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Orientational order in nematic and smectic A phases of three closely related compounds

4,4′-di-*n*-heptylazobenzene, 4,4′-di-*n*-heptyl- and 4,4′-di-*n*-octylazoxybenzene

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The orientational ordering in the three related compounds 4,4′-di-*n*-heptyl-d_2-azobenzene-d_8 (HB-d_{12}), 4,4′-di-*n*-heptyl-d_2-azoxybenzene-d_8 (HAB-d_{12}) and 4,4′-di-*n*-octyl-d_2-azoxybenzene-d_8 (OAB-d_{12}) has been monitored using deuteron N.M.R. spectroscopy. In these non-rigid molecules it is possible to obtain only the elements of local order matrices. For the aromatic rings these are found to be axially symmetric within the precision of our measurements. The temperature dependences of the local order parameters for the aromatic rings are compared with those predicted by McMillan's theory of smectic A phases.

1. Introduction

There have been a number of studies of the orientational order of solutes dissolved in 4,4′-di-*n*-heptylazobenzene (HAB), a liquid-crystalline solvent which exhibits both nematic and smectic A phases (C–S_A 307 K; S_A–N 327·0 K; N–I 342·9 K) [1–4]. An unusual behaviour has been observed for some solutes in that their major order parameters decrease on lowering the temperature in the smectic A phase. For rigid solutes with less than cylindrical symmetry their biaxial order parameters show in some cases a dramatic increase on entering the smectic A phase of HAB, whilst for others no such major change occurs. In order to investigate this behaviour in more detail, a simultaneous study of the orientational ordering of both solute and solvent is required, and such a study is described in the following paper. Firstly, however, we describe the measurement of the orientational order of HAB itself and of two related compounds: 4,4′-di-*n*-octylazoxybenzene (OAB) (C–S_A 312·0 K; S_A–N 337·6 K; N–I 339·8 K) which has a shorter nematic range, and 4,4′-di-*n*-heptylazobenzene (HB) (C–N 306 K; N–I 321 K) which differs in structure from HAB only by having an azo rather than azoxy link between the two rings. The structures of these three compounds are shown in figure 1.

There have been attempts to obtain the second rank order parameter $\bar{P}_2$ for HAB and OAB [5] and mixtures of these compounds [6] via measurements of χ, the volume magnetic susceptibility. However, this method is unsuitable for the simultaneous measurement of orientational order of both solute and solvent in a mixture since only the total susceptibility can be determined. For the pure liquid crystals the order parameter determined from measurement of the magnetic susceptibility is an unknown

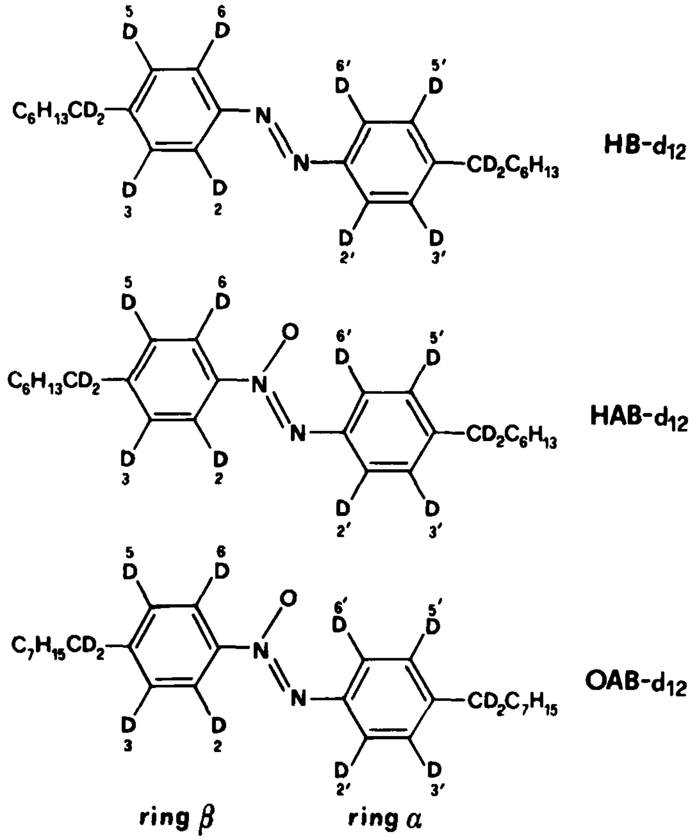

Figure 1. Structure and labelling of atoms for 4,4′-di-*n*-heptylazobenzene (HB), 4,4′-di-*n*-heptylazoxybenzene (HAB) and 4,4′-di-*n*-octylazoxybenzene (OAB).

average over the conformations adopted by the molecule, and refers to the principal axes for the order matrix, whose location in the structure is unknown.

