A ^1H NMR Investigation of the Conformational Properties of 1,2-Dimethoxybenzene

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The ^1H NMR spectrum of a sample of 1,2-dimethoxybenzene dissolved in a nematic solvent (I35) has been analysed to yield a set of partially-averaged dipolar couplings, D_{ij}. These are used to test models for the conformations adopted for the two OCH_3 groups relative to the ring. It is concluded that a single conformation, or a set of symmetry-related conformations is not consistent with the data. The dipolar couplings are used to derive the distribution among the 16 minimum energy structures which are possible if it is assumed that the C–O–C planes can only be either coplanar with, or perpendicular to, the phenyl ring plane.

Phenyl rings containing two methoxy groups in adjacent positions occur in many compounds of pharmaceutical importance. The two methoxy groups rotate about the Ar–O bonds in gas or liquid phases, and it is clear from their size that not all conformations can be equally probable. Designating the rotation angles about the two bonds as φ_1 and φ_2, with the in-plane structure having φ_1 and φ_2 as 0 or 180°, then a 'conformation' is a position of local minimum energy. If the barriers to rotation are sufficiently large, then the molecule can be regarded as being an equilibrium mixture of conformations, with relative weights given by eqns. (1) and (2)

$$p(\varphi_1, \varphi_2) = Q^{-1} \exp\{-U(\varphi_1, \varphi_2)/kT\} \qquad (1)$$

$$Q = \int \exp\{-U(\varphi_1, \varphi_2)/kT\}\, d\varphi_1\, d\varphi_2 \qquad (2)$$

In sterically unhindered anisoles the single minimum energy conformation has $\varphi = 0°$ in the gas,[1] liquid[2,3] and solid[4] phases, and introducing bulky substituents at both adjacent sites shifts the minimum to $\varphi = 90°$ in the solid state,[4] and probably also in liquids.[3,5] In the case of 1,2-dimethoxybenzene, which we shall refer to as ODMB, it has been suggested that the minimum energy structures are those in which the OCH_3 groups are either coplanar with, or perpendicular to, the phenyl plane in liquids and in the gas, so that there are 16 possible conformers, which can be divided into seven sets of symmetry related structures as shown in Fig. 1. Anderson *et al.*[6] interpreted the gase phase photoelectron spectrum of ODMB as showing **3** to be of lowest energy, whilst measurements of ^{13}C shifts and spin-lattice relaxation times[7] were used to support in-plane structures as being of lowest energy, with **1** regarded as the most probable form. Exner and Jehlicke[8] have measured the dipole moments of a number of polymethoxy benzenes, including ODMB, and conclude that four possibilities fit their data: (*a*) a single conformer with $\varphi_1 = 110°$, $\varphi_2 = 0°$; (*b*) a single conformer with $\varphi_1 = 145°$, $\varphi_2 = 35°$; (*c*) a mixture of **1** and **2** in the ratio 70:30; (*d*) a mixture of **1** and **3** in the ratio 40:60. Breen *et al.*[3] conclude from time of flight mass spectroscopy that ODMB is in a single conformation when prepared by the supersonic jet expansion technique, but its structure could not be assigned. Schaefer and Laatikainen[9] studied the long range $^5J_{HH}$ coupling constant and concluded that ODMB is mainly in planar conformations. Molecular mechanics calculations by Dodzuick,[10] using the MM2 method, found the free energies to be in the order **1** < **3** < **2** < **6**.

We have developed a new method of determining the conformations of flexible molecules in solution.[11] This relies on the sensitivity of dipolar couplings, D_{ij}, between nuclei to geometry and to any internal motion which changes the magnitude or orientation of internuclear vectors, r_{ij}. The dipolar couplings average to zero in isotropic liquids, because of rapid, isotropic rotational motion, but to non-zero values in liquid crystal solutions. The advantages of this method are that dipolar couplings are observed between all magnetic nuclei in a molecule, and they are very sensitive to the nature of internal motion. We report here on the analysis of the ^1H NMR spectra of a sample of ODMB dissolved in a nematic liquid crystal, and show that the dipolar couplings obtained can be used to obtain a conformational distribution.

