\phi. \quad (4)$$

The minimum energy structure for biphenyl in the liquid state has been investigated by comparing observed with calculated dipolar couplings for samples dissolved in liquid-crystalline solvents and found to have a value of about $32°$ if it is assumed that only this structure is populated [4]. Note that allowing for an uncertainty in ϕ of $\pm 2°$ introduces an error into $S_{xx} - S_{yy}$ of about $\pm 2·5$ per cent.

We shall assume that ϕ is $32°$ for each of the solutes, and for the 4-cyano- and 4-bromo-compounds we shall also assume the same location for the principal axes x and y; z is still located as the 4,4'-axis. In the case of 4-methoxybiphenyl the location of the principal axes x, y, z is unknown. It has been assumed by analogy with anisole that the COC and phenyl ring are coplanar. The experiments yield S_{xx}^R, S_{yy}^R and S_{xz}^R, from which it is possible to obtain $S_{z'z'}$ and $S_{x'x'} - S_{y'y'}$, where x', y', z' are principal axes for the
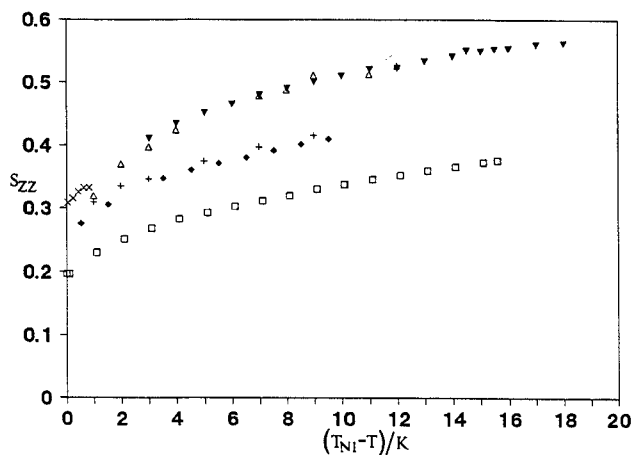
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Figure 7.   Dependence of S_{zz} on the shifted temperature, $T_{NI} - T$, for pure 1-OCB ($\blacktriangledown$), biphenyl ($\square$), 4-cyano-($+$), 4-bromobiphenyl ($\blacklozenge$), and of $S_{z'z'}$ for pure 1-OCB ($\triangle$) and 4-methoxybiphenyl ($\times$).
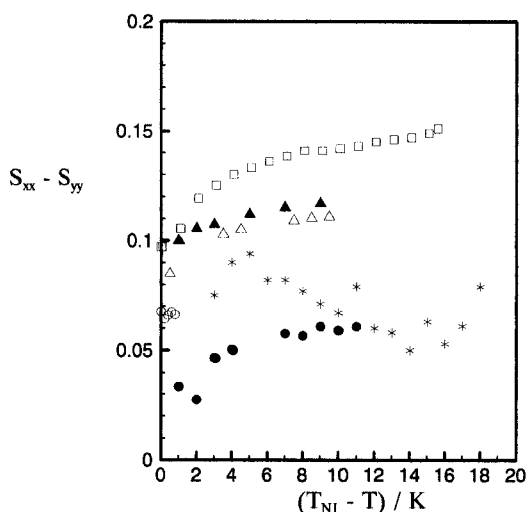

Figure 8.   Dependence of $S_{xx} - S_{yy}$ on the shifted temperature, $T_{NI} - T$, for pure 1-OCB ($*$), biphenyl ($\square$), 4-cyano-($\blacktriangle$), 4-bromobiphenyl ($\triangle$), and of $S_{x'x'} - S_{y'y'}$ for pure 1-OCB ($\bullet$) and 4-methoxybiphenyl ($\bigcirc$).

anisole fragment, and these can be compared with similar order parameters obtained [5] for pure 1-OCB. Maintaining a supercooled nematic phase for 4-methoxybiphenyl-d_5 in 1-OCB was difficult, and spectra could be obtained only within 1°C of T_{NI}.

