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An investigation by N.M.R. spectroscopy of the dependence on internal motion of the orientational ordering of ethoxybenzene and 4-fluoroethoxybenzene when dissolved in a nematic solvent

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The proton N.M.R. spectra of samples of ethoxy-d_3-benzene and 4-fluoroethoxy-d_3-benzene dissolved in the nematic solvent I52 have been recorded and analysed to yield sets of dipolar coupling $\tilde{D}_{ij}$. The dipolar couplings are used together with the theoretical model of Emsley, Luckhurst and Stockley to obtain $V(\varphi)$ the potential governing rotation about the O–CH_2 bond, and the dependence on φ of the orientational order parameters $S_{\alpha\beta}$.

1. Introduction

The molecules which form liquid crystals almost invariably have internal motion about some of their constituent bonds. This has the consequence that $f(\omega, \chi)$, the singlet orientational distribution function, will depend, in principle, on both ω, the orientation of the mesophase director in a molecular frame and χ, the coordinates defining the shape of the molecule [1]. The dependence of $f(\omega, \chi)$ on molecular shape means that measurements of quantities which are averaged by the two kinds of motion yield an ensemble average which depends upon the orientational order parameters $S_{\alpha\beta}(\chi)$, which are dependent on χ, and on potentials $V(\varphi_i)$ for rotation about bonds. It has been demonstrated [2] that $S_{\alpha\beta}(\chi)$ can be obtained by comparing observed deuterium quadrupolar splittings $\Delta\tilde{v}_i$ with values calculated with parameterized models of $f(\omega, \chi)$. In these investigations the number of $\Delta\tilde{v}_i$ available from the N.M.R. spectrum is limited to one for each group of equivalent deuterons, and this is too small a data set to enable the form of $V(\varphi_i)$ to be characterized in detail. Thus, $V(\varphi_{cc})$, the potential for rotation about the C–C bonds in an alkyl chain was assumed in these calculations on mesogens to be such that only the three positions of minimum energy are populated, which is known as the rotational isomeric state model. This limitation on studying $V(\varphi_i)$, and in consequence in characterizing $S_{\alpha\beta}(\chi)$, can be removed by comparing observed with calculated dipolar couplings involving protons, $\tilde{D}_{ij}$. There are $n(n-1)/2$ values of $\tilde{D}_{ij}$ between n non-equivalent nuclei and although symmetry reduces this number it is potentially a much larger data set to use in characterizing $f(\omega, \chi)$. There are, however, two important factors which have acted as a deterrent to using sets of $\tilde{D}_{ij}$ for the characterization of the shape dependence of $f(\omega, \chi)$ and these are that the proton spectra are extremely complex and their analysis presents a formidable challenge, and that the form of the dependence of $f(\omega, \chi)$ on χ is not known with certainty. Mesogens contain many interacting protons and usually several bond rotation axes, and this combination makes the characterization of $f(\omega, \chi)$ for these molecules extremely difficult.

These difficulties can be reduced by studying solutes dissolved in liquid crystal solvents, thus enabling the methods of characterizing $f(\omega, \chi)$ to be tested on molecules which whilst being non-mesogenic do contain the same structural elements as mesogens. Thus, we have described [3] a test of the method of characterizing $f(\omega, \chi)$ devised by Emsley, Luckhurst and Stockley [2], the ELS model, using a set of $\tilde{D}_{ij}$ obtained by analysing the proton spectrum of a sample of 4-chloroethoxybenzene dissolved in the nematogen I52. This molecule was chosen for study because the alkyloxyphenyl group is a common feature in many mesogens, and the potentials governing interal rotation and the geometry of the molecule are known to a reasonable accuracy so that this molecule can be used to test the method [3, 4]. The conclusion reached from this investigation is that the ELS method, whilst not giving exact agreement between theory and experiment, does provide a means of testing models for bond rotational potentials, and of characterising the conformational dependence of orientational ordering.

We now explore the effect on both $S_{\alpha\beta}(\chi)$ and $V(\varphi_{oc})$, the potential for rotation about the O–CH_2 bond, of replacing the chlorine with either hydrogen or fluorine. We choose to study the para fluorine substituted molecule because of the aid to spectral analysis of having proton and fluorine resonances which are completely separated from each other whilst having the advantage, which is shared with unsubstituted ethoxybenzene, of increasing the number of $\tilde{D}_{ij}$. For both these molecules the methyl group was fully deuteriated in order to simplify the proton spectrum.

2. Experimental

The analysis of the proton spectra of 10 interacting spins is a formidable problem and our strategy, whenever possible, is first to record and analyse the deuterium and proton—{deuterium} spectra from fully or partially deuteriated samples. In the present case this was practicable for ethoxybenzene, and hence the compounds $C_6D_5OC_2D_5$, $C_6D_5OCH_2CH_3$ and $C_6H_5OCH_2CD_3$ were synthesized from appropriate starting materials. All the ethoxybenzenes were synthesized by the method of Williamson [5].