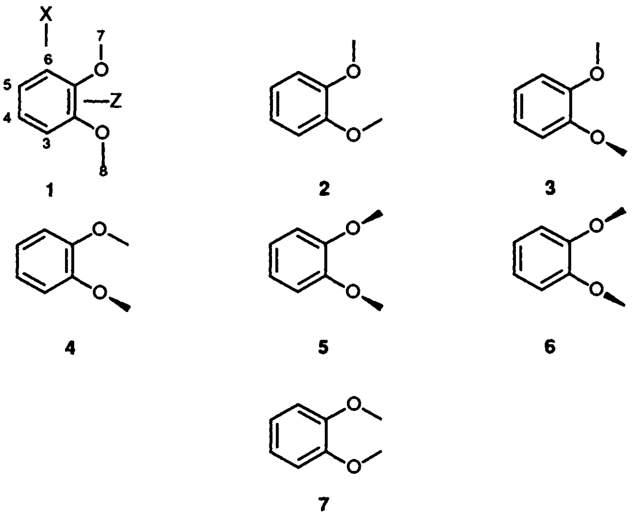

Fig. 1 The 16 minimum energy structures of 1,2-dimethoxybenzene divided into symmetry related sets of equal energy

Experimental

The ^1H NMR spectrum of *ca.* 20% by weight solution of ODMB in the nematic liquid crystal I35 (BDH Chemicals Limited) is shown in Fig. 2. The free induction decays were accumulated with a spectral width of 10 416 Hz into 32K words of computer store, giving a digital resolution on the transform of 0.6 Hz. The analysis of such a spectrum is a formidable task,

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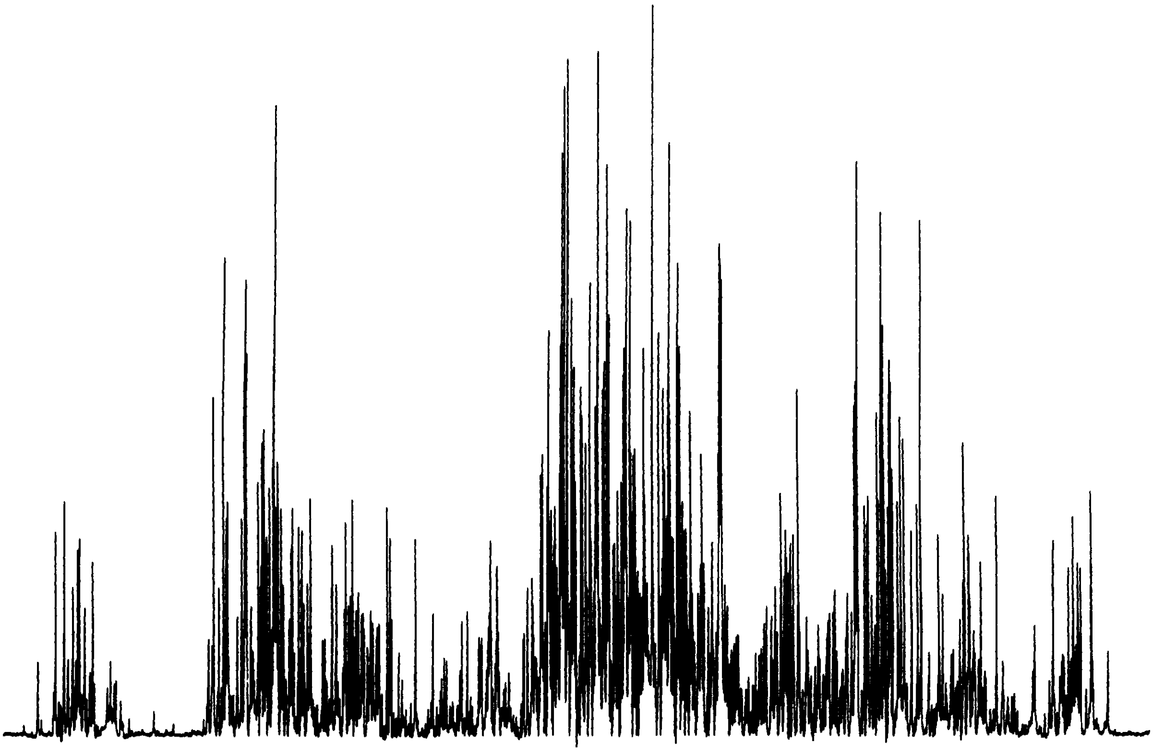


Fig. 2 300 MHz ^1H NMR spectrum of a sample of 1,2-dimethoxybenzene dissolved in the nematic solvent I35. Temperature, 300 K; spectral width displayed, 9550 Hz.

