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Dipolar coupling study of the conformations and ordering of 4-chloroethoxybenzene in a nematic solvent

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The observed dipolar couplings of 4-chloroethoxybenzene in a nematic solvent are used to study the internal rotations about the O-C(H₂) bond. Accurate theoretical reproductions of these couplings are obtained using the standard three state (*trans*, *gauche*[±]) rotational isomer model with *gauche* rotation angle $\varphi^* = 96^\circ$ and the *trans-gauche* energy difference $E_{tg} = 5.52 \text{ kJ mol}^{-1}$. The probabilities and ordering matrix components of the *trans* and *gauche* forms are calculated.

1. Introduction

The 'soft' internal motions of 4-chloroethoxybenzene consist of rotations about the C_{Ar}-O bond (angle φ_1 in figure 1), the O-C(H₂) bond (angle φ_2) and the C(H₂)-C(D₃) bond (angle φ_3). For many practical purposes a sufficiently accurate model of the internal molecular motions is obtained in the context of the Rotational Isomeric State (RIS) approximation [1] where firstly we ignore all excitations of the 'hard' modes of internal motions (i.e. bond length and bond angle vibrations) and use for the respective variables certain fixed values which are understood to represent ground state averages or equilibrium values, and secondly we assume that the 'soft' mode variables, i.e. the torsion angles, take only certain discrete values, representing the local minima of the rotation potential (alternatively we assume that the torsion angles perform sufficiently small oscillations in the neighbourhood of the local minima of the potential surface so that we may use discrete effective values for these variables).

Obviously for the RIS approximation to give accurate results the temperature should be sufficiently low (i.e. kT much smaller than the typical excitation energy of the 'hard' modes), the local minima of the rotational potential should be sufficiently narrow and deep and the quantities to be calculated should not depend critically on small oscillations of the variables (of either the 'soft' or the 'hard' modes) about their equilibrium values.

The RIS methodology has been used extensively to study the orientational ordering exhibited by non-rigid molecules in liquid solvents and has provided consistent analysis of a wide variety of NMR data on such systems [2, 3]. These studies have established that the conditions of applicability of the RIS approximation are generally met in the liquid crystal regime and have also determined in some instances [3] the degree of quantitative detail to which this approximation can be used.

In the context of the RIS approximation the description of the internal motion of the 4-chloroethoxybenzene molecule requires the determination of the discrete values taken by the rotation angles φ_1 , φ_2 , φ_3 and the respective conformation energy values

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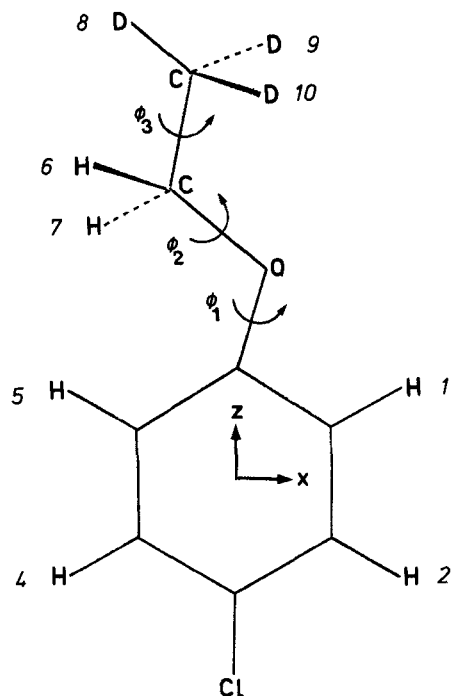


Figure 1. Molecular diagram and atomic labelling of 4-chloroethoxybenzene with a deuterated methyl group.

$E(\varphi_1, \varphi_2, \varphi_3) = E_n$ from which the statistical weight $\exp(-E_n/kT)$ of each conformation is obtained.

The φ_3 rotations are well understood [1]. There are three statistically equivalent φ_3 values related by the threefold rotational symmetry about the $C(H_2)-C(D_3)$ axis. Ignoring minor perturbations caused by the proximity to the ring, the values of φ_3 are independent of φ_1 and φ_2 and correspond to each of the C-D bonds of the methyl group being coplanar with the $O-C(H_2)-C(D_3)$ bonds as shown in figure 1.

The φ_1 rotations are twofold symmetric ($\varphi_1 \leftrightarrow -\varphi_1$) due to the planar symmetry of the ring structure and there are strong indications [4] that the $C_{Ar}-O-C(H_2)$ plane coincides with the ring plane. This would restrict φ_1 to two equivalent values, 0° and 180° (shown in figure 1).

