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Solute-solvent interactions in the nematic and smectic A phases of 4,4'-di-*n*-heptylazoxybenzene studied by deutron N.M.R.

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The orientational order parameters have been measured by deutron N.M.R. of both solute (at low dilution) and solvent in various binary mixtures involving the liquid crystal 4,4'-di-*n*-heptylazoxybenzene (HAB). The solutes studied were azoxybenzene- d_{10} and *n*-heptylbenzene- d_7 , which are fragments of HAB, azobenzene- d_{10} because of its similarity to azoxybenzene, and anthracene- d_{10} because of its known structure and symmetric shape. The major and biaxial order parameters of the solutes are analysed in terms of a molecular field model for the potential of mean torque for biaxial particles. The behaviour of the solute order parameters on approaching and entering the smectic A phase is interpreted in terms of a temperature and phase dependent partitioning of the solute between aromatic and aliphatic regions of the solvent.

1. Introduction

The orientational order of solutes dissolved in liquid-crystalline solvents has often been studied because the solute may be chosen so that the effect on orientational order of particular molecular features may be explored. Thus, it is an advantage when testing molecular theories of ordering to study the orientational order of rigid molecules of well-defined symmetry and geometry. Our aim here, however, is to investigate the way in which solute and solvent molecules interact with one another in the case of a liquid crystal solvent which has both nematic and smectic A phases. The particular solvent chosen for study is 4,4'-di-*n*-heptylazoxybenzene (C-S_A 307 K; S_A-N 327 K; N-I 343.9 K), HAB, which has been involved in several investigations of orientational ordering, both as a solvent [1-3] and as a pure liquid crystal. In the preceding article [4] we show how the orientational order of the aromatic rings in HAB may be monitored by deutron N.M.R., a technique which can also be used to study the ordering of solutes and solvent simultaneously.

The stimulus for studying solutes in HAB stems from the observation of an unusual temperature dependence for the order parameters of some solutes in this solvent. A solute such as anthracene- d_{10} when dissolved in HAB has principal order parameters S_{zz} and $(S_{xx} - S_{yy})$ which vary with temperature in a similar manner to that observed for the same solute dissolved in solvents which have only a nematic phase [3], except that there is a more rapid change in the order parameters in the region close to, and centred on, $T_{S_A N}$. A dramatically different behaviour is observed for solutes such as alkylbenzenes and alkanes [5, 6], when the local order parameters reach a maximum close to the smectic A-nematic transition and then decrease as

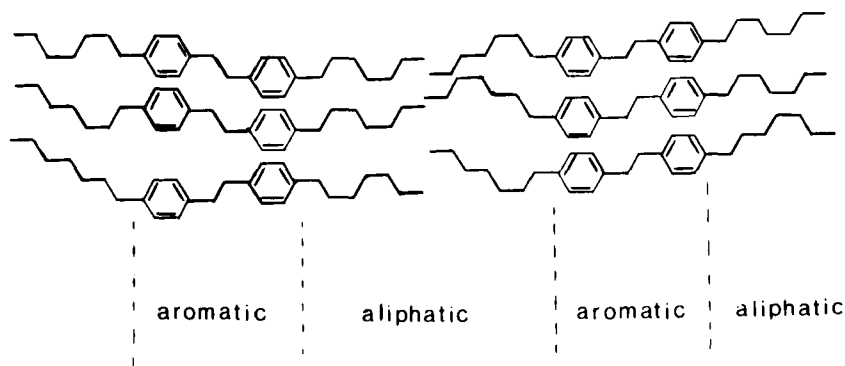


Figure 1. Idealized structure of the smectic A phase of HAB.

temperature is decreased. This unusual behaviour is thought to reflect the layer structure in the smectic A phase. In HAB the layer spacing is of the order of the length of the molecule in its most extended conformation, and this is consistent with the idealized structure of the smectic A phase shown in figure 1; the aromatic cores prefer to be surrounded within a layer with other aromatic cores, and similarly the aliphatic chains prefer themselves as neighbours. The potential of mean torque $U(\Omega_1, z_1)$ for the solvent in the smectic A phase is a function of both Ω , the orientation of the director in the molecular frame, and z_1 , the displacement of the centre of mass along a layer normal. In the nematic phase the potential of mean torque depends only on Ω_1 , so that orientational order parameters are expected to show a discontinuity at $T_{S_A N}$ and to have different temperature dependence in the two phases. In practice the local order parameters of the aromatic rings in HAB do not show a discontinuity but rather a rapid but smooth change, possibly because of a pretransitional development of smectic-like order [4].

A solute molecule may have a preference for aromatic or aliphatic neighbours and hence the nature of its average environment may change markedly on entering the smectic A phase, but now we can expect a greater variation of how the potential of mean torque $U(\Omega_2, z_2)$ differs from its form in the nematic phase. Some solutes could show little or no preference for particular types of neighbours whereas for others the preference will be strong, and hence the temperature dependences of the orientational order parameters of solutes in smectic A phases can be expected, as observed, to depend markedly on the nature of the solute.

To study the microheterogeneity of the smectic A phase in more detail we have measured orientational order parameters of both solute and solvent by deuterium N.M.R. The solvent, HAB, is deuteriated in both aromatic rings and at the two α -methylene positions. Two of the solutes, azoxybenzene and *n*-heptylbenzene, are fragments of the liquid crystal solvent and hence their interaction with HAB can be expected to be related to the way the molecules of HAB interact with each other. Azobenzene- d_{10} was chosen as a solute because of its similarity to azoxybenzene. These three solutes are however all non-rigid and of low symmetry and it is possible to measure only local order parameters, which can be related only approximately to the predictions of theory. We have included, therefore, a solute, anthracene- d_{10} , which is rigid and of sufficient symmetry that the principal axes of its ordering matrix can be located with certainty. It is also similar in size and shape to the aromatic core, and to the core-like solutes. The order parameters of this solute dissolved in HAB have been measured previously [3], but here we shall also measure the ordering

of the solvent which allows a more detailed comparison to be made between theory and experiment.

2. Experimental

The fully deuteriated azoxy and azobenzene were prepared by standard methods from aniline- d_5 [7]. The sample of *n*-heptylbenzene- d_5 was prepared by an exchange reaction with benzene- d_6 catalysed by ethylaluminium-dichloride [8], whilst *n*-heptyl- d_2 -benzene- d_5 was synthesized by acylation of benzene- d_6 and subsequent reduction of the ketone with DCl on zinc amalgam.

