

Interconversion Kinetics and Ordering of *cis*-Decalin in Liquid-Crystalline Solvents by 1D and 2D Deuterium NMR

C. Boeffel,[†] Z. Luz,* R. Poupko, and H. Zimmermann[‡]

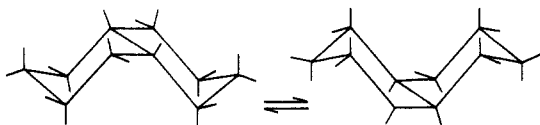
Contribution from The Weizmann Institute of Science, Rehovot 76100, Israel.
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Abstract: The deuterium NMR spectrum of perdeuterated *cis*-decalin in liquid-crystalline solvents is studied over the temperature range -5 to ~160 °C. The spectrum exhibits dynamic features due to the interconversion process of the *cis*-decalin molecules. For the quantitative analysis of the spectra, complete peak assignment is performed (i) by using selectively deuterated *cis*-decalin in the β -position, (ii) by using 2D exchange spectroscopy at low temperatures, and (iii) by fitting the observed spectrum with that expected from the minimum energy structure derived from molecular mechanics calculations. The analysis also provides all components of the ordering matrix of *cis*-decalin in the nematic solvents used. It is found that the orientations of the principal directions of this ordering matrix in the molecular frame is temperature dependent, apparently due to solvation effects. A quantitative analysis is made of the spectrum line shape over the whole experimental temperature range in terms of the interconversion reaction of *cis*-decalin, yielding the rate equation $k = 3.9 \times 10^{14} \exp(-15.5/RT)$, where R is in kcal mol⁻¹ K⁻¹. The results are compared with those previously obtained by ¹³C NMR.

I. Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy has been extensively used to study the mechanisms and associated kinetic parameters of molecular rearrangement reactions in liquid solutions. Most of these studies employ spin $I = 1/2$ nuclei like ¹H, ¹⁹F, ¹³C, and ³¹P, in isotropic liquids. More recently the method was extended to liquid-crystalline solutions with both spin $I = 1/2$ (¹H and ¹³C) and $I = 1$ (²H) nuclei.¹⁻⁵ The application of deuterium NMR in liquid-crystal solutions is particularly useful for such studies for several reasons. The ²H spectra are relatively simple, exhibiting for each group of equivalent deuterons an isolated quadrupole doublet, usually with no internuclear interactions or chemical shift effects. Dynamic effects on the line shape can therefore readily be interpreted, and due to the relatively large quadrupole splittings, the kinetic parameters can be studied over wide dynamic ranges. Moreover by using special pulse techniques, the dynamic range can be extended to well above and well below the usual range over which complete line-shape analysis can be made.⁶⁻⁸ Another advantage of deuterium is the lack of background signals, which sometimes complicate the interpretation of ¹H NMR in liquid-crystalline solutions. The method has however certain limitations, particularly the necessity of labeling, sometimes specifically, the compounds to be investigated. Also the low deuterium gyromagnetic ratio results in relatively weak NMR signals that may require long averaging periods, and often exchange-independent relaxation mechanisms result in excess line broadening, which masks the dynamic effects.

In the present work we apply the method of dynamic deuterium NMR in liquid-crystalline solutions to the ring interconversion of *cis*-decalin. Perdeuterated *cis*-decalin is commercially available,



and it provides an excellent system for demonstrating the method of dynamic deuterium NMR including the new 2D exchange technique.^{7,8} The interconversion of *cis*-decalin was first studied by proton NMR in a normal isotropic CS₂ solution, but the spectra were too complicated for exact analysis and therefore only estimates of the kinetic parameters could be obtained.⁹ A more complete investigation was done in neat *cis*-decalin by using ¹³C

NMR spectroscopy under conditions of proton decoupling that yielded kinetic parameters in the range -30 to +50 °C.¹⁰ More recently this system was used to demonstrate the 2D and 3D exchange techniques in NMR spectroscopy.^{11,12} The method of NMR spectroscopy in liquid-crystalline solutions allowed us to extend the dynamic measurements on this system to over 150 °C, corresponding to an interconversion rate of almost 10⁷ s⁻¹.

The structure of the paper is as follows: After a short Experimental Section (II) we first describe the interpretation of the low-temperature (nearly static) spectrum of perdeuterated *cis*-decalin (*cis*-decalin-*d*₁₈) in the liquid-crystalline solution (IIIA). To do so we employ a 2D exchange method,^{7,8} which allows us to identify the interchanging NMR peaks. We also use a specifically labeled *cis*-decalin species (in the β -position) for further classification of the NMR peaks. In section IIIB, we perform a quantitative analysis of the low-temperature splitting pattern in terms of the molecular geometry (obtained from molecular mechanics calculations) and derive values for all components of the ordering matrix of *cis*-decalin. This analysis is subsequently extended to the whole temperature range of the experiments. Once the spectrum is interpreted we determine the kinetic parameters (IIIC) for the interconversion reaction by fitting the experimental line shapes with simulated dynamic spectra.

