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Interconversion kinetics and ordering of 1,4- and 1,1-dimethylcyclohexane in liquid-crystalline solutions by 1D and 2D deuterium NMR

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Deuterium NMR spectra of perdeuteriated 1,4-dimethylcyclohexane-d_{16} and 1,1-dimethylcyclohexane-d_{16} dissolved in the nematic solvent ZLI 2452 are reported for the temperature range −40 to +80°C. Between −30 and +60°C the spectra exhibit characteristic exchange broadening and coalescence due to the ring inversion process. In the extreme slow exchange regime, peak assignment and determination of relative signs of the deuterium quadrupole interactions were made using 2D exchange spectroscopy and structural parameters derived from molecular mechanics calculations. In the intermediate temperature range the lineshapes were interpreted quantitatively in terms of the ring interconversion kinetics yielding the kinetic equations, $k = 1{\cdot}38 \times 10^{13} \exp(-45{\cdot}2/RT)\,\mathrm{s}^{-1}$ for 1,4-dimethylcyclohexane, and $k = 4{\cdot}05 \times 10^{13} \exp(-49{\cdot}0/RT)\,\mathrm{s}^{-1}$ for 1,1-dimethylcyclohexane, where R is in $\mathrm{kJ\,mol^{-1}}$. The complete ordering matrix of both compounds was determined over the whole temperature range of the measurements.

1. Introduction

Deuterium NMR of deuteriated solutes dissolved in liquid crystals provides a powerful tool for the investigation of their ordering properties and dynamics [1]. The advantage of using deuterium NMR lies predominantly in the fact that each group of equivalent deuterons exhibits a single quadrupole doublet whose splitting, $2\langle \nu_Q \rangle$, is to a very good approximation, simply related to the orientation of the corresponding C–D bond in the molecule [2]. With the development of techniques for complete and selective deuteriation of organic compounds [3] this method has become an effective practical tool for dynamic studies of molecular rearrangement in liquid-crystalline solutions [4, 5]. In the present paper we apply this method to the investigation of the order parameters and the ring interconversion kinetics of two dimethyl cyclohexanes, i.e. 1,4-(*cis*)- and 1,1-dimethylcyclohexane (1,4-DMC and 1,1-DMC respectively) dissolved in a nematic solvent. Both compounds undergo chair–chair interconversion [6] but since the two interconverting conformers have identical structures the equilibrium constant between the two forms is unity and their deuterium NMR spectra in liquid-crystalline solutions correspond to single species. The low symmetry of the

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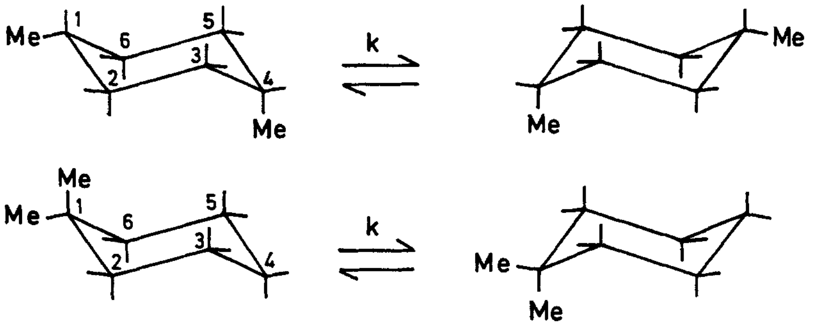
molecules (both having only a single reflection plane) requires, however, that three order parameters should be determined by the experiments. To derive these parameters and to simulate dynamic NMR spectra a complete assignment of the spectral peaks is required as well as knowledge of the relative signs of the associated quadrupole coupling constants. We derive this information by recording two dimensional exchange spectra [7, 8] of the solutions in the low temperature (ultraslow) regime and by best fitting the splitting patterns in terms of the molecular geometries obtained from molecular mechanics calculations.



Following an experimental section containing details about the preparation of the deuteriated compounds and the NMR experiments, the peak assignment and the determination of the complete ordering matrix at low and high temperatures is described. The analysis also provides information on the relative signs of the quadrupole interactions of the various deuterons. Finally we perform a complete lineshape analysis of the spectra in terms of the kinetic parameters of the interconversion reaction and compare the results with the earlier ^{13}C NMR results of the neat liquids [6].

2. Experimental

2.1. *Materials*

Perdeuteriated 1,4-DMC-d_{16} was prepared by hydrogenation of perdeuteriated *p*-xylene with deuterium gas using Adam's catalyst. The latter was activated by pre-reducing $PtO_2 \cdot xH_2O$ with D_2 gas in CH_3COOD. 10 ml of *p*-xylene-d_{10} were mixed with 0·5 g of catalyst in 70 ml of acetic acid-d_1 under an atmosphere of deuterium gas and allowed to react under constant shaking at room temperature. When about half of the gas was consumed a fresh amount of the pre-reduced catalyst was added and the reaction continued. After three days the reaction was stopped and the product, consisting of a mixture of *cis* and *trans* (perdeuteriated) 1,4-dimethylcyclohexane was subject to fractional distillation using a column with 30 equivalent theoretical plates. The fraction corresponding to 1,4-(*cis*)-DMC-d_{16} had a boiling point of 124·5°C and its purity was confirmed by gas-chromatography.

