The structure and orientational ordering of 4-methoxy-4'-cyanobiphenyl in the nematic mesophase

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The structure and orientational ordering of 4-methoxy-4′-cyanobiphenyl in the nematic mesophase

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The proton N.M.R. spectra of two partially deuteriated samples of the mesogen 4-methoxy-4′-cyanobiphenyl (1-OCB) have been obtained. The spectra were simplified by decoupling the interactions between protons and deuterons and analysed to yield sets of dipolar couplings, $\tilde{D}_{ij}$. The $\tilde{D}_{ij}$ are used to investigate the angle ϕ between the two ring normals and the conformation of the methoxy group relative to the attached phenyl ring. If the potential governing rotation, $V(\phi)$, is assumed to have a deep minimum such that only structures with the minimum value of ϕ are appreciably populated, then ϕ_{min} is determined to be $30\cdot4° \pm 0\cdot4°$. However, adopting a continuous form for $V(\phi)$ changes ϕ_{min} to $36°$. For the methoxy group the data are consistent with the potential governing rotation about the ring–oxygen bond being zero when the carbon atom is in the ring plane and infinite otherwise; in addition, we have investigated the consequences for the structure and ordering of adopting more realistic forms for this potential. The 24 structures of equal, minimum energy, which are generated by rotation about the inter ring bond, the phenyl–O bond and the O–CH$_3$ bond, all have the same shape, and hence each of these conformations has the same ordering matrix, with principal elements S_{zz} and $S_{xx} - S_{yy}$. The magnitudes of S_{zz} and $S_{xx} - S_{yy}$ have been obtained, together with the orientation of x, y and z with respect to a frame fixed in the methoxylated ring, with the assumption that only these minimum energy structures are populated. The magnitudes of these principal order parameters are used to test the form of a potential of mean torque.

1. Introduction

Liquid crystals are fluids in which there is some long range orientational order, and for single molecules this is characterized by a singlet orientational distribution function, $f(\chi, \omega)$, which depends on both the orientation, ω, of the mesophase director in a frame fixed in a rigid sub-unit of the molecule, and on χ, a set of coordinates describing internal modes of motion [1]. There is a considerable amount of internal, bond rotational motion in most mesogenic molecules and it has proved possible to characterize $f(\chi, \omega)$ only by adopting simplified models of their internal modes of motion. Thus, all attempts to derive $f(\chi, \omega)$ have either ignored the problems imposed by the internal motions, that is, they have assumed that the molecules can be regarded as being rigid, or they have adopted the rotational isomeric state (RIS) approximation

for the motion [2]. The RIS model assumes that all of the rotational potentials are such that the molecule can be regarded as existing in a discrete set of conformers, n, which correspond to the minimum energy structures generated by rotations about bonds. With this approximation the singlet orientational distribution function depends on n and ω. For a uniaxial phase $f(n, \omega)$ can be expressed as the sum of order parameters $\bar{C}_{L,m}^{n}$, which are averages of reduced spherical harmonics, thus

$$f(n, \omega) = \sum_{L,m} \overline{C_{L,m}^{n}} C_{L,m}(\omega(n))4\pi/(2L + 1). \tag{1}$$

The order parameters vary with the conformational state, reflecting the variation of intermolecular forces with molecular shape.

It would appear from equation (1) that to characterize $f(n, \omega)$ fully would require the ability to obtain an infinite set of order parameters from experiments, and clearly this is an impossible task. However, it is possible to test models for $f(n, \omega)$ by comparing observed with calculated values of second rank quantities. Thus, the component, $\tilde{A}_{\parallel}$, along the director of a second rank quantity is related to $A_{\alpha\beta}^{n}$, the components in a molecular frame, by

$$\tilde{A}_{\parallel} = A_0 + 2/3 \sum_{n} p^{n} \sum_{\alpha,\beta} A_{\alpha\beta}^{n} S_{\alpha\beta}^{n}, \tag{2}$$

where $S_{\alpha\beta}^{n}$ are components of a second rank order matrix (equivalent to $\bar{C}_{2,m}^{n}$), given by

$$S_{\alpha\beta}^{n} = \tfrac{1}{2} \int (3\cos\theta_a \cos\theta_\beta - \delta_{\alpha\beta}) f(n, \omega) d\omega, \tag{3}$$

and p^{n} is the statistical weight of the nth conformation.

The mesogen 4-methoxy-4'-cyanobiphenyl (1-OCB) is of particular value as a model compound because of its simple structure, which is shown in figure 1. There are three bonds about which internal rotation takes place. Rotation about the inter ring C–C bond is subject to a potential $V(\phi)$ whose simplest form is

$$V(\phi) = V_2(1 - \cos 2\phi) + V_4\cos 4\phi, \tag{4}$$

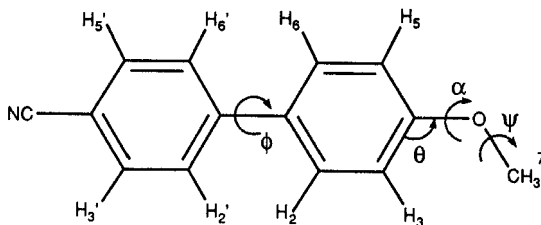which has a minimum determined by the relative values of V_2 and V_4.