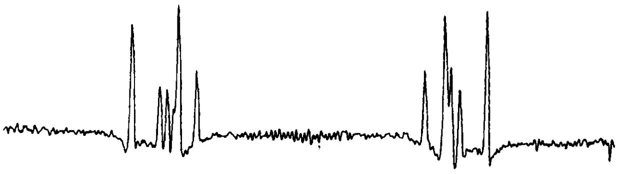
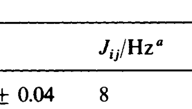


Fig. 3 Deuterium-decoupled 200 MHz spectrum of a sample of [$^2H_6$]1,2-dimethoxybenzene with both methyl groups deuteriated. Solvent, I35; temperature, 300 K; spectral width displayed, 7250 Hz.

Table 1 NMR parameters obtained from the analysis of the 300 MHz ^1H NMR spectrum of a sample of 1,2-dimethoxybenzene dissolved in the nematic solvent I35



i,j	D_{ij}/Hz	J_{ij}/Hz[a]	$(\delta_i - \delta_j)$/Hz
3,4	-1200.06 ± 0.04	8	-142.87 ± 0.05
3,5	-112.74 ± 0.06	2	
3,6	-35.69 ± 0.08	0	
3,7	-34.80 ± 0.03	0	
3,8	-865.65 ± 0.03	0	
4,5	$\pm 277.72 \pm 0.08$	8	
4,7	-56.63 ± 0.05	0	784.90 ± 0.06
4,8	-153.21 ± 0.05	0	
7,8	-16.92 ± 0.05	0	
7,7	215.96 ± 0.04	0	

[a] Estimated as being couplings between protons in benzene derivatives, and kept constant in the spectral analysis.

which was achieved by the following strategy. A sample of ODMB containing two CD_3 groups was synthesized by the method of Williamson.[12] The deuterium-decoupled, ^1H spectrum of a sample of this [$^2H_6$] compound dissolved in I35 is shown in Fig. 3 and its analysis yields D_{34}, D_{35}, D_{36} and D_{45}. The deuterium spectrum is essentially a doublet with splitting $\Delta\nu$, which arises from the nuclear electric quadrupole interaction with the electric field gradient at the deuterons. It has been established[5] that for some unhindered anisoles $\Delta\nu$ is $7.17 \times D_{77}$ ($= D_{88}$), the dipolar coupling between protons within the methyl groups, and hence this dipolar coupling can also be obtained.

Having obtained five dipolar couplings in this way it still proved impossible to analyse the spectrum in Fig. 2, and so the compound containing one CD_3 group was synthesized. The starting material, 2-methoxyphenyl, was obtained from the Aldrich Chemical Company Limited and the CD_3 group introduced by the Williamson synthesis. The deuterium-decoupled ^1H spectrum of a sample of this compound in I35 is shown in Fig. 4, and its analysis yielded all the dipolar couplings and chemical shifts necessary to analyse the spectrum of the fully protonated compound, except D_{78}. With this information it was possible to analyse the proton spectrum of ODMB; an rms error between observed and calculated line positions of 0.48 Hz was obtained, and the dipolar couplings are given in Table 1. Note that the errors on the D_{ij} values do not take into account the errors on the line positions in the experimental spectrum, which are ± 0.3 Hz, nor the effect of using estimates for the magnitudes of the J_{ij} values. These factors are estimated as reducing the precision on the D_{ij} values to *ca.* ± 0.5 Hz.