Perdeuteriated 1,1-DMC-d_{16} was prepared by catalytic deuteriation of the corresponding isotopically normal compound. 3·5 g of the latter was mixed with 50 ml of D_2O and 0·25 g of platinum on carbon (10 per cent) catalyst in a stainless steel container. The reaction mixture was stirred for four days at 200°C followed by distillation of the desired 1,1-DMC-d_{16} product (bp 119–120°C).

The liquid-crystalline solvent used was the nematic mixture ZLI 2452 (Merck, Darmstadt) which consists of cyano and alkyl substituted phenylcyclohexanes and biphenylcyclohexanes alkylcyclohexylbiphenylcyclohexanes as well as cyclohexylcarboxylates. Its nematic range is between −40 and 110°C. Solutions containing about three weight per cent solute were made up gravimetrically and vacuum sealed in 5 mm tubes of about 2 cm length for the NMR measurements.

2.2. *NMR measurements*

The deuterium NMR measurements were performed at 46·07 MHz on a Bruker CXP300 spectrometer. The 1D spectra were recorded by the quadrupole echo method using $\pi/2$ pulses of 2 to 3 μs, and time intervals between pulses of 20 μs. The 2D spectra were obtained by three-pulse sequences [7, 8] augmented with an extra quadrupole echo detection pulse. Two data sets were collected corresponding to the cos–cos and sin–sin components of the two dimensional spectra [8] and Fourier transformed according to the method of States *et al.* [9]. The data size in these experiments was 128 with increments of 10 μs and zero filling up to 512 in t_1, and 1024 (5 μs dwell time) in t_2. This corresponds to a spectral width of 100 kHz in both dimensions.

2.3. *Molecular mechanics calculations*

No crystallographic structures of the two little compounds are available and so their geometries were determined by molecular mechanics calculations [10] using the MM2(85) force field parameters for deuterium. The resulting coordinates for the carbon and ring deuterium atoms in the molecule fixed coordinate system x', y', z', as defined in figure 1 are summarized in the table. This coordinate system is chosen so that x' and y' lie in the symmetry plane of the molecule with the origin 0, 0, 0, at the middle of

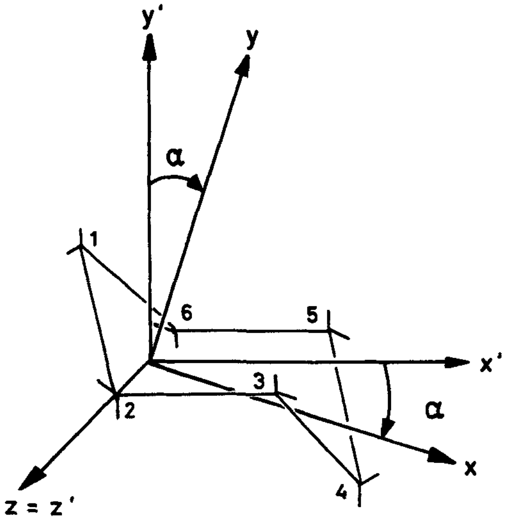


Figure 1. Numbering convention and coordinate systems used in the present work. The molecular system x', y', z', is chosen such that x' and y' lie in the symmetry plane of the molecule, the origin is at the midpoint between carbons 2 and 6 and the positive z' axis passes through atom 2. The positive x' axis is oriented along the projection of the C_2–C_3 (C_6–C_5) bond on to the symmetry plane and y' completes the set into an orthogonal right handed coordinate system. The coordinates x, y and z are the principal axes of the ordering matrix. They are rotated with respect to x', y', z' by an angle α about $z'(=z)$. A positive α rotates y from y' in the direction of x'.

Carbon and deuterium coordinates in the molecular-fixed system x', y', z' (see figure 1) obtained from molecular mechanics calculations.[†]

	1,1-DMC-d_{16}			1,4-DMC-d_{16}		
	x'/Å	y'/Å	z'/Å	x'/Å	y'/Å	z'/Å
C_1	−0·604	0·662	0	−0·555	0·685	0
$C_{2,6}$	0	0	±1·258	0	0	±1·261
$C_{3,5}$	1·536	0	±1·262	1·536	0	±1·259
C_4	2·082	−0·681	0	2·119	−0·668	0
M_e^a	−0·358[‡]	2·186[‡]	0[‡]	1·923[§]	−2·193[§]	0[§]
M_e^e	−2·134[‖]	0·438[‖]	0[‖]	−2·092[‖]	0·675[‖]	0[‖]
D_1^a	—	—	—	−0·218	1·745	—
$D_{2,6}^a$	−0·343	−1·055	±1·314	−0·381	−1·040	±1·324
$D_{2,6}^e$	−0·378	0·507	±2·171	−0·368	0·528	±2·167
$D_{3,5}^a$	1·923	1·040	±1·326	1·890	1·052	±1·308
$D_{3,5}^e$	1·910	−0·529	±2·165	1·919	−0·508	±2·170
D_4^a	1·785	−1·752	0	—	—	—
D_4^e	3·193	−0·649	0	3·220	−0·495	0