All three compounds studied are non-rigid, and this has important consequences for the description of their orientational order; thus, if we make the reasonable assumption that the molecules exist in a set of discrete conformations generated by rotations about bonds, then each conformation must be described by its own second rank order matrix S^n [7]. If a measurement is made of A, some second rank property of the molecules, then the partially-averaged component along the mesophase director $\tilde{A}_{\parallel}$, is related to the S^n by

$$\tilde{A}_{\parallel} = A_0 + 2/3 \sum_{n}^{N} p_n \sum_{\alpha\beta}^{xyz} S^n_{\alpha\beta} A^n_{\alpha\beta}. \qquad (1)$$

A_0 is the orientation independent part of A and is the isotropic average value; $A^n_{\alpha\beta}$ are components in a molecule fixed frame of the value of A in the *n*th conformation, which has a statistical weight p_n. The individual conformers lack cylindrical symmetry and hence there are two non-zero independent principal components of each S^n; moreover the location of the principal axes will be conformationally dependent so that for each conformation five quantities are required. Each of the liquid crystals studied adopts more than 5×10^4 conformations, so that it is clearly impractical to measure a sufficient number of orientationally dependent experimental quantities to

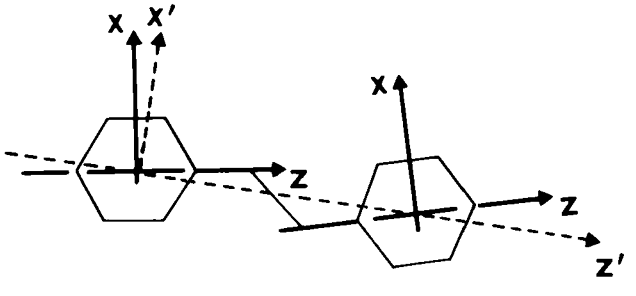

Figure 2. Location of the principal axes for the local ordering matrices of each benzene ring (x, y, z) and for the central aromatic core (x', y', z') in HB, HAB and OAB. The two rings are equivalent in HB but non-equivalent in HAB and OAB.

uniquely define the $\mathbf{S}^n$. We must therefore limit the description to the order of fragments of the molecule, measuring matrices $\mathbf{S}^L$ for individual rigid sub-units in the molecule [8]. For example, the aromatic rings are rigid (neglecting small amplitude vibrational motion) and the axes xyz shown in figure 2 are principal axes for the local ordering matrices

$$S^L_{\alpha\beta} = \sum_n p_n S^n_{\alpha\beta}, \tag{2}$$

because the conformations are symmetrical with respect to the xy, xz and yz planes.

In order to measure the elements of the local ordering matrices for the aromatic rings, we have replaced the hydrogens in these groups with deuterium and recorded the deuteron N.M.R. spectra. Such spectra can be analysed to yield quadrupolar splittings, $\Delta\tilde{\nu}_i$, and dipolar couplings $\tilde{D}_{ij}$, which are both related to elements of $\mathbf{S}^L$ for the ring containing the deuterons. Thus

$$\Delta\tilde{\nu}_i = (3/2)q^i_{\text{ar}}[S^L_{zz}(l^2_{zi} + l^2_{xi}\eta^i_{\text{ar}}/3) + S^L_{xx}(l^2_{xi} + l^2_{zi}\eta^i_{\text{ar}}/3) - \eta^i_{\text{ar}}S^L_{yy}/3], \tag{3}$$

and

$$\tilde{D}_{ij} = -\gamma^2_{\text{D}}h[S^L_{zz}(3l^2_{ijz} - 1) + (S^L_{xx} - S^L_{yy})l^2_{ijx}]/8\pi^2 r^3_{ij}. \tag{4}$$

The direction cosines $l_{\alpha i}$ are between the ith C–D bond and the α axis, whilst $l_{ij\alpha}$ are those for the internuclear vector $\mathbf{r}_{ij}$; q^i_{ar} and η^i_{ar} are the quadrupolar coupling constant and asymmetry parameter for the ith deuteron, and γ_{D} is the deuteron gyromagnetic ratio.

We have also incorporated deuterium into the α-methylene groups; the quadrupolar splittings for these deuterons, whilst insufficient to define the local ordering matrix for this rigid unit, yield the order parameter for the C–D bonds, which is an additional measure of the orientational order of the liquid crystals.

2. Experimental

The samples of the partially deuteriated liquid crystals were synthesized by the procedure described by Van der Veen *et al.* [9], and the aromatic deuterons were incorporated by using appropriately perdeuteriated starting materials. The benzene rings were alkylated by first synthesizing the ketones and subsequently reducing the carbonyl group with DCl on zinc amalgam. Deuterium spectra at various temperatures were recorded at 30·7 MHz with a Bruker CXP 200 spectrometer. A two-dimensional deuteron-N.M.R. spectrum of HAB-d_{12} was also recorded at 304 K, in order to clarify the interpretation of the one-dimensional spectrum [10].

3. Spectral analysis

The simplest deuteron spectrum is that of the azobenzene, HB-d_{12}, shown in figure 3. The relative intensities of the peaks make assignment unambiguous, so that A and A′ can be attributed to the eight aromatic deuterons, and B and B′ stem from the four α-methylene deuterons. We expect the α-methylenes to have a common quadrupolar splitting since they are chemically equivalent. Rapid motion of the rings between two equivalent conformations generated by 180° rotation about the 4,4′ axes renders the deuterons 3,3′, 5,5′ equivalent but, in principle, this group remains different from the other group of equivalent deuterons, 2,2′, 6,6′. We would expect, therefore, two different quadrupolar splittings for the aromatic deuterons. Peaks A and A′ can be analysed satisfactorily as being from pairs of deuterons with identical quadrupolar splittings and interacting via one dominant dipolar coupling [11]. The vector $\mathbf{r}_{23}$ is essentially parallel to the z axis and hence $\tilde{D}_{23}$ depends on only one order parameter, S^L_{zz}, which is expected to be positive, so that $\tilde{D}_{23}$ ($= \tilde{D}_{56} = \tilde{D}_{2'3'} = \tilde{D}_{5'6'}$) will be negative, as shown by equation (4). The shape of the peaks A and A′ then determines $\Delta\tilde{v}_2$ ($= \Delta\tilde{v}_3 = \Delta\tilde{v}_5 = \Delta\tilde{v}_6 = \Delta\tilde{v}_{2'} = \Delta\tilde{v}_{3'} = \Delta\tilde{v}_{5'} = \Delta\tilde{v}_{6'}$) to be negative [11].