Figure 1.   Structure, atomic labelling and angles for 4-methoxy-4'-cyanobiphenyl.

Rotation about the phenyl–O bond through an angle α is found to be predominantly two-fold in character in anisoles which lack bulky substituents in the ortho positions [3], so that the potential has the form

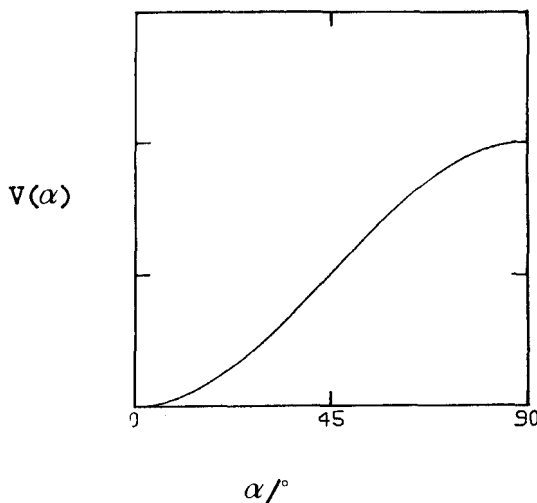$$V(\alpha) = V_2(1 - \cos 2\alpha), \tag{5}$$

$V(\alpha)$

Figure 2. Shape of $V(\alpha)$, the potential for rotation about the phenyl–O bond.

which is shown schematically in figure 2. The third rotation is about the $O–CH_3$ bond and is three fold in character,

$$V(\psi) = V_3(1 - \cos 3\psi). \qquad (6)$$

The particular importance of 1-OCB is that the 24, equivalent, most probable structures all have the same shape. Thus, applying the RIS approximation to this mesogen gives the result that the principal components S_{zz} and $S_{xx} - S_{yy}$ for the 24 conformers all have the same magnitude and that the orientation of the principal axes xyz varies in a predictable way provided that the value of ϕ for which $V(\phi)$ is a minimum is known.

We shall show that it is possible to obtain $\phi_{\min}$, the values of S_{zz} and $S_{xx} - S_{yy}$ and the location of the xyz axes by analysing the proton N.M.R. spectra of suitably deuteriated samples of 1-OCB. We shall show too how relaxing the RIS approximation and allowing for the ϕ and α dependence of the order parameters changes the values derived for $\phi_{\min}$ and the order parameters. Finally, we shall use the values obtained for the order parameters to test the simplest form of $f(\omega)$ which is appropriate for a biaxial, effectively rigid mesogen.

2. Experimental

Analysable proton spectra were obtained by partially deuteriating the molecules and recording deuterium decoupled proton spectra in the nematic phase; 1-OCB exists in a supercooled nematic phase from 85·5°C to approximately 62°C. Two deuteriated samples were used in these experiments: a sample deuteriated in positions 3 and 5 of the biphenyl group and in the methoxy group (1-OCB-d_5), and a sample deuteriated in positions 2,6,2′,3′,5′ and 6′ of the biphenyl group (1-OCB-d_6). The synthesis of the sample of 1-OCB-d_5 has been described by Emsley *et al.* [4] and the methods which were used to synthesise both compounds have been discussed by Zimmermann [5].
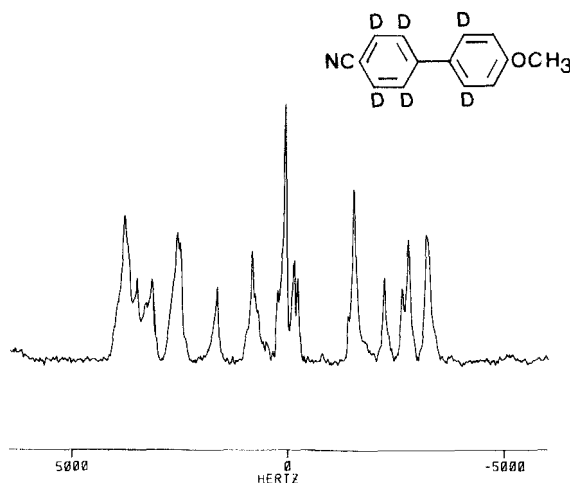
The deuterium decoupled proton spectra were obtained with a Bruker CXP 200 spectrometer, and their analysis yielded the dipolar couplings given in tables 1 and 2. Examples of the $^1H–\{^2H\}$ spectra are shown in figures 3 and 4.

Table 1. Dipolar couplings $\tilde{D}_{ij}$ obtained from the proton-{deuterium} spectra of 1-OCB-d_5 at different scaled temperatures, $T_{NI} - T$.