Calculations.—The method that we use to relate the dipolar couplings to the structure, flexibility and orentational order of a molecule dissolved in a liquid crystal phase has been described in detail elsewhere.[11] It has been used to study internal rotation in molecules such as ethoxybenzenes,[11,13] 4,4-disubstituted biphenyls,[14,15] and benzyl halides,[16,17] where the positions of the minima in $V(\varphi)$ are known, at least approximately. These studies suggest that the method can be used to test conformational models, although it should be kept in mind that

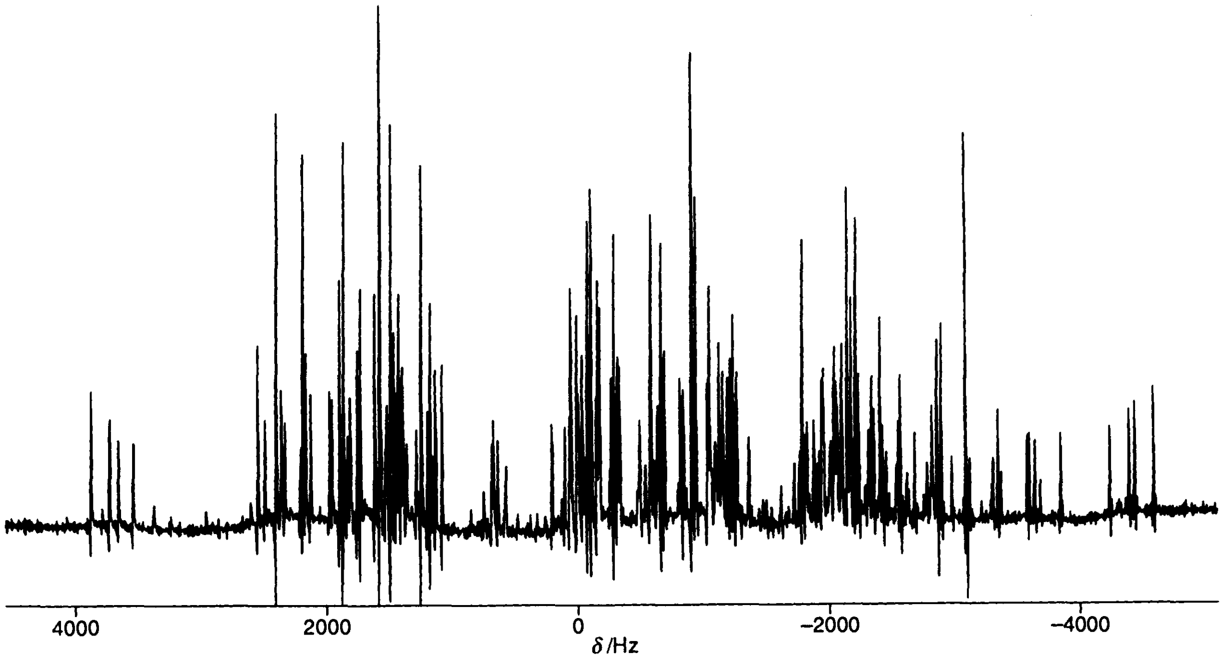


Fig. 4 Deuterium-decoupled 200 MHz proton spectrum of [$^2H_3$]1,2-dimethoxybenzene containing one deuteriated methyl group. Solvent, I35; temperature 300 K; spectral width displayed, 9660 Hz.

it is not an exact method and the present study is part of a continuing process of discovering whether the results obtained are reasonable. To present sufficient detail that the strengths and weaknesses of the method can be appreciated we begin by considering rigid molecules. The partially-averaged dipolar couplings for a rigid molecule are given by eqn. (3) where

$$D_{ij} = (2/3)\,\Sigma_{\alpha\beta}\, D_{ij\alpha\beta}\, S_{\alpha\beta} \qquad (3)$$

$D_{ij\alpha\beta}$ are the components of the dipolar coupling tensor in a molecule fixed frame, and $S_{\alpha\beta}$ is an element of the Saupe order matrix. The $D_{ij\alpha\beta}$ are related to structure by eqn. (4) where $\theta_{ij\alpha}$

$$D_{ij\alpha\beta} = -\gamma_i\gamma_j h(3\cos\theta_{ij\alpha}\cos\theta_{ij\beta} - \delta_{\alpha\beta})/8\pi^2 r_{ij}{}^3 \qquad (4)$$

is the angle between the inter-nuclear vector, r_{ij}, and axis α, $\delta_{\alpha\beta}$ is 1 if $\alpha = \beta$ and zero otherwise, and γ_i and γ_j are the gyromagnetic ratios of the two nuclei. If there is intramolecular rotation through an angle φ, subject to a potential $V(\varphi)$, then $D_{ij\alpha\beta}$ and $S_{\alpha\beta}$ become φ dependent, so that the observed dipolar coupling is given by eqn. (5).

