Molecular Motion of *trans*-1,4-Dichlorocyclohexane in the Solid and in Solution

Bjørn Pedersen

Kjemisk Institutt, Universitetet i Oslo, Postboks 1033 Blindern, N-0315 Oslo 3, Norway

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The temperature dependence of the ^1H spin-lattice relaxation and linewidth reveal the presence of two kinds of molecular reorientation in the high-temperature phase of *trans*-1,4-dichlorocyclohexane stable above 285 K. The slowest motion is hindered by a potential barrier of 11.3(5) kJ mol^{-1} and the fastest by a potential barrier of 15.6(2) kJ mol^{-1}. The high-resolution ^{13}C NMR spectrum of the solid shows that 90 % of the molecules are in the *ee* conformation and 10 % in the *aa* conformation at room temperature. In acetone solution the *aa* conformer is found to be 1.72(3) kJ mol^{-1} higher in Gibbs free energy than the *ee* conformer. The *ee* to *aa* interconversion in solution is found to be hindered by a potential barrier with $\Delta H^{\neq} = 48.8(8)$ kJ mol^{-1} and $\Delta S^{\neq} = 1(2)$ J K^{-1}. The interconversion rate is found to be at least three orders of magnitude lower in the solid at the same temperature.

Dedicated to Professor Otto Bastiansen on his 70th birthday

That a homogeneous substance may give rise to different conformers when dissolved or evaporated is important to know in order to properly understand the properties of the substance, but that such a structural diversity exists is an almost trival fact to us. We know from both theory and experiment that all geometrical forms of a molecule will be present to the extent that the corresponding state is populated at a given temperature. Today, when the study of this structural diversity is well established (and called conformational analysis) it should be remembered that it was only 42 years ago when Bastiansen and Hassel[1] published the paper entitled "Equilibrium between Non-separable Stereo-isomeric Forms of Cyclohexane Derivatives" that the finding of this structural diversity in the gas phase was a surprise to them and to the world.

This structural diversity does not in general apply to the crystalline state. In the crystal, intermolecular forces in general exclude all but one conformer. However, there are exceptions: in particular in the plastic or semi-liquid phases that may appear in the temperature region not far from the melting point for some compounds.[2] Solid *trans*-1,4-dichlorocyclohexane (DCC) is such a compound. In crystals of DCC both the diequatorial *ee* and the diaxial *aa* conformer have been detected in the temperature region from 190 K to the melting point at 375 K.[3]

In DCC vapour the *ee* and *aa* conformers exist in equal amounts.[4] About equal amounts of both conformers are observed when DCC is dissolved in non-polar solvents.[5] In more polar solvents, however, the equlibrium is shifted in favour of the *ee* conformer with its larger electric quadrupole moments (both conformers have zero electric dipole moment).[6]

Solid DCC undergoes a phase transition at 285 K.[7] In the early days of conformational analysis it was thought that the phase transition was due to a conformation change from *ee* to *aa*. However, all experimental data available today (to be discussed in more detail below) show that the *ee* conformer dominates in both phases stable at atmospheric pressure (a phase that is only metastable at low temperature and stable at high pressure has been shown by Klaeboe *et al.*[8] to contain predominantly the *aa* conformer).

Yoshino[3] estimated the *aa*/*ee* ratio to be about

1:5 in the high-temperature phase at room temperature by comparing relative intensities of infrared absorption bands. He reported that the bands of the *aa* conformer disappear at 193 K. Ellestad and Klaeboe[9] also observed the *aa* conformer above 193 K "even for large-sized crystals", but they gave no quantitative estimates of the conformer concentration at different temper-