[†] Using MM2 (85) force field parameters [10].
[‡] Carbon coordinates of the axial methyl group at C_1.
[§] Carbon coordinates of the axial group at C_4.
[‖] Carbon coordinates of the equatorial methyl groups at C_1.

the line connecting carbons 2 and 6. The positive z' axis lies parallel to this line in the direction from carbon 6 to carbon 2. The positive x' axis is parallel to the projection of the C_2–C_3 (C_6–C_5) bond onto the molecular symmetry plane and y' is oriented such that x', y', z', form a right handed coordinate system.

3. Results and interpretation

3.1. *Interpretation of the NMR spectra*

Deuterium NMR spectra of the two solutions studied are shown in the left hand columns of figures 2 and 3. In both solutions relatively narrow lines are observed below about −30°C where the interconversion rate is slow, as well as above 60°C where the exchange rate is extremely fast, while in the intermediate region the spectra are broadened by the ring inversion process. From the symmetry of the molecules we expect, in the slow exchange regime of both compounds, to observe eight doublets with relative intensities 3 : 3 : 2 : 2 : 2 : 2 : 1 : 1 corresponding to the two methyl groups, the four symmetry related pairs 2a 6a, 2e 6e, 3a 5a, 3e 5e and either 4a, 4e in 1,1-DMC or 1a, 4e in 1,4-DMC (where a and e refer to axial and equatorial deuterons respectively). At high temperatures coalescence of signals should result in four line spectra with relative intensities 6 : 4 : 4 : 2. The experimental spectra at high temperatures are indeed nearly as expected, allowing partial identification of the peaks as indicated in the top traces of figures 2 and 3. Note that in 1,1 DMC we cannot distinguish between the peaks corresponding to the groups of nuclei (2a, 6a, 2e, 6e) and (3a, 5a, 3e, 5e) solely on the basis of their relative intensities, while in 1,4-DMC the signals due to the groups (2a, 6a, 3e, 5e) and (2e, 6e, 3a, 5a) superpose on top of each other. In the low temperature spectra the situation is more complicated due to excessive overlap between lines. From the relative intensities of the peaks as indicated in the bottom traces of figures 2 and 3 we can only assign with certainty the two pairs of peaks with relative intensities 3, as due to the methyl deuterons. Partial assignment can also be made of the single intensity peaks as due to either deuteron 4e or 4a in 1,1-DMC, and either 1a or 4e in 1,4-DMC; the other single deuterons in each case must be part of the unresolved bands of intensity 5.

Additional information was obtained from 2D exchange spectra of the 1,1-DMC and 1,4-DMC solutions in the ultraslow exchange regime. A general discussion of 2D exchange spectra for deuterium in nematic solutions is given in [1, 8]. For 1,1-DMC exchange cross peaks are expected between the pairs (Me1a, Me1e), (2a 6a, 2e 6e), (3a 5a, 3e 5e) and (4a, 4e), while for the 1,4-DMC isomer cross peaks should appear connecting the pairs (Me1e, Me4a), (2a 6a, 3e 5e), (2e 6e, 3a 5a) and (1a, 4e). Two dimensional exchange spectra of the 1,4-DMC-d_{16} solutions at −30°C are shown in