$$D_{ij} = (2/3)\int p(\varphi)\mathrm{d}\varphi\; \Sigma_{\alpha\beta}\, D_{ij\alpha\beta}(\varphi)\, S_{\alpha\beta}(\varphi) \qquad (5)$$

The φ dependence of dipolar coupling depends on the bond lengths, angles and the location of the rotation axis, and for a molecule like ODMB these are either known with reasonable precision, or can be determined as part of the data analysis. The φ dependence of orientational order parameters is not known *a priori* and must be calculated from a theoretical model. We adopt here the model proposed by Emsley, Luckhurst and Stockley[18] (ELS) in which $S_{\alpha\beta}(\varphi)$ is calculated from a mean potential energy $U(\omega,\varphi)$, which is partitioned into a part, $U_{\mathrm{ext}}(\omega,\varphi)$, which depends on the orientation, ω, of the mesophase director with respect to a molecular frame fixed in a rigid, sub-unit of the molecule, and $U_{\mathrm{int}}(\varphi)$, which depends only on φ, and which, for a single rotation axis, is identified with $V(\varphi)$. In practice the integral over φ is replaced by a summation over n. The value of n is chosen to approximate most closely to the integral, and when the rotational barrier has deep minima, then it is usual to set its value to be equal to or less than the number of local minima, so that for ODMB $n \leq 16$. For a discrete set of n conformations eqn. (5) becomes eqn. (6) where p_n is the

$$D_{ij} = (2/3)\,\Sigma_n\, \Sigma_{\alpha\beta}\, p_n D_{ij\alpha\beta}(n) S_{\alpha\beta}(n), \qquad (6)$$

probability of the nth conformation. The ELS model expresses the potential of mean torque for a molecule in conformation n

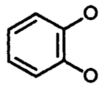
$$U_{\mathrm{ext}}(\omega,n) = -\varepsilon_{2.0}{}^n\, C_{2.0}(\omega,n) - 2\varepsilon_{2.2}{}^n\, C_{2.2}\,(\omega,n), \qquad (7)$$

as eqn. (7) where the $C_{2.m}(\omega,n)$ values are modified spherical harmonics, and the $\varepsilon_{2.m}{}^n$ values are interaction coefficients. The conformational dependence of the $\varepsilon_{2.m}{}^n$ values is obtained by expressing them as a sum of tensors $\varepsilon_{2.m}{}^j$ which represent the interaction of rigid molecular fragments, and which are independent of the conformation. Thus, eqn. (8) holds, where

$$\varepsilon_{2.m}{}^n = \Sigma_j\, \Sigma_p \varepsilon_{2.p}{}^j D_{mp}{}^2(\Omega_j{}^n), \qquad (8)$$

$D_{mp}{}^2(\Omega_j{}^n)$ is a Wigner rotation matrix and $\Omega_j{}^n$ is the orientation of segment j in conformer n relative to the reference frame in which $\varepsilon_{2.m}{}^n$ is calculated.

In the case of ODMB the rigid segments are **8**, which requires



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two interaction tensor elements, $\varepsilon_{2.0}{}^R$ and $\varepsilon_{2.2}{}^R$, and OCH_3 which requires just $\varepsilon_{2.0}{}^{OC}$. The probabilities p_n in eqn. (6) refer to the liquid crystal phase and differ from those in the isotropic phase, p_n(iso), which are simply given by eqn. (9).

$$p_n(\mathrm{iso}) = \exp\{-V(n)/kT\}/\Sigma_n \exp\{-V(n)/kT\} \qquad (9)$$

The p_n values are given by eqn. (10), where Q_n and Z are as defined in eqns. (11) and (12) respectively.