The liquid crystal solvent used was (1-(4-trans-pentylcyclohexyl)-2-(2′-fluoro-4′-ethyl-4-biphenyl)ethane (I52) which was obtained from BDH Ltd. The concentration of the solutes was approximately 10 per cent by weight. The deuterium and proton echo spectra were recorded on a Bruker CXP 200, whereas the proton and fluorine spectra were recorded on a Bruker AM 360 spectrometer. The temperature of the sample in each experiment was 300 K. Figure 1 shows the 30·7 MHz deuterium spectrum from $C_6D_5OCD_2CD_3$ and the 360 MHz proton spectrum from $C_6H_5OCH_2CD_3$. Figure 2 shows the fluorine and proton spectra from $FC_6H_4OCH_2CD_3$.

3. Results and discussion

The quadrupolar splittings for the deuterons in $C_6D_5OCD_2CD_3$ are given in table 1. They were used to determine good estimates for the interproton dipolar couplings within the aromatic ring, which were then used as starting parameters in the analysis of the proton spectrum. The signs of $\Delta\tilde{\nu}_i$ are those which agree with the

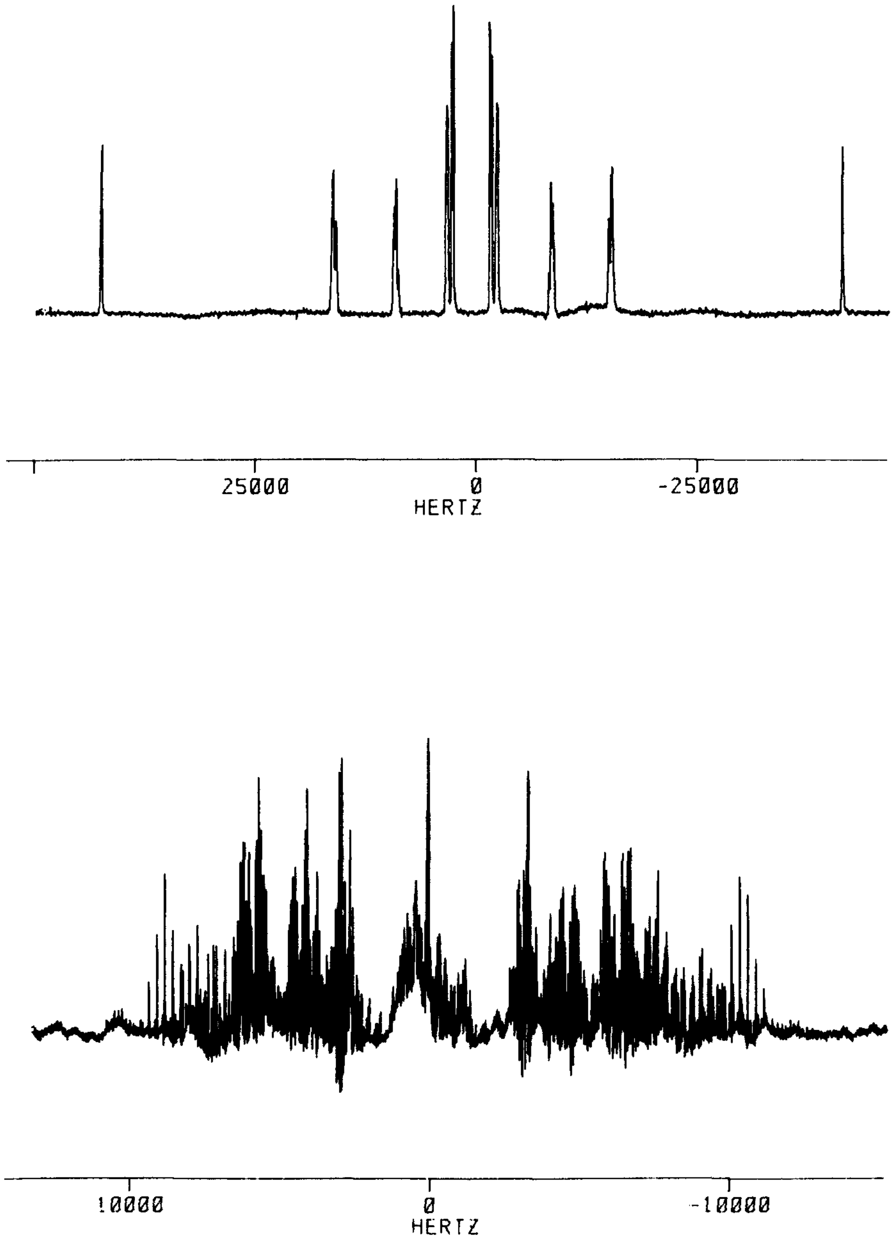

Figure 1. 30·7 MHz deuterium spectrum of perdeuteriated ethoxybenzene (top) and 360 MHz proton spectrum of ethoxybenzene containing a CD3 group (bottom). Both samples were dissolved in the nematic solvent I52 at 300 K.

structure and orientational ordering determined from analysis of the set of dipolar couplings obtained from the proton spectrum of a sample of $C_6H_5OCH_2CD_3$ dissolved in I52, which are given in table 2. We shall not comment further on the values of the $\Delta\tilde{\nu}_i$, except to note that $\Delta\tilde{\nu}_1 \neq \Delta\tilde{\nu}_2$. This inequality can arise from either different orientations of the principal axes of the quadrupolar tensors of the two deuterons, or different magnitudes of these two tensors.