$(T_{NI}-T)/K$	$\tilde{D}_{2'3'}$/Hz	$\tilde{D}_{23}$/Hz	$\tilde{D}_{2'5'}$/Hz	$\tilde{D}_{3'5'}$/Hz	$\tilde{D}_{22'}$/Hz
22·5	-4587 ± 4	-394 ± 4	55 ± 4	391 ± 1	-1864 ± 3
20·5	-4504 ± 4	-387 ± 4	54 ± 4	384 ± 3	-1827 ± 3
18·0	-4374 ± 4	-391 ± 5	48 ± 4	370 ± 3	-1764 ± 4
17·0	-4365 ± 1	-375 ± 1	47 ± 1	368 ± 1	-1765 ± 1
16·0	-4322 ± 1	-369 ± 1	46 ± 1	363 ± 1	-1747 ± 1
15·5	-4287 ± 4	-371 ± 4	53 ± 4	359 ± 3	-1729 ± 3
15·0	-4271 ± 1	-364 ± 2	49 ± 2	358 ± 1	-1724 ± 1
14·5	-4212 ± 2	-366 ± 3	41 ± 3	355 ± 2	-1700 ± 2
14·0	-4217 ± 1	-361 ± 2	47 ± 2	352 ± 1	-1704 ± 1
13·0	-4163 ± 2	-358 ± 2	43 ± 2	347 ± 2	-1678 ± 1
12·0	-4103 ± 2	-351 ± 2	46 ± 2	341 ± 2	-1652 ± 2
11·0	-4046 ± 2	-349 ± 2	43 ± 2	339 ± 2	-1625 ± 2
10·0	-3969 ± 1	-336 ± 1	44 ± 1	329 ± 2	-1595 ± 1
9·0	-3897 ± 1	-332 ± 1	42 ± 1	321 ± 1	-1564 ± 1
8·0	-3818 ± 1	-325 ± 2	41 ± 2	314 ± 1	-1530 ± 1
7·0	-3727 ± 2	-318 ± 2	41 ± 2	304 ± 2	-1491 ± 2
6·0	-3622 ± 2	-310 ± 3	37 ± 3	297 ± 2	-1451 ± 2
5·0	-3510 ± 2	-302 ± 3	37 ± 3	287 ± 2	-1401 ± 2
4·0	-3367 ± 2	-287 ± 2	35 ± 2	272 ± 2	-1345 ± 2
3·0	-3207 ± 2	-273 ± 3	26 ± 3	255 ± 2	-1279 ± 2

Table 2. Dipolar couplings $\tilde{D}$ obtained from the proton-{deuterium} spectra of 1-OCB-d_6.

$(T_{NI} - T)/K$	$\tilde{D}_{37}$/Hz	$\tilde{D}_{77}$/Hz	$\tilde{D}_{35}$/Hz
18·0	-1397 ± 1	690 ± 1	372 ± 1
14·0	-1335 ± 1	664 ± 1	354 ± 1
11·0	-1263 ± 2	635 ± 1	330 ± 1
7·0	-1165 ± 1	592 ± 1	303 ± 1
3·0	-1018 ± 6	515 ± 3	253 ± 3
1·0	-888 ± 5	460 ± 2	219 ± 3

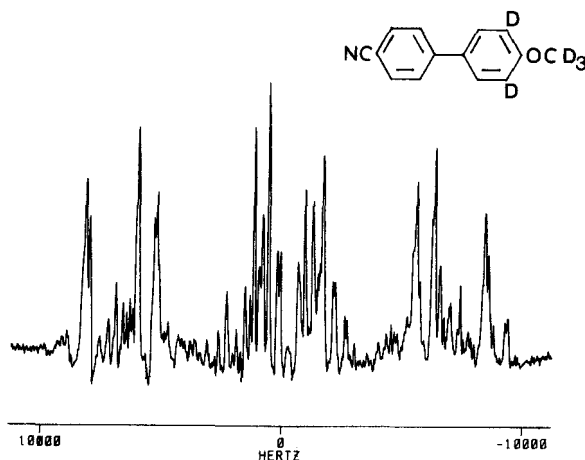Figure 3. The deuterium decoupled 200 MHz proton spectrum of 1-OCB-d_5 at $T_{NI} - T$ of 10 K.

Figure 4.   The deuterium decoupled 200 MHz proton spectrum of 1-OCB-d_5 at $T_{NI} - T$ of 10 K.

3.   Results and discussion

3.1. *The structure and orientational order of the biphenyl fragment*

The dipolar couplings obtained for the 1-OCB-d_5 sample can be used to investigate the minimum in the potential $V(\phi)$. To do this we fix axes abc so that a is the para axis of the biphenyl group, and b the normal to the plane bisecting the planes of the two phenyl rings. With these axes, and invoking the RIS approximation, the local order matrix $\mathbf{S}^B$ for the biphenyl fragment is in diagonal form and the dipolar couplings between the six biphenyl protons are given by

$$\tilde{D}_{ij} = -\gamma_i\gamma_j h\{S_{aa}^B(3\cos^2\theta_{ija} - 1)$$
$$+ (S_{cc}^B - S_{bb}^B)(\cos^2\theta_{ijc} - \cos^2\theta_{ijb})\}/8\pi^2 r_{ij}^3. \qquad (7)$$