II. Experimental Section

A. Materials. Perdeuterated *cis*-decalin (*cis*-decalin-*d*₁₈) and the nematic liquid-crystal solvents (ZLI2452 and S1131BCH) were obtained commercially from Aldrich and Merck (Darmstadt), respectively. The solvent ZLI2452 consists of a mixture of three mesogens including alkyl-substituted cyanophenylcyclohexane and cyanobiphenylcyclohexane, as well as an unspecified ester compound. Its nematic range is between -40 and 110 °C. The S1131BCH solvent consists of the single compound 4-pentyl-(4'-cyanobiphenyl-4)cyclohexane, which is nematic between 96 and 222 °C. A specifically (but not stereospecifically) deuterated

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* Address correspondence to this author.

[†] Permanent address: Max-Planck-Institut für Polymerforschung, Ackermannweg 10, Postfach 3148 D-6500 Mainz, West Germany.

[‡] Permanent address: Max-Planck-Institut für Medizinische Forschung, AG Molekulkristalle, Jahnstrasse 29, Postfach 103820, D-6900 Heidelberg, West Germany.

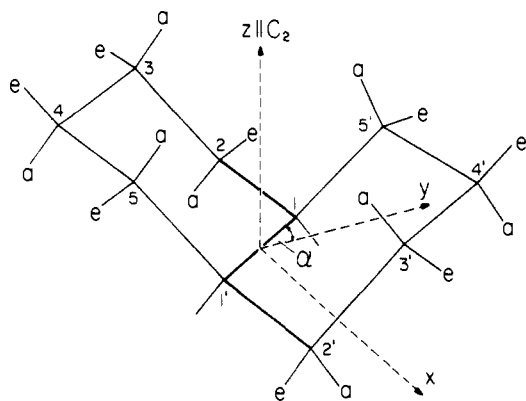


Figure 1. The molecular structure of *cis*-decalin and the numbering system for the deuterons used in the text. The coordinates X , Y , Z represent the principal directions of the ordering matrix in the molecular frame, with Z parallel to the C_2 symmetry axis and α the angle between Y and the carbon-carbon bridging bond.

cis-decalin labeled in the β -position (*cis*-decalin- d_1) was prepared as follows: A mixture of *cis*- and *trans*-decahydro-2-naphthol (Aldrich) was brominated at 0 °C with PBr_3 to β -bromodecalin and subsequently debrominated by refluxing with $\text{D}_2\text{O}/\text{CH}_3\text{COOD}$ and zinc. The product which contained a mixture of *cis*- and *trans*-decalin- β - d_1 was distilled by using a Vigreux column and the fraction boiling at 193–194 °C was collected. Mass spectrometry, NMR spectroscopy, and GLC (2% Silicone OV17, 50% phenyl, methyl) indicated a 95% deuteration of the β -position and a *cis*-*trans* ratio of 4/1.

B. NMR Measurements. The deuterium 1D NMR measurements were mostly made at 46.07 MHz with a Bruker CXP300 spectrometer with use of the quadrupole echo method ($\pi/2$ pulse width, 2.1 μs ; time interval between pulses, 30 μs). Some measurements were also made on a AM500 high-resolution spectrometer at 76.77 MHz by using single $\pi/2$ pulses (of 14- μs width) and broad-band proton decoupling (3–10 W). The deuterium 2D experiments were made on the CXP300 spectrometer by coadding quadrupole- and Zeeman-order signals as described in detail previously.^{7,8} The data size was 256 (with an increment time of 10 μs) and 1024 (5 μs dwell time) in the t_1 and t_2 dimensions, respectively. Zero filling to 1024 points along t_1 and Fourier transformation gave 2D spectra with a 100-kHz spectral width in both dimensions.

III. Results and Interpretation

A. Interpretation of the NMR Spectra. The *cis*-decalin molecule consists of two condensed cyclohexane rings in the chair conformation with an overall C_2 symmetry. Consequently there are nine inequivalent pairs of deuterons in the molecule, which we label according to the numbering system of Figure 1. The deuterium NMR spectrum of *cis*-decalin- d_{18} in a liquid-crystalline solution in the absence of interconversion should therefore exhibit nine equally intense quadrupole doublets. In practice the experimental spectrum at low temperatures (see trace a in Figure 2) can indeed be interpreted in terms of nine doublets, although with a certain degree of overlap. As the temperature is raised to above 0 °C the spectrum line shape undergoes changes characteristic of dynamic effects (left column in Figure 3), which we ascribe to the ring-interconversion process. The lines first broaden, then coalesce, and finally, at high temperatures, yield an average spectrum with just five pairs of narrow peaks. Note that one pair of lines remains sharp throughout the whole temperature range. Referring to the structural diagram in Figure 1, it may be seen that the interconversion process interchanges between the following pairs of deuterons: (1, 1'); (2a, 5'e); (2e, 5'a); (3a, 4'e); (3e, 4'a); etc. Since however the C_2 symmetry of the molecule relates the primed and unprimed hydrogens, the interconversion process effectively corresponds to interchange between the deuteron pairs (2a, 5e), (2e, 5a), (3a, 4e), (3e, 4a), while the deuterons bonded to carbons 1 and 1' remain unaffected by the exchange process. Consequently in the fast exchange limit just five doublets are expected, as observed experimentally at high temperatures (Figure 3), and we assign the invariant doublet in the spectra to deuteron 1.