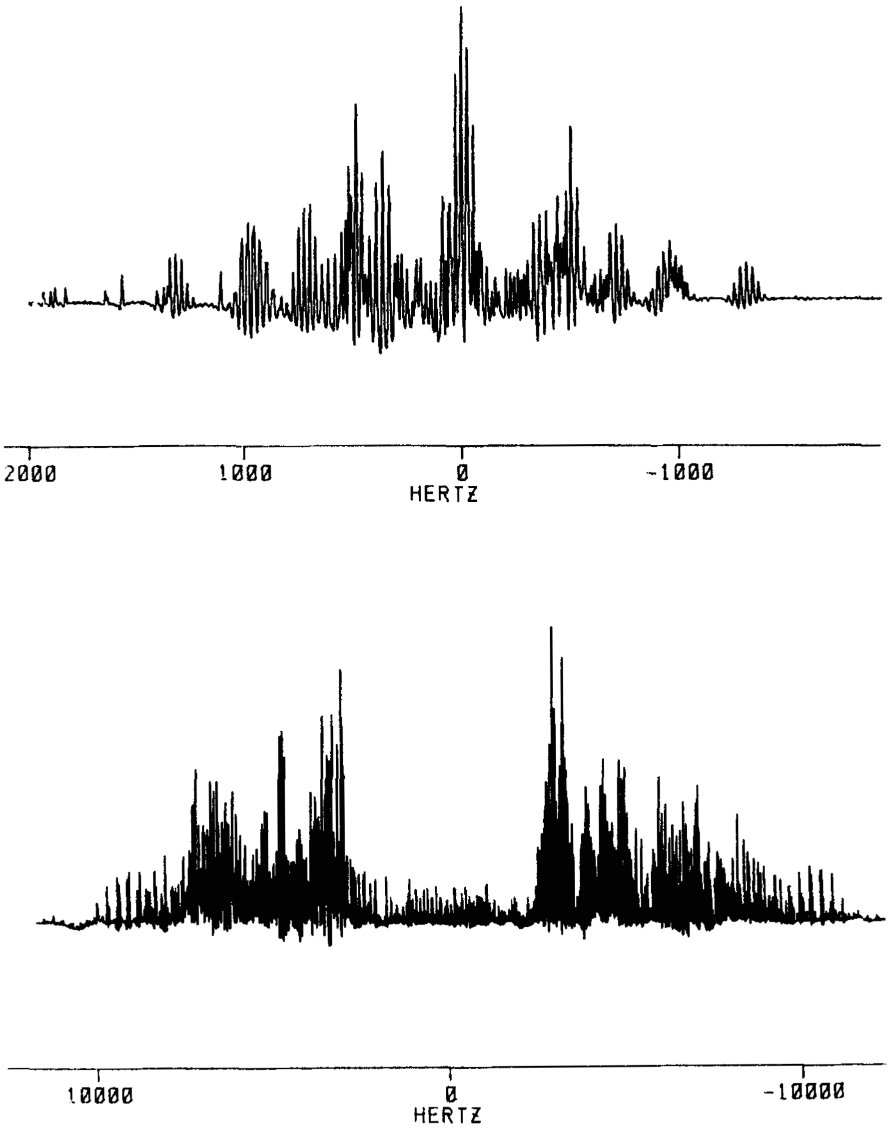

Figure 2. 360 MHz proton (bottom) and 338 MHz fluorine (top) spectra of a sample of 4-fluoroethoxybenzene deuteriated in the methyl group and dissolved in the nematic solvent I52 at 300 K.

Table 1. Quadrupolar splittings observed for a sample of perdeuteriated ethoxybenzene dissolved in I52.

$\Delta\tilde{\nu}_1 = 5616 \pm 20\,\mathrm{Hz}$
$\Delta\tilde{\nu}_2 = 4319 \pm 20\,\mathrm{Hz}$
$\Delta\tilde{\nu}_3 = 83860 \pm 20\,\mathrm{Hz}$
$\Delta\tilde{\nu}_6 = -31287 \pm 20\,\mathrm{Hz}$
$\Delta\tilde{\nu}_8 = -17518 \pm 20\,\mathrm{Hz}$

Table 2. Dipolar couplings, $\tilde{D}_{ij}$, and chemical shifts, δ_{ij}, obtained from the analysis of the 360 MHz proton spectrum of a sample of ethoxybenzene-d_3 dissolved in I52 at 300 K. The calculated values are those for the model discussed in the text.