The following solutions in HAB + HAB- d_{12} were prepared: 2.4 mole per cent azobenzene- d_{10} ; 3.6 mole per cent azoxybenzene- d_{10} ; 7.5 mole per cent *n*-heptyl- d_2 -benzene- d_5 ; approximately 15 mole per cent *n*-heptylbenzene- d_5 ; 1.8 mole per cent anthracene- d_{10} .

The deuteron spectra were recorded on a Bruker CXP 200 spectrometer at 30.7 MHz.

3. Spectral analysis

A deuteron spectrum of azobenzene- d_{10} in HAB is shown in figure 2 and the structure and atomic labelling in figure 3. The deuterons in positions 4 and 4' give the largest quadrupolar splittings, peaks a, a', and do not have any resolvable structure from dipolar coupling to other deuterons. The assignment of these peaks is unambiguous because of their intensity relative to that of peaks b, b' which stem from the deuterons at positions 2, 3, 5, 6 and 2', 3', 5' and 6'. The deuterons 2, 6, 2', 6' are equivalent to one another because of rapid 180° ring flips, but their equivalence with deuterons 3, 5, 3', 5' is accidental. The same near equivalence of deuterons at these positions has been observed for the liquid crystal 4,4'-di-*n*-heptyl-azobenzene [4]. The dipolar couplings $\tilde{D}_{23} = \tilde{D}_{2'3'}$ (which are equal to \tilde{D}_{56} and $\tilde{D}_{5'6'}$) are large compared with all other inter-deuteron couplings, and in addition are larger than the difference, if any, between the quadrupolar splittings of deuterons 2 and 3. This can be inferred from the shape of the peaks b, b', which also shows that $\Delta\tilde{\nu}_2$ and $\Delta\tilde{\nu}_3$ are of opposite sign to \tilde{D}_{23} .

A spectrum from a sample of azoxybenzene- d_{10} dissolved in HAB is shown in figure 4; it reflects the lower symmetry of this solute compared with azobenzene. Thus,

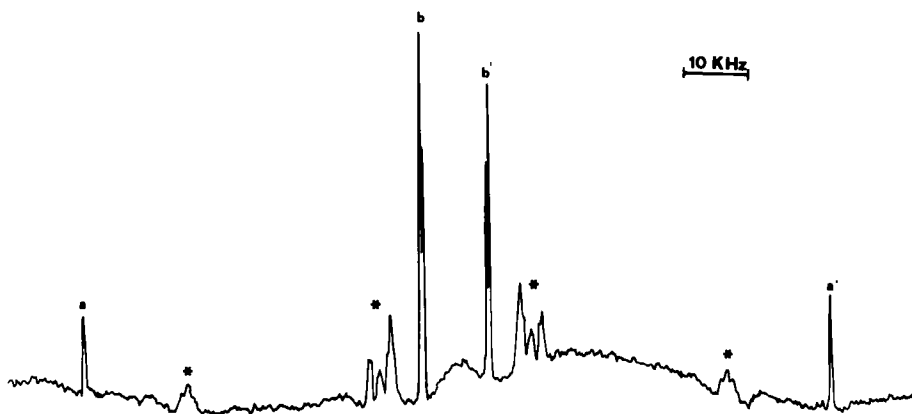


Figure 2. 30.7 MHz N.M.R. spectrum of deuterons in azobenzene- d_{10} dissolved in HAB + HAB- d_{12} . Peaks marked with * are from deuterons in HAB- d_{12} .

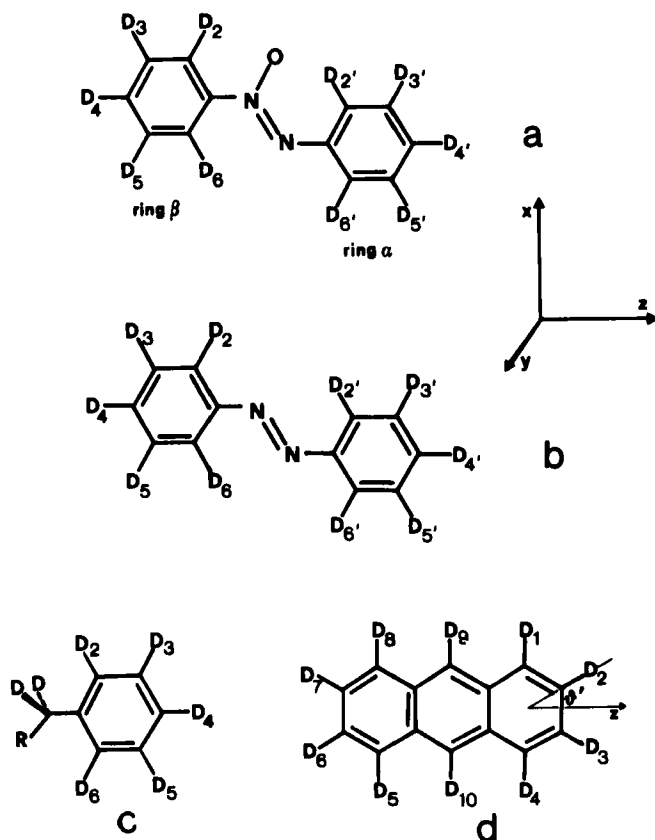


Figure 3. Structure, atomic labelling and location of axes for (a) azoxybenzene, (b) azobenzene, (c) *n*-heptylbenzene and (d) anthracene.

the deuterons 4 and 4' are no longer equivalent and give quadrupolar doublets a,a' and b,b'. The rest of the deuterons give rise to the groups of peaks c,c', d,d' and e,e'. The peaks d,d' and e,e' have intensities and spacings which allow us to assign them as being from four deuterons in one ring, and on the assumption that proximity to oxygen is the major factor in changing $\Delta\tilde{\nu}$ values in this molecule, then we assign them to ring β . Thus, $\Delta\tilde{\nu}_2 = \Delta\tilde{\nu}_6 \neq \Delta\tilde{\nu}_3 = \Delta\tilde{\nu}_5$, and the fine structure is caused by $\tilde{D}_{2,3} = \tilde{D}_{5,6}$. The four deuterons in ring α have accidentally equal quadrupolar splittings and give the peaks c,c'. The spectrum from the ring deuterons in azoxybenzene is therefore of the same form as that from the corresponding deuterons in the solvent HAB [4], but with smaller quadrupolar and dipolar splittings so that, as shown in figure 4, the two spectra do not overlap. We can also deduce that the quadrupolar splittings of the aromatic deuterons are all of opposite sign to the dipolar couplings \tilde{D}_{23} and $\tilde{D}_{2,3}$, which we expect to be negative, so that the quadrupolar splittings are positive.