The angles θ_{ija} etc. are between the inter proton vector $\mathbf{r}_{ij}$ and the molecule fixed a axis. The phenyl rings were assumed to have identical geometries with $r_{23} = r_{56} = r_{2'3'} = r_{5'6'} = 2\cdot48$ Å. The distances $r_{26}, r_{35}, r_{2'6'}$, and $r_{3'5'}$ were assumed equal and their values varied, together with the proton coordinate a_2 (which is equal to a_6, $-a_{2'}$ and $-a_{6'}$), ϕ_{min}, S_{aa}^B and $(S_{cc}^B - S_{bb}^B)$ to fit the five observed dipolar couplings at all the temperatures for which spectra were recorded. The values obtained for ϕ_{min} show a random scatter about a value of $30\cdot4° \pm 0\cdot4°$, and a_2 and r_{26} are similarly independent of temperature with values of $a_2 = 0\cdot920 \pm 0\cdot005$ Å and $r_{26} = 4\cdot342 \pm 0\cdot005$ Å. Thus, within the RIS approximation the structure of this fragment of 1-OCB is independent of temperature. The value obtained for ϕ_{min} is very similar to that found for the corresponding angle in the mesogen 4-*n*-pentyl-4′-cyanobiphenyl by Sinton and Pines [6]. They analysed the dipolar couplings between all the protons in the biphenyl group of this molecule and adopted the RIS approximation for the conformational possibilities. An investigation of the structure of 1-OCB in the solid, crystalline state by X-ray diffraction by Walz, Paulus and Haase [7] found ϕ_{min} to be 40°. Such a large difference in ϕ_{min} on changing from the nematic to crystalline phase is perhaps not too surprising in view of the change in ϕ_{min} for biphenyl itself from about 45° in the isotropic liquid or gaseous phases to a value of zero in the solid. However, it is possible that the value of ϕ_{min} that we have determined for the nematic

phase of 1-OCB is dependent on the adoption of the RIS approximation in analysing our data and so we have explored the effect of relaxing this approximation and instead adopting a continuous form for $V(\phi)$.

The dipolar couplings are averaged over a continuous potential by using equation (2) with $\bar{\mathbf{A}}$ as the dipolar coupling thus,

$$\tilde{D}_{ij} = (2/3) \sum_n p^n \sum_{\alpha,\beta} D_{ij\alpha\beta}^n S_{\alpha\beta}^n, \tag{8}$$

where p^n is the statistical weight of the nth conformation, that is the nth point on a continuous potential function. The dipolar coupling in the nth conformation is

$$D_{ij\alpha\beta}^n = -\gamma_i\gamma_j h(3 l_{ij\alpha n} l_{ij\beta n} - \delta_{\alpha\beta})/8\pi^2 r_{ijn}^3, \tag{9}$$

where $l_{ij\alpha n}$ is the direction cosine of the vector $\mathbf{r}_{ijn}$ with the molecular fixed axis α. To obtain the values of p^n and $S_{\alpha\beta}^n$ it is necessary to know the conformationally dependent singlet orientational distribution function, $f(n, \omega)$, for which we adopt the theoretical model proposed by Emsley, Luckhurst and Stockley [8], in which $f(n, \omega)$ is written in terms of a conformationally dependent potential of mean torque, $U_{\text{ext}}(n, \omega)$, and a potential energy, $U_{\text{int}}(n)$, which depends only on the conformational state, thus

$$f(n, \omega) = \exp\{-(U_{\text{ext}}(n, \omega) + U_{\text{int}}(n))/RT\}/Z. \tag{10}$$

The partition function Z is

$$Z = \sum_n \int \exp\{-(U_{\text{ext}}(n, \omega) + U_{\text{int}}(n))/RT\}d\omega. \tag{11}$$

The potential of mean torque is approximated as

$$U_{\text{ext}}(n, \omega) = -\varepsilon_{2,0}^n C_{2,0}(\omega) - 2\varepsilon_{2,2}^n C_{2,2}(\omega), \tag{12}$$

where the $C_{2,m}(\omega)$ are modified spherical harmonics, and the $\varepsilon_{2,m}^n$ are conformationally dependent interaction parameters whose values are related to conformationally independent interaction parameters $\varepsilon_{2,p}^j$ by

$$\varepsilon_{2,m}^n = \sum_p \sum_j D_{2,p}^2(\Omega_j^n)\varepsilon_{2,p}^j, \tag{13}$$

where Ω_j^n represents the three Euler angles which relate the jth sub-unit to the reference axes in the nth conformation.

For the biphenyl fragment there are two rigid sub-units that have to be considered, the cyanylated (A) and the methoxy-substituted (B) rings. Both of these fragments have sufficient symmetry that two of the principal axes (and hence the third) for the interaction tensors can be identified as the ring normals and the para axes. Therefore, there are four interaction tensor elements required, $\varepsilon_{2,0}^{RA}$, $\varepsilon_{2,2}^{RA}$, $\varepsilon_{2,0}^{RB}$ and $\varepsilon_{2,2}^{RB}$, but since the para axes are collinear then only their mean value $(\varepsilon_{2,0}^{RA} + \varepsilon_{2,0}^{RB})/2 = \varepsilon_{2,0}^R$ determines the principal order parameters for the biphenyl fragment. Similarly the tensor elements $\varepsilon_{2,2}^{RA}$ and $\varepsilon_{2,2}^{RB}$ cannot be distinguished because the ring normals make equal angles with the principal axes of the biphenyl fragment, and therefore we need to determine only their mean value $\varepsilon_{2,2}^R$.