	$\tilde{D}_{ij}$/Hz	
i, j	Observed	Calculated
1, 2	−2806·52 ± 0·06	−2807·09
1, 3	−358·78 ± 0·09	−358·91
1, 4	−6·56 ± 0·07	−6·24
1, 5	163·58 ± 0·13	163·63
1, 6	−1202·17 ± 0·06	−1203·10
1, 8	−45·27 ± 0·05	−44·43
2, 3	−69·35 ± 0·10	−68·87
2, 4	163·18 ± 0·13	163·35
2, 6	−241·77 ± 0·08	−233·87
2, 8	−17·98 ∓ 0·05	−18·47
3, 6	−168·48 ± 0·06	−160·39
3, 8	−14·16 ± 0·06	−13·76
6, 7	4020·81 ± 0·06	4021·34
6, 8	−137·85 ± 0·03	−138·10
Chemical shifts δ_{ij}/Hz		
1, 2	144·0 ± 0·1	
1, 3	218·8 ± 0·2	
1, 6	−588·2 ± 0·1	
	Scalar coupling J_{ij}/Hz†	
1, 2	8·30	
1, 3	1·03	
1, 4	0·44	
1, 5	2·74	
2, 3	7·36	
2, 4	1·76	
6, 8	0·00	

† Assumed values and kept fixed in the analysis; only non-zero J_{ij} values given.

The analysis of the proton and fluorine spectra of 4-fluoroethoxybenzene-d_3 proved to be possible without the need to first record the spectra of deuteriated samples. The results are given in table 3.

The analysis of the dipolar couplings in terms of the structure and orientational ordering of the solute molecules proceeds by the method described by Celebre *et al.* [3], which used the model for $f(\omega, \chi)$ proposed by Emsley, Luckhurst and Stockley [2]. Thus, the partially averaged dipolar couplings are related to $S^n_{\alpha\beta}$, the elements of a Saupe order matrix for the molecule in the nth conformation, and p_n, the statistical weight of that conformation, by

$$\tilde{D}_{ij} = (2/3) \sum_n p_n \sum_{\alpha,\beta} D^n_{ij\alpha\beta} S^n_{\alpha\beta}, \tag{1}$$

where α and β refer to molecular axes. The dipolar coupling $D^n_{ij\alpha\beta}$ in the nth conformation is,

$$D^n_{ij\alpha\beta} = -\gamma_i\gamma_j h(3l_{ij\alpha}l_{ij\beta} - \delta_{\alpha\beta})/8\pi^2 r^3_{ijn}, \tag{2}$$

Table 3. Dipolar couplings, $\tilde{D}_{ij}$, and chemical shifts, δ_{ij}, obtained from the analysis of the proton spectrum of a sample of 4-fluoroethoxybenzene-d_3 dissolved in I52 at 300 K. The calculated values of $\tilde{D}_{ij}$ are those from the model discussed in the text.

	$\tilde{D}_{ij}$/Hz	
i, j	Observed	Calculated
1, 2	−3104·78 ± 0·09	−3106·52
1, 3	−342·05 ± 0·11	−342·21
1, 4	10·23 ± 0·10	10·55
1, 5	225·72 ± 0·17	226·21
1, 6	−1334·82 ± 0·08	−1335·86
1, 8	−50·38 ± 0·06	−50·06
2, 3	−158·02 ± 0·11	−156·93
2, 4	228·21 ± 0·16	228·73
2, 6	−268·99 ± 0·10	−254·80
2, 8	−19·95 ± 0·08	−19·55
3, 6	−163·89 ± 0·07	−153·75
3, 8	−13·91 ± 0·05	−13·11
6, 7	4061·48 ± 0·09	4062·51
6, 8	−151·61 ± 0·04	−148·51
	δ_{ij}/Hz	
1, 2	176·4 ± 0·3	
1, 6	−660·95 ± 0·25	
	Scalar coupling J_{ij}/Hz†	
1, 2	9·15	
1, 3	4·80	
1, 4	0·35	
1, 5	3·20	
2, 3	7·80	
2, 4	3·20	
6, 8	0·00	

† Assumed values and kept fixed in the analysis; only non-zero J_{ij} values given.

where $l_{ij\alpha}$ and $l_{ij\beta}$ are direction cosines of the internuclear vector $\mathbf{r}_{ijn}$ in the molecular frame and $\delta_{\alpha\beta} = 1$ if $\alpha = \beta$ and is zero otherwise. The elements $S^n_{\alpha\beta}$ are given by

$$S^n_{\alpha\beta} = Q_n^{-1} \int ((3l_\alpha l_\beta - \delta_{\alpha\beta})/2) \exp(-U_{\text{ext}}(n, \omega)/RT\}\, d\omega, \tag{3}$$

where l_α and l_β are direction cosines of the director with respect to molecular axes α and β, and integration over the orientation of the director is represented by $d\omega$. The orientational partition function Q_n is

$$Q_n = \int \exp\{-U_{\text{ext}}(n, \omega)/RT\}\, d\omega, \tag{4}$$

where $U_{\text{ext}}(n, \omega)$ is a potential of mean torque which depends on both ω, the orientation of the director in the molecular frame, and the conformation of the molecule.