A similar analysis of the shape of the peaks B and B′ determines the dipolar coupling $\tilde{D}_\alpha$, which is that between two deuterons in the same methylene group, to have the opposite sign to the quadrupole splitting, $\Delta\tilde{v}_\alpha$. The nature of the rotational potential of the CD_2 group about the phenyl–C bond is not known with certainty, but we expect that most of the conformations adopted by rotation about the two phenyl–C bonds have ordering matrices which are close to being axially symmetric about the z axes of the rings. In this case, therefore, $\tilde{D}_\alpha$ will be positive and $\Delta\tilde{v}_\alpha$ negative.

The deuteron spectrum of HAB-d_{12} is similar to that from OAB-d_{12} and is shown in figure 4(a), together with an auto-correlation two-dimensional spectrum. Both the

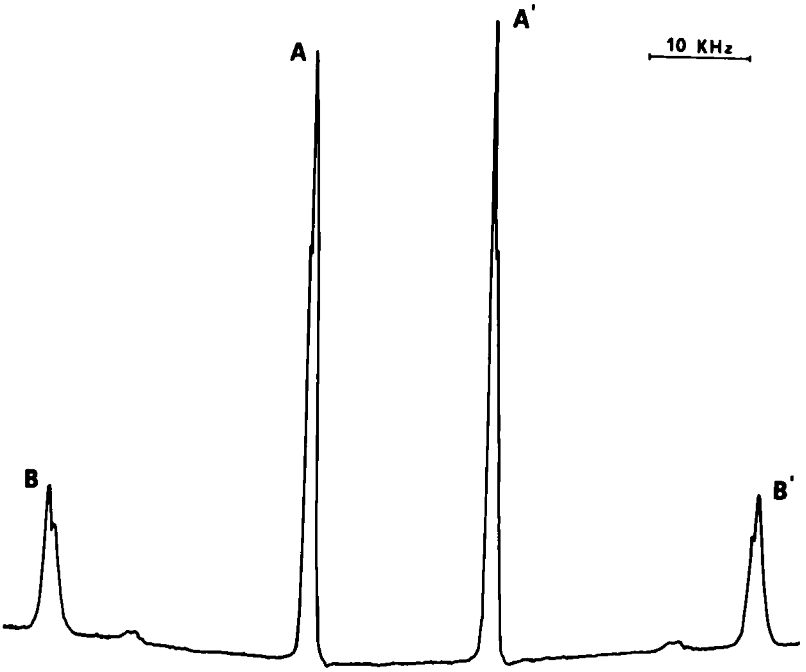

Figure 3. 30·7 MHz deuteron spectrum of 4,4′-di-n-heptylazobenzene-d_{12} (HB-d_{12}) at T = 307 K.

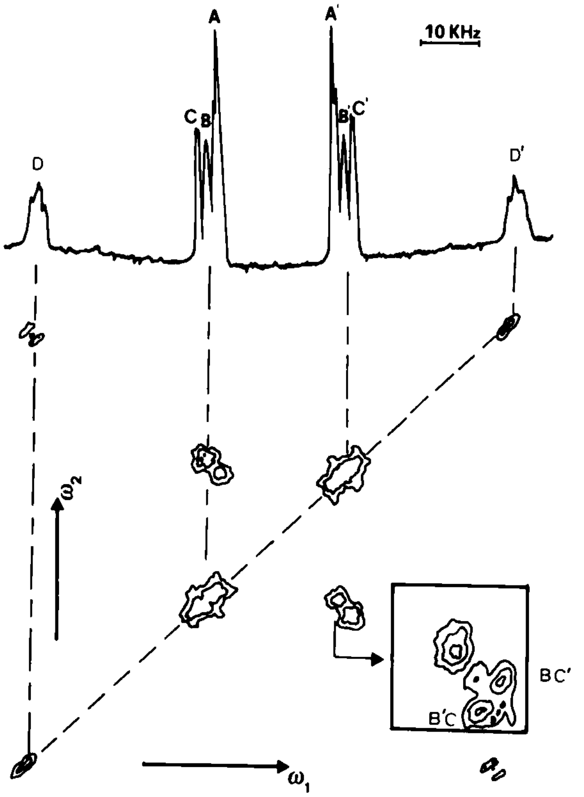

Figure 4. 30·7 MHz deuteron spectrum of 4,4'-di-*n*-heptylazoxybenzene-d_{12} (HAB) at 304 K (upper trace) and (below) the two-dimensional auto-correlation spectrum.