The calculations proceed by choosing a form for $V(\phi)$, which defines $U_{\text{int}}(n)$ in this case, varying $\varepsilon_{2,0}^R$, $\varepsilon_{2,2}^R$ and the inter-ring separation in order to obtain the best agreement between observed and calculated inter-proton dipolar couplings for 1-OCB-d_5. The form of $V(\phi)$ is then changed and the procedure repeated in order to
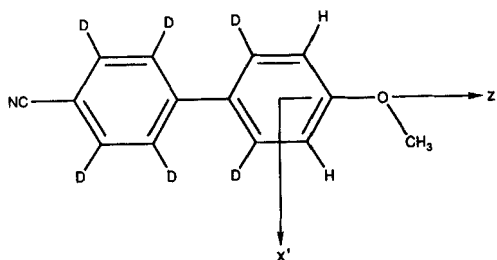
Figure 5. Molecular axes $x'y'z'$ fixed in the methoxylated ring.

locate a global minimum. The calculations were carried out on the data for the two shifted temperatures $(T_{NI} - T)$ of 10 K and 22·5 K. It was found that the potential $V(\phi)$ is independent of temperature, having the shape shown in figure 6 and for which ϕ_{min} is 36°. The Fourier components, V_q, in equation (4) giving the best agreement with experiment are shown in table 3, and the ϕ dependence of the order parameters, $S^B_{\alpha\beta}$, is shown in figure 7.
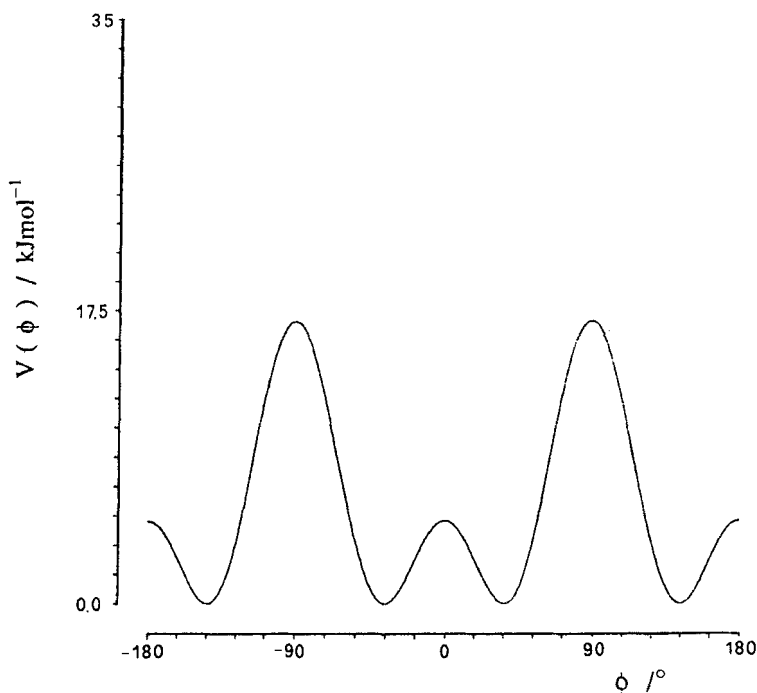
Figure 6. The dependence of the potential energy $V(\phi)$ on ϕ, the angle of rotation about the inter-ring bond in 1-OCB.

The value found for ϕ_{min} is changed considerably on going from the RIS model for the structure to one with a continuous potential for rotation about the inter-ring C–C bond, and the difference between the structure found for the solid form of 1-OCB and the minimum energy structure for the nematic phase has diminished. Note, however, that the order parameters for the minimum energy structure are very similar to those found for the RIS model.

$S_{\alpha\beta}$

Figure 7.   The ϕ dependence of the local order parameters $S_{\alpha\beta}^{B}$.

Table 3.   Coefficients V_q describing the potential $V(\phi)$ for rotation about the inter-ring bond in 1-OCB.
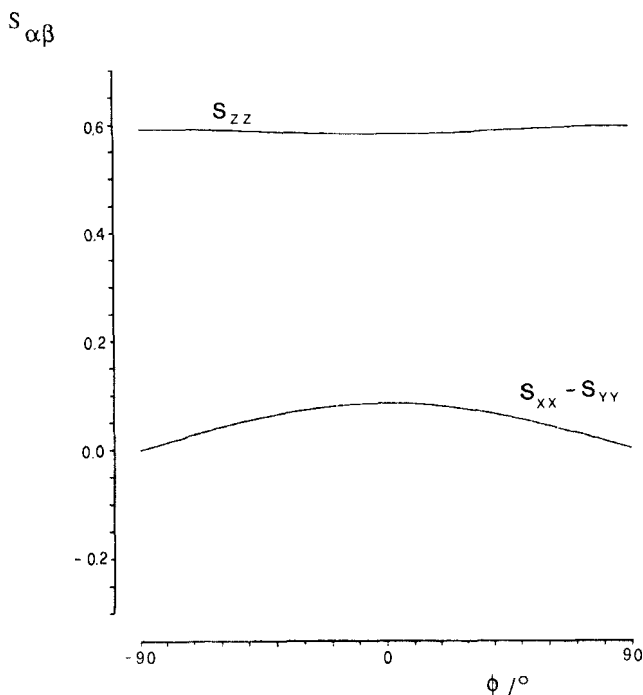
$(T_{NI}-T)/K$	10·0	22·5
$V_2/\mathrm{kJ\,mol}^{-1}$	5·85 ± 0·05	5·91 ± 0·05
$V_4/\mathrm{kJ\,mol}^{-1}$	5·10 ± 0·05	5·00 ± 0·05