The statistical weights, p_n, are determined by $U_{\text{ext}}(n, \omega)$, but also by $U_{\text{int}}(n)$ an orientation independent contribution to the distribution function

$$f(n, \omega) = \exp\{(-U_{\text{int}}(n) - U_{\text{ext}}(n, \omega))/RT\}. \tag{5}$$

Thus,

$$p_n = \exp\{(-U_{\text{int}}(n))/RT\}Q_n Z^{-1}, \tag{6}$$

where Z is the total partition function,

$$Z = \sum_n \int f(n, \omega)\, d\omega. \tag{7}$$

The form of $U_{\text{int}}(n)$ is determined by the nature of the bond rotational potentials. There are three bond rotations in ethoxybenzene, those about ring–O, O–CH_2 and CH_2–CH_3 bonds, and to explore the detailed shape of all three potentials and their effect on the form derived for the orientational dependence of orientational ordering was beyond the computational power available to us. Moreover, it is probable that the sets of dipolar couplings obtained for each molecule are such that it is not possible to characterize separately the effects of rotations about the three bonds. We have, therefore, made simplifying assumptions about the nature of the barriers about the ring–O and C–CH_3 bonds. Rotation about the ring–O bond is assumed to be two-fold in character with minima when the O–CH_2 bond is coplanar with the phenyl ring. This is in agreement with both experimental and theoretical studies of anisoles [6–11]. The rotation about the C–CH_3 bond is assumed to have three-fold symmetry with minima when the C–H bonds on CH_2 and CH_3 carbons are in the staggered conformations. The experimental evidence for the heights of the barriers to rotation for both these bonds suggests that in each case the values are greater than about 12 kJ mol^{-1}, which means that it is a reasonable approximation in our calculations to take into account only the minimum energy positions when calculating the averaged dipolar couplings. The shape of the potential for rotation about the O–CH_2 bond has been explored in greater detail, in the same way as described previously for 4-chloroethoxybenzene [3]. Thus, $V(\varphi)$ for this bond has been sampled at 73 equally spaced values of φ.

The conformationally dependent potential of mean torque is expressed as,

$$U_{\text{ext}}(n, \omega) = -\varepsilon^n_{2,0}(3\cos^2\beta - 1)/2 - \varepsilon^n_{2,2}(3/2)^{1/2}\sin^2\beta\cos 2\gamma, \tag{8}$$

where β and γ are the spherical polar angles of the director in a reference frame fixed in a rigid molecular sub-unit, which in the case of the ethoxybenzenes is chosen to be the phenyl ring, as shown in figure 3. The interaction energies $\varepsilon^n_{2,m}$ are expressed as tensorial sums of conformationally independent contributions $\varepsilon^j_{2,p}$ from each rigid sub-unit in the molecule,

$$\varepsilon^n_{2,m} = \sum_p \sum_j \varepsilon^j_{2,p} D^2_{p,m}(\Omega^n_j). \tag{9}$$

The Wigner rotation matrix $D^2_{p,m}(\Omega^n_j)$ describes the transformation from a frame fixed in sub-unit j to the reference frame through Euler angles Ω^n_j. The $\varepsilon^j_{2,p}$ in the present case are chosen to be $\varepsilon^R_{2,0}$ and $\varepsilon^R_{2,2}$ for the fragments C_6H_5–O and F–C_6H_4–O, $\varepsilon^{\text{oc}}_{2,0}$ for the O–CH_2 bond, and $\varepsilon^{\text{cc}}_{2,0}$ for the C–CH_3 bond. Studies on other aromatic ethers suggest that $\varepsilon^{\text{oc}}_{2,0}$ and $\varepsilon^{\text{cc}}_{2,0}$ are similar in magnitude, and so as to make the computational model as simple as possible we have made them equal in our calculations.