The deuteron spectrum of *n*-heptyl- α - d_2 -benzene- d_5 in HAB shows three sets of quadrupolar splittings which can be assigned unambiguously because of their relative intensities. The deuterons at positions 2, 3, 5 and 6 give rise to one, unresolved quadrupolar doublet and it is not possible from the spectrum to determine the relative sign of $\Delta\tilde{\nu}_4$ and $\Delta\tilde{\nu}_2 = \Delta\tilde{\nu}_3 = \Delta\tilde{\nu}_5 = \Delta\tilde{\nu}_6$. To resolve this problem we recorded the

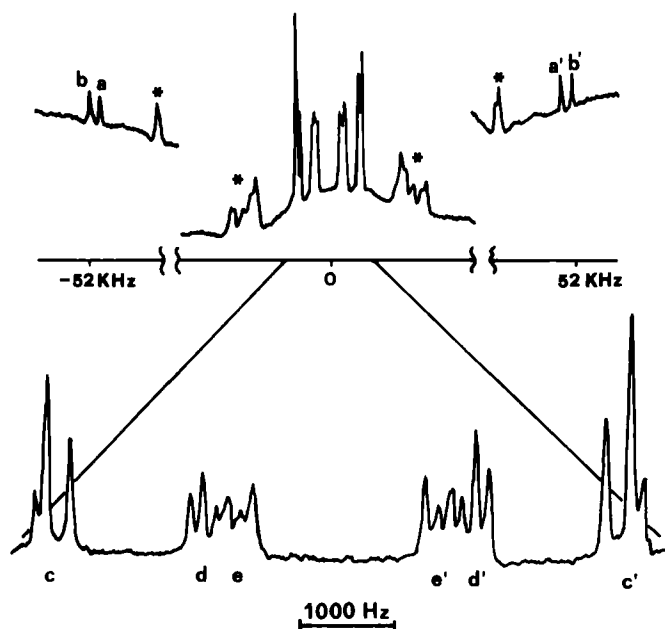


Figure 4. 30.7 MHz N.M.R. spectrum of deuterons in azoxybenzene- d_{10} dissolved in HAB + HAB- d_{12} . The peaks marked with * are from deuterons in HAB- d_{12} .

spectrum of *n*-heptyl-benzene- d_5 in the same solvent and improved the resolution on the peaks resulting from ortho and meta deuterons (peaks a, a' in figure 5) by recording an echo spectrum [9]. The pulse sequence $90_x^\circ-t-180_x^\circ-t$ -echo was applied to the deuterons in a sample of *n*-heptylbenzene- d_5 dissolved in HAB. One sample point was taken at a time $2t$ from the application of the 90° pulse and an interferogram $S(t)$ developed by incrementing t in equal steps. The Fourier transform of $S(t)$ yielded the echo spectrum shown as the lowest trace in figure 5, and which now clearly shows structure on the quadrupolar doublet from dipolar coupling $\tilde{D}_{23} = \tilde{D}_{56}$; from the intensities we conclude that $\Delta\tilde{\nu}_2 = \Delta\tilde{\nu}_3$, and is opposite in sign to this dipolar coupling.

The deuteron spectrum of anthracene- d_{10} in HAB is shown in figure 6 and has been analysed previously [3]. There is a large splitting from the group of four equivalent deuterons 2, 3, 6 and 7, and the remaining six deuterons, whilst not all equivalent, give in HAB an unresolved doublet so that only a single, averaged quadrupolar splitting can be measured for these positions.

4. Measurement of order parameters

The solutes which we have studied, and HAB itself, apart from anthracene, are all non-rigid and hence the quadrupolar and dipolar splittings can yield only local order parameters, S^L [10]. For azo- and azoxybenzene and *n*-heptylbenzene we locate axes in individual phenyl rings, as shown in figure 3. Rapid motion of the molecules about the para axes of the phenyl groups means that for each of these molecules the quadrupolar and dipolar couplings are averages over the values in individual conformers, and the symmetry of the rotational potential, assuming the molecules to be rigid rotors, gives the relationship between the quadrupolar splittings and the local