Further classification of the peaks into the groups of deuterons bonded to the α -carbons (2a, 2e, 5a, 5e) and those bonded to the

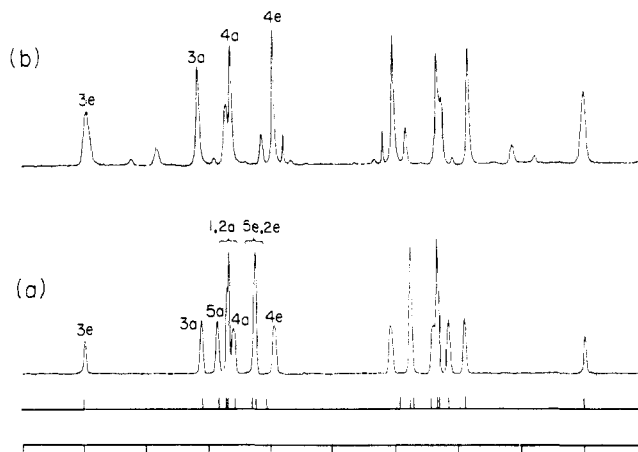


Figure 2. Deuterium NMR of *cis*-decalin in the nematic solvent ZL12452 at -5 °C: (a) a 1.4 wt % solution of *cis*-decalin- d_{18} ; (b) a 8.4 wt % solution of *cis*-decalin- d_1 with broad-band proton decoupling (3 W). The labeling of the peaks refers to the numbering system of Figure 1. The stick diagram below trace a corresponds to the calculated spectrum with use of the best-fit parameters of the ordering matrix given in Figure 7. Spectra a and b have different overall widths but are plotted so that corresponding peaks will fall on top of each other. The overall scale at the bottom of the figure corresponds to 9.50 kHz for trace a and 6.70 kHz for trace b.

β -carbons (3a, 3e, 4a, 4e) could be made on the basis of the deuterium NMR spectrum of *cis*-decalin specifically deuterated in the β -position (trace b of Figure 2). As indicated in the Experimental Section this sample contained about 20% *trans*-decalin, and the deuterium labeling which affected both isomers was not stereospecific, i.e., all β -positions were deuterated. Accordingly we identify the four strong peaks in the spectrum of this species with the deuterons bonded to carbons 3 and 4 and the weaker peaks to deuterated impurities, mainly β -deuterated *trans*-decalin. With these assignments we are thus able to divide the nine doublets in the *cis*-decalin- d_{18} spectrum into three groups corresponding to the deuterons bonded to the bridging carbons 1, the four β -deuterons 3a, 3e, 4a, and 4e, and the remaining four α -deuterons 2a, 2e, 5a, and 5e.

In the next stage of the assignment we employed the method of 2D exchange spectroscopy for spin $I = 1$ nuclei^{7,8} in order to identify the pairs of doublets that are related by the interconversion process. By properly combining Zeeman- and quadrupole-order experiments a 2D spectrum may be obtained consisting of the normal 1D peaks along the main diagonal and off-diagonal cross-peaks reflecting the connectivities induced by the exchange process. Such a 2D spectrum for the same solution and temperature used to obtain spectrum a in Figure 2 is shown in Figure 4. It may be seen that all diagonal peaks are indeed pairwise connected by cross peaks as expected from the mechanism of the interconversion reaction. This allows further classification of the α - and β -deuterium peaks into pairs of exchanging deuterons, but it still does not provide a complete assignment of all the peaks. On the basis of qualitative geometrical considerations we may guess that the largest splitting in the spectrum is due to the 3e deuterons because their C-D bond directions lie approximately parallel to the long dimension of the *cis*-decalin molecule, while for all other deuterons the C-D bonds are more nearly perpendicular to this direction and should therefore exhibit approximately half the maximum splitting. As may be seen in trace a of Figure 2, eight of the nine doublets are clustered in a narrow range with splittings corresponding to approximately half that of the single doublet with the largest splitting. Assuming that the molecules prefer to align with their long axis parallel to the director, the quadrupole interaction of the 3e deuterons should be positive while that of all other deuterons should be negative. Thus, we tentatively assign the doublet with the largest splitting to the 3e deuterons and the pair connected to it in the 2D exchange spectrum to the 4a deuterons. As may be seen in the 2D spectrum (Figure 4) these two pairs of exchanging deuterons indeed correspond to quadrupole