The barrier to rotation about the O–CH_2 bond is represented by the expansion

$$V(\varphi) = \sum_{q=0}^{m} V_q \cos(q\varphi) \tag{10}$$

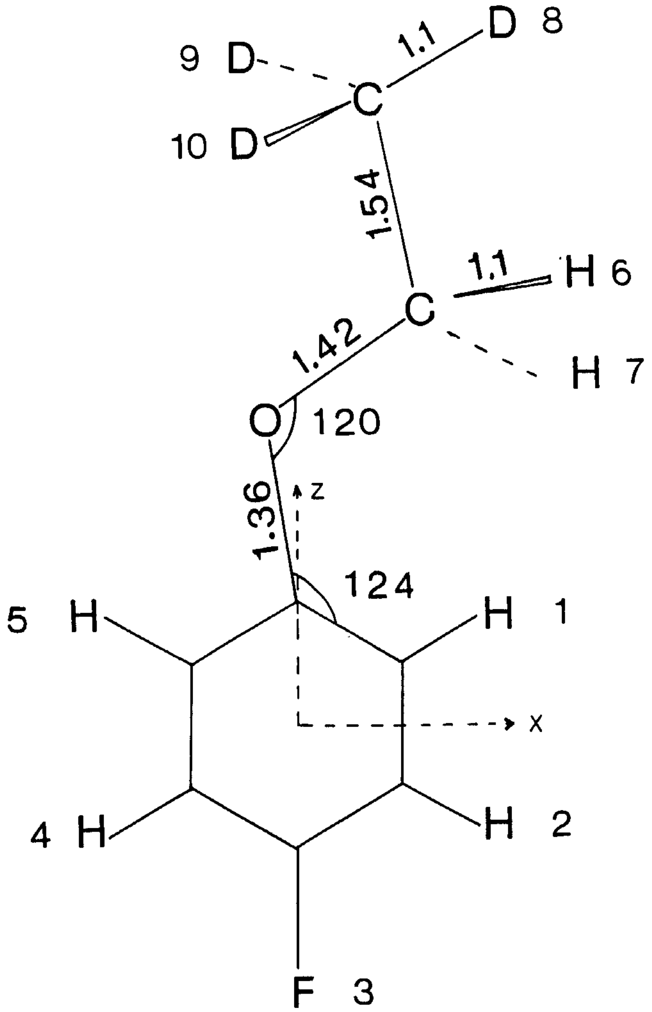

Figure 3. Structure, atomic labelling and location of axes for 4-fluoro- and ethoxybenzene.

Table 4. Relative positions of protons and fluorine nuclei in the phenyl rings of ethoxybenzene and 4-fluoroethoxybenzene based on $r_{12} = 2{\cdot}48$ Å.

Nuclear position	Ethoxybenzene		4-Fluoroethoxybenzene	
	x/Å	z/Å	x/Å	z/Å
1	2·156	1·258	2·138	1·196
2	2·157	−1·221	2·130	1·283
3	0·0	−2·480	0·0	−2·730

and the calculations proceed by seeking values of the V_q, the $\varepsilon^j_{2,p}$ and geometry which minimize the error function

$$R = \left\{ \sum_{i<j} (\tilde{D}_{ij}\ (\text{calculated}) - \tilde{D}_{ij}\ (\text{observed}))^2/F \right\}^{1/2}. \tag{11}$$

All 45 dipolar couplings are used in the calculation of R, that is including those which are equal by symmetry. In each minimization cycle the geometry and V_q were held constant and only the three interaction constants were varied, so that F, the number of degrees of freedom, is 42. The relative positions of the interacting nuclei in the phenyl ring were varied so as to minimize the difference between observed and calculated $\tilde{D}_{ij}$ between these nuclei, giving the coordinates in table 4. These ring coordinates were then kept fixed when exploring the nature of $V(\varphi)$. The variation of the positions of the CH$_2$ protons and the CD$_3$ deuterons, in addition to varying the $\varepsilon^{j}_{2,p}$ and V_q was not practical with the computing resources available, and hence these nuclei were fixed at positions determined by the bond lengths and angles shown in figure 3, together with tetrahedral geometries at the aliphatic carbon atoms. With these geometrical restrictions the values of V_q and $\varepsilon^{j}_{2,p}$ are given in tables 5 and 6 where we also give data obtained previously for 4-chloroethoxybenzene [3]. The functions $V(\varphi)$ for the three compounds are plotted in figure 4, and this shows very clearly that the form of the potential for the para fluorinated compound is substantially different from that of the other two ethoxybenzenes. It should be noted, however, that the error function R for the data for 4-fluoroethoxybenzene (5.08) is greater than for either ethoxybenzene (3·05) or 4-chloroethoxybenzene (4·58) data sets, and that the differences in the $V(\varphi)$ may be caused in part by changes in geometry which have not been properly allowed for in these calculations. The constraints that we have imposed on $U_{\mathrm{ext}}(n, \omega)$ may also be affecting the V_q that are determined, and it would be interesting to see if alternative methods of constructing $f(\omega, \varphi)$, such as that proposed by Di Bari *et al.* [12], produce similar potential functions.

The order parameters for ethoxybenzene and 4-fluoroethoxybenzene are shown as a function of φ in figure 5. These are similar in that the molecules are most strongly ordered in their trans forms, as shown quantitatively by the data given in table 7. Ethoxybenzene, however, differs strikingly from the 4-F and 4-Cl derivatives in

Table 5. Coefficients V_q in kJ mol^{-1} in the expansion for $V(\varphi)$, the potential for rotation about the O–CH$_2$ bond in ethoxybenzene and the 4-F and 4-Cl derivatives.

	Ethoxybenzene-d_3	4-Fluoroethoxybenzene-d_3	4-Chloroethoxybenzene-d_3†
V_0	13·2 ± 0·2	10·7 ± 0·2	12·3 ± 0·2
V_1	−3·61 ± 0·06	−5·55 ± 0·09	−4·04 ± 0·07
V_2	−0·22 ± 0·04	1·33 ± 0·27	0·29 ± 0·06
V_3	−8·16 ± 0·04	−5·83 ± 0·03	−7·84 ± 0·04
V_4	−0·11 ± 0·01	0·66 ± 0·08	0·23 ± 0·03
V_5	−0·72 ± 0·01	−1·11 ± 0·01	−0·78 ± 0·01
V_6	−0·36 ± 0·02	−0·16 ± 0·01	−0·18 ± 0·01

† Note that these are opposite in sign to those given in error in [3].

Table 6. Interaction energies $\varepsilon^{j}_{2,p}$ for the XC$_6$H$_4$O group (X = H, Cl, F) and the O–CH$_2$ and CH$_2$–CH$_3$ bonds of ethoxybenzenes dissolved in I52 at 300 K.