The situation for the φ_2 rotations is not as straightforward aside from the existence of the local minimum at $\varphi_2 = 0^\circ$ (giving the *trans* conformation shown in figure 1) and the symmetry imposed equivalence $\varphi_2 \leftrightarrow -\varphi_2$. In many instances in the literature [5-7] these rotations were treated by analogy to the rotations in long chain molecules where the minima are located at 0° (primary minimum) and at roughly $\pm 120^\circ$ (secondary minima producing the *gauche*[±] conformers). This analogy is obviously inconsistent [7] because, rotations of $\varphi_2 \geq 100^\circ$ would cause severe overlapping between the ring and (in the present case) the CD_3 group. One would therefore intuitively expect that the *gauche* (g^\pm) rotational minima (if present in the 4-chloroethoxybenzene molecule) would be shifted (relative to those of the long chain) towards smaller φ_2 values and that their energy would be elevated. This is illustrated in more quantitative terms in figure 2 where the total rotational potential about the $O-C(H_2)$ bond is approximated by the

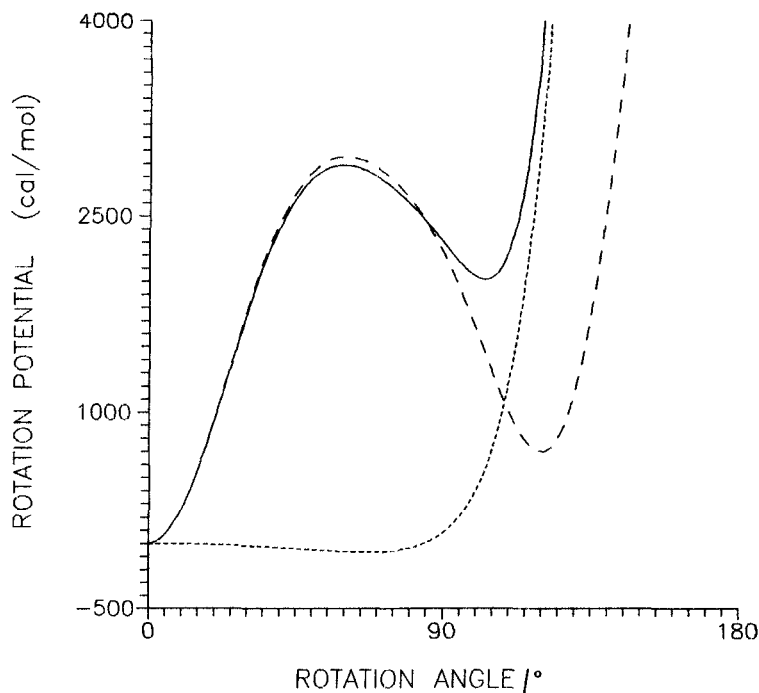


Figure 2. Plots of the potential energy of the 4-chloroethoxybenzene molecule as a function of the angle of rotation about the O-C(H₂) bond. The long-dashed curve represents the part of the potential energy arising from intramolecular interactions within the C_{Ar}-O-C(H₂)-C(D₃) structure (ignoring the phenyl ring) as approximated by the Ryckaert-Bellemans [8] potential for butane. The short-dashed curve represents the potential energy arising from Lennard-Jones type interactions [9] between the phenyl ring and the C(D₃) group. The solid curve represents the total potential energy (sum of the two dashed curves).

sum of the standard Ryckaert-Bellemans (R-B) potential [8] (with parameterization appropriate for butane) and a static additive Lennard-Jones potential of the form

$$V_{ij} = \frac{Q_6}{r_{ij}^6} - \frac{Q_{12}}{r_{ij}^{12}},$$

for the interactions between the ring (united) atoms and the CD₃ group. The parameters used are [9] $Q_6 = 0.9393 \times 10^7 \text{ \AA}^6 \text{ kJ mol}^{-1}$, and $Q_{12} = 0.4556 \times 10^4 \text{ \AA}^{12} \text{ kJ mol}^{-1}$. The main effect of the latter potential, as figure 2 clearly shows, is to shift the *gauche* minima from the 120° values for the pure R-B potential to about 100° and to raise considerably the relative value of the potential at these minima.

From the RIS point of view this would suggest three conformations corresponding to $\varphi_2 = \varphi' = 0^\circ$ and $\varphi_2 = \pm \varphi^g \cong 100^\circ$ with energy difference $E_{tg} = E(\textit{gauche}) - E(\textit{trans})$ appreciably higher than the typical values [1] ($E_{tg} \cong 2.09 \text{ kJ mol}^{-1}$) found for alkyl chains. To our knowledge there is no direct experimental information on the values of φ^g and E_{tg} that would be applicable to the C_{Ar}-O-C(H₂)-C(D₃) bond sequence. Calculations [5, 6] of dipolar couplings based on the assumption that $\varphi^g = 120^\circ$ give rather poor agreement with experiment and have led to questioning the applicability of the RIS methodology to the description of the rotations about the O-C(H₂) bond.

The primary objective of the present work is to establish whether the RIS approximation can give a quantitatively correct description of conformational averaging in the 4-chloroethoxybenzene molecule and to determine the appropriate values of φ^g and E_{ig} . Our interest in this objective stems from the importance in understanding the conformation energetics of the core-chain linkage structure in a variety of liquid crystal forming molecules (monomer, oligomer and polymer mesogens). Typically such molecules consist of a mesogenic core formed by two or more rings and of pendant (or spacer) alkyl or alkoxy chains. The alignment properties of such flexible mesogens depend sensitively [7] on the geometrical and statistical mechanical details of the core-chain linkage structure. The 4-chloroethoxybenzene molecule is particularly advantageous for the study of this structure because, at the RIS level of approximation, E_{ig} and φ^g , being essentially the only conformation parameters, are decoupled from factors that could otherwise complicate the problem and introduce ambiguities.

Our study is based on the analysis of NMR data [5] on the dipolar couplings of 4-chloroethoxybenzene (deuteriated at the methyl group) dissolved in the nematic solvent I52 [5]. These data provide a complete set of dipolar couplings thus allowing the evaluation of all the basic parameters that determine the conformation energetics and the orientational ordering of the solute molecule.

2. Calculation of dipolar couplings

The dipolar couplings D_{ij} for a pair of nuclei i and j of a molecule dissolved in a nematic solvent are defined by [10]

$$D_{ij} = -(\gamma_i \gamma_j h / 8\pi^2) \langle [3(\hat{r}_{ij} \cdot \hat{N})^2 - 1] / r_{ij}^3 \rangle, \quad (1)$$

where r_{ij} is the magnitude and \hat{r}_{ij} is the direction respectively of the internuclear vector, \hat{N} is the director of the nematic medium and γ_i, γ_j are the gyromagnetic ratios of nuclei i, j ($\gamma_i \gamma_j h / 8\pi^2 = 6.0034 \times 10^4 \text{ Hz } \text{\AA}^3$ for proton pairs and $9.206 \times 10^3 \text{ Hz } \text{\AA}^3$ for proton-deuteron pairs). The thermal averages appearing in equation (1) are determined from the geometry of the conformers, their statistical weights and also by the orientational ordering of each conformer in the nematic solvent. Accordingly, by comparing the experimental values of dipolar couplings obtained by NMR spectra with the predictions of a specific conformation-orientation model for the solute molecule one may obtain information on the essential parameters of such a model, provided one has analysable measurements of dipolar couplings for a sufficient number of independent nuclear pairs. The molecular model used in our calculation of the dipolar coupling of 4-chloroethoxybenzene is specified as follows:

- (a) The geometrical data [5, 11] for bond lengths and angles are shown in table 1. For simplicity an exact hexagonal geometry is assumed for the ring. Details regarding the oscillations [10] of these quantities about their equilibrium values are not introduced in the analysis.
- (b) The molecular conformations are assumed to be generated by (i) threefold φ_3 rotations, (ii) φ_2 rotations of 0° and $\pm \varphi^g$ with respective energies $E(\text{trans}) = 0$ and $E(\text{gauche}) = E_{ig}$, and (iii) φ_1 rotations of $0^\circ, 180^\circ$, each with probability $0.5 P_{\parallel}$ and also $\varphi_1 = 90^\circ, 270^\circ$, each with probability $0.5 P_{\perp}$. The latter values of φ_1 were initially allowed in order to detect possible deviations from coplanarity of the ring with the $C_{Ar}-O-C(H_2)$ plane [4, 12, 13]. However, the analysis of the

dipolar couplings gave negligible probability for the non-planar configuration ($P_{\perp} < 0.002$) and therefore the final calculations were performed using only $\varphi_1 = 0^\circ$ and 180° . Accordingly, there are altogether $3 \times 3 \times 2 = 18$ conformers.

Various theoretical determinations [1, 12, 13] of the rotational energy surface suggest that a rigorous treatment of the internal rotations $\varphi_1, \varphi_2, \varphi_3$ should allow for deviations from the simple additive form $E(\varphi_1, \varphi_2, \varphi_3) = E(\varphi_1) + E(\varphi_2) + E(\varphi_3)$. Although there is no general agreement on the detailed form of these deviations in the literature, their presence implies that the equilibrium values of φ_3 (and the respective values for the energy barriers) are not in general strictly independent of the values of φ_2 and φ_1 . Similarly φ_2 could in principle exhibit different equilibrium values for the planar structure ($\varphi_1 = 0^\circ, 180^\circ$) and the non-planar one ($\varphi_1 = 90^\circ, 270^\circ$). These interdependences among the potential rotations are readily incorporated in the RIS description. However, a preliminary analysis of the dipolar couplings of 4-chloroethoxybenzene allowing for reasonable correlated variations of the equilibrium values of $\varphi_1, \varphi_2, \varphi_3$, showed that these rotations are essentially uncorrelated in the context of the RIS approximation. We have therefore proceeded by using the additive form of $E(\varphi_1, \varphi_2, \varphi_3)$ in our RIS modelling. Due to the symmetry of the φ_1 and φ_3 rotations, this form leads to just two distinct values of the conformation energy namely $E_n = 0$ for the six conformers with $\varphi_2 = 0^\circ$ (collectively referred to as *trans* conformers in what follows) and $E_n = E_{tg}$ for the twelve conformers with $\varphi_2 = \pm \varphi^g$ (referred to as *gauche* $^\pm$ conformers). Consequently the geometry and statistics of the conformations of 4-chloroethoxybenzene are completely specified by the two RIS parameters E_{tg} and φ^g . Obviously all the *trans* conformers have identical molecular shapes and similarly for all the *gauche* $^+$ (g^+) and all the *gauche* $^-$ (g^-) conformers. Thus there are two distinct conformer shapes the *trans* and the *gauche* shape (the *gauche* g^\pm shapes are mirror images of each other with respect to the ring plane).

- (c) The orientational averaging required for the calculation of the dipolar couplings is described in terms of a conformation dependent potential of mean torque. Following the modular approach [7, 14], this potential is formed

Table 1. Geometrical data of the 4-chloroethoxybenzene molecule.

Bond lengths	$C_{Ar}-C_{Ar}$	1.39 Å
	$C_{Ar}-O$	1.36 Å
	$O-C$	1.42 Å
	$C-C$	1.54 Å
	$C_{Ar}-H$	1.10 Å
	$C-H$	1.10 Å
	$C-D$	1.10 Å
	Bond angles	$C_{Ar}-C_{Ar}-C_{Ar}$
$C_{Ar}-C_{Ar}-O$		124.0°
$C_{Ar}-O-C$		120.0°
$O-C-C$		112.5°
$C_{Ar}-C_{Ar}-H$		120.0°
$H-C-H$		109.0°
$C-C-D$		109.5°
$D-C-D$		109.5°

additively with anisotropic tensor contributions up to rank two from all the rigid submolecular units into which the molecule is decomposed. Previous studies [2, 3, 7, 14] of orientational ordering of flexible molecules have shown that it is sufficient to consider just two types of such tensor contributions, namely those associated with the ordering of individual units (single unit terms) and those associated with the correlated ordering of neighbouring pairs of units (correlation terms).

The 4-chloroethoxybenzene molecule can be conveniently subdivided into three rigid units consisting of the Cl-C₆H₄-O core, the O-C(H₂) bond and the C(H₂)-C(D₃) bond. To write down the potential of mean torque appropriate to the above modular decomposition we use the bond labels $s=0, 1, 2$ to represent the C_{Ar}-O, O-C(H₂) and C(H₂)-C(D₃) bonds respectively and we introduce a molecular frame with its z axis along the ring *para*-axis and the y axis normal to the ring plane (see figure 1). Assuming axial symmetry for bonds 0, 1, 2, we have the following expression for the potential of mean torque [7, 14] of the 4-chloroethoxybenzene molecule

$$\begin{aligned}
 V(\omega, n) = & -A\left[\frac{3}{2}(\hat{\mathbf{N}} \cdot \hat{\mathbf{z}})^2 - \frac{1}{2}\right] - B\left[\frac{3}{2}(\hat{\mathbf{N}} \cdot \hat{\mathbf{x}})^2 - \frac{3}{2}(\hat{\mathbf{N}} \cdot \hat{\mathbf{y}})^2\right] \\
 & - \frac{1}{2} \sum_{s=1}^2 [\tilde{w}_0(s)[3 \cos^2 \vartheta_s - 1] \\
 & + \tilde{w}_1(s-1, s)[3 \cos \vartheta_{s-1} \cos \vartheta_s - \cos \vartheta_{s-1, s}]]. \quad (2)
 \end{aligned}$$

In this expression $\omega = \omega(\vartheta, \varphi)$ denotes the orientation of the molecular frame ($\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$) relative to the nematic director $\hat{\mathbf{N}}$. The angle of $\hat{\mathbf{N}}$ with the s th bond axis is denoted by ϑ_s and the angle of bond s with bond s' is denoted by $\vartheta_{s, s'}$. A and B are the two coupling constants required to describe the second rank tensor coupling of the (biaxial) ring to the (uniaxial) medium of the nematic solvent. The coefficients $\tilde{w}_0(s)$, $\tilde{w}_1(s-1, s)$ are coupling constants associated respectively with the single bond terms and neighbouring bond correlation terms.

Since bonds 0, 1, 2 are inequivalent there are in principle four different couplings constants $\tilde{w}_0(1)$, $\tilde{w}_0(2)$, $\tilde{w}_1(0, 1)$ and $\tilde{w}_1(1, 2)$. It is possible, however, to reduce the number of independent coupling constants by making use of certain approximate relations [2, 3, 7] that were found to give sufficiently accurate results in simulations of NMR dipolar and quadrupolar spectra of flexible molecules. According to these results (i) the ratios of coupling constants pertaining to different bonds can be related [7] to the ratios of bond lengths l_s as follows:

$$\left. \begin{aligned}
 \tilde{w}_0(s)/\tilde{w}_0(s') &= (l_s/l_{s'})^2, \\
 \tilde{w}_1(s-1, s)/\tilde{w}_1(s, s+1) &= l_{s-1}/l_{s+1}
 \end{aligned} \right\} \quad (3)$$

and (ii) for C(H₂)-C(H₂)(or C(D₃)) bonds $\tilde{w}_1(s, s-1)$ is slightly smaller than $\tilde{w}_0(s)$. Ratios of $\tilde{w}_1(s-1, s)/\tilde{w}_0(s) \approx 0.85$ for these bonds give consistently excellent simulations of alkane dipolar and quadrupolar NMR spectra [2, 3].

Using these relations we may express $\tilde{w}_0(1)$ and $\tilde{w}_1(1, 2)$ in terms of $\tilde{w}_0(2)$ as follows:

$$\begin{aligned}
 \tilde{w}_0(1) &= [l_{\text{O-C(H}_2\text{)}}/l_{\text{C(H}_2\text{)-C(D}_3\text{)}}]^2 \tilde{w}_0(2) = 0.85 \tilde{w}_0(2) \\
 \tilde{w}_1(1, 2) &= 0.85 [l_{\text{O-C(H}_2\text{)}}/l_{\text{C(H}_2\text{)-C(D}_3\text{)}}] \tilde{w}_0(2) = 0.78 \tilde{w}_0(2). \quad (4)
 \end{aligned}$$

An analogue expression that would relate $\tilde{w}_1(0, 1)$ to $\tilde{w}_0(2)$ was not independently tested in any previous study and is not expected to be as accurate since $\tilde{w}_1(0, 1)$

essentially describes the correlated ordering of bond 1 and the entire Cl-C₆H₄-O core (rather than with just the C_{Ar}-O bond). We therefore treat $\tilde{w}_1(0, 1)$ as an independent parameter.

It should be noted that the expression of equation (2) does not include an explicit single bond contribution for the C_{Ar}-O bond (with coupling constant $\tilde{w}_0(0)$). Such contribution is essentially included in the core contribution (coupling constants A, B) aside from a small part which results from the slight deviation ($\sim 4^\circ$) of the direction of the C_{Ar}-O bond from the ring *para*-axis [11, 13]. The latter part, however, can be rigorously absorbed in the term $\tilde{w}_1(0, 1)$ [$3 \cos \vartheta_0 \cos \vartheta_1 - \cos \vartheta_{0,1}$] since $\tilde{w}_1(0, 1)$ is treated as an independent parameter. Accordingly, the complete potential of mean torque for the 4-chloroethoxybenzene molecule is parameterized by the four independent coupling constants $A, B, \tilde{w}_0 = \tilde{w}_0(2)$ and $\tilde{w}_1 = \tilde{w}_1(0, 1)$. The details of the above parameterization of $V(\omega, n)$ were found not to be critical to the final results of the present calculations and in particular to the determination of E_{tg} and φ^g . More crude parameterizations (such as using a common value of $\tilde{w}_0(s) = \tilde{w}_0$ and $\tilde{w}_1(s-1, s) = \tilde{w}_1 = 0.85 \tilde{w}_0$ for all bonds) were also found to be fairly accurate and to give marginal differences (one to two per cent) in the values of E_{tg} and φ^g .

Having specified the geometry, the energy E_n and ordering potential for each conformer, the dipolar coupling D_{ij} are obtained according to the following averaging procedure:

$$D_{ij} = -(\gamma_i \gamma_j / 8\pi^2) \sum_n \int d\omega \frac{1}{r_{ij}^3} (3[\hat{\mathbf{f}}_{ij} \cdot \hat{\mathbf{N}}]^2 - 1) f(\omega, n), \quad (5)$$

where the orientation-conformation distribution function $f(\omega, n)$ is given by

$$f(\omega, n) = \zeta^{-1} \exp[-[E_n + V(\omega, n)]/kT] \quad (6)$$

with

$$\zeta = \sum_n \int d\omega \exp[-[E_n + V(\omega, n)]/kT]. \quad (7)$$

The index n runs over the 18 conformations of the 4-chloroethoxybenzene molecule. Since these conformers can have one of three distinct shapes (*trans* or *gauche*[±]) it is useful to express the dipolar couplings in terms of the ordering matrices associated with these shapes. The ordering matrix for the n th conformer is given by

$$S_{ab}^{(n)} = (\zeta^{(n)})^{-1} \int d\omega \left[\frac{3}{2} [\hat{\mathbf{a}} \cdot \hat{\mathbf{N}}][\hat{\mathbf{b}} \cdot \hat{\mathbf{N}}] - \frac{1}{2} \delta_{ab} \right] \exp(-V(\omega, n)/kT) \quad (8)$$

where $\hat{\mathbf{a}}, \hat{\mathbf{b}} = \hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the unit vectors of the molecular frame and

$$\zeta^{(n)} = \int d\omega \exp(-V(\omega, n)/kT). \quad (9)$$

The probability of the n th conformer is given by

$$p^{(n)} = \int d\omega f(\omega, n) = \zeta^{-1} \zeta^{(n)} \exp(-E_n/kT). \quad (10)$$

It is straightforward to show that an equivalent expression to that of equation (5) relating the dipolar couplings to the ordering matrices of individual conformers $S_{ab}^{(n)}$ is given by

$$D_{ij} = -(\gamma_i \gamma_j h / 4\pi^2) \sum_n P^{(n)} (d_{ij})_{ab}^{(n)} S_{ab}^{(n)}, \quad (11)$$

where the factors $(d_{ij})_{ab}^{(n)} = (\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{a}})(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{b}}) / r_{ij}^3$ are completely determined from the conformer geometry alone.

Due to the particular choice of the molecular frame and the symmetries of the conformers of the 4-chloroethoxybenzene molecule there are just 8 independent components of the conformed ordering matrices entering in equation (11). These are the three components $S_{zz}^t, S_{xx}^t - S_{yy}^t, S_{xz}^t$ for the ordering matrix of the *trans* conformers and the five components $S_{zz}^{g\pm}, S_{xx}^{g\pm} - S_{yy}^{g\pm}, S_{xy}^{g\pm}, S_{xz}^{g\pm}, S_{yz}^{g\pm}$ for the *gauche* conformers.

3. Results and discussion

3.1. Fitting of dipolar couplings

The complete set of observed [5] proton dipolar couplings of 4-chloroethoxybenzene is represented by the ten D_{ij} values listed in the first column of table 2, using the nuclear site labelling of figure 1. The remainder of the 33 in all couplings are related to these ten by symmetry. The theoretical fitting is done by calculating the ten independent D_{ij} values according to equation (6) and varying the six fitting parameters $A, B, \tilde{w}_0, \tilde{w}_1, E_{tg}, \varphi^g$ in order to obtain the best agreement with the observed values. To allow direct comparison with the results of earlier studies [6] of the same set of data the agreement between calculated and observed values is monitored by the error measure

$$R = \left(33^{-1} \left[\sum_{ij} [D_{ij}(\text{calcd}) - D_{ij}(\text{obsd})]^2 \right] \right)^{1/2}, \quad (12)$$

Table 2. Observed [5] and calculated dipolar couplings of 4-chloroethoxybenzene dissolved in the nematic solvent I52 at 300 K.

	Observed dipolar coupling/Hz	Calculated dipolar coupling/Hz	
		6 parameter fit†	5 parameter fit‡
D_{12}	-3699.83	-3700.12	-3701.55
D_{14}	27.21	26.09	28.38
D_{15}	292.64	290.92	295.71
D_{16}	-1574.06	-1573.21	-1571.92
D_{18}	-58.08	-55.20	-55.28
D_{24}	293.55	290.92	295.71
D_{26}	-313.78	-316.76	-317.28
D_{28}	-23.25	-22.72	-22.66
D_{67}	4438.25	4439.07	4438.15
D_{68}	-176.14	-176.65	-177.27
		$R = 1.8 \text{ Hz}$	$R = 2.1 \text{ Hz}$

† Optimal values of fitting parameters $\varphi^g = 96^\circ$, $E_{tg} = 5.52 \text{ kJ mol}^{-1}$, $\tilde{w}_0 = 0.435 \text{ kJ mol}^{-1}$, $\tilde{w}_1 = 0.335 \text{ kJ mol}^{-1}$, $A = 5.77 \text{ kJ mol}^{-1}$, $B = 1.720 \text{ kJ mol}^{-1}$.

‡ Optimal values of fitting parameters $\varphi^g = 95.5^\circ$, $E_{tg} = 5.65 \text{ kJ mol}^{-1}$, $\tilde{w}_0 = 0.406 \text{ kJ mol}^{-1}$, $\tilde{w}_1 = 0.343 \text{ kJ mol}^{-1}$, $A = 5.69 \text{ kJ mol}^{-1}$, $B = 1.548 \text{ kJ mol}^{-1}$.

where the summation over i, j covers the 33 proton-proton (deuteron) pairs of the 4-chloroethoxybenzene molecule.

The results of the fit obtained with this procedure are shown in the second column of table 2. It is interesting to note that (a) the fit is remarkably accurate particularly in view of the simple RIS description of the conformations and of the use of standard geometrical data without any fine adjustments of bond lengths or angles. The value of $R = 1.8$ Hz obtained in this fit is substantially lower than the values ($R = 4.57$ Hz) obtained in earlier studies [6] with a fitting procedure of 11 adjustable parameters using a different ordering potential together with a more extensive sampling of conformations. (b) The optimal value of $\varphi^g = 96^\circ$ is in good agreement with expectations based on atomic overlapping considerations and static potential estimates discussed in §1 and is considerably below the value of 120° used in earlier calculations [5, 6]. The optimal value of $E_{tg} = 5.52$ kJ mol⁻¹ is also in accord with these expectations. (c) The optimal value of $\tilde{w}_0 = 0.44$ kJ mol⁻¹ is in the typical range found for this coupling constant in calculations on alkane solutes [2, 3] in nematic solvents. Also the optimal value of the ratio $\tilde{w}_1/\tilde{w}_0 = 0.77$ is only slightly above the value of 0.75 that we would obtain from direct application of the relations of equation (4) to the C_{Ar}-O bond (i.e. by setting $\tilde{w}_1 = (1.36/1.54) 0.85 \tilde{w}_0$, therefore ignoring any correlated ordering effects between the ring and the O-C(H₂) bond).

To investigate the degree of sensitivity of the fitting to variations of φ^g and E_{tg} , and thus to determine how restrictive the dipolar coupling data are with respect to the optimal values $\varphi^g = 96^\circ$ and $E_{tg} = 5.52$ kJ mol⁻¹, we have performed calculations of R with predetermined values of φ^g and E_{tg} and using the four parameters $A, B, \tilde{w}_0, \tilde{w}_1$ of the ordering potential as fitting parameters. The results of these calculations for two different values of E_{tg} and with φ^g in the range 80° to 120° are shown in figure 3. It is clear from the plots of figure 3 that the accuracy of the fitting rapidly deteriorates on departing to either side of the region around $\varphi^g = 96^\circ$.

Finally, to explore the effects of the parameterization of $V(\omega, n)$ on the accuracy of the fitting, and in particular the importance of differentiating between the coupling constants \tilde{w}_0, \tilde{w}_1 of inequivalent bonds, we have performed a fitting where instead of using the relations of equation (4) we have set $\tilde{w}_0(s) = \tilde{w}_0$ and $\tilde{w}_1(s-1, s) = 0.85 \tilde{w}_0$ irrespective of bond type. The results of this five parameter ($A, B, \tilde{w}_0, \varphi^g, E_{tg}$) fit are shown in the third column of table 2. It is worth noting that the accuracy of this simpler fit is rather good ($R = 2.1$ Hz) and that the optimal value of φ^g ($= 95.5^\circ$) is practically identical to the value of the more accurate fit although there are minor differences in the optimal values of the other fitting parameters.

3.2. Conformer ordering matrix

Conformer probabilities and the nonvanishing components of the ordering matrix for the *trans* and *gauche* conformers are calculated by inserting into equations (8) and (9) the optimal values of the parameters $A, B, \tilde{w}_0, \tilde{w}_1, E_{tg}, \varphi^g$ found in the 6 parameter fit of table 2. The probability of the *trans* conformers is found to be $p^t = 0.843$. This is somewhat higher than the *trans* probability $p^t_{(iso)} = 1/(1 + 2 \exp(-E_{tg}/kT)) = 0.821$ in the isotropic phase, indicating that the interaction with the nematic medium slightly favours the *trans* conformations over the *gauche*. The values of the weighted ordering matrix components $\Sigma'_{ab} = p^t S'_{ab}$ and $\Sigma^{g\pm}_{ab} = 0.5(1 - p^t) S^{g\pm}_{ab}$ are shown in table 3.

An independent determination of the ordering matrix components that does not make use of any specific form for the potential of mean torque is given by equation (11). Using the observed values of D_{ij} from table 2 in equation (11) we obtain a linear

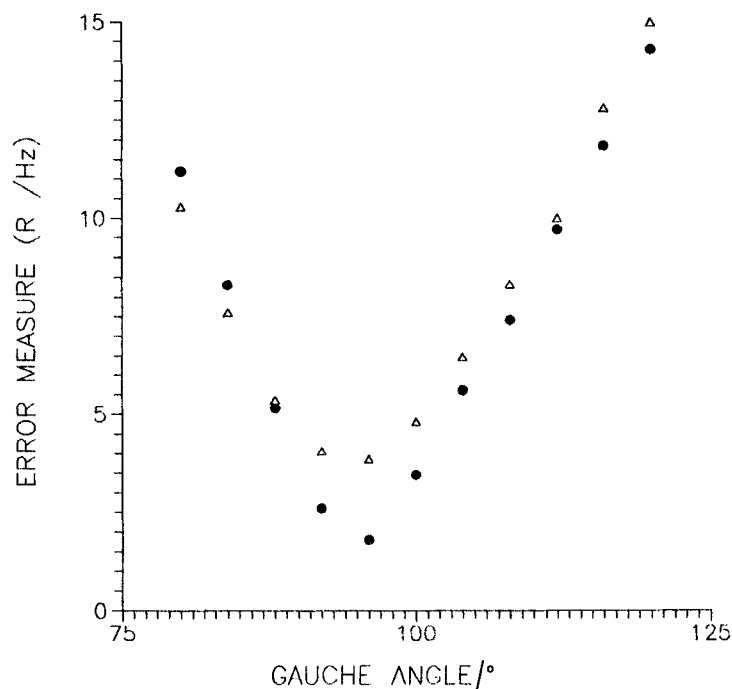


Figure 3. Plots of the accuracy of the fits of the observed [5] dipolar couplings of 4-chloroethoxybenzene as a function of the *gauche* angle φ^g for the optimal value for *gauche* energy $E_{tg} = 5.52 \text{ kJ mol}^{-1}$ (filled circles) and $E_{tg} = 0.9 \times 5.52 \text{ kJ mol}^{-1} = 4.79 \text{ kJ mol}^{-1}$ (triangles). The values of R are obtained by varying the parameters $A, B, \tilde{w}_0, \tilde{w}_1$ of $V(\omega, n)$ to optimize the agreement of the theoretical D_{ij} values of equation (5) with the observed dipolar couplings at fixed φ^g and E_{tg} .

Table 3. Weighted components of the ordering matrix for the *trans* and *gauche* conformers of 4-chloroethoxybenzene as calculated from equation (8) with optimal parameters of $V(\omega, n)$ ($A = 5.77 \text{ kJ mol}^{-1}$, $B = 1.720 \text{ kJ mol}^{-1}$, $\tilde{w}_0 = 0.435 \text{ kJ mol}^{-1}$, $\tilde{w}_1 = 0.335 \text{ kJ mol}^{-1}$) and as obtained by direct calculation from equation (11). In both cases $\varphi^g = 96.0^\circ$.

Weighted order parameters	From optimized $V(\omega, n)$	Direct calculation
Σ_{zz}^t	0.410	0.396
$\Sigma_{xx}^t - \Sigma_{yy}^t$	0.072	0.092
Σ_{xz}^t	-0.041	-0.029
Σ_{zz}^g	0.033	0.040
$\Sigma_{xx}^g - \Sigma_{yy}^g$	0.007	-0.003
Σ_{xy}^g	± 0.001	± 0.002
Σ_{xz}^g	-0.004	-0.006
Σ_{yz}^g	∓ 0.001	∓ 0.004

algebraic system of 8 independent equations (only 8 of the 10 equations are linearly independent because as a result of the hexagonal structure of the C_6H_4 ring one has $D_{15} = D_{24}$ and $D_{14} = (1/2^5)D_{12} + (3^{5/2}/2^5)D_{24}$). These can be solved to give the values of the eight weighted ordering matrix components. The results of this calculation are shown in the last column of table 3. Note that the only parameter in this calculation is φ^g which fixes the geometry of the *gauche* conformers and therefore determines all the respective $(d_{ij})_{ab}^{(n)}$. The results of the direct calculation in table 3 are obtained for $\varphi^g = 96^\circ$ and are quite reasonable, in contrast to the unrealistic results obtained in calculations with $\varphi^g = 120^\circ$ [5]. Although the latter results were interpreted [5, 6] as indications of the failure of the RIS modelling, our findings make it clear that the discrepancies of these earlier studies are due to the use of inappropriately large values for φ^g and not to the application of the RIS approximation.

Comparison of the results in two columns of table 3 shows that there is reasonable agreement between the direct calculation and the one using $V(\omega, n)$. The minor differences in the results of the two calculations mainly reflect the sensitivity of the ordering matrix components to the geometrical details. For example variations of 2° in φ^g cause rather large relative variations (comparable to the differences between the two columns) in the results of the direct calculation. Analogous variations, particularly in the *gauche* ordering matrix elements, are observed when slight geometrical deformations of the rigid submolecular units are introduced.

4. Concluding remarks

Our results on the fits of the proton dipolar couplings and the conformer ordering matrix show that a satisfactory quantitative description of the conformation statistics and the ordering of the 4-chloroethoxybenzene molecule in a nematic medium can be obtained by combining the simple RIS modelling of internal motions with the modular formulation of the potential of mean torque. The results are sensitive to the angle φ^g of *gauche* rotations about the O–C(H₂) bond and exhibit a clear preference to values in the neighbourhood of $\varphi^g = 96^\circ$, in agreement with atomic interaction considerations.

Our findings differ from those of [5, 6] where it was suggested that the 3-state RIS description of rotations about the O–C(H₂) bond is inadequate and that sampling of a larger number of rotation angles is required. However, the fits of the dipolar couplings obtained [6] with such detailed sampling were substantially less accurate ($R = 4.57$ Hz) than the ones obtained here. The primary difference between our calculations and those of [6] is in the positioning of the *gauche* minima of the rotational potential (96° versus 120°).

A secondary difference is in the form of the potential of mean torque. The potential used in [6] is a special case of the one used here in the limit $\tilde{w}_1(s-1, s) = 0$, i.e. when correlated ordering of molecular segments is completely ignored. The deficiencies associated with the neglect of correlated ordering of bond segments in flexible molecules have been discussed extensively in the literature [2, 14]. It appears, however, that these deficiencies do not constitute the major source of error in the fitting of [6]. In particular we have found that the neglect of such correlations generates a modest error because of the limited flexibility of the 4-chloroethoxybenzene molecule (only the C(H₂)–C(D₃) bond moves relative to the rest of the molecule). Moreover, this is overshadowed by the more significant error associated with use of the unrealistic value of 120° for the *gauche* dihedral angle minima by Emsley *et al.* [5, 6].

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