3.2. *The structure and ordering of the anisole fragment*

We now consider the information which can be obtained from the inter-proton dipolar coupling constants determined from the spectra of the sample of 1-OCB-d_6. In this case the molecular fragment containing the protons is a substituted anisole, and we expect the lowest energy structures to have the phenyl ring coplanar with the COC plane. Invoking the RIS approximation and fixing axes x', y', and z' in the ring *B*, as shown in figure 5, such that z' is the para axis and y' the ring normal, there are three non-zero order parameters $S_{z'z'}$, $S_{x'x'} - S_{y'y'}$, and $S_{x'z'}$. The two benzene rings are assumed to have the same structure so that $\tilde{D}_{26}$ should equal $\tilde{D}_{35}$, which allows us to relate the dipolar couplings obtained from the sample of 1-OCB-d_6 with those obtained for the d_5 sample. Thus, from the value of $\tilde{D}_{35}$ we determine both $S_{x'x'}$ and $S_{z'z'}$ which leaves $S_{x'z'}$ and the structure and conformation of the O–CH$_3$ group to be determined from the two couplings $\tilde{D}_{37}$ and $\tilde{D}_{77}$. To do this we have assumed the methyl group to have a tetrahedral geometry with a C–H bond length of 1·09 Å, and the O–CH$_3$ and phenyl-O bonds were taken to be 1·42 Å and 1·36 Å respectively, which are the values determined for anisole [9]. The COC angle is assumed to be 120° and the unknown factors to be determined from the dipolar couplings are the C$_3$C$_4$O

angle, θ, and the three order parameters. The values of these parameters were determined for each temperature studied, with the result that θ is found to be independent of temperature and to have the value of $124\cdot4° \pm 0\cdot4°$. This compares with a value of $125\cdot0°$ found for 1-OCB in the solid state [7].

The similarity of the values of θ determined for 1-OCB in solid and nematic phases implies that the RIS model is a good approximation; nevertheless, we have considered the effect of adopting a continuous form for $V(\alpha)$. There are two sub-units to consider when constructing the interaction tensor elements $\varepsilon^n_{2,m}$. These are ring B, for which $\varepsilon^B_{2,0}$ and $\varepsilon^B_{2,2}$ are required, and the O–CH$_3$ fragment, which is effectively cylindrically symmetric by virtue of the three-fold nature of the potential for rotation of the methyl group about this bond, and which, therefore, requires just $\varepsilon^{OC}_{2,0}$. The angle θ is expected to change with rotation about the O–CH$_3$ bond, but in these exploratory and approximate calculations it will be given a fixed value. However, it is not appropriate to use the value found for the planar structure in the solid state. Ideally the value of θ should be included as a variable in the calculations but in the present case there are insufficient experimental data to determine the value of θ independently of the form of $V(\alpha)$. It is also simpler to fix θ at 120° and to allow the $\widehat{COC}$ angle to vary in the calculations. Thus, changing $\widehat{COC}$ to range between 127° and 123° changes the value of V_2 in equation (5) which produces the optimum agreement between observed and calculated dipolar couplings from 18 to 6 kJ mol^{-1}. The interdependence of θ and V_2 can be removed only by determining more dipolar couplings, for example by recording and analysing the spectrum of the fully protonated mesogen. The important conclusion to be drawn from the calculations using the existing, limited data set, is that adopting realistic forms for $V(\alpha)$ has only a small effect on the structure derived for this fragment and the order parameters for the minimum energy structure are virtually independent of the values of θ and V_2.

3.3. *The ordering matrix for the whole molecule*

The calculations which take into account the continuous nature of the rotational potentials show that the effect on the order matrix elements for the most probable structure is small. We have therefore determined the ordering matrix for the whole molecule when the RIS approximation is used. For 1-OCB, this means that for a fixed set of molecular axes the 24 sets of elements $S^n_{\alpha\beta}$ have magnitudes which are independent of n, but whose signs change when $\alpha \neq \beta$ as the molecule changes conformation. To determine these ordering matrix elements the dipolar couplings obtained for the d_5 and d_6 molecules were combined into one set at each temperature. To do this the dipolar couplings obtained from the d_6 compound were fitted to polynomials of the form

$$\tilde{D}_{ij} = A_0 + A_1 T_S + A_2 T_S^2 + A_3 T_S^3 + A_4 T_S^4,$$

where $T_S = T_{NI} - T$. These curves were then used to obtain a set of proton–proton couplings at the temperatures shown in table 4. The molecular structure used had the protons fixed at the average values obtained by separately analysing the data for the two isotopomers within the RIS approximation, with $\phi_{min} = 30\cdot4°$ and $\theta = 124\cdot4°$. The calculations were done with the axes x', y', z' since in this axis system $S_{y'z'}$ is zero. The values of the four non-zero matrix elements obtained at each temperature were then used to obtain the elements in the principal frame xyz, which are shown in table 4. The angles $\theta_{zz'}$, $\theta_{xx'}$ and $\theta_{yy'}$ between the principal

Table 4. Principal order parameters for 1-OCB.