	Ethoxybenzene-d_3	4-Fluoroethoxy-benzene-d_3	4-Chloroethoxy-benzene-d_3 [3]
$\varepsilon^{R}_{2,0}$/kJ mol^{-1}	4·12 ± 0·02	4·13 ± 0·04	5·02 ± 0·05
$\varepsilon^{R}_{2,2}$/kJ mol^{-1}	1·34 ± 0·01	0·83 ± 0·02	0·72 ± 0·02
$\varepsilon^{co}_{2,0} = \varepsilon^{cc}_{2,0}$/kJ mol^{-1}	0·09 ± 0·01	0·65 ± 0·02	0·75 ± 0·02

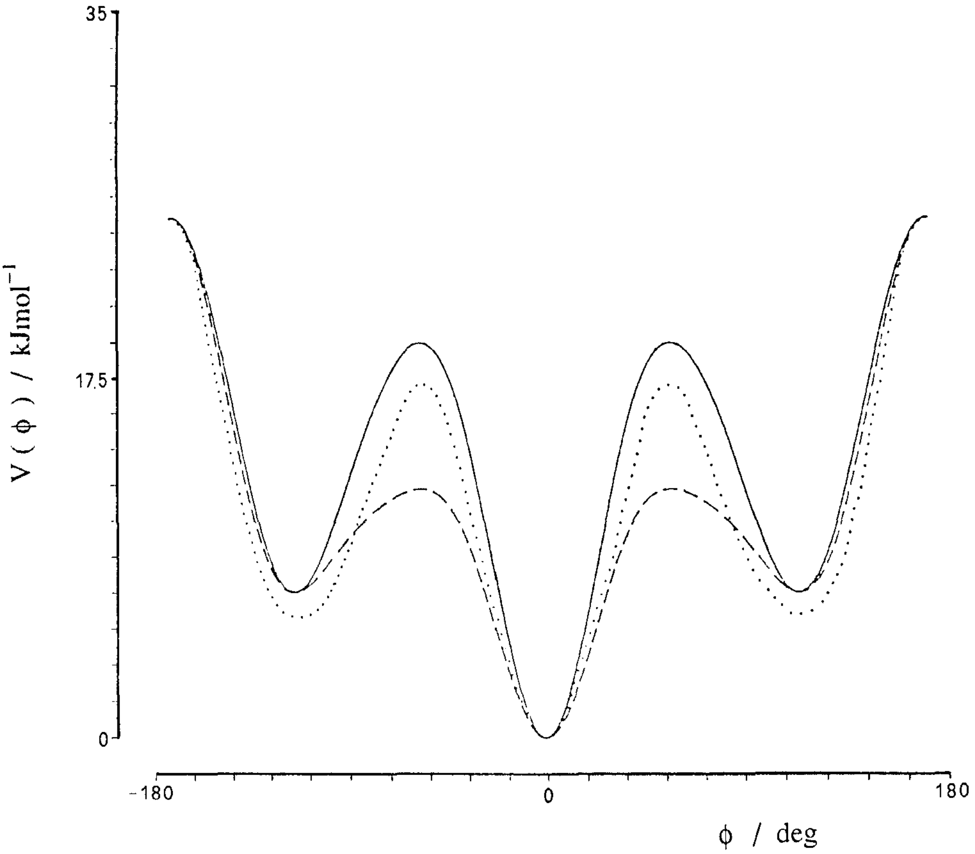

Figure 4. The potential energy $V(\varphi)$ as a function of the angle of rotation φ about the O–CH$_2$ bond in ethoxybenzene (——), and the 4-fluoro (– – –) and 4-chloro (· · ·) derivatives.

Table 7. Ordering matrix elements for ethoxybenzene, 4-fluoroethoxybenzene, and 4-chloroethoxybenzene dissolved in I52 at 300 K and in the trans ($S^T_{\alpha\beta}$) and gauche ($S^G_{\alpha\beta}$) forms. The *xyz* axes are fixed in the phenyl ring in each case.

	Ethoxybenzene	4-Fluoroethoxybenzene	4-Chloroethoxybenzene [3]
S^T_{zz}	0·358	0·406	0·484
$S^T_{xx} - S^T_{yy}$	0·138	0·101	0·077
S^T_{xz}	0·002	0·014	0·016
S^G_{zz}	0·348	0·332	0·406
$S^G_{xx} - S^G_{yy}$	0·139	0·103	0·078
S^G_{xy}	−0·002	−0·018	−0·018
S^G_{xz}	0·004	0·026	0·030
S^G_{yz}	0·002	0·012	0·014

having virtually no dependence of ordering on φ, which is also revealed by the small value of $\varepsilon^{oc}_{2,0}$ for this compound. The additivity principle that we have used to construct the conformation dependence of the potential of mean torque (see equation (9)) suggests that the values of $\varepsilon^{oc}_{2,0}$ should be transferable for compounds dissolved in I52 and at the same reduced temperature. The three samples were only approximately at