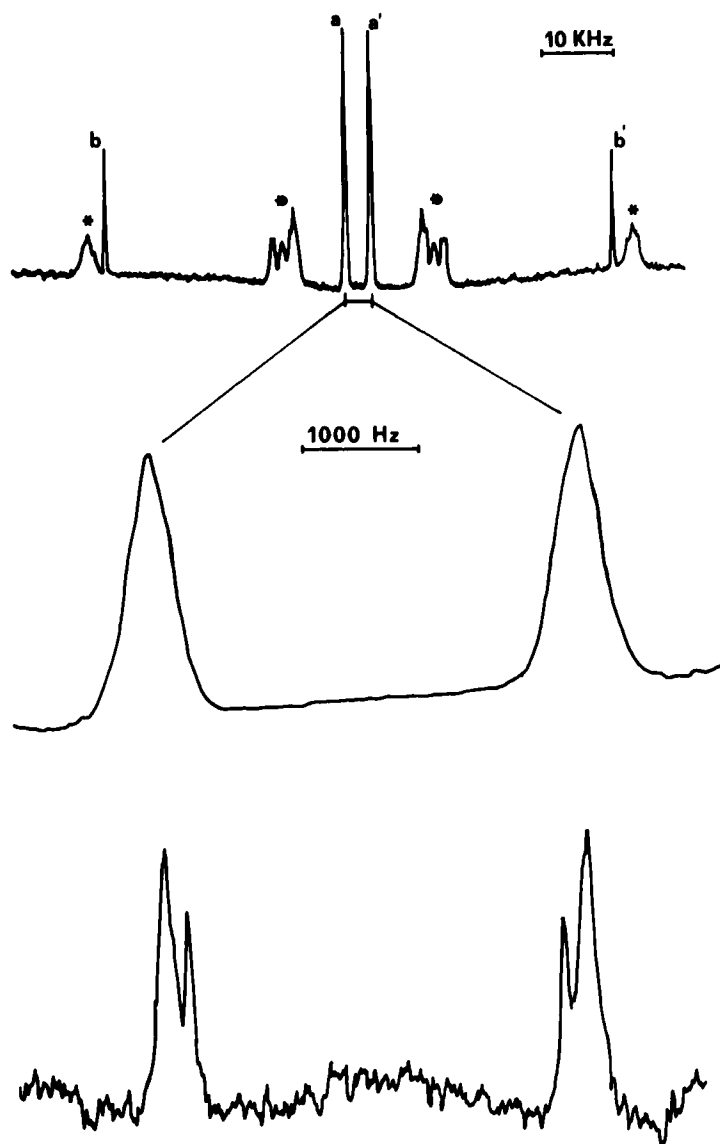


Figure 5. 30.7 MHz spectrum of partially deuteriated *n*-heptylbenzene- d_5 dissolved in HAB + HAB- d_{12} ; the peaks marked with * are from HAB- d_{12} . The top trace is the full spectrum whilst the middle trace is an expansion of the centre pair of peaks a,a'. The lower trace is a spin echo spectrum of the d_5 compound. It is the result of Fourier transforming the interferogram obtained by incrementing t in the sequence $90_x^\circ-t-180_x^\circ-t$ -echo. The spectral window was chosen so as to include only the peaks from the ortho and meta deuterons.

order parameters as

$$\Delta\tilde{\nu}_i = (3/2)q_{bb}[S_{zz}^L\{3I_{zbi}^2 - 1 + \eta^i(I_{zai}^2 - I_{zci}^2)\}/2 + (S_{xx}^L - S_{yy}^L)\{I_{xbi}^2 - I_{ybi}^2 + \eta^i(I_{xai}^2 - I_{yci}^2 - I_{yai}^2)/3\}/2]. \quad (1)$$

The principal axes of the quadrupole tensor at the i th site are denoted as abc with b along the i th C-D bond and c parallel to the ring normals, and the $I_{\alpha\beta i}$ etc. are the

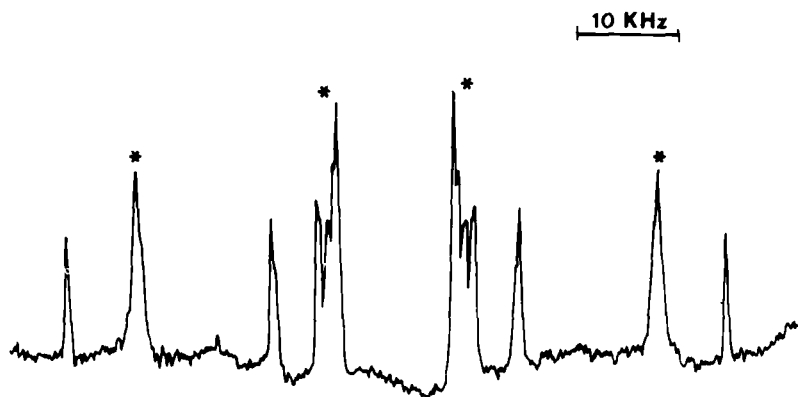


Figure 6. 30.7 MHz spectrum of deuterons in a sample of anthracene- d_{10} dissolved in HAB + HAB- d_{12} . The peaks marked with * are from HAB- d_{12} .

direction cosines between axes α and β . The values of the quadrupolar coupling constant, q_{bb} , for the aromatic deuterons, except those in anthracene, is taken to be 185 kHz at all positions, whereas the asymmetry parameter $\eta = (q_{aa} - q_{cc})/q_{bb}$ is taken to be 0.04 [11]. For anthracene we use the values determined by Ellis and Bjorkstam [12] of 181 kHz and 0.064 respectively.

There has been a study of the crystal and molecular structure of azobenzene [13], but the positions of the hydrogen atoms were not located; the phenyl rings were found to be essentially undistorted from a regular hexagon. There have not been any structural studies reported on the other two compounds and we have therefore assumed a regular geometry for the rings in azo-, azoxy- and heptylbenzene with the CCD angles as 120° , unless the N.M.R. spectrum suggests a distorted structure.

The only case where the deuteron spectrum does indicate that there is a distortion from this geometry is for ring β of azoxybenzene, in which $\Delta\tilde{\nu}_2 \neq \Delta\tilde{\nu}_3$, so that if the quadrupolar tensors for these two positions are identical in magnitude, as we assume, then the angles between the C-D bonds and the x axis must differ. Note that our assumption about the quadrupolar tensors may also be incorrect but this will make little difference to the error in our calculation of local order parameters. Choosing the angle to be 30° for the C-D (3') bond, as argued for the same position in the same ring fragment in HAB [4], and assigning $\Delta\tilde{\nu}_2 < \Delta\tilde{\nu}_3$, also as in HAB, then we obtain a value of 30.4° for the angle between C-D (2') and x . The distortion from a regular geometry for ring β is small, but note that it is opposite in sign to that deduced for the same position in HAB.

The geometry of anthracene in the solid state has been investigated by neutron diffraction [14, 15], and we use the angles obtained to derive S_{zz} and $(S_{xx} - S_{yy})$. The angle between C-D (2) and z was found to be 29.3° , rather than 30° if the structure was the idealized one used for the other solutes, and we have also calculated the order parameters with this standard geometry. The two calculations give essentially the same values of S_{zz} , but the idealized geometry gives $(S_{xx} - S_{yy})$ as 8-14 per cent larger depending on the temperature. Systematic errors of this magnitude could therefore be present in the values we have derived for the solute order parameters, even in the case of anthracene whose structure in the liquid phase may differ from that in the solid; however errors of this magnitude do not affect the conclusions that we reach.