Table 2 Co-ordinates of ring protons and local order parameters, $S_{\alpha\beta}{}^{R}$, for 1,2-dimethoxybenzene dissolved in I35[a]

i	x_i/Å	z_i/Å
3	2.48	0.0
4	1.251 5	−2.162 1
5	−1.251 5	−2.162 1
6	−2.48	0.0

[a] $S_{zz}{}^{R} = 0.191\,6$; $S_{xx}{}^{R} - S_{yy}{}^{R} = 0.264\,1$.

$$p_n = Q_n Z^{-1} \exp\{-V(n)/kT\} \tag{10}$$

$$Q_n = \exp\{-U_{\text{ext}}(n,\omega)/kT\}\text{d}\omega \tag{11}$$

$$Z = \int \Sigma_n \exp\{-U(n,\omega)/kT\}\text{d}\omega \tag{12}$$

The calculations proceed by fixing a geometry for the molecule, the bond lengths and angles being assumed independent of n, and testing a particular conformational model, *i.e.* a set of values for $V(n)$, by finding whether the error function given in eqn. (13), where F is the number of degrees of

$$R = F^{-1}(\Sigma_{i<j}[D_{ij}(\text{observed}) - D_{ij}(\text{calculated})]^2)^{1/2} \tag{13}$$

freedom, can be brought to an acceptable minimum by varying $\varepsilon_{2.0}{}^{R}$, $\varepsilon_{2.2}{}^{R}$ and $\varepsilon_{2.0}{}^{\text{OC}}$.

Results and Discussion

Does the Molecule Exist in a Single Set of Symmetry Related Structures?—The simplest conformational model is that only one set of symmetry-related structures exists. In this case the molecule can be regarded as being pseudo-rigid, because the only change in $S_{\alpha\beta}$ with conformation is in the sign, but not the magnitude of the off-diagonal elements.

To test whether the dipolar couplings are consistent with a particular conformation, we first determine the values of the local order parameters for the phenyl ring, $S_{zz}{}^{R}$ and $S_{xx}{}^{R} - S_{yy}{}^{R}$, from D_{34}, D_{35}, D_{36} and D_{45}. To do this it is necessary to fix one interproton distance, and we chose $r_{36} = 4.96$ Å, which corresponds to the separation in a regular hexagon with $r_{\text{CC}} = 1.4$ Å and $r_{\text{CH}} = 1.08$ Å. The four calculated dipolar couplings are brought into exact agreement with those observed by varying the two order parameters and the x and z co-ordinates of 4-H and 5-H. The results are shown in Table 2.

The six dipolar couplings D_{37}, D_{38}, D_{47}, D_{48}, D_{77} and D_{78} can now be used to test each of the single conformational sets. For conformations **1** and **7** the only other variables determining these dipolar couplings are the bond lengths and angles. In planar anisoles the angles C_2–C_1–O is close to 125°, and C_1–O–C(CH_3) is close to 117°. When the C^1–O–C(CH_3) plane is orthogonal to the ring the C_2–C_1–O angle decreases to 120°, and C_1(CH_2)–O–C decreases to *ca.* 116°.[4] In our calculations we have assumed for simplicity that the bond lengths and angles do not change with conformation, and we have chosen the values $r_{\text{CO}} = 1.36$ Å, $r_{\text{OC}} = 1.42$ Å, r_{CH}(methyl) = 1.1 Å and H–C–H = 109.47°.

In unhindered anisoles the minimum energy conformation of the methyl group has one C–H bond in the C_1–O–C plane, and we have assumed this to be the case for both methyls in all the conformations of 1,2-dimethoxybenzene. The calculations on single conformations were performed with C_2–C_1–O and C_1–O–C both equal to 120°, although the effect on the calculated values of dipolar couplings of changing these angles has been investigated.

When the molecule is assumed to be either structure **1** or **7**, the calculated value of R is unacceptably large (36 and 650 Hz, respectively), and so we conclude that the molecule does not exist in either of these forms alone.

The remaining five conformational sets require off-diagonal order parameters to calculate the six conformationally-sensitive D_{ij} values, thus set **2** requires S_{xz}, sets **3** and **4** require S_{xz}, S_{yz} and S_{xy}, set **5** requires S_{yz} as also does set **6**. In each case, variation of the off-diagonal order parameters, together with reasonable changes in bond lengths and angles, does not reduce $R < 80$ Hz, and so these single conformational sets are judged to be unacceptable.