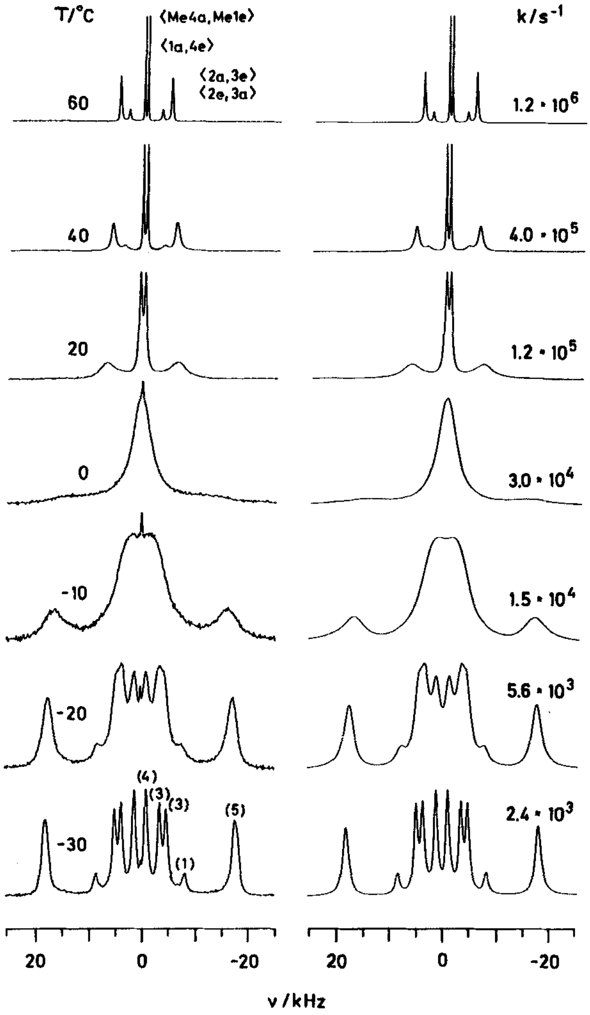


Figure 2. Left hand side: experimental spectra of 1,4-DMC-d_{16} dissolved in the nematic solvent ZLI 2452 (3·1 wt%) at different temperatures. The bracketed numbers on the bottom trace indicate rounded off relative intensities of the various peaks. In the top trace are given the assignments of the coalesced peaks. Right hand side: simulated dynamic spectra calculated with the indicated rate constants, the quadrupole splittings from figure 6 and an exchange independent linewidth parameter, $1/T_2$, ranging from 30 to 300 s^{-1}.

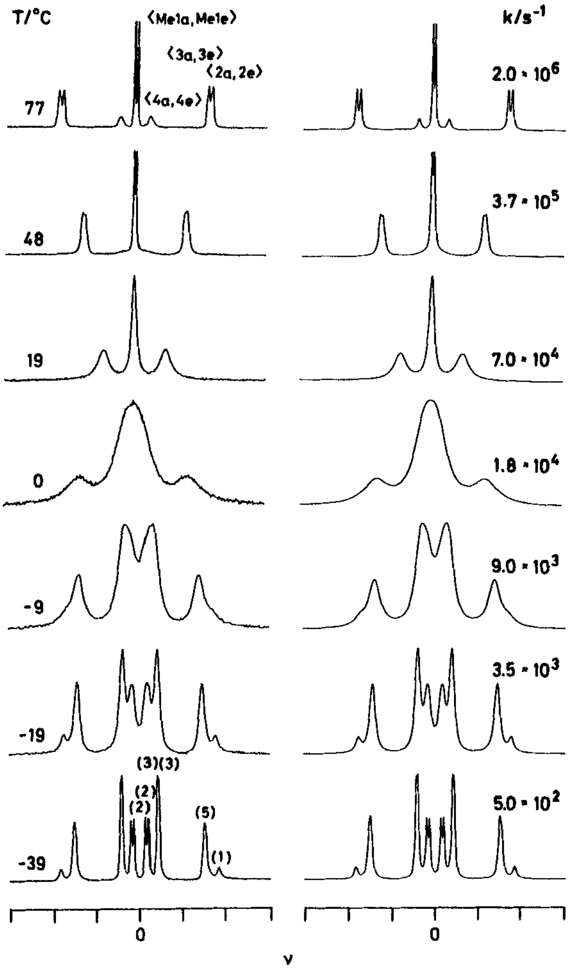


Figure 3. As in figure 2 but for a 1,1-DMC-d_{16} (2·5 wt%) solution. The quadrupole splitting parameters used in the simulation were taken from figure 7. The overall frequency scale is 60 kHz for the bottom five traces (10 kHz per division) 30 kHz for the sixth trace (48°C) and 15 kHz for the top one.

figures 4 and 5, respectively. They exhibit well resolved diagonal and off diagonal peaks from which information about the exchange connectivities as well as the relative signs of the quadrupole interactions of the interchanging deuterons can be obtained. It may be seen that in both compounds the axial and equatorial methyl deuterons have very similar quadrupole splittings but their interactions are of opposite signs. It is also interesting to note that in 1,1-DMC-d_{16} the two methyl signals are not resolved in the 1D spectrum shown at the top of figure 5 although they are clearly separated in both the diagonal and off diagonal signals of the 2D diagram. This is apparently due to the $\sqrt{2}$ effect, reflecting the spreading of the 1D spectrum along the diagonal. The 2D spectra also confirm that the exchange partners of the isolated single-intensity peaks are, in both compounds, included in the unresolved intensity-5 peaks and that their quadrupole interactions are of opposite signs (see the dashed lines in figures 4 and 5). The rest of the intensity-5 peaks must be assigned to the four axial (or four equatorial) deuterons attached to carbons 2, 6, 3 and 5. As may be seen they are connected through exchange cross peaks to the inner signals in the 2D spectra which must therefore be assigned to the corresponding equatorial (or axial) deuterons.

This is as far as peak assignment can be made from 1D intensity and 2D exchange connectivity considerations. In principle this is sufficient for simulation of the dynamic spectra since this only requires identification of pairs of exchanging peaks, and not a complete spectral assignment. A complete interpretation of the spectrum is nevertheless useful since this would allow us to determine the ordering matrix at both the low and the high temperature ends of the dynamic range and by interpolation determine the quadrupole splittings over the whole temperature range, which can then be used for the lineshape simulation.