HAB and OAB molecules lack any symmetry and hence the two α-methylene groups are non-equivalent and have different quadrupolar splittings; they produce the peaks D, D', which are superimpositions of two spectral envelopes of the same shape as those from the methylene deuterons in HB-d_{12} (peaks B and B' in figure 3). The peaks from the aromatic deuterons can be assigned on the basis of their fine structure, relative intensities and analysis of the two-dimensional spectrum. Thus, peaks A and A' correspond in intensity to four deuterons, while the sets B,B' and C,C' correspond to two deuterons each. The 2D auto-correlation spectrum used a 45° refocusing pulse [10] and in this case we expect two kinds of off-diagonal peaks, those closest to the diagonal and caused by connections via the largest dipolar couplings, and those furthest from the diagonal and which result from both quadrupolar and dipolar coupling connectivities. The signal-to-noise ratio in the 2D spectrum of HAB-d_{12} precluded a clear interpretation of the former but not the latter off-diagonal peaks. Thus in figure 4 we show an enlargement of one of the off-diagonal peaks from the aromatic deuterons which stems from quadrupolar and dipolar coupling, and it is clear that peaks A,A' are connected only to each other. These peaks also have the same shape as those from the aromatic deuterons in HB-d_{12} (peaks A and A' in figure 3). We assign them, therefore, to the four deuterons in ring α, since this ring is more similar to those in HB; the lineshapes show $\Delta\tilde{\nu}_{2'}$ $(=\Delta\tilde{\nu}_{3'} = \Delta\tilde{\nu}_{5'} = \Delta\tilde{\nu}_{6'})$ to be the same sign as $\tilde{D}_{2'3'}$ and hence to be negative. The presence of the peaks labelled B'C and BC' in the 2D spectrum clearly reveals that peaks B',C and B,C' are connected to each other. Peaks B,B′ and C,C′, therefore, stem from the two pairs of different deuterons in ring β; this is also confirmed by a closer examination of their fine structure, which is caused by dipolar coupling between deuterons which have unequal quadrupolar splittings. The peaks B and B′ are less resolved and broader than C and C′; this too suggests that the former are from deuterons 3 and 5, which are more strongly coupled with the chain deuterons and protons via dipolar interactions. For our aims, however, it is not essential to assign the two pairs of resonances to particular sets of equivalent deuterons. Again the dipolar coupling $\tilde{D}_{23}$ $(=\tilde{D}_{56})$ is expected to be negative and the lineshapes show that the quadrupolar splittings $\Delta\tilde{\nu}_2$ $(=\Delta\tilde{\nu}_3)$ and $\Delta\tilde{\nu}_5$ $(=\Delta\tilde{\nu}_6)$ are also negative.

4. Results and discussion

We discuss first the derivation of $\mathbf{S}^{R\alpha}$ and $\mathbf{S}^{R\beta}$, the local ordering matrices for the aromatic rings in the three compounds. For HB-d_{12} the two rings are equivalent so that $\mathbf{S}^{R\alpha} \equiv \mathbf{S}^{R\beta}$ and the eight aromatic deuterons should form two groups of chemically equivalent nuclei and thus produce two different quadrupolar splittings. The spectrum, however, shows only one quadrupolar splitting, and the shapes of the peaks are consistent with there being only one large dipolar coupling. These two quantities can be used, in principle, to determine both $S_{zz}^{R\alpha}$ $(=S_{zz}^{R\beta})$ and $S_{xx}^{R\alpha} - S_{yy}^{R\alpha}$ $(=S_{xx}^{R\beta} - S_{yy}^{R\beta})$. In practice, the dipolar coupling is obtained with a low precision, and although the quadrupolar splitting is measured with high accuracy we do not know the quadrupolar tensor elements nor the geometry accurately, so that both the order parameters cannot be obtained with good precision. Choosing q_{ar} as 185 kHz and η_{ar} as 0·04, which are typical values for aromatic compounds [12], and using a regular hexagonal geometry for the phenyl groups, yields a biaxiality in $\mathbf{S}^{R\alpha}$ which is close to zero. Changes in θ_z, the angle between the C–D bonds and the z axis, of $\pm 1^\circ$ changes $S_{xx}^{R\alpha} - S_{yy}^{R\alpha}$ about zero by about ± 5 per cent of $S_{zz}^{R\alpha}$. In view of these uncertainties we have chosen to set the biaxiality to zero and to derive $S_{zz}^{R\alpha}$ from the quadrupolar splitting alone, with θ_z as 60°. There is therefore a systematic error in the values of $S_{zz}^{R\alpha}$ whose magnitude is uncertain, thus changing θ_z by $\pm 1^\circ$ alters $S_{zz}^{R\alpha}$ by ± 16 per cent. The temperature dependence of $S_{zz}^{R\alpha}$ obtained in this way for HB-d_{12} is shown in figure 5.

The deuteron spectra for the two azoxy compounds are much richer in information. However, it is again not possible to determine $S_{xx}^{R\alpha} - S_{yy}^{R\alpha}$ or $S_{xx}^{R\beta} - S_{yy}^{R\beta}$ with a great enough precision to differentiate these biaxialities from zero. This is again principally because the geometry and quadrupolar tensors are not known and have to be assumed.