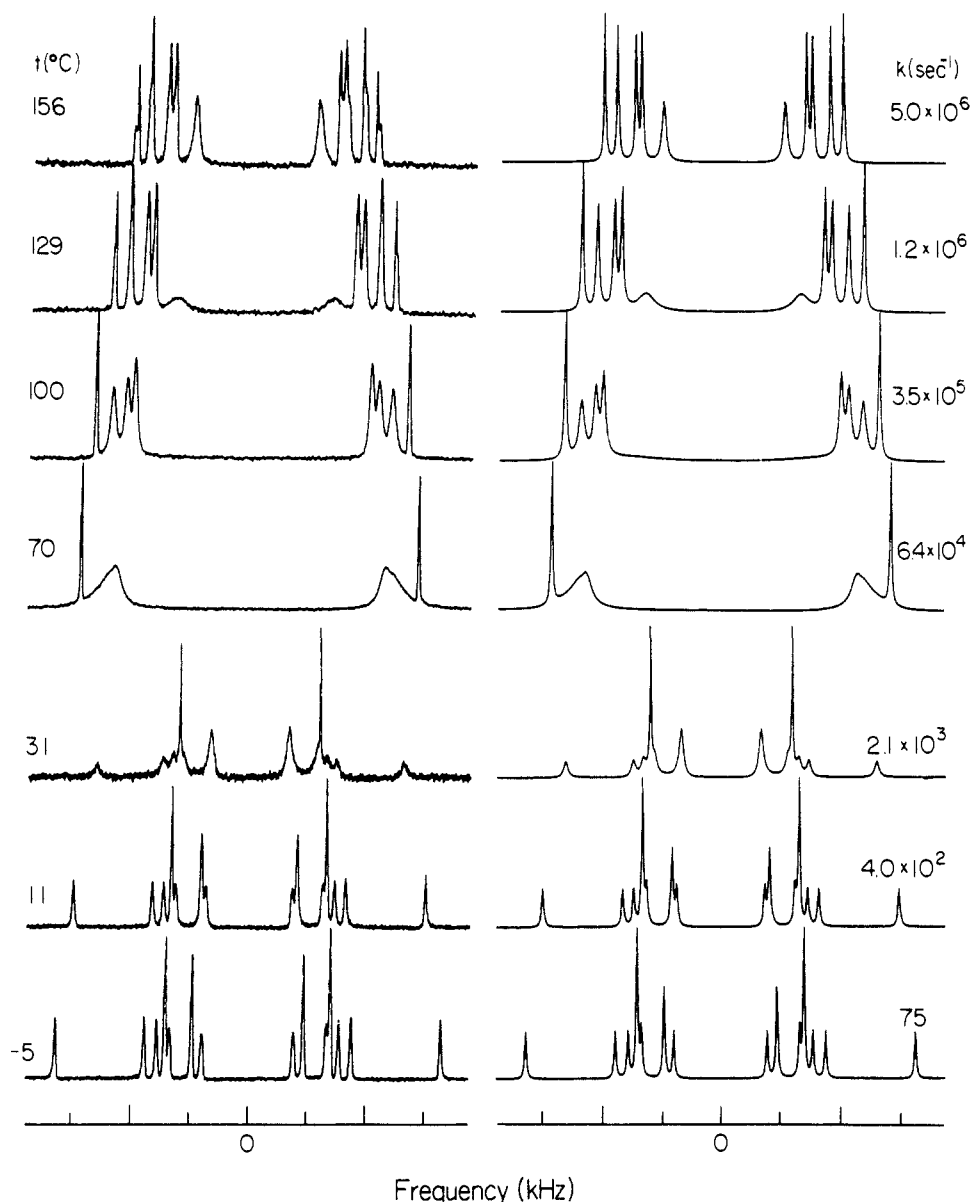


Figure 3. Left: Experimental deuterium NMR spectra of *cis*-decalin- d_{18} in nematic solutions at various temperatures as indicated. The bottom three spectra are for a 4.2 wt % solution in ZLI2452, while the four top spectra are for a 3.2 wt % solution in S1131BCH. Right: Dynamic spectra simulated to best-fit the corresponding experimental results. The interval between neighboring ticks in the frequency scale, in both columns, is 10 kHz for the bottom three traces and 5 kHz for the top four traces.

splittings with opposite signs, reflected by the fact that the high-field component of one pair is connected via cross-peaks to the low-field component of the other (and vice versa), while the quadrupole interactions of all other exchanging deuterons have identical signs.

Although the information obtained from the exchange connectivities between pairs of doublets is sufficient for a quantitative kinetic analysis of the experimental spectra, for the sake of completeness we first present an analysis that yields a full assignment of all spectral peaks. As described below this also leads to the complete determination of the ordering matrix of *cis*-decalin in the nematic solvents.

B. Complete Spectral Assignment and Derivation of the Ordering Matrix. The quadrupole splitting of a deuteron i of *cis*-decalin in a liquid-crystalline solution is given by

$$\nu_Q^i = \nu_Q(S_X \cos^2 \theta_X^i + S_Y \cos^2 \theta_Y^i + S_Z \cos^2 \theta_Z^i) \quad (1)$$

where $\nu_Q = 3/4 e^2 q Q / h$ is the principal component of the static quadrupole interaction tensor of a deuteron which we assume to be the same for all sites and cylindrically symmetric about the respective C-D bonds, the coordinates X , Y , and Z are the principal directions of the ordering matrix in the molecular frame, S_γ are the diagonal elements of this matrix (also often referred

to as motional constants), and θ_γ^i are the angles between the C-D bond direction of the i th deuteron and the γ principal axis of the ordering matrix. The symmetry of *cis*-decalin requires that the C_2 axis is a principal direction of the ordering matrix which we label Z . The X and Y axes must therefore lie in the plane perpendicular to C_2 , which also contains the bridging bond between carbons 1 and 1'. The orientation of the X and Y axes in this plane is not known a priori, and we define (see Figure 1) an angle α to indicate the orientation of Y relative to the 1-1' bond direction. Since we expect the major ordering axis to be along X , it is convenient to rewrite eq 1 in the form

$$\nu_Q^i = \nu_Q S_X [1/2(3 \cos^2 \theta_X^i - 1) + 1/2 \eta (\cos^2 \theta_Y^i - \cos^2 \theta_Z^i)] \quad (2)$$