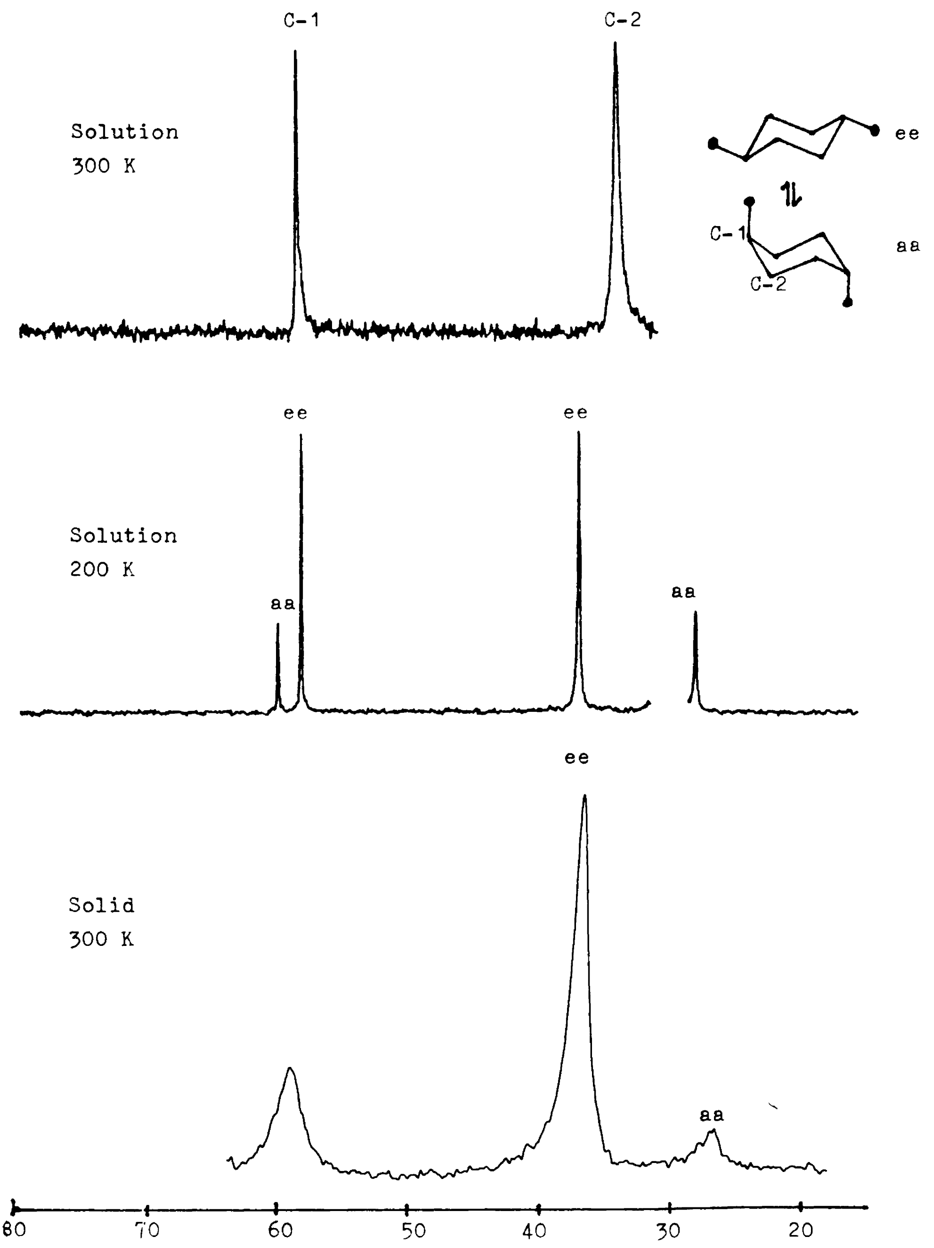

Fig. 1. ^{1}H-decoupled 50.3 MHz ^{13}C NMR spectra of *trans*-1,4-dichlorocyclohexane in acetone solution and of the solid high-temperature phase.

atures. They observed a sudden increase in the intensity of the *aa* band when the temperature of the sample was increased above the phase transition temperature. We will in this paper report on a determination of the conformer concentration from a high-resolution ^{13}C NMR spectrum.

The low-temperature phase of DCC is isomorphous with other *trans*-1,4-disubstituted cyclohexane derivatives and has been shown by X-ray diffraction to consist of *ee* conformers.[7] An X-ray study of the high temperature phase showed extraordinarily strong thermal damping and only 69 independent reflections could be measured.[10] The structure is evidently disordered. The intensity data could be interpreted on the basis of a structure consisting of *ee* conformers reorienting between two sets of resting positions. That the disorder was dynamic and not static was concluded from observed changes in the ^1H NMR spectrum above and below the phase transition temperature. We will in this paper discuss the molecular motion in the high-temperature phase in more detail based on more extensive ^1H NMR data.

In solution, cyclohexane and cyclohexane derivatives are known (since 1960) to invert between the two chair conformations at a rate well suited to be studied by NMR methods.[11] The rate of inversion can be determined directly from the NMR data in a limited temperature region.[12] From the temperature dependence of the rate of inversion it is possible to determine the free energy of activation. As this has not been done for DCC earlier, and we need to know the inversion rate, we have also recorded and analyzed ^1H and ^{13}C NMR spectra of DCC in solution.

Experimental

DCC was purchased from K&K and used as received (purity > 99 %). The NMR data for the solid were obtained using a Bruker CXP spectrometer with a 4.7 T magnet. T_1 was measured using a 180–190 pulse sequence (inversion recovery). The data were analyzed using non-linear regression with three parameters. The solution spectra used in the band-shape analysis were recorded on a Varian XL 300. The temperature was calibrated using a methanol sample.

Results

In solution. Fig. 1 shows the high-resolution ^1H-decoupled ^{13}C spectra of DCC in acetone solution