Figure 7 shows the temperature dependence of S_{zz} and $S_{z'z'}$ for the solutes and for 1-OCB, from which it is apparent that introducing each of the substituents Br, CN or OCH$_3$ into the 4-position of biphenyl increases S_{zz} substantially at a constant shifted temperature $T_{NI} - T$. In order to shed further light on this phenomenon, and also to understand the variation of the biaxial order parameter, $S_{xx} - S_{yy}$, whose dependence on $T_{NI} - T$ is shown in figure 8, with molecular structure, we use the order parameters to

obtain the interaction coefficients, $\epsilon_{2,m}$, in the potential of mean torque, $U(\beta_2\gamma_2)$, for the solute in the nematic solvents. Thus, $U(\beta_2\gamma_2)$ is expressed as [6]

$$U(\beta_2, \gamma_2) = -\epsilon_{2,0}C_{2,0}(\beta_2, \gamma_2) - 2\epsilon_{2,2}\,\mathrm{Re}\,C_{2,2}(\beta_2, \gamma_2), \tag{5}$$

where the $C_{2,m}(\beta_2, \gamma_2)$ are modified spherical harmonics and β_2 and γ_2 are the spherical polar angles made by the mesophase director in the principal molecular frame for the solute ordering matrix. The order parameters are related to $U(\beta_2, \gamma_2)$ by

$$S_{zz} = Q^{-1}\int C_{2,0}(\beta_2, \gamma_2)\exp\{-U(\beta_2, \gamma_2)/kT]\sin\beta_2\,d\beta_2\,d\gamma_2, \tag{6}$$

and

$$S_{xx} - S_{yy} = \sqrt{6}Q^{-1}\int C_{2,2}(\beta_2, \gamma_2)\exp\{-U(\beta_2, \gamma_2)/kT]\sin\beta_2\,d\beta_2\,d\gamma_2 \tag{7}$$

with

$$Q = \int \exp\{-U(\beta_2, \gamma_2)/kT\}\sin\beta_2\,d\beta_2\,d\gamma. \tag{8}$$

The interaction coefficients, $\epsilon_{2,m}$, depend on the solvent order parameters, $\bar{C}_{2,m}$, via

$$\epsilon_{2,0} = \bar{u}_{200}C_{2,0} + 2\bar{u}_{220}\bar{C}_{2,2} \tag{9}$$

and

$$\epsilon_{2,2} = \bar{u}_{202}\bar{C}_{2,0} + 2\bar{u}_{222}\bar{C}_{2,3}. \tag{10}$$

In the simplest molecular field theory, the solute–solvent interaction constants, $\bar{u}_{2mn}$, are averages over the solute–solvent distances, $\mathbf{r}_{ij}$, and are independent of temperature at constant volume. This is consistent with the solute–solvent anisotropic interaction being sufficiently long range that the vectors $\mathbf{r}_{ij}$ have a uniform, spherical distribution. For 1-OCB, $\bar{C}_{2,2}$ is less than 8 per cent of $\bar{C}_{2,0}$ so that to a good approximation,

$$\epsilon_{2,0} = \bar{u}_{200}\bar{C}_{2,0} \tag{11}$$

and

$$\epsilon_{2,2} = \bar{u}_{202}C_{2,0}, \tag{12}$$

and the ratio

$$\lambda = \epsilon_{2,2}/\epsilon_{2,0} = \bar{u}_{202}/\bar{u}_{200}. \tag{13}$$

The observed values of S_{zz} and $S_{xx} - S_{yy}$ enable values of $\epsilon_{2,0}$, $\epsilon_{2,2}$ and an experimental value, λ^{exp}, to be obtained at each temperature. Similarly, $S_{z'z'}$ and $S_{x'x'} - S_{y'y'}$ can be used to obtain $\epsilon'_{2,0}$, $\epsilon'_{2,2}$ and λ'^{exp} for 1-OCB, and for 4-methoxybiphenyl-d_5 dissolved in 1-OCB. Figure 9 shows the temperature dependence of λ^{exp} and λ'^{exp} for the samples studied. Note that λ^{exp} and λ'^{exp} for pure 1-OCB differ as T_{NI} is approached. Part of this difference stems form the systematic errors in $S_{x'x'} - S_{y'y'}$ because of assumptions made in their calculation, but it should also be noted that there is a large, random error in $S_{xx} - S_{yy}$ for pure 1-OCB which stems from the poor quality of the proton spectra, particularly at temperatures close to T_{NI}.