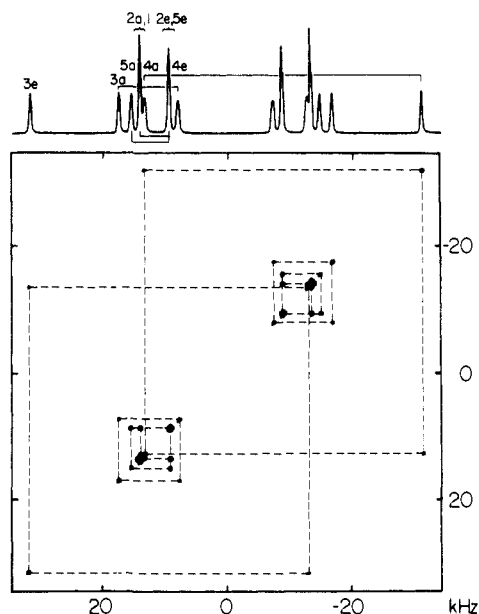
where

$$\eta = (S_Y - S_Z) / S_X \quad (3)$$

and for the transformation we have used the equalities $\sum_\gamma S_\gamma = 0$ and $\sum_\gamma \cos^2 \theta_\gamma^i = 1$. The angles θ_γ^i depend on the molecular geometry and on the angle α . It should therefore be possible to determine the parameters defining the ordering matrix (S_X , η , and α) from the structure of *cis*-decalin by best fitting the experimental ν_Q^i 's to eq 2. Since however not all of the ν_Q^i 's were definitively identified, we employed a somewhat more elaborate procedure

Table I. Geometrical Parameters for *cis*-Decalin- d_{18} Derived from Molecular Mechanics Calculations with MM2(85) Force Field Parameters^a

<i>i</i>	bond lengths, Å			bond angles, deg			torsional angles, deg		
	$\text{C}_i\text{-C}_{i+1}$	$\text{C}_i\text{-D}_i^{\text{ax}}$	$\text{C}_i\text{-D}_i^{\text{eq}}$	$\text{C}_{i-1}\text{C}_i\text{C}_{i+1}$	$\text{C}_{i-1}\text{C}_i\text{D}_i^{\text{ax}}$	$\text{C}_{i-1}\text{C}_i\text{D}_i^{\text{eq}}$	$\text{C}_{i-2}\text{C}_{i-1}\text{C}_i\text{C}_{i+1}$	$\text{C}_{i-2}\text{C}_{i-1}\text{C}_i\text{D}_i^{\text{ax}}$	$\text{C}_{i-2}\text{C}_{i-1}\text{C}_i\text{D}_i^{\text{eq}}$
1	1.538	1.116	1.116	110.913	107.629	107.629	-52.132	-67.982	-167.925
2	1.532	1.113	1.111	113.261	110.233	110.233	52.213	-67.982	175.595
3	1.531	1.110	1.112	111.127	110.238	109.463	-54.029	67.845	-174.993
4	1.533	1.112	1.111	111.270	109.421	109.635	55.167	-65.930	176.724
5	1.538	1.109	1.112	111.490	108.688	108.758	-55.846	67.059	-176.952
6	1.541	1.116	1.116	112.240	106.120	106.120	54.636	-62.618	

^a Notation as in Figure 1.**Figure 4.** A two-dimensional deuterium NMR spectrum for the 4.2 wt % solution of *cis*-decalin- d_{18} in ZLI2452 at -5 °C. The dashed lines indicate the exchange connectivities of the cross-peaks. The assignment of the deuterons and the exchange connectivities are also indicated on the 1D spectrum at the top.

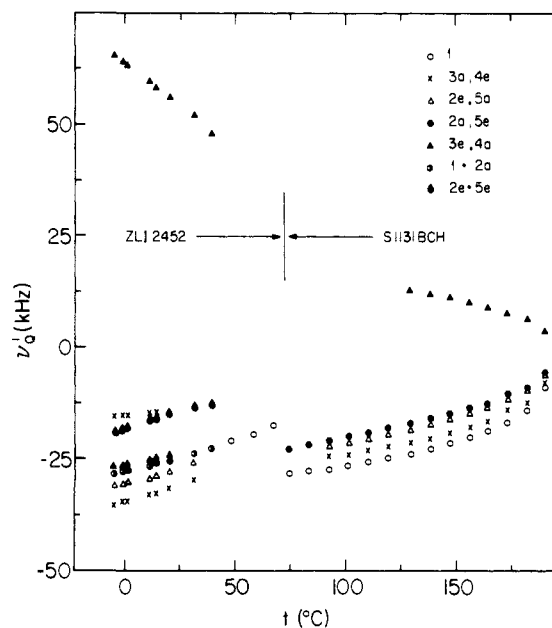
which also provided a complete assignment of the spectral peaks. As S_X is a multiplicative factor in eq 2, we may define dimensionless quadrupole interaction parameters, ν'_p , as the ratio

$$\nu'_p = \frac{-\nu_Q}{\nu_Q} = \frac{-[3(\cos^2 \theta_X - 1) + \eta(\cos^2 \theta_Y - \cos^2 \theta_Z)]}{[3(\cos^2 \theta_X - 1) + \eta(\cos^2 \theta_Y - \cos^2 \theta_Z)]} \quad (4)$$