3.2. *Complete peak assignment and determination of the ordering matrix*

In general five order parameters are required for a complete spectrum simulation of a molecule dissolved in a nematic solvent [11]. They may be identified with the three Euler angles relating molecular fixed coordinate axes (x', y', z') with the principal coordinate system of the ordering matrix (x, y, z), and two orientational constants, for example S_{xx} and $(S_{zz}-S_{yy})/S_{xx}$, where the $S_{\gamma\gamma}$ are the components of the ordering matrix in the x, y, z, coordinate system [11]. Both the 1,4-DMC and 1,1-DMC molecules have a symmetry reflection plane, so that the perpendicular axis to this plane, z' (see figure 1),

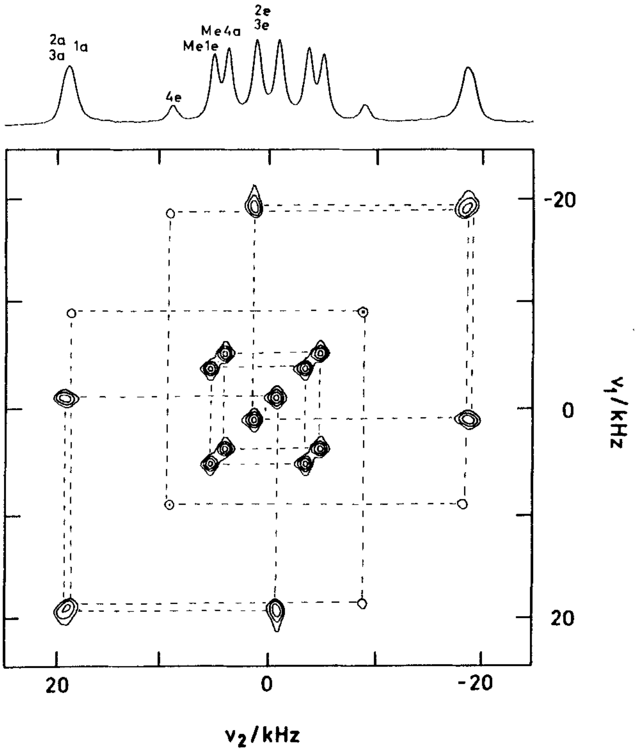


Figure 4. A two dimensional exchange spectrum of the 1,4-DMC-d_{16} solution at −30°C. The dashed lines were drawn to indicate the exchange connectivities. A corresponding 1D spectrum is shown at the top.

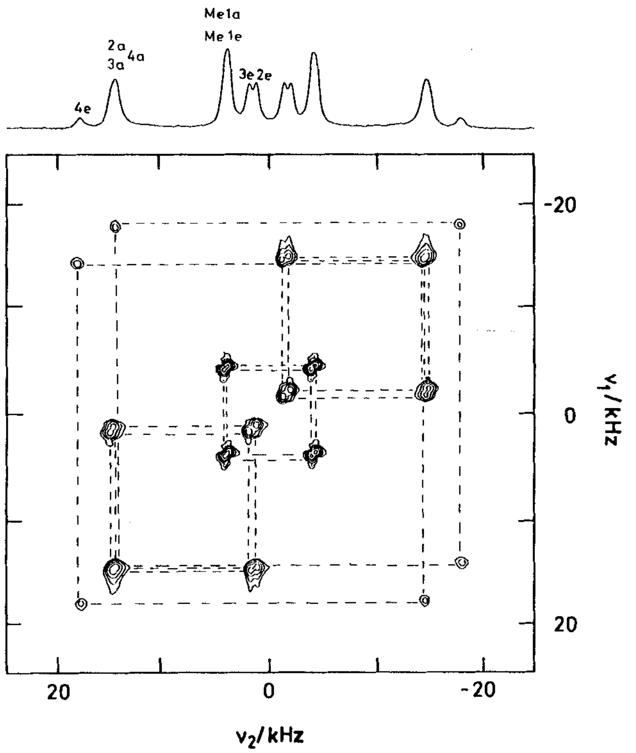


Figure 5. A two dimensional exchange spectrum of the 1,1-DMC-d_{16} solution at −30°C. The dashed lines were drawn to indicate the exchange connectivities. A corresponding 1D spectrum is shown at the top.

must also be a principal axis of the molecular diffusion tensor, z. The other two principal directions of the ordering matrix, x and y lie in the $x'y'$ plane, rotated at an (unknown) angle, α, about $z=z'$. In the x, y, z coordinate system the average quadrupole interactions of the various deuterons, $\langle \nu_Q^i \rangle$, (half of the observed splitting) is given by

$$\begin{aligned}\langle \nu_Q^i \rangle &= \nu_Q^i (S_{xx} \cos^2 \theta_x^i + S_{yy} \cos^2 \theta_y^i + S_{zz} \cos^2 \theta_z^i), \\ &= \nu_Q^i S_{xx} [\tfrac{1}{2}(3 \cos^2 \theta_x^i - 1) + \tfrac{1}{2}\eta(\cos^2 \theta_z^i - \cos^2 \theta_y^i)].\end{aligned} \tag{1}$$