The temperature dependences of λ^{exp} and λ'^{exp} for the samples studied are of the same general shape as those found for other solutes in a wide range of solvents [6–12].
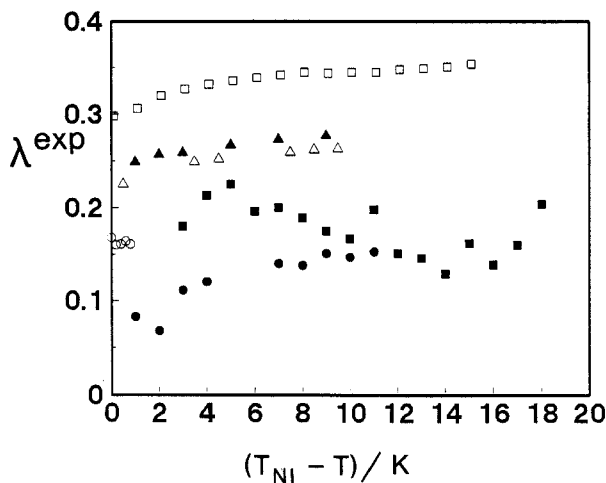
Figure 9.   Dependence on the shifted temperature, $T_{NI} - T$, of λ^{exp} for pure 1-OCB (■), biphenyl (□), 4-cyano-(▲), 4-bromobiphenyl (△) and for λ'^{exp} for pure 1-OCB (●) and 4-methoxybiphenyl (○).

There will be a contribution to this temperature dependence which arises because the samples are at constant pressure, rather than constant volume as assumed in the theory, but the evidence from a study of the pressure and temperature dependence of the ordering of anthracene in a nematic solvent is that this effect does not account for the major part of the temperature dependence [12].

In deriving equation (13) it is assumed that the solvent is rigid and cylindrically symmetric. Both of these are good assumptions for 1-OCB, but not for most mesogens. The similar nature of the temperature dependences of λ^{exp} for all the solute–solvent systems studied so far strongly suggests a common origin for this effect, and therefore it is unlikely that it is a consequence of either molecular flexibility of lack of symmetry. It is more probably the result of more than one interaction making an appreciable contribution to $U(\beta_2, \gamma_2)$, and to a breakdown in some of the assumptions in the simplest molecular field models [13,14].

Despite these reservations about the validity of the simple potential of mean torque, it is useful to extend the analysis of the data to examining the dependence of both $\epsilon_{2,0}$ and $\epsilon_{2,2}$ on the solvent order parameter $C_{2,0}$, which is shown in figure 10 for biphenyl, 4-cyano- and 4-bromobiphenyl. This shows that equation (11) is obeyed to good precision enabling values of $\bar{u}_{200}$ to be obtained for these solute–solvent pairs, and these are given in table 2, where we also give the solvent–solvent interaction coefficient u_{200} for pure 1-OCB. The variations of $\epsilon_{2,2}$ with $\bar{C}_{2,0}$ show significant deviations from linearity, however, averaging the ratios $\epsilon_{2,2}/\bar{C}_{2,0}$ gives a reasonably precise value of $\bar{u}_{202}$, as shown in table 2.

For 4-methoxybiphenyl in 1-OCB we have calculated the ratios $\epsilon'_{2,n}/\bar{C}'_{2,0}$, where $\bar{C}'_{2,0}$ is the major, local order parameter for the anisole fragment of 1-OCB. This can be expected to yield a good estimate for $\bar{u}_{200}$ because $\bar{C}'_{2,0}$ and $\bar{C}_{2,0}$ are almost identical (see figure 7). Thus, calculating the ratio $\epsilon'_{2,0}/\bar{C}'_{2,0}$ for pure 1-OCB yields a value of $\bar{u}_{200} = 13\cdot5 \pm 0\cdot1\,\text{kJ mol}^{-1}$, compared with the value of $13\cdot75 \pm 0\cdot01\,\text{kJ mol}^{-1}$ obtained for $\epsilon_{2,0}/C_{2,0}$. The correspondence between $\epsilon'_{2,2}/\bar{C}'_{2,0}$ and $\epsilon_{2,2}/\bar{C}_{2,0}$ is much worse.
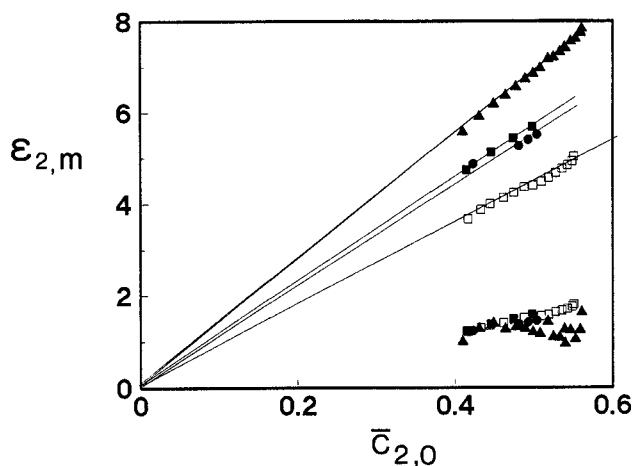
Figure 10. Dependence on the solvent (1-OCB) order parameter, $\bar{C}_{20}$, of $\epsilon_{2,0}$ and $\epsilon_{2,2}$, the solute–solvent interaction coefficients for biphenyl ($\square$), 4-cyano- ($\blacksquare$) and 4-bromo-biphenyl ($\bullet$). Data for pure 1-OCB ($\blacktriangle$) is included for comparison. The lines are drawn to illustrate the linear dependence of $\epsilon_{2,0}$ on $\bar{C}_{2,0}$; the values of $\epsilon_{2,2}$ cluster in the bottom right of the diagram.