which is independent of S_X . We have used deuteron 1 as a reference because its peaks have been definitively assigned and they remain invariant to the exchange over the whole experimental range. The negative sign in eq 4 ensures that the signs of ν_Q and ν'_p are the same since in the analysis (based on the assumption that ν_Q^{ref} is positive) ν_Q turns out to be negative. To proceed we need to know the geometry of the *cis*-decalin molecule. Although the structure of several *cis*-decalin derivatives has been determined by X-ray¹³ analysis, this was not done for unsubstituted *cis*-decalin. We therefore use in the analysis geometrical parameters determined by molecular mechanics calculations. The results of such calculations are free from distortions due to chemical substitution or crystal packing forces, they give reliable bond angles for the hydrogens, which are not always accurately obtained by X-ray, and they even permit introduction of isotope effects on the geometry due to deuterium substitution. We have performed such molecular mechanics calculations for perdeuterated *cis*-decalin using the MM2(85) force field parameters.¹⁴ The resulting bond lengths, bond angles, and torsional angles are summarized in Table

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**Figure 5.** The quadrupole interaction parameters, ν'_Q , for the various deuterons of the *cis*-decalin- d_{18} in the two nematic solvents ZLI2452 and S1131BCH. The data below 70 °C correspond to ZLI2452 in the slow-exchange regime where all peaks are observed separately. Interchanging peaks as well as partially overlapping peaks are labeled by the same symbols. For complete identification of the peaks in this region, trace a in Figure 2 must be consulted. The data above 70 °C correspond to S1131BCH in the fast-exchange region where only exchange-narrowed peaks are observed. The symbols of the combined peaks are the same as those of the corresponding separate peaks in the slow-exchange region. The relative signs of the ν_Q 's follow from the analysis as described in the text assuming that for ν_Q^{ref} it is positive.

I. With use of these results and the coordinate system of Figure 1, expressions for the direction cosines ($\cos \theta_i$) of the various C-D bonds relative to the X, Y, Z coordinate system, in terms of the angle α , were derived. The procedure used in this derivation follows closely that described in detail in Appendix A of ref 15. With these expressions the parameters α and η at -5 °C were determined by best fitting the experimental ν'_p 's to eq 4. In practice a search for α and η was made that minimized the error function $\sum_i |\nu'_p(\text{exp}) - \nu'_p(\text{calc})|$. The search was made with different assignments of the spectral peaks until the best fit was obtained. Thus the analysis also gave a complete assignment of all peaks as well as the relative signs of their quadrupole interactions. Finally, taking $\nu_Q = 126$ kHz, the last missing parameter, S_X , was calculated from the experimental ν'_p 's and eq 2. The stick diagram below trace a in Figure 2 shows the peak positions calculated from eq 2 by using the best-fit parameters derived by the above analysis. Considering the assumptions and approximations made in this analysis (identical ν_Q for all deuterons, neglect of possible biaxiality of the static quadrupole interaction tensor, geometry based solely on molecular mechanics calculations, and neglect of possible effects due to molecular vibrations), the fit of nine ν'_p 's by just three parameters (S_X , η , and α) is quite satisfactory, with only one peak

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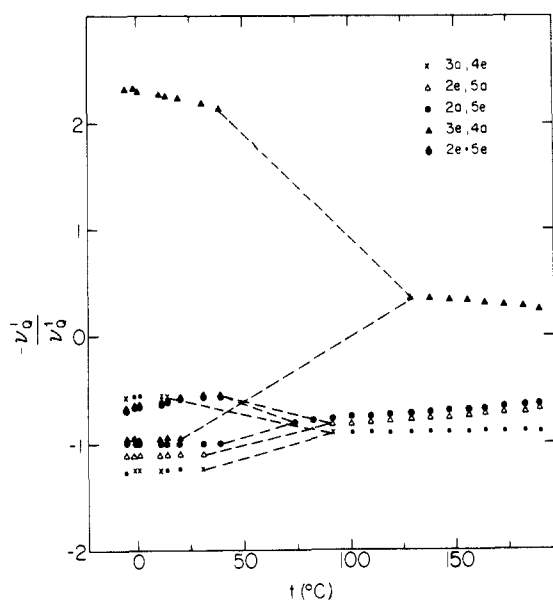


Figure 6. Reduced quadrupole splitting parameters $\nu_p^1 = -\nu_Q^1/\nu_Q^0$ derived from the results in Fig. 5. The dashed lines indicate the pairs of interchanging peaks.

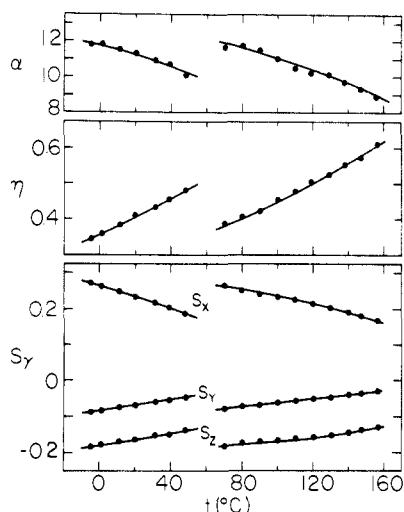


Figure 7. Best-fit results for the various parameters of the ordering matrix of *cis*-decalin- d_{18} as determined from the experimental data in the two nematic solvents, ZLI2452 (below 60 °C) and S1131BCH (above 70 °C). S_x , S_y , and S_z are the principal components of the ordering matrix (assuming S_x to be positive), $\eta = (S_y - S_z)/S_x$ is the asymmetry parameter, and α is the angle between the principal Y axis of the ordering matrix and the direction of the bridging 1-1' bond (see Figure 1).