For ring α, whose deuterons have the same spectrum as those in the aromatic rings of HB-d_{12}, the dipolar coupling is not measured with good precision and $S_{zz}^{R\alpha}$ is obtained from the quadrupolar splitting. The deuterons in ring β show different quadrupolar splittings, and the dipolar coupling between adjacent deuterons is measured with better precision than that between similar deuterons in ring α. The difference in quadrupolar splittings could reflect unequal quadrupolar tensors, as found, for example, in some monosubstituted benzenes [13], or it could stem from unequal angles between the C–D bonds and the z axis. Assuming the quadrupolar tensors to be equal and setting the biaxiality in $\mathbf{S}^{R\beta}$ at zero enables us to evaluate the difference in the values of θ_z for bonds C–D(2) and C–D(3). To do so we determine $S_{zz}^{R\beta}$ from the dipolar coupling $\tilde{D}_{23}$, assuming $\mathbf{r}_{23}$ to be parallel to z and of magnitude 2·5 Å. The angles obtained for C–D(2) and C–D(3) of 61·0° and 60·3° respectively in

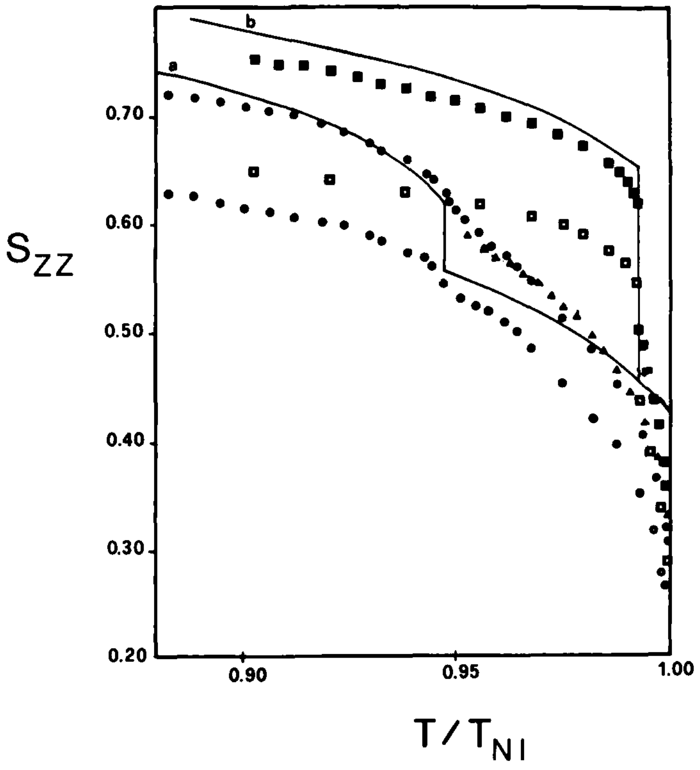

Figure 5. Variation with reduced temperature, T/T_{NI}, of the local order parameters for the aromatic rings: $S_{zz}^{R\alpha}$ in HB (▲), $S_{zz}^{R\alpha}$ (○) and $S_{zz}^{R\beta}$ (●) in HAB, $S_{zz}^{R\alpha}$ (□) and $S_{zz}^{R\beta}$ (■) in OAB. The continuous curve show the trends predicted by the modified McMillan theory for (*a*) HAB-d_{12} with model parameters α/u_0 = 0·41, γ/u_0 = 0·65; (*b*) OAB-d_{12} with model parameters α/u_0 = 0·60, γ/u_0 = 0·386.

HAB-d_{12} and of 60·7° and 60·1° in OAB-d_{12} represent small and hence reasonable distortions from a hexagonal geometry. Four HAB-d_{12} spectra and two OAB-d_{12} spectra respectively were analysed in this way, corresponding to temperatures of 319, 326, 328 and 342 K for the former, and of 330·6 and 335·6 K for the second liquid crystal. The same spectra could, alternatively, be used to evaluate the possible ring biaxiality, with the same $S_{zz}^{R\beta}$ values but assuming fixed angles within a sensible range. If the C–D(3) bond, which presumably is the less distorted one, is considered and an angle between 59·5° and 60·5° is chosen, then $S_{xx}^{R\beta} - S_{yy}^{R\beta}$ is obtained to be less than 0·025 for both HAB-d_{12} and OAB-d_{12}, that is less than 5 per cent of $S_{zz}^{R\beta}$. It is reasonable, therefore, to set the biaxiality in $S^{R\beta}$ to zero and obtain $S_{zz}^{R\beta}$ from one of the two quadrupolar splittings by using the appropriate value of θ_z. Moreover the ratio between any two quadrupolar splittings of the ring deuterons remains constant, within the limits of the experimental error, throughout the large range of temperature studied (see figure 6); this is consistent with an essentially zero biaxiality for both $\mathbf{S}^{R\alpha}$ and $\mathbf{S}^{R\beta}$, although this cannot be exactly satisfied for both rings simultaneously if $S_{zz}^{R\alpha} \neq S_{zz}^{R\beta}$. The values of $S_{zz}^{R\beta}$ shown in figure 5 are averages at each temperature of values determined from the two quadrupolar splittings.