Table 2. Interaction parameters $\bar{u}_{20n}$ for the solutes biphenyl, 4-cyano-, 4-bromo- and 4-methoxybiphenyl dissolved in 1-OCB.

Solute	$\bar{u}_{200}/\mathrm{kJ\,mol^{-1}}$	$\bar{u}_{202}/\mathrm{kJ\,mol^{-1}}$
Biphenyl	$8{\cdot}99 \pm 0{\cdot}12$	$3{\cdot}0 \pm 0{\cdot}2$
4-Bromobiphenyl	$11{\cdot}17 \pm 0{\cdot}03$	$2{\cdot}9 \pm 0{\cdot}1$
4-Cyanobiphenyl	$11{\cdot}62 \pm 0{\cdot}04$	$3{\cdot}1 \pm 0{\cdot}1$
4-Methoxybiphenyl	$13{\cdot}4 \pm 0{\cdot}5$	$2{\cdot}2 \pm 0{\cdot}1$
Pure 1-OCB†	$13{\cdot}75 \pm 0{\cdot}07$	$2{\cdot}42 \pm 0{\cdot}36$
	$(13{\cdot}5 \pm 0{\cdot}1)\ddagger$	$(1{\cdot}6 \pm 0{\cdot}2)\ddagger$

† From [1].
‡ Obtained from the orientational order parameters for the anisole fragment.

Thus, for 1-OCB the values are $\epsilon'_{2,2}/\bar{C}'_{2,0} = 1{\cdot}6 \pm 0{\cdot}2\,\mathrm{kJ\,mol^{-1}}$ and $\epsilon_{2,2}/\bar{C}_{2,0} = 2{\cdot}42 \pm 0{\cdot}36\,\mathrm{kJ\,mol^{-1}}$. The estimate for $\bar{u}_{202}$, therefore, for 4-methoxybiphenyl in 1-OCB obtained from the average value of the ratio $\epsilon'_{2,2}/\bar{C}'_{2,0}$ of $2{\cdot}2 \pm 0{\cdot}1\,\mathrm{kJ\,mol^{-1}}$ may be considerably in error.

The surprising feature of the effect on $\bar{u}_{200}$ of introducing substituents into biphenyl is that the introduction of OCH_3 has a larger effect than CN, which is a better mesogenic group [15]. Thus, $\bar{u}_{200}$ for 4-methoxybiphenyl is almost equal to that for pure 1-OCB. The increase in $\bar{u}_{200}$ on introducing CN, Br or OCH_3 into biphenyl can be rationalized in terms of an increase in L/B, the length-to-breadth ratio; both anisotropic dispersion and repulsion are expected to increase with L/B. Thus the value of L/B for 4-methoxybiphenyl is larger than that of L/B for 4-cyanobiphenyl.

The values obtained for $\bar{u}_{202}$ for biphenyl, bromobiphenyl and cyanobiphenyl are identical within experimental error, and the small decrease in $\bar{u}_{202}$ on going to 1-OCB is barely significant and possibly reflects the systematic errors in obtaining values of these interaction parameters.

5. Conclusion

Studies of the orientational order of solutes in the model, fully characterized solvent 1-OCB have the considerable advantage of yielding values of the molecular field interaction parameters $\bar{u}_{200}$ and $\bar{u}_{202}$ rather than just their ratio λ. In the present case this reveals that the decrease in values of λ^{exp} on going from biphenyl to pure 1-OCB is mainly the result of increases in the values of $\bar{u}_{200}$, and can be rationalized in terms of an increase in the length-to-breadth ratio in the series biphenyl $<$ bromobiphenyl $\approx$ cyanobiphenyl $<$ methoxybiphenyl $<$ 1-OCB. It is interesting to note that introducing OCH_3 into biphenyl has a larger effect than CN on $\bar{u}_{200}$.

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