(4e) deviating noticeably from its calculated position.

The analysis described above was subsequently extended to the whole temperature range of the measurements by using the experimentally determined quadrupole splittings as plotted in Figure 5. In the slow-exchange region (below ~ 60 °C) the splittings correspond to the separate deuterium sites, while in the fast-exchange region (above 70 °C) they correspond to the average values of the pairwise interchanging deuterons. The corresponding reduced interaction parameters, ν_p^1 , are plotted in Figure 6. In the next section we present a quantitative analysis of the experimental spectra in terms of the *cis*-decalin interconversion process. This analysis also yields ν_Q^0 values and hence ν_p^1 for the separate deuterons in the fast-exchange region permitting us to derive the elements of the ordering matrix over the whole range of the measurements. The results for the two nematic solvents used in the present work are summarized in Figure 7.

As expected, from the structural formula of *cis*-decalin (Figure 1) the largest component of the ordering matrix is S_x , which we have assumed to be positive. The result that $|S_z| > |S_y|$ reflects

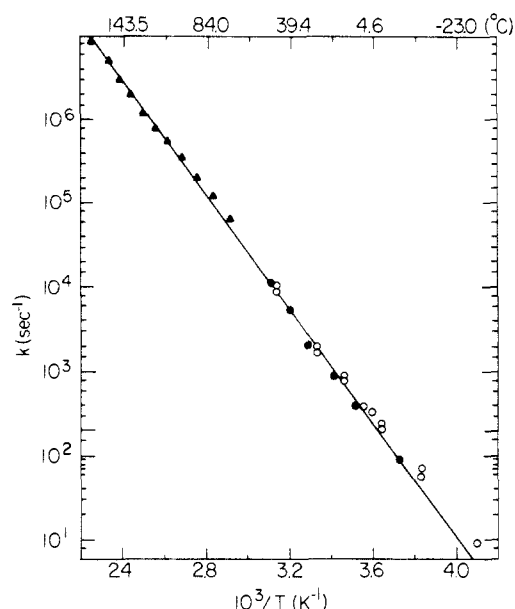


Figure 8. Arrhenius plot of the interconversion rate of *cis*-decalin. The full symbols are from the present work in ZLI2452 (circles) and S1131BCH (triangles), while the open circles are from the ^{13}C NMR results of Dalling et al.¹⁰ The overall rate equation represented by the full line is, $k = 3.9 \times 10^{14} \exp(-15.5/RT) \text{ s}^{-1}$, where R is in $\text{kcal mol}^{-1} \text{ K}^{-1}$.

the fact that when the molecular X-axis is inclined with respect to the director, there is a certain preference for the molecular Z-axis to lie perpendicular to the director over that of the Y-axis. This preference is quantified by the asymmetry parameter η , which is plotted in the middle part of Figure 7. As expected the direction of largest S_y is roughly along the line connecting atoms 3 and 3', i.e. along the "long molecular axis" about which the moment of inertia is minimum, but an exact inverse relation between the principal values of the ordering matrix and of the moment of inertia tensor is not obeyed.¹⁶ Thus the relative values of the principal components of the moment of inertia tensor along the principal directions, X, Y, Z, obtained from the molecular mechanics calculations are 1:0.53:0.43, as compared to the relative magnitudes of the experimental S_y 's at, e.g., 20 °C, 1:0.30:0.70. Moreover the principal Y axis of the moment of inertia tensor is rotated from the 1-1' bond direction by 4.2°, which must be compared with $\alpha = 11.3^\circ$ for the corresponding angle of the ordering tensor. In fact α is not constant and, as may be seen in the top part of Figure 7, in both solvents this angle changes with temperature.

C. Dynamic Line-Shape Analysis and the Rate of Interconversion. We next refer again to Figure 3 where the deuterium NMR spectra of *cis*-decalin- d_{18} over the whole temperature range studied are depicted. As indicated above these spectra can be understood in terms of superpositions of four dynamically broadened subspectra, each involving two pairs of doublets (2a, 5e), (2e, 5a), (3a, 4e), (3e, 4a) and a single dynamically invariant doublet due to deuterons 1. Each dynamic subspectrum exhibits characteristic effects of line broadening and exchange narrowing, so that in the fast-exchange region the spectrum exhibits just five doublets. (The small doubling of the spectral lines in the 156 °C spectrum is due to the instability of the nematic solution at temperatures close to the clearing point, resulting in partial phase separation.)