5. Results and discussion

Our principal aim is to compare the ordering of the solutes with each other and with that of the solvent HAB. The latter is non-rigid and we characterize its orientational order with local ordering matrices $\mathbf{S}^{R\alpha}$ and $\mathbf{S}^{R\beta}$ whose elements are defined with respect to axes fixed in the α and β aromatic rings, as discussed in the preceding paper. Within the precision with which we can measure the elements of the ordering matrices for HAB, the biaxialities of $\mathbf{S}^{R\alpha}$ and $\mathbf{S}^{R\beta}$ are zero. Moreover, $S_{zz}^{R\beta} > S_{zz}^{R\alpha}$ at all temperatures in the liquid crystal phases and we shall use $S_{zz}^{R\beta}$ as a measure of the order of the whole molecule since this will be closer in value to either S_{zz}^R , the major principal component of the local ordering matrix for the aromatic core of HAB, or to $\langle S_{zz} \rangle$, the major principal component of the average ordering matrix,

$$\langle \mathbf{S} \rangle = \sum_n p_n \mathbf{S}^n, \quad (2)$$

where p_n is the statistical weight of the n th conformer with ordering matrix \mathbf{S}^n .

The ordering matrices for the solutes are not axially symmetric, and for anthracene we measure S_{zz} and $(S_{xx} - S_{yy})$, the two principal order parameters for the molecule, whereas for the other molecules we obtain the principal elements of local ordering matrices of phenyl rings, \mathbf{S}^R . We do not know the relationship between \mathbf{S} and \mathbf{S}^R for azo and azoxybenzene, and hence our interpretation of the ordering of these molecules is necessarily less exact than for anthracene.

In figure 7 we show the major order parameters for HAB and the solutes as a function of reduced temperature T/T_N . For the mixtures there is, as expected, a region where nematic and isotropic phases coexist and T_N is the temperature at which an isotropic component first appears. The continuous line in figure 7 is the variation of $S_{zz}^{R\beta}$ for pure HAB and there are small but significant deviations from this curve for this order parameter in the mixtures. Part of this discrepancy results from the difficulty in locating T_N , which in these experiments was obtained to within 1°C. A more significant discrepancy occurs at T_{SN} where for pure HAB there is a marked change in the slope of the order parameter temperature profile. The values of T_{SN} for the mixtures were not obtained independently of the N.M.R. measurements, but these temperatures can be located approximately by noting the change in slope of the temperature dependence of S_{zz} for both HAB and the solutes which occurs for all samples near the value of $T_{S_{AN}}/T_{NI}$ for pure HAB. This change in slope is diminished for HAB in the mixtures relative to the pure solvent, and has virtually disappeared when *n*-heptylbenzene is the solute. There was no evidence of the formation of a region where nematic and smectic A phases coexist, possibly because such a biphasic region is very narrow, but it is also possible that this region is undetected because the deuteron spectra in the two phases are not sufficiently different.

Even allowing for the use of local rather than total order parameters it is clear that the solutes align less well in HAB than does the liquid crystal itself. Before discussing this in more detail we turn our attention first to the variation of $(S_{xx} - S_{yy})$ with S_{zz} for the solutes, which we show in figure 8. The curves for anthracene and azoxybenzene are similar to those found for solutes in nematic phases [2, 3] and no change is apparent at $T_{S_{AN}}$. This is not true however for *n*-heptylbenzene, which shows a major change on entering the smectic A phase [5], and to a lesser extent a similar effect is seen for azobenzene. To obtain an insight into the possible causes of this change in behaviour we analyse the data to yield coefficients which are a measure of the strength of the solute-solvent interactions. To do so we use the molecular field theory

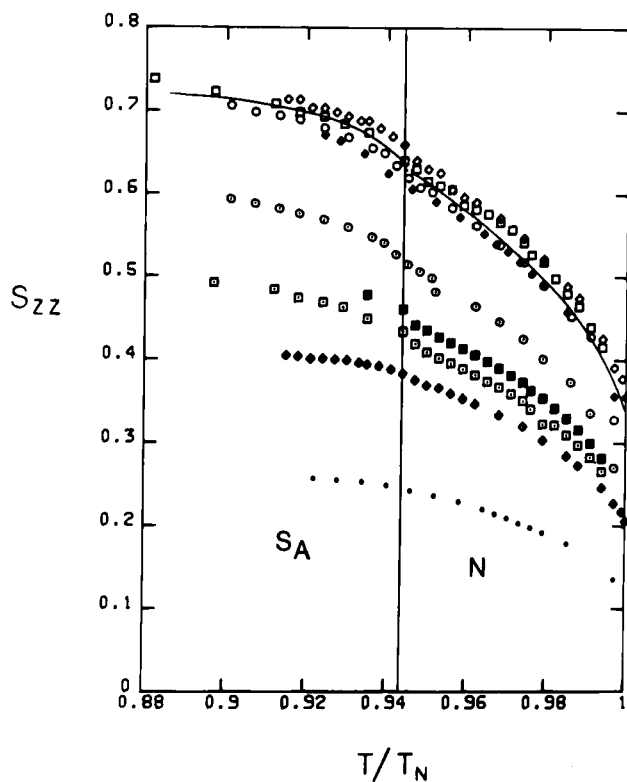


Figure 7. Major order parameter S_{zz} , or S_{zz}^R , and its dependence on reduced temperature T/T_N for: HAB- d_{12} (\circ) and anthracene (\circ); HAB- d_{12} (\square) and azobenzene (\square); HAB- d_{12} (\blacklozenge) and n -heptylbenzene (\bullet); HAB- d_{12} (\diamond) and azoxybenzene (\diamond) ring α , \blacksquare ring β). The continuous curve represents the temperature dependence of $S_{zz}^{R\beta}$ for pure HAB- d_{12} , and the vertical line marks $T_{S_{AN}}$ for pure HAB.