In this equation ν_Q^i is the static quadrupole interaction constant of the ith deuteron

$$(\nu_Q^i) = \frac{3}{4} \frac{e^2 qQ}{h},$$

$\theta_\gamma^i = \theta_\gamma^i(\alpha)$ are the angles between the C–D^i bond direction and the γ principal axes, and

$$\eta = \frac{S_{zz} - S_{yy}}{S_{xx}}, \tag{2}$$

is the asymmetry parameter of the ordering matrix. Here we have assumed that the static quadrupole tensor is axially symmetric with its unique axis parallel to the C–D bond direction and we have chosen x as the major axis for the ordering matrix since it appears to be the longest molecular axis. The splittings thus depend on the three parameters, S_{xx}, η and α. To determine these parameters we performed a best fit analysis of the experimental splittings in terms of equation (1) as described in detail in [1]. For each molecule we tried various assignments of the peaks with different relative signs for the observed $\langle \nu_Q^i \rangle$s, subject to the restrictions dictated by the results of the 2D exchange experiment. For each assignment we varied the three parameters S_{xx}, η and α until a minimum in the error function

$$\sum_i |\langle \nu_Q^i \rangle_{\text{exp}} - \langle \nu_Q^i \rangle_{\text{cal}}|,$$

was found. Two additional restrictions were imposed in the analysis. One was to keep $|\alpha|$ less than 45°; lifting this restriction would yield equivalent solutions, but with S_{xx} and S_{yy} interchanged. The second restriction was to keep S_{xx} positive in order to ensure that the long axis of the molecule will be associated with a positive order parameter. While this is chemically sound it cannot be deduced from the experimental results; inverting the signs of all $\langle \nu_Q^i \rangle$s would yield an identical fit but with opposite signs for all the S_{yy}s. In practice for the best fit analysis the angles θ^i were calculated, for each value of α, from the molecular coordinates given in the table. The static quadrupole interaction parameter ν_Q^i was taken as 126 kHz for all deuterons except for those of the methyl groups for which $\nu_Q^{\text{Me}} = -\frac{1}{3}\nu_Q^i = -42$ kHz was assumed. The factor $-\frac{1}{3}$ accounts for the fast three fold rotation of the methyl group assuming an average tetrahedral angle for the C–C–D bonds. The angle θ^{Me} was identified with that of the

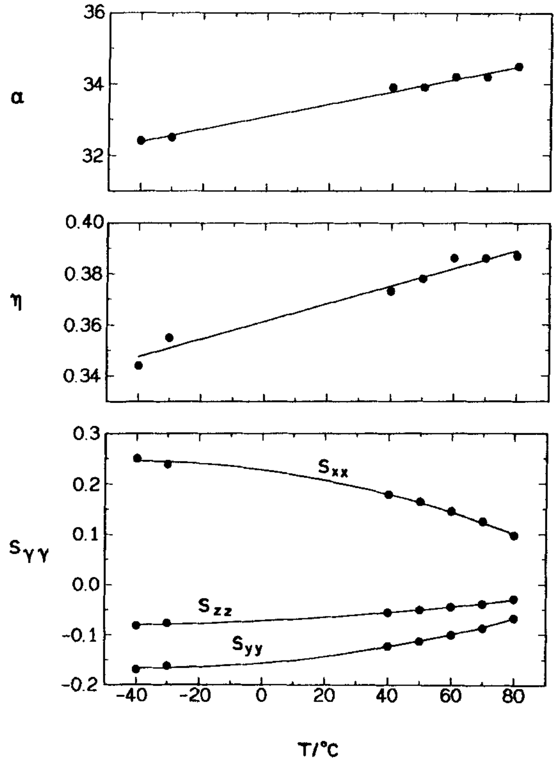


Figure 6. Best fit results for the various parameters of the ordering matrix for the 1,4-DMC-d_{16} solution. The points are experimental, while the continuous curves are interpolation lines connecting the low and high temperature results.

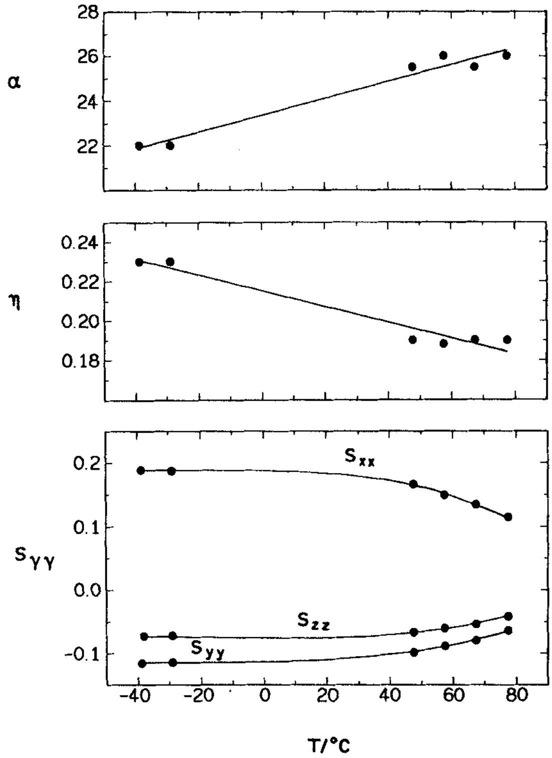


Figure 7. Best fit results for the various parameters of the ordering matrix for the 1,1-DMC-d_{16} solution. The points are experimental, while the continuous curves are interpolation lines connecting the low and high temperature results.