The procedure and assumptions described lead to $S_{zz}^{R\alpha} \neq S_{zz}^{R\beta}$ at the same temperature for both HAB and OAB. This inequality implies that the two z axes, $z(\alpha)$ and $z(\beta)$,

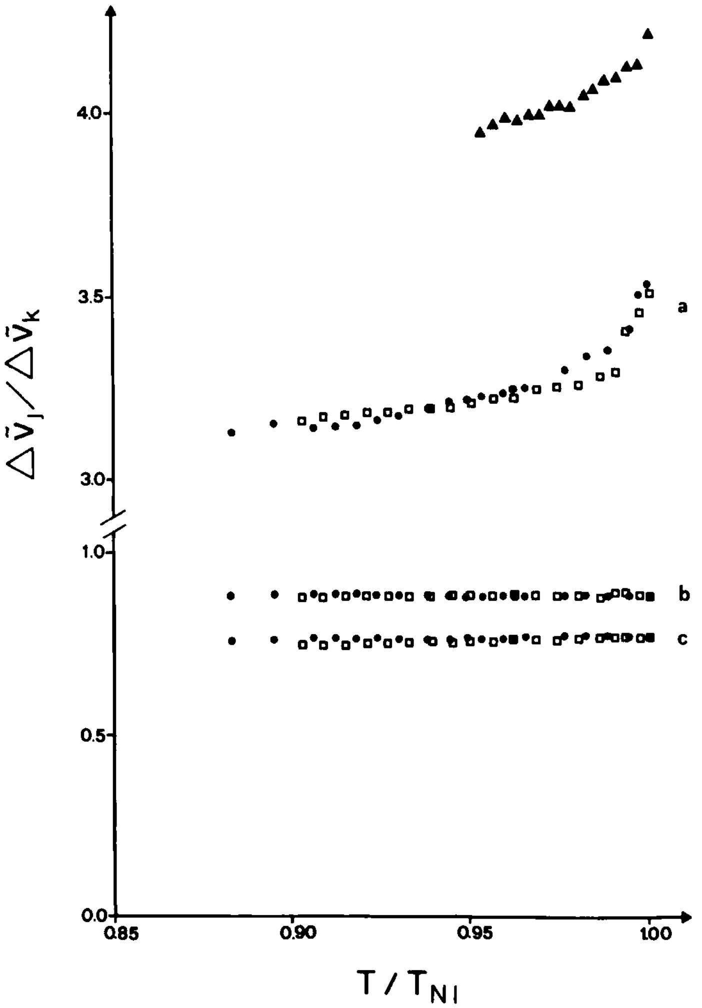

Figure 6. Ratios of quadrupolar splittings versus reduced temperature for HAB-d_{12} (●) and OAB-d_{12} (□): (*a*) $\Delta\tilde{v}_{CD_2}/\Delta\tilde{v}_2$; (*b*) $\Delta\tilde{v}_1/\Delta\tilde{v}_2$; (*c*) $\Delta\tilde{v}_3/\Delta\tilde{v}_2$. The ratio $\Delta\tilde{v}_{CD_2}/\Delta\tilde{v}_1$ is shown (▲) for HB-d_{12}.

are not collinear in all the conformations adopted by the aromatic core. An estimate of the average angle between the two z axes can be obtained by assuming that on average the aromatic core is cylindrically symmetric with a local order matrix $\mathbf{S}^R$ with principal axes $x'y'z'$ (see figure 2). In this case, if it also has an essentially axially symmetric local ordering matrix $\mathbf{S}^R$ with principal axes x', y', z', then

$$S_{zz}^{R\alpha} = S_{z'z'}^{R}(3l_{zz'\alpha}^2 - 1)/2 \tag{5}$$

and

$$S_{zz}^{R\beta} = S_{z'z'}^{R}(3l_{zz'\beta}^2 - 1)/2. \tag{6}$$

From the observed constant ratio $S_{zz}^{R\alpha}/s_{zz}^{R\beta}$ of 0·872 for HAB and of 0·887 for OAB we cannot determine both the unknowns $l_{zz'\alpha}^2$ and $l_{zz'\beta}^2$. However, in the hypothesis that the z axis of the β ring, i.e. the more orientated one, coincides with the axis of maximum order of the molecular core z', a value of 17·0° and 16·6° is found for the angle between $z(\alpha)$ and $z(\beta)$ in HAB and OAB respectively. These values are close to the value of 13° found for 4,4′-dimethoxyazoxybenzene in the solid state [14] and hence are not unreasonable.

The values of $S^{R\beta}_{zz}$ for the aromatic rings of the three compounds studied are shown together in figure 5. In comparing these order parameters with each other, and with values of order parameters derived by other methods, we must remember that they refer to axes fixed in particular rigid sub-units, and hence have different proportionality factors with $S^{R}_{z'z'}$. For HAB and OAB the values of $S^{R\beta}_{zz}$ must be closer than $S^{R\alpha}_{zz}$ to $S^{R}_{z'z'}$ for their respective aromatic cores, and we expect the ratio $S^{R\beta}_{zz}/S^{R}_{z'z'}$ to be essentially equal for the two molecules. Thus, we can conclude that $S^{R}_{z'z'}(\mathrm{OAB}) > S^{R}_{z'z'}(\mathrm{HAB})$ at all reduced temperatures. This is in contrast with the observation by de Jeu and Claassen [5] that order parameters $\bar{P}_2$ derived from measurements of diamagnetic susceptibilities are in the order $\bar{P}_2(\mathrm{OAB}) > \bar{P}_2(\mathrm{HAB})$ for $T/T_{\mathrm{NI}} > 0{\cdot}94$ but are reversed in order below this point. The diamagnetic susceptibility is a property of the whole molecule, averaged over the conformational distribution, and therefore $\bar{P}_2$ cannot be identified with $S^{R}_{z'z'}$. However, the diamagnetic susceptibility anisotropy is expected to be dominated by contributions from the aromatic rings and hence the different behaviour of the order parameters $S^{R}_{z'z'}$ and $\bar{P}_2$ is surprising.