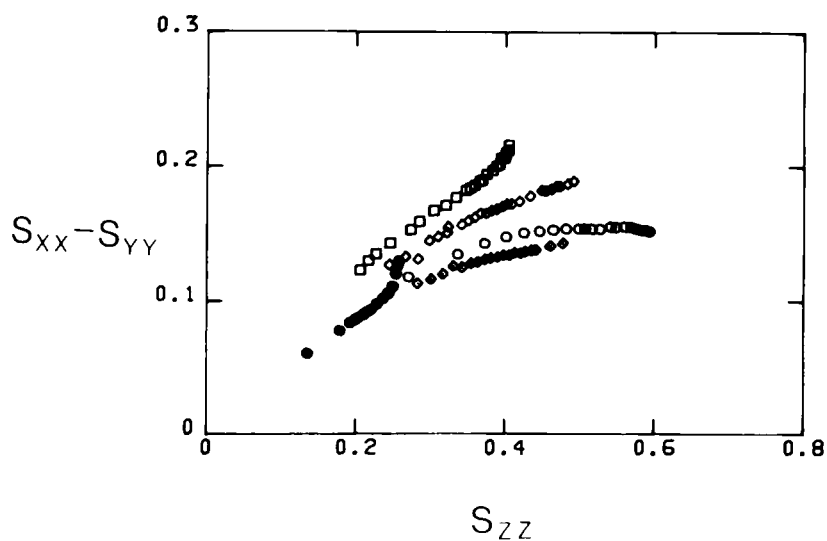


Figure 8. Dependence of $(S_{xx} - S_{yy})$ on S_{zz} for anthracene (\circ), and of $(S_{xx}^R - S_{yy}^R)$ against S_{zz}^R for azobenzene (\square), azoxybenzene (\diamond ring α , \blacklozenge ring β) and n -heptylbenzene (\bullet).

developed by Luckhurst *et al.* [16] to describe the properties of uniaxial liquid crystals comprised of rigid biaxial molecules, and modified by Emsley *et al.* [2] to describe the behaviour of solutes dissolved in these phases.

The theory expresses the potential of mean torque $U(\beta\gamma)$ to terms in second rank as

$$U(\beta\gamma) = -kT \{a d_{00}^2(\beta) + b d_{02}^2(\beta) \cos 2\gamma\}, \quad (3)$$

where β and γ are spherical polar angles describing the orientation of the director in the molecular frame which diagonalizes \mathbf{S} , and the $d_{0m}^2(\beta)$ are elements of the reduced Wigner rotation matrices. The two coefficients a and b take on different meanings depending on whether we are describing the potential of mean torque of the pure solvent, or of a solute effectively at infinite dilution. Thus for the pure solvent

$$a_{\text{LC}} = -(\bar{u}_{200}^{\text{LC}} \bar{C}_{2,0} + 2\bar{u}_{220}^{\text{LC}} \bar{C}_{2,2})/kT \quad (4)$$

and

$$b_{\text{LC}} = -2(\bar{u}_{220}^{\text{LC}} \bar{C}_{2,0} + 2\bar{u}_{222}^{\text{LC}} \bar{C}_{2,2})/kT, \quad (5)$$

where $\bar{C}_{2,0}$ and $\bar{C}_{2,2}$ are the principal order parameters for the liquid crystal molecules expressed as averages of reduced spherical harmonics. The coefficients $\bar{u}_{2mn}^{\text{LC}}$ are averages over the radial distribution function of the anisotropic intermolecular interactions. For HAB our experiments suggest that b_{LC} and $\bar{C}_{2,2}$ are small and can be neglected (see the preceding paper). For solutes at infinite dilution the two coefficients are still dependent on the order parameters of the solvent alone, so that when $\bar{C}_{2,2}$ is negligible we obtain,

$$a_s = -\bar{u}_{200}^s \bar{C}_{2,0}/kT, \quad (6)$$

$$b_s = -2\bar{u}_{202}^s \bar{C}_{2,0}/kT, \quad (7)$$

and the coefficients \bar{u}_{2mn}^s depend upon solute-solvent interactions alone; the subscripts m and n refer to the solvent and solute respectively. The ratio $\lambda = b_s/2a_s$ is expected to be temperature independent, and its value for a particular solute should determine the dependence on S_{zz} of $(S_{xx} - S_{yy})$ [1]. Studies on several solutes dissolved in a range of liquid crystal solvents, including HAB, have shown that the dependence of $(S_{xx} - S_{yy})$ on S_{zz} is usually close to that predicted with temperature independent values of λ , but that there are significant deviations from the theoretical curves; these deviations are similar to that observed in figure 8. At each temperature for a particular solute the two measured order parameters S_{zz} and $(S_{xx} - S_{yy})$ can be used to obtain λ_{eff} , an effective value of the biaxiality in $U(\beta\gamma)$. The dependence on T/T_N of these effective λ values is shown in figure 9 which demonstrates more clearly the similar behaviour in the nematic phase and the differences in the smectic A phase of the solutes. This suggests that the dependence of λ_{eff} on temperature in the nematic phase has a common origin which is mainly determined by the nature of the liquid crystal solvent, whereas the change in behaviour in the smectic A phase is determined by properties of the solute. We note, however, that the change from nematic-like to smectic-like behaviour of λ_{eff} is continuous and for *n*-heptylbenzene there is a strong pretransitional effect.

To pursue our analysis further we note that equations (6) and (7) predict a linear dependence on $\bar{C}_{2,0}$ of $a_s kT$ and $b_s kT$. The order parameter $S_{zz}^{R\beta}$ is a good approximation to $\bar{C}_{2,0}$ and we show in figure 10 the variation of $a_s RT$ and $b_s RT$ for the four solutes with this order parameter. We note first that for all the solutes

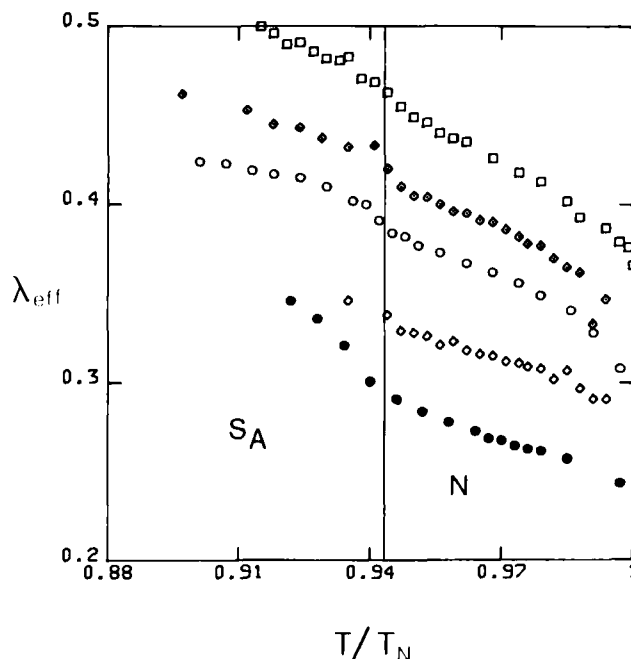


Figure 9. Dependence of λ_{eff} on T/T_N for anthracene (\circ), azobenzene (\square), azoxybenzene (\diamond α , and \diamond β) and *n*-heptylbenzene (\bullet) in HAB. The vertical line at $T/T_N = 0.941$ marks $T_{S_A N}$ for pure HAB.