C–Me bond. A similar analysis was performed on the averaged, high temperature spectra, except that the best fit calculation were performed with respect to the average splittings

$$\langle \nu_Q^{i,j} \rangle = \tfrac{1}{2}(\nu_Q^i + \nu_Q^j), \qquad (3)$$

where the superscript represents pairs of interchanging deuterons.

The peak assignments resulting from this analysis are shown on the 1D spectra at the top of figures 4 and 5 for the low temperature regime and on the top traces in figures 2 and 3 for the high temperature spectra. The results for the S_{yy}s and α are shown in figures 6 and 7 together with the calculated asymmetry parameters. The points in these figures correspond to experimental results while the curves represent continuous interpolation between the low and high temperature regions. In figures 8 and 9 are plotted the experimental quadrupole splittings with the appropriate signs and assignment as obtained from the analysis.

3.3. *Analysis of the dynamic lineshapes*

The lineshape of the NMR spectra in the intermediate temperature range −30 to 60°C is dominated by the ring inversion process and the rate of the latter can be determined by comparison with simulated lineshapes. These can readily be calculated

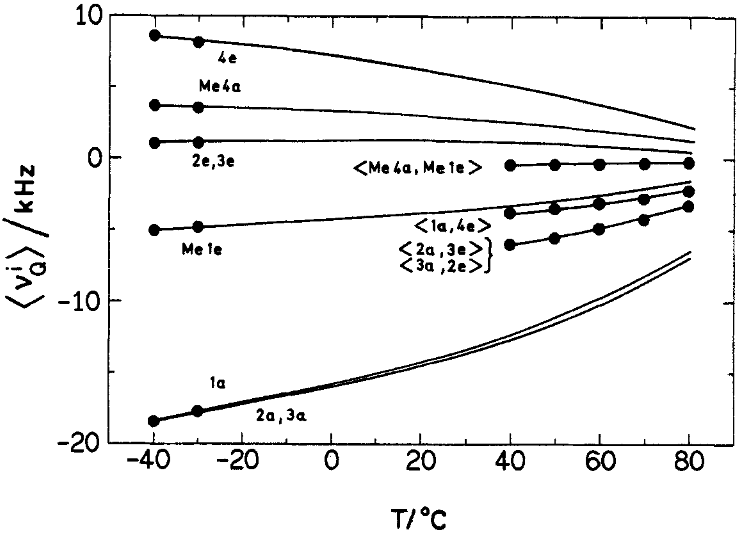


Figure 8. Experimental quadrupole interactions (half of the full splitting) for the various deuterons observed in the 1,4-DMC-d_{16} solution. The points are experimental for the deuterons indicated or group of deuterons at high and at low temperatures. The continuous curves extrapolated from the low temperature results were calculated from the order parameters in figure 6. The signs of the $\langle\nu_Q^i\rangle$s are fixed by the choice that S_{xx} be positive.

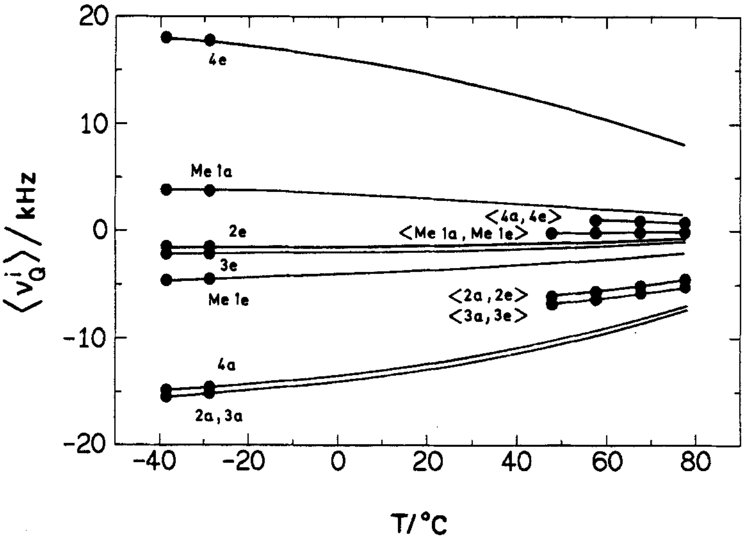


Figure 9. Experimental quadrupole interactions (half of the full splitting) for the various deuterons observed in the 1,1-DMC-d_{16} solution. The points are experimental for the deuterons indicated or group of deuterons at high and low temperatures. The continuous curves extrapolated from the low temperature results were calculated from the order parameters in figure 7. The signs of the $\langle\nu_Q^i\rangle$s are fixed by the choice that S_{xx} be positive.