$(T_{NI} - T)/K$	S_{zz}	$S_{xx} - S_{yy}$
18·0	0·56	0·078
17·0	0·56	0·061
16·0	0·55	0·053
15·5	0·56	0·061
15·0	0·55	0·063
14·5	0·54	0·066
14·0	0·54	0·050
13·0	0·53	0·057
12·0	0·53	0·060
11·0	0·52	0·079
10·0	0·51	0·067
9·0	0·50	0·071
8·0	0·49	0·077
7·0	0·48	0·082
6·0	0·46	0·082
5·0	0·45	0·094
4·0	0·43	0·090
3·0	0·41	0·075

and reference frames have the values:

$$\theta_{xx'} = 20 \cdot 6° \pm 4 \cdot 2°,$$

$$\theta_{yy'} = 20 \cdot 1° \pm 4 \cdot 2°,$$

and

$$\theta_{zz'} = 4 \cdot 4° \pm 0 \cdot 3°.$$

The angle $\theta_{zz'}$ is obtained with a small error because it is determined mainly by $S_{z'z'}$, which is obtained with high precision, whilst the poor accuracy with which $S_{x'x'} - S_{y'y'}$ is known leads to the large uncertainties in the angles $\theta_{xx'}$ and $\theta_{yy'}$. The errors in the values obtained for S_{zz} and $S_{xx} - S_{yy}$ are estimated from the derivations of their temperature dependences from smooth curves to be about ± 2 and ± 10 per cent respectively.

3.4. *The relationship between the deuterium quadrupolar splittings and the principal order parameters*

The quadrupolar splitting, $\Delta\tilde{v}_i$, for a deuteron at the ith site is given by

$$\Delta\tilde{v}_i = 3q^i_{zz}S_{zz}/2 + (q^i_{xx} - q^i_{yy})(S_{xx} - S_{yy})/2, \tag{14}$$

where q^i_{zz}, q^i_{xx} and q^i_{yy} are components of the quadrupolar tensor $\mathbf{q}_i$ in the principal frame of $\mathbf{S}$, and which will be independent of temperature for a rigid molecule. The quadrupolar splittings for the ring and methyl deuterons are well resolved for the d_5 compound [4], and they were measured using a double tuned probe at the same temperatures at which the dipolar couplings were obtained. This means that both the order parameters and the quadrupolar splittings (including their signs [4]) are known over a range of temperature from $(T_{NI} - 3)$ K to $(T_{NI} - 18)$ K. We have investigated the possibility of using this data to obtain the values of $q^{Me}_{\alpha\alpha}$ and $q^R_{\alpha\alpha}$ ($\alpha = x, y, z$) by a least squares fitting procedure. A very good fit was obtained between observed and

calculated quadrupolar splittings, but the values obtained for q_{zz}^{Me}, $q_{xx}^{Me} - q_{yy}^{Me}$, q_{zz}^{R} and $q_{xx}^{R} - q_{yy}^{R}$ are very different from those that can be predicted with confidence from estimates of the magnitudes of the deuterium quadrupolar tensors. The reason for this discrepancy is that $(q_{xx} - q_{yy}) \gg q_{zz}$ so that the term in equation (14) involving $S_{xx} - S_{yy}$ is appreciable in magnitude compared with the term involving S_{zz} even though the biaxiality in ordering is small. This in itself would not create a problem except that the errors involved in obtaining $S_{xx} - S_{yy}$ are large. We conclude, therefore, that the components of $\mathbf{q}^{R}$ and $\mathbf{q}^{Me}$ in the principal frame for the ordering matrix cannot be obtained in this way.

3.5. *Comparison with theory*

The values of the principal order parameters can be used to test theories of the orientational ordering of rigid biaxial mesogens. Thus, the potential of mean torque for a rigid mesogen can be expressed generally as

$$U(\beta, \gamma) = - \sum_{L,m} \varepsilon_{L,m} C_{L,m}(\beta, \gamma), \qquad (15)$$

where β and γ are the polar angles that the director makes in the principal frame, and the $\varepsilon_{L,m}$ are interaction coefficients averaged over both the separations and orientations of the surrounding molecules. It is often assumed that the infinite sum in equation (15) can, to a reasonable approximation, be truncated at the first terms, those with $L = 2$, so that [10]