there is an approximately linear relationship between $S_{zz}^{R\beta}$ and $a_s RT$ which passes through the origin. This is shown for all the solutes together in figure 11, where the straight lines connect the origin with the point at highest temperature; we shall return to a discussion of these slopes later. The coefficient $b_s RT$ shows a non-linear variation with $S_{zz}^{R\beta}$ for all the solutes in the nematic phase, but like $a_s RT$ it does not show any significant change in behaviour with $S_{zz}^{R\beta}$ in the vicinity of $T_{S_A N}$ even though this order parameter is changing rapidly in this temperature range.

We concentrate our discussion first on the behaviour of anthracene. For this solute both $a_s RT$ and $b_s RT$ show an increasing deviation from the linear dependence on $S_{zz}^{R\beta}$ as the temperature is lowered into the smectic A phase. It is possible that this behaviour reflects an increasing magnitude of $\bar{C}_{2,2}$ for HAB, but this is unlikely since theory predicts this order parameter to decrease when $\bar{C}_{2,0}$, and hence $S_{zz}^{R\beta}$, is greater than 0.5. It is more probable that the marked increase in non-linearity observed in figure 10 reflects a change in the average environment experienced by the solute. If we consider HAB to be comprised of aromatic and aliphatic parts, and the parameters $a_s RT$ and $b_s RT$ to depend on interactions of anthracene with these parts, then we express equations (6) and (7) as

$$a_s = -\{x \bar{u}_{200}^{sa} \bar{C}_{2,0}^a + (1-x) \bar{u}_{200}^{sc} \bar{C}_{2,0}^c\} / RT, \quad (8)$$

$$b_s = -2\{x \bar{u}_{202}^{sa} \bar{C}_{2,0}^a + (1-x) \bar{u}_{202}^{sc} \bar{C}_{2,0}^c\} / RT. \quad (9)$$

Here \bar{u}_{200}^{sa} and \bar{u}_{220}^{sa} measure the strength of the interaction of the anthracene with the aromatic core whilst \bar{u}_{200}^{sc} and \bar{u}_{220}^{sc} relate to the interaction with the aliphatic chains of HAB, and x is the probability that anthracene is interacting with the core. $\bar{C}_{2,0}^a$ is the major local order parameter for the aromatic core and is given to a good approximation

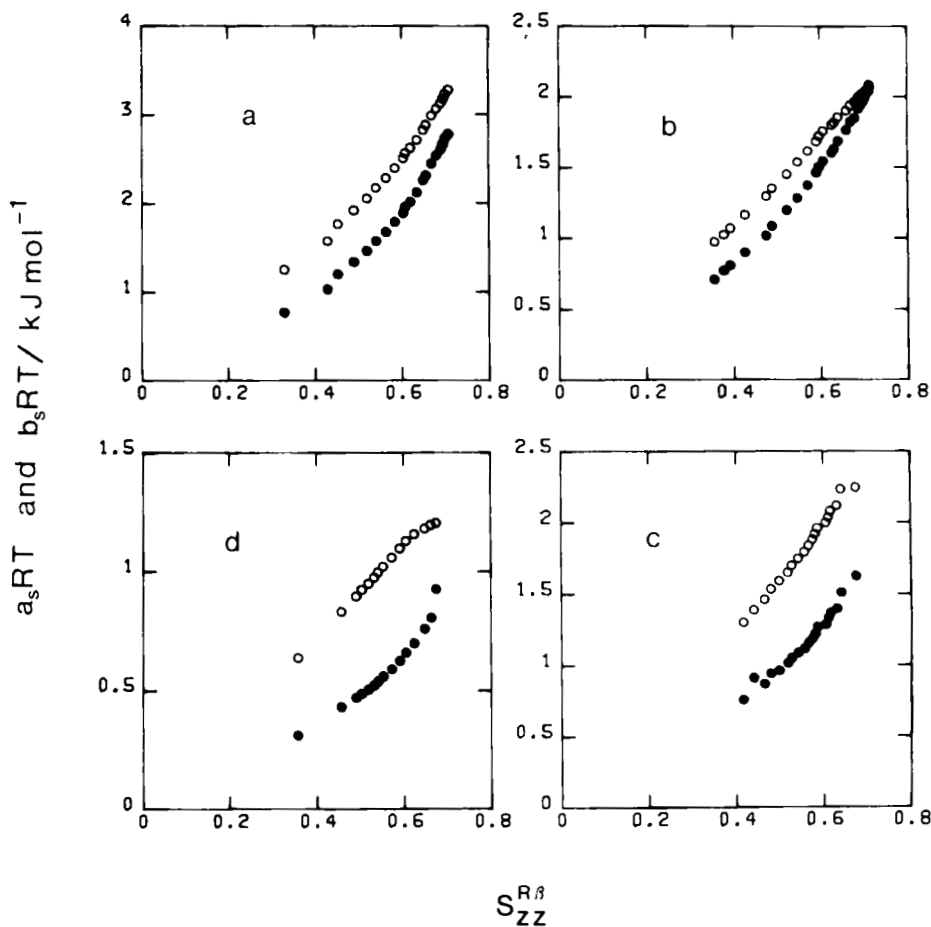


Figure 10. The variation of $a_s RT$ (○) and $b_s RT$ (●) with $S_{zz}^{R\beta}$, the major order parameter for the β ring in HAB, for (a) anthracene, (b) azobenzene, (c) azoxybenzene (ring β) and (d) *n*-heptylbenzene.

by $S_{zz}^{R\beta}$. The order parameter $\bar{C}_{2,0}^c$ is an average for the aliphatic chains over all conformations, which we expect on the basis of calculations on flexible liquid crystals [17] to be linearly related to $\bar{C}_{2,0}^a$. If the solute has no specificity for the two sections of the solvent when x will reflect the volume fraction of the core and will be essentially temperature independent. In this case $a_s RT$ and $b_s RT$ should be linear in $S_{zz}^{R\beta}$, whereas a curvature will be introduced if x varies with temperature which will be different for $a_s RT$ and $b_s RT$, as observed. The continuous nature of the curves in figure 10 suggests that the solutes begin to show a temperature dependent preference for the core or chains of HAB in the nematic phase and that this preference becomes steadily more pronounced in the smectic A phase.