We have also tested some symmetry related sets of conformations, but which have either φ_1 or φ_2 different from 0°, 90° or 180°. All three off-diagonal order parameters are non-zero for these conformations. Structures were tested with $\varphi_1 = 0°$ and φ_2 varied between 100° and 140°, and also the structure suggested by Exner and Jehlicka[8] on the basis of the value of the dipole moment, which has $\varphi_1 = 35°$ and $\varphi_2 = 145°$. However, none of these structures gives an rms error, R, less than 50 Hz, and are, therefore rejected as possible solutions. We can conclude, therefore, that 1,2-dimethoxybenzene must exist in more than one conformational form.

Testing Conformational Distributions.—When more than one conformational set is involved in a distribution, it is necessary to calculate the D_{ij} values from eqn. (6) and to use a model, such as the ELS model, to calculate the order parameters.

Our aim is to test the most probable conformational distribution, rather than to attempt a search for all possible distributions which will fit our data. From the other structural evidence on this molecule discussed earlier, the most probable distribution should include **1** and **3**, and possibly some of the other conformations, except **7**, which is severely sterically hindered. With the geometry discussed earlier, the dipolar couplings are consistent with **1** being the most populated (74%), followed by **3** (25%) and **6** (1%). Table 3 gives the differences between observed and calculated dipolar couplings, ΔD_{ij}, for this conformational distribution. The value of R for this distribution is 2.7 Hz, but the large value obtained for the ratio $\Delta D_{78}/D_{78}$ suggests that the distribution is flawed in some respect. In fact, changing the angles C_2–C_1–O and C_1–O–C, whilst giving a small increase in R, does decrease ΔD_{78} to *ca.* 1 Hz. Table 4 shows the conformational distributions which give the best fits to the data for some other, fixed values of C_2–C_1–O and C_1–O–C. It is clear from the results in Table 4 that the conformational probabilities determined by this method have an uncertainty of *ca.* 5% for the two most probable structures, so that the probability of **1** lies between 74 and 79%, and that of **3** between 25 and 20%, with **6** being no more than 1%.

Finally, it is important to remember that the p_n values in Table 4 refer to those calculated from eqn. (10) and include a contribution which depends on the conformational dependence of the potential of mean torque $U_{\text{ext}}(n,\omega)$. The ELS model allows p_n(iso) to be obtained from eqn. (9), and in the present case the difference $p_n(\text{iso}) - p_n$ is negligibly small (<0.5%).

Conclusion

The values of the partially-averaged inter-proton dipolar couplings are clearly inconsistent with 1,2-dimethoxybenzene existing as a single set of symmetry-related conformers. Analysing the data with the ELS model gives the conformational distribution with **1** as most probable (74–79%), followed by **3** (25–20%), and with a negligible amount of the other conformers. The reliability of these conformational probabilities depends on how well the ELS model approximates the true conformational dependence of orientational ordering. This is

Table 3(a) The differences, ΔD_{ij}, between observed dipolar couplings and those calculated by the ELS model[a] and (**b**) the order parameters for each conformation. The angles C_2–C_1–O and C_1–O–C are both fixed at 120°

i,j	ΔD_{ij}/Hz
3,4	0.39
3,5	0.37
3,6	0.34
3,7	−3.30
3,8	0.28
4,5	2.63
4,7	−3.80
4,8	−1.26
7,8	−3.83
8,8	−0.15

Table 3(b)

Conformation	S_{zz}	$S_{xx} - S_{yy}$	S_{xy}	S_{xz}	S_{yz}
1	0.279	0.186	0	0	0
3	0.207	0.227	0.006	0.006	−0.014
6	0.227	0.176	0.012	0	0

[a] Interaction parameters, $\varepsilon_{2,}{}^{j}{}_{m}$/kJ mol^{-1}: $\varepsilon_{2,0}{}^{R} = 2.03 \pm 0.02$; $\varepsilon_{2,2}{}^{R} = 1.42 \pm 0.02$; $\varepsilon_{2,0}{}^{OC} = 0.35 \pm 0.01$.

Table 4 Conformational probabilities obtained for 1,2-dimethoxybenzene dissolved in the nematic phase of I35

Bond angles/°		Probability (%)	
C_2–C_1–O	C_1–O–C	**1**	**3**
120	120	74	25
125	117	79	20
125	115	75	24

difficult to assess at the present time, but it is encouraging that the conformational distribution obtained for 1,2-dimethoxybenzene is in accord with most of the other estimates of the relative free energies of the structures shown in Fig. 1.

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