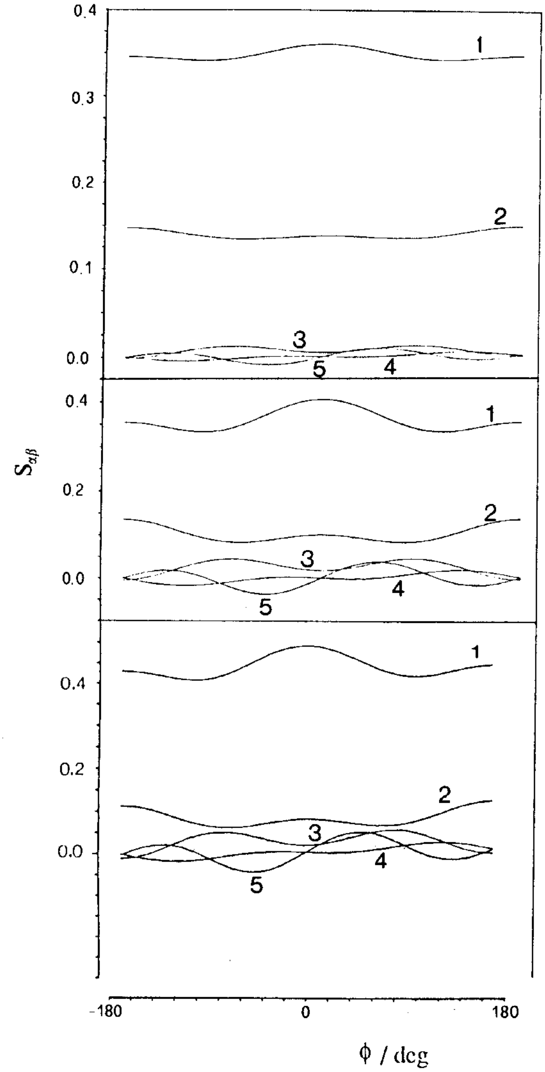

Figure 5. The dependence of the order parameters $S_{zz}(1)$, $S_{xx} - S_{yy}(2)$, $S_{xz}(3)$, $S_{yz}(4)$ and S_{xy} on φ the angle of rotation about the O–CH_2 bond in ethoxybenzene (top), and the 4-fluoro (middle) and 4-chloro (bottom) derivatives.

the same shifted temperature (within 10 K centred on a value of $T_{NI} - T$ of 50 K), but these differences are small at such a low temperature below T_{NI}. The very small value of $\varepsilon^{oc}_{2,0}$ for ethoxybenzene compared with the larger, and similar, values for the two para substituted ethoxybenzenes suggests that there is a fundamental difference in the nature of the mean field experienced by these molecules. Thus, the unusual value of $\varepsilon^{oc}_{2,0}$ for ethoxybenzene could arise because this molecule samples a different part of the I52 solvent molecules than do the other two compounds.

4. Conclusion

The data presented here for the three ethoxybenzenes shows the information on structure and orientation which can be obtained by application of the theoretical model of Emsley, Luckhurst and Stockley for a series of related molecules dissolved in a common solvent. The variations found in $V(\varphi)$ for the three molecules will not be easy to verify by other experimental techniques. It would, however, be interesting to see if the changes which we find are predicted by *ab initio* molecular orbital calculations, even though such calculated $V(\varphi)$ refer to isolated molecules, whereas our results are for molecules in a condensed phase.

The large change found in $\varepsilon_{2,0}^{\mathrm{oc}}$ when fluorine or chlorine is introduced at the para position of ethoxybenzene shows that in this case the segmental interaction parameters cannot be transferred between molecules even when the same solvent is involved and the solute molecules have very similar structures. In one sense this is a dissapointing observation since it diminishes the predictive capability of the theory. However, it does present an interesting challenge to our understanding of how solutes and solvents interact in liquid crystal phases.

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References

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

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

[3] Celebre, G., Longeri, M., and Emsley, J. W., 1988, *J. chem. Soc. Faraday Trans. II*, **84**, 1041.

[4] Emsley, J. W., Heaton, N. J., Kimmings, M. K., and Longeri, M., 1987, *Molec. Phys.*, **61**, 433.

[5] Williamson, A. W., 1852, *J. chem. Soc.*, p. 4229.

[6] Seip, H. M., and Seip, R., 1973, *Acta chem. scand.*, **27**, 4024.

[7] Diehl, P., Huber, H., Kunwar, A. C., and Reinhold, M., 1977, *Org. magn. Reson.*, **9**, 374.

[8] Sax, M. M., Desiderato, R., and Dakin, T. W., 1969, *Acta crystallogr.* B, **25**, 362.

[9] Konschin, H., Tylli, H., and Westermark, B., 1983, *J. molec. Struct.*, **102**, 279.

[10] Schaefer, T., and Penner, H. G., 1987, *J. molec. Struct.*, **152**, 179.

[11] Konschin, H., 1983, *J. molec. Struct.*, **105**, 213.

[12] DiBari, L., Forte, C., Veracini, C. A., and Zannoni, C., 1988, *Chem. Phys. Lett.*, **143**, 263.