In comparing the behaviour of the four solutes in HAB we concentrate first on $a_s RT$. We expect $\bar{C}_{2,0}^a > \bar{C}_{2,0}^c$, and for the wholly aromatic solutes we expect $\bar{u}_{200}^a > \bar{u}_{200}^c$, so that the upward curve for the dependence on $S_{zz}^{R\beta}$ of $a_s RT$ for anthracene and azoxybenzene suggests that x increases as temperature decreases and these solutes prefer to be close to the aromatic cores in the smectic A phase. The dependence of $a_s RT$ on $S_{zz}^{R\beta}$ for azobenzene is close to being linear throughout both nematic and

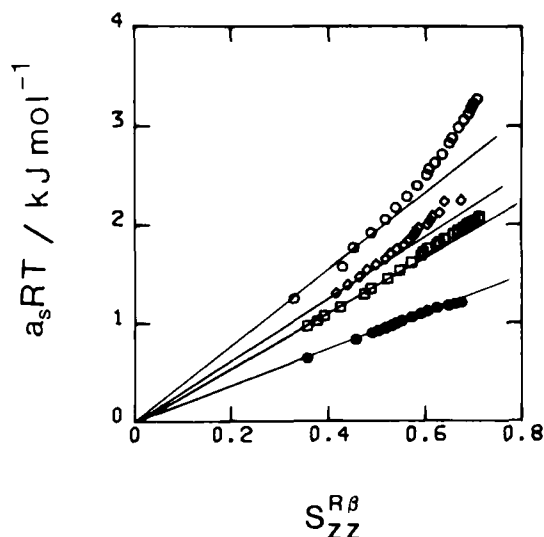


Figure 11. Dependence of $a_s RT$ on $S_{ZZ}^{R\beta}$ for anthracene (O), azobenzene (□), azoxybenzene (ring β (◇)) and *n*-heptylbenzene (●) in HAB. The straight lines pass through the origin and the point at the lowest value of $S_{ZZ}^{R\beta}$.

smectic A phases, which indicates that this solute does not discriminate between aromatic and aliphatic regions. The downward curvature of $a_s RT$ against S_{ZZ}^R for *n*-heptylbenzene suggests that for this solute x decreases with a temperature decrease so that a preference for the aliphatic region develops in the smectic A phase.

The straight lines in figure 11 have slopes which are given approximately as $[x\bar{u}_{200}^{sa} + (1-x)\bar{u}_{200}^{sc}\bar{C}_{2,0}^c/\bar{C}_{2,0}^a]$ and their relative values for the different solutes reflect differences in both the strength of solute-solvent interactions and the probability that the solute has an aromatic core of HAB as a neighbour. We expect x to approach similar values for these solutes as $S_{ZZ}^{R\beta}$ decreases (and hence temperature increases) because they are similar in size. In this case the slopes, whose values are given in the table, change because the interaction constants \bar{u}_{200}^{sa} and \bar{u}_{200}^{sc} increase in the order anthracene > azoxybenzene > azobenzene > *n*-heptylbenzene. The interaction of azobenzene and azoxybenzene with HAB are clearly very similar, and their apparently weaker interaction than anthracene may be, in part, a consequence of deriving $a_s RT$ for the two non-rigid solutes from local rather than total order parameters.

Slopes of the dependence of $a_s RT$ on the solvent order parameter $S_{ZZ}^{R\beta}$ for solutes in HAB.

	Slope/kJ mol ⁻¹
Anthracene	5.3
Azobenzene	2.7
Azoxybenzene ring α	3.0
ring β	3.2
<i>n</i> -heptylbenzene	1.8

The heptyl chain in *n*-heptylbenzene can adopt 243 conformations, many of which deviate considerably in shape from the elongated form of the most probable rotational isomer, the all-trans form. The interactions which determine the magnitude of \bar{u}_{200}^{sa} and \bar{u}_{200}^{sc} are expected to be shape dependent so that there are three factors contributing

to the value of the slope of $a_s RT$ against $S_{zz}^{R\beta}$ for this solute: the strength of the interactions in each conformer, the value of x in each conformer, and the nature of the conformational average.

The coefficients $b_s RT$ for all the mixtures studied show a similar upward curve as $S_{zz}^{R\beta}$ increases, so that if our explanation for the dependence of $a_s RT$ with this order parameter is correct, this means that the biaxiality in the solute-solvent potential of mean torque increases independently of whether the solute prefers to interact with the aromatic cores or the aliphatic chains. This is not impossible, but it does seem to be rather surprising. An alternative explanation of the curved nature of the dependence of $b_s RT$ on $S_{zz}^{R\beta}$ is that this coefficient is more sensitive to general defects in the potential of mean torque, such as our neglect of the biaxiality and flexibility of the solvent molecules, and the truncation of the potential of mean torque at the second rank term.

6. Conclusion

When studying liquid-crystalline mixtures it is clearly an advantage to be able to monitor the orientational order of both solute and solvent simultaneously. For some solutes in HAB, such as *n*-heptylbenzene, the dependence of the solute order parameters on temperature does indicate that an unusual change occurs in the solute-solvent interaction on entering the smectic A phase. For others, such as anthracene, the solute order parameters are not so informative, but the dependence on solvent ordering of the quantities $a_s RT$ and $b_s RT$, which determine the magnitude of the potential of mean torque for the solute, reveals that changes in the nature of the solute-solvent interaction do take place as the smectic A phase is approached and entered even for this solute. Our explanation of these changes as stemming from a different interaction between the solute and the core and chains of the liquid crystal is undoubtedly an over-simplification. A more realistic treatment would take into account a continuous variation of the solute-solvent interaction with the relative positions of solute and liquid crystal molecules in the two phases, and also with the distance along the direction of a layer normal in the smectic phase.

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