The line shapes of the experimental spectra can readily be simulated by using theoretical procedures developed previously.³⁻⁵ As usual in such calculations we assume the molecular transformation to be instantaneous and neglect the time interval the molecule spends in the transition state. For the simulation it is necessary to fit (at each temperature) the interconversion rate,

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k , the full set of quadrupole interactions, ν_Q^i , and an exchange-independent line width parameter, $1/T_2$. Examples of such best-fit spectra are shown in the right column of Figure 3. These were calculated by using the same ν_Q^i 's used to derive the results of Figure 7 and the rate constants shown in the figure. The overall best-fit results for the interconversion rate are plotted in Figure 8 vs reciprocal absolute temperature. Also shown in this figure are the earlier results of Dalling et al.¹⁰ obtained from ¹³C NMR spectroscopy of neat liquid *cis*-decalin. It may be seen that within experimental accuracy, all data fall on the same Arrhenius plot, yielding an overall rate equation $k = 3.9 \times 10^{14} \exp(-15.5/RT)$. This corresponds to the activation parameters $\Delta E = 15.5$ kcal mol⁻¹, $\Delta H = 14.9$ kcal mol⁻¹, and (with $\kappa = 0.5$) $\Delta S = 7.6$ eu, which are reasonably close to those determined for the ¹³C results ($\Delta H = 13.6$ kcal mol⁻¹, $\Delta S = 3.5$ eu). Thus there does not seem to be a significant effect of the solvent on the reaction rate, irrespective of its state, isotropic liquid, or a liquid crystal. A similar lack of solvent effects was noticed previously for other intramolecular rearrangement reactions.^{1,4}

IV. Summary and Conclusions

We have used deuterium NMR spectroscopy to determine the ordering characteristics and the interconversion rate of *cis*-decalin in liquid-crystalline solutions. Combining the kinetic results of the present work with those obtained previously¹⁰ in neat *cis*-decalin gives an overall dynamic range of six decades for the interconversion rate (see Figure 8). The large quadrupole splittings and consequently the large dynamic range over which the reaction

can be studied in liquid crystalline solution render this method most favorable. This is particularly so, also because the spectra are quite simple and readily lend themselves to quantitative analysis. We thus believe that when the problem of deuteration can be solved this method will find many more applications in studying dynamic processes.

We have also determined the full ordering matrix of the *cis*-decalin in two nematic solvents over the temperature range -5 to 160 °C. The results show that the actual values of the principal components depend not only on the temperature but also on their direction in the molecular frame. This is most likely due to solvation effects on the ordering matrix. The structure of the solvation complex, consisting of the solute and several closely associated solvent molecules, changes with temperature through association and dissociation equilibria, and consequently also its rotational diffusion properties are affected. Clearly such solvation effects must be included in any exact theory of solute ordering in liquid-crystal solutions.¹⁷

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Conformational *s*-Cis/*Trans* Isomerization in Free Radicals Observed by Muon Level Crossing Resonance Spectroscopy

Mary V. Barnabas, Krishnan Venkateswaran, and David C. Walker*

Contribution from the Department of Chemistry and TRIUMF, University of British Columbia, Vancouver, British Columbia, V6T 1Y6, Canada. Received February 27, 1990

Abstract: A rare type of *cis*-*trans* isomerism arises from restricted rotation about a single C-C bond and has been seen here by level crossing resonance spectroscopy (LCR) in muonated free radicals. It is observed as a splitting of the proton's LCR when the C-atom adjacent to the unpaired electron density is an asymmetric sp² hybrid. Free radicals which contain C's with sp³, symmetric sp², or sp hybrid bonds do not show this geometric isomerism. The α -protons on these radicals show resolvable splitting less easily than the β -protons. The radicals observed are those resulting from formal addition of muonium to the C=C bonds of acrylates, and they occur regardless of whether the compounds are studied in dilute aqueous solution or as pure liquids.

Introduction

Free radicals of the type $R_2\dot{C}-C(=X)-R_3$ have recently been found to exhibit conformational *s*-*cis*-*trans* isomerism, due to the partial double bond character of the (formal) single bond as a result of p- π delocalization. The first example reported for this type of stereoisomerism seems to be the radical $MuCH_2\dot{C}(CH_3)COOC_2H_5$, which was observed by transverse-field muon spin rotation (TF- μ SR)¹ (Mu being a muonium atom, the hydrogen isotope with a positive muon as its nucleus). This radical showed two isotropic muon hyperfine coupling constants separated by 1.6 MHz and was assigned as a *cis*-*trans* pair when high-resolution ESR showed that the two methyl groups in $(CH_3)_2\dot{C}COOC_2H_5$ were magnetically inequivalent.² Recently, Strub, Roduner, and Fischer³ have determined the actual heights of the barriers to free rotation for five muonated free radicals (with

α -carbonyl, α -carboxyl, or α -carbamide groups). These authors again employed TF- μ SR to look directly at the muon hyperfine coupling constants from the pairs of precession frequencies formed in these compounds as pure liquids, as a function of temperature.

We report here a study using muon level crossing resonance spectroscopy to determine the extent of this *cis*-*trans* stereoisomerism. About half the compounds selected contained the structure sketched above and the others had C atoms in sp³ or sp hybrid orbitals or were symmetric or ring sp² configurations. They were studied as solutes in dilute aqueous solution (or in micelles to solubilize them) and for comparison as pure liquids. In the former case, free thermalized muonium atoms are the free-radical precursors, whereas in the pure liquid state, "hot" muonium atom interactions, or ionic processes of μ^+ , are also possible precursors to the muonated radicals.

Experimental Section

The level crossing resonance technique (LCR) has been fully described previously.⁴⁻⁶ It is based on the transfer of spin polarization from a muon to that of another nucleus of nonzero spin which is coupled to it through their mutual hyperfine interactions in a free radical. Resonant conditions

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