In comparing HB with OAB and HAB, it is reasonable to assume that in each case the relationship between $S^{R\alpha}_{zz}$ or $S^{R\beta}_{zz}$ and $S^{R}_{z'z'}$ is very similar; a 10° difference between the relative orientations of the principal axes z and z' would change the proportionality factor between the order parameters by only 5 per cent. Thus, the observation that $S^{R\alpha}_{zz}$ or $S^{R\beta}_{zz}$ for HB is almost identical with $S^{R\beta}_{zz}$ for HAB in the nematic phase suggests that the orientational ordering in these two compounds is very similar in this phase. However, there is a small but significant difference between the temperature dependences of these two order parameters. At the nematic–isotropic transition the azo compound is more ordered than the azoxy, but this relative magnitude of $S^{R\alpha}_{zz}(\mathrm{HB})$ and $S^{R\beta}_{zz}(\mathrm{HAB})$ changes as $T_{\mathrm{S_AN}}$ for HAB is approached. This reversal in the relative degree of orientational ordering probably reflects a pretransitional development of smectic A character in HAB as the transition to the smectic phase is approached.

The most striking feature shown in figure 5 is the increase in the order parameters for HAB and OAB on entering the smectic A phase. The change in both $S^{R\alpha}_{zz}$ and $S^{R\beta}_{zz}$ for OAB is of the order of 20 per cent whereas both order parameters for HAB change by an order of magnitude less. Such a difference is in approximate accord with the predictions of McMillan's molecular field theory of smectic A phases [15], and has been noted previously by both de Jeu [16], who monitored the change by measuring optical birefringence, and Achard *et al.* [6] who measured the volume magnetic susceptibility. The theory of McMillan and its most recent modification [17] assume the molecules to be rigid and axially symmetric, thus describing the purely orientational order of the molecules with only one molecular order parameter $\bar{P}_2$. For the molecules considered in the present work, the order of the aromatic core can be expressed by one parameter to a reasonable approximation, but it is less certain how well a single-order parameter can represent the ordering of the whole molecule. We do not expect the predictions of McMillan's theory to exactly match with the experimental data, but none the less, it is interesting to compare the predicted behaviour of $\bar{P}_2$ with the observed temperature profile of $S^{R\beta}_{zz}$, the order parameter which most closely represents an order parameter for the whole molecule. We note too that McMillan's theory does not take into account the flexibility of the molecules, which it is now known from studies on nematic phases is an important factor in determining liquid-crystalline behaviour [18–20].

The singlet distribution function, $f(\beta, z)$, proposed by McMillan depends on β, the orientation of the director with the molecular symmetry axis, and z, the displacement of the centre of mass along the layer normal

$$f(\cos\beta, z) = Z^{-1}\exp\{(u_0/kT)[\bar{P}_2P_2(\cos\beta) + \alpha\sigma P_2(\cos\beta)\cos(2\pi z/d) + \gamma\tau\cos(2\pi z/d)]\}, \tag{7}$$

where Z is the partition function

$$Z = \int_{-d/2}^{d/2}\int_{-1}^{1}\exp\{(u_0/kT)[\bar{P}_2P_2(\cos\beta) + \alpha\sigma P_2(\cos\beta)\cos(2\pi z/d) + \gamma\tau\cos(2\pi z/d)]\}\,dz\,d\cos\beta. \tag{8}$$

The translational order parameter τ is defined as the ensemble average of $\cos(2\pi z/d)$, and σ is a mixed translation–orientation order parameter and it is the ensemble average of $P_2(\cos\beta)\cos(2\pi z/d)$; d is the layer spacing in the smectic A phase. Knowing the three parameters u_0, α and γ it is possible to predict T_{NI}, T_{S_AN}, the entropy change, ΔS_{S_AN}, at the smectic A–nematic transition, and the dependence of $\bar{P}_2$ on reduced temperature T/T_{NI}. Conversely, we can in principle obtain the ratios α/u_0 and γ/u_0 from experimental values of ΔS_{S_AN} and T_{S_AN}/T_{NI} and then predict the variation with reduced temperature of $\bar{P}_2$. The results of such a calculation for OAB are shown in figure 5, where we have used the experimental value of 0·82R [21] for ΔS_{S_AN} together with T_{S_AN}/T_{NI} to determine α/u_0 and γ/u_0, and hence to predict the variation of $\bar{P}_2$ with T/T_{NI}.

Comparing the predicted value of $\bar{P}_2$ with the observed values of $S_{zz}^{R\beta}$ we note that they have very similar temperature profiles in the smectic phase, but the changes at T_{S_AN} are very different. This discrepancy at T_{S_AN} may be because the experimental value of ΔS_{S_AN} includes not only the entropic change at the transition, but also part of the entropy variation which accompanies the strong pretransitional effect observed just above T_{S_AN}. A similar hypothesis has been used by Van der Veen *et al.* [21] to explain the unusually large change in entropy at T_{NI} for OAB, thus ΔS_{NI} is measured to be 0·81R whilst the Maier–Saupe theory, which usually overestimates this quantity, predicts 0·417R [22].