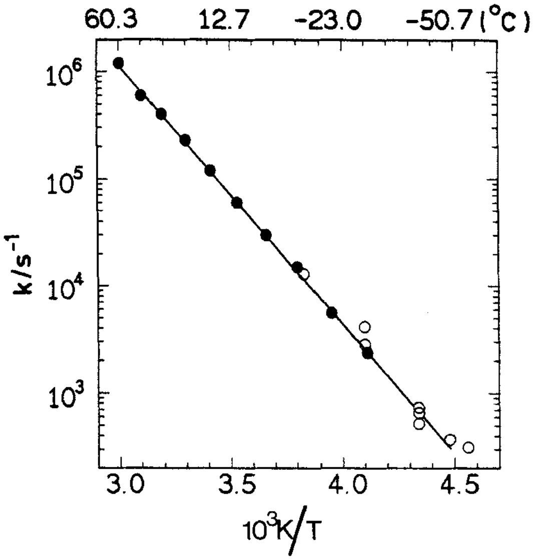


Figure 10. Arrhenius plot for the ring inversion process in 1,4-DMC-d_{16}. The full points are from the present work in the nematic solvent ZLI 2452, while the open points are from [6], obtained from ^{13}C NMR of the neat liquid.

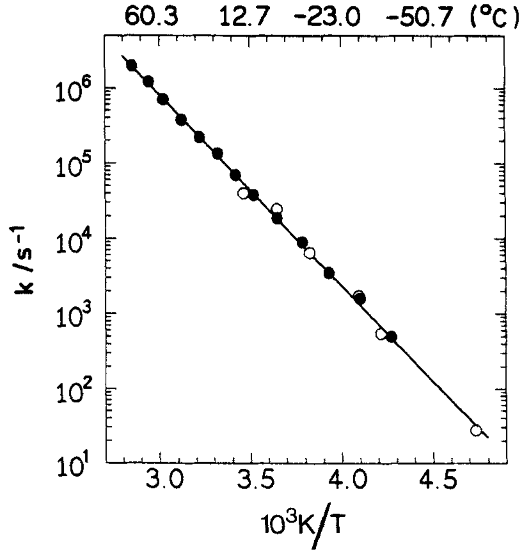


Figure 11. Arrhenius plot for the ring inversion process in 1,1-DMC-d_{16}. The full points are from the present work in the nematic solvent ZLI 2452, while the open points are from [6], obtained from ^{13}C NMR of the neat liquid.

by superposing with proper weights two-site exchange spectra of the four interchanging pairs of peaks. In practice the peak positions at the different temperatures were taken from figures 8 and 9 and an exchange independent linewidth parameter ranging between 30 and 300 s^{-1} was included in the calculation. The rate constant for the ring inversion, k, was taken as a common variable for all exchanging pairs and the calculated traces obtained by superposition of the exchange broadened spectra were compared visually with the experimental results. Examples of calculated spectra that best fit the corresponding experimental results are shown in the right hand columns of figures 2 and 3. In figures 10 and 11 the results for k so obtained are plotted versus the reciprocal absolute temperature, yielding the kinetic equations, $k = 1{\cdot}38 \times 10^{13} \exp(-45{\cdot}2/RT)\,s^{-1}$ for 1,4-DMC and $k = 4{\cdot}05 \times 10^{13} \exp(-49{\cdot}0/RT)\,s^{-1}$ for 1,1-DMC, where R is in kJ mol^{-1}.

4. Summary and conclusions

In figures 10 and 11 are also indicated (by open circles) the results for the kinetic parameters of the ring inversion of 1,4- and 1,1-DMC of Dalling *et al.* [6] obtained by ^{13}C-NMR of the neat compounds in the liquid state. It may be seen that these results fall essentially on the same Arrhenius curves as those for the nematic solutions. This indicates that within the experimental accuracy of the measurements there is no effect on the ring interconversion rate of the solute ordering in the liquid-crystalline solution. This lack of solvent effect has been observed in several other studies of monomolecular reactions in liquid-crystalline solvents [1, 4, 5, 8]. The results in figures 10 and 11 also demonstrate the power of the dynamic deuterium NMR method in liquid-crystalline solvents where because of the large splittings the range over which processes can be studied is increased by several orders of magnitude compared with those in isotropic liquids.

Relatively few ordering matrices have been determined for molecules with more than two independent elements [12]. In general the orientational order parameters for the 1,4- and 1,1-DMC are somewhat smaller than for aromatic molecules of comparable size. This most likely reflects the more nearly globular shape of the cyclohexane moiety and is also manifested by the very small biaxial order parameter $(S_{zz} - S_{yy})$. This parameter has an opposite temperature dependence for the two compounds studied. Such an effect was predicted for rigid solutes by the mean torque theory of Emsley *et al.* [13]. It is interesting to note that the most ordered principal axis (x) is very nearly parallel to the line connecting carbons 1 and 4 (which makes an angle of 27° with x'). This line corresponds to the chemist's intuitive view of the molecular long axes [14]. It should, however, be emphasized that the principal directions of the ordering matrix (which are not fixed by symmetry) are temperature dependent as manifested by the variation of α with temperature. The effect is small (less than 4° over a range of 100°C) but it reflects the effect of solvation on the ordering of the solute molecules. Clearly such effects need be included in any theory that aims at accurately calculating order parameters of solute molecules [13–21].

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