$$U(\beta, \gamma) = - \varepsilon_{2,0} C_{2,0}(\beta, \gamma) - 2\varepsilon_{2,2} C_{2,2}(\beta, \gamma). \qquad (16)$$
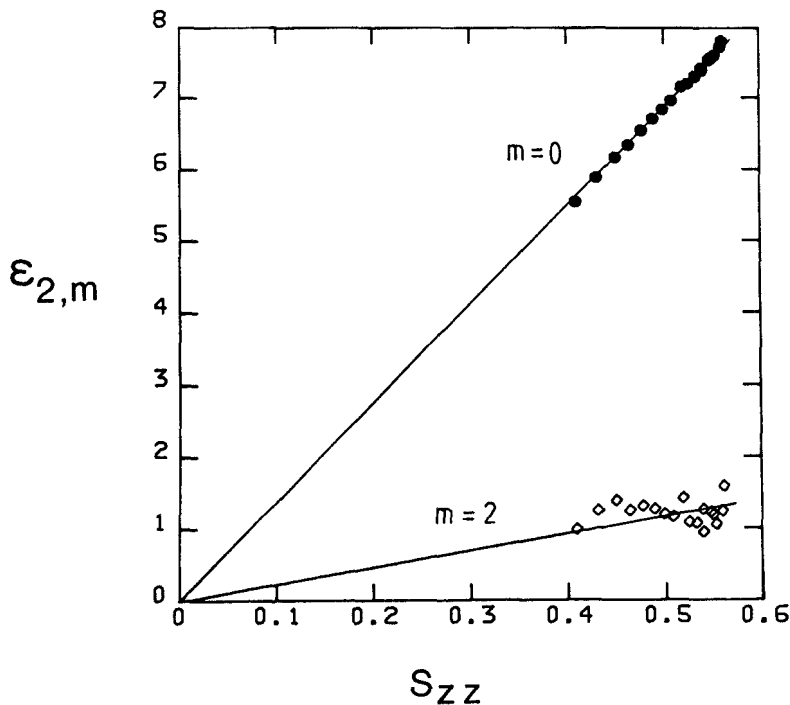

Figure 8. Dependence of $\varepsilon_{2,m}$ on S_{zz} for 1-OCB; the continuous lines are the result of fitting the data to a linear relationship.

The order parameters S_{zz} and $S_{xx} - S_{yy}$ are related to the $\varepsilon_{2,m}$ by

$$S_{zz} = Z^{-1} \int C_{2,0}(\beta, \gamma) \exp\{-U(\beta, \gamma)/RT\} \sin\beta d\beta d\gamma, \qquad (17)$$

$$S_{xx} - S_{yy} = 6^{-1/2} Z^{-1} \int C_{2,2}(\beta, \gamma) \exp\{-U(\beta, \gamma)/RT\} \sin\beta d\beta d\gamma, \qquad (18)$$

so that at each temperature the two interaction coefficients can be determined. The $\varepsilon_{2,m}$ vanish in the isotropic phase so they must depend directly on the order parameters. The simplest form that this dependence can have is

$$\varepsilon_{2,0} = \bar{u}_{200} S_{zz} + (2/3)^{1/2} \bar{u}_{202}(S_{xx} - S_{yy}), \qquad (19)$$

$$\varepsilon_{2,2} = \bar{u}_{220} S_{zz} + (2/3)^{1/2} \bar{u}_{222}(S_{xx} - S_{yy}), \qquad (20)$$

with the $\bar{u}_{2mn}$ being averages over intermolecular separations.

Figure 8 shows the $\varepsilon_{2,m}$ plotted against S_{zz}. The dependence of $\varepsilon_{2,0}$ on S_{zz} is linear within the small experimental error, and passes through the origin, showing that the second term in equation (19) is small. The slope gives $\bar{u}_{200}$ as $13{\cdot}66 \pm 0{\cdot}08\,\mathrm{kJ\,mol^{-1}}$. The coefficient $\varepsilon_{2,2}$ is determined with a larger experimental error and it is not possible to detect any non-linearity in the dependence on S_{zz}. It is possible, therefore to determine only the coefficient $\bar{u}_{220} = 2{\cdot}4 \pm 0{\cdot}4\,\mathrm{kJ\,mol^{-1}}$.

4. Conclusion

It is not yet possible to establish uniquely from experiment the shape and orientational order of a flexible molecule in a liquid-crystalline phase, both these quantities being dependent on the model chosen for the variation of the intermolecular potential with molecular shape. Here we have explored the consequences of adopting two particular models for interpeting the dipolar couplings obtained from proton N.M.R. spectra. The simpler model assumes that the molecule exists only in the minimum energy conformations (RIS model), whilst the Emsley–Luckhurst–Stockley model allows for a distribution of conformations weighted by appropriate probabilities. For 1-OCB, the most important conformational feature is the distribution in the inter-ring angle ϕ. Thus the dipolar couplings yield ϕ_{min} as $30{\cdot}4°$ when the RIS model is adopted, whereas interpreting the data with the ELS model yields $\phi_{min} = 36°$. Both methods of treating the data yield temperature independent structures over the whole of the nematic range. The two methods of treating the data lead to quantitative measurements of the second rank order matrix for 1-OCB. Adopting the Emsley–Luckhurst–Stockley model leads to a conformational dependence of both the magnitude of the principal components and location of the principal axes of the ordering matrix. However, for 1-OCB, this conformational dependence is small and it is a good approximation to determine the ordering matrix with the RIS model. In this case, only one matrix is required for 1-OCB since all minimum energy conformations have the same shape. This means that within the RIS model, the molecules of 1-OCB are effectively rigid and hence for the first time it is possible to test quantitatively the theories for the anisotropic potential for a single component mesogen. We have derived the interaction parameters for a general potential of mean torque, truncated at second rank terms and found good agreement with the predicted dependence on the orientational order parameters.

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