For HAB-d_{12} there is a similar, but more substantial, discrepancy between theory and experiment concerning ΔS_{S_AN}. In this case the experimental value of ΔS_{S_AN} is 0·06R, but such a small value is inconsistent with the value of T_{S_AN}/T_{NI} for positive values of α and γ. To obtain the correct value of T_{S_AN}/T_{NI} it is necessary that ΔS_{S_AN} should be at least double the observed value and we have computed the temperature profile of $\bar{P}_2$ from α and γ values determined from a value of $\Delta S_{SN} = 0{\cdot}12R$ as shown in figure 5. However, the change in $\bar{P}_2$ is too large, although the behaviour in the smectic A phase is in good accord with that of $S_{zz}^{R\beta}$, and as with OAB, the explanation is probably the development of translational order in the nematic phase.

The order parameters σ and τ vanish in the nematic phase so that the McMillan potential reduces to that of Maier and Saupe and a universal curve is predicted for the variation of $\bar{P}_2$ with reduced temperature. This is in poor agreement with the temperature profiles of HAB, OAB and HB in the nematic phase, as shown in figure 5. Such a discrepancy between theory and experiment is, however, well known [23] and is probably a consequence of the neglect of the molecular flexibility and the assumption of cylindrical symmetry.

The ratios of the quadrupolar splittings of the α-methylene deuterons to those of the aromatic deuterons are strongly temperature dependent for all three liquid crystals, as shown in figure 6, therefore revealing the necessity of more than one parameter to describe the order of the CD_2-phenyl fragments. Consequently, the presence of a single conformation for these fragments can be excluded. In order to explain the value of these splittings and their variation with temperature, it should be necessary to introduce other order parameters and a model for the internal motion. The experimental information is however insufficient to allow a quantitative treatment of this kind.

5. Conclusion

Our principal conclusion is that the quadrupolar splittings of the aromatic deuterons are consistent with local ordering matrices for the separate benzene rings, or for the whole aromatic cores, which are axially symmetric within the precision of our measurements and with our uncertain knowledge of the quadrupolar tensors and the molecular geometry. This defines the precision with which we can monitor the orientational order in these partially-deuteriated compounds, but despite the uncertainties discussed here, deuteron N.M.R. provides the most precise way of measuring orientational order on pure systems, and it is virtually the only method available for measuring solute and solvent ordering in mixtures.

References

[1] Viloria, F. R., 1982, Ph.D. thesis, University of Southampton.

[2] Catalano, D., Forte, C., Veracini, C. A., and Zannoni, C., 1983, *Israel J. Chem.*, **23**, 283.

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

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

[5] de Jeu, W. H., and Claassen, W. A. P., 1978, *J. chem. Phys.*, **68**, 102.

[6] Achard, M. F., Hardouin, F., Sigaud, G., and Gasparoux, H., 1976, *J. chem. Phys.*, **65**, 1387.

[7] Emsley, J. W., and Luckhurst, G. R., 1980, *Molec. Phys.*, **41**, 19.

[8] Emsley, J. W., 1985, *NMR of Liquid Crystals*, edited by J. W. Emsley (Reidel).

[9] Van der Veen, J., de Jeu, W. H., Grobben, A. H., and Boven, J., 1972, *Molec. Crystals liq. Crystals*, **17**, 291.

[10] Emsley, J. W., and Turner, D. L., 1981, *Chem. Phys. Lett.*, **82**, 447.

[11] Luz, Z., Hewitt, R. C., and Meiboom, S., 1974, *J. chem. Phys.*, **61**, 1758. Hsi, S., Zimmermann, H., and Luz, Z., *J. chem. Phys.*, **69**, 4126.

[12] Veracini, C. A., 1985, *NMR of Liquid Crystals*, edited by J. W. Emsley (Reidel).

[13] Ambrosetti, R., Catalano, D., Forte, C., and Veracini, C. A., 1985, *Z. Naturf.* (*a*), **41**, 431.

[14] Krigbaum, W. R., Chatani, Y., and Barber, P. G., 1970, *Acta crystallogr.* B, **26**, 97.

[15] McMillan, W. L., 1971, *Phys. Rev.* A, **4**, 1238; 1972, *Ibid.*, **6**, 936.

[16] de Jeu, W. H., 1973, *Solid St. Commun.*, **13**, 1521.

[17] Kventsel, G. F., Luckhurst, G. R., and Zewdie, H. B., 1985, *Molec. Phys.*, **56**, 589.

[18] Marcelja, S., 1974, *J. chem. Phys.*, **60**, 3599.

[19] Emsley, J. W., Luckhurst, G. R., and Stockley, C. P., 1982, *Proc. R. Soc.* A, **381**, 117.

[20] Luckhurst, G. R., 1985, *NMR of Liquid Crystals*, edited by J. W. Emsley (Reidel).

[21] Van der Veen, J., de Jeu, W. H., Wanninkhof, M. W. M., and Tienhoven, C. A. M., 1973, *J. phys. Chem.*, **77**, 2153.

[22] Maier, W., and Saupe, A., 1958, *Z. Naturf.* (*a*), **13**, 564; 1959, *Ibid.*, **14**, 882; 1960, *Ibid.*, **15**, 287.

[23] Luckhurst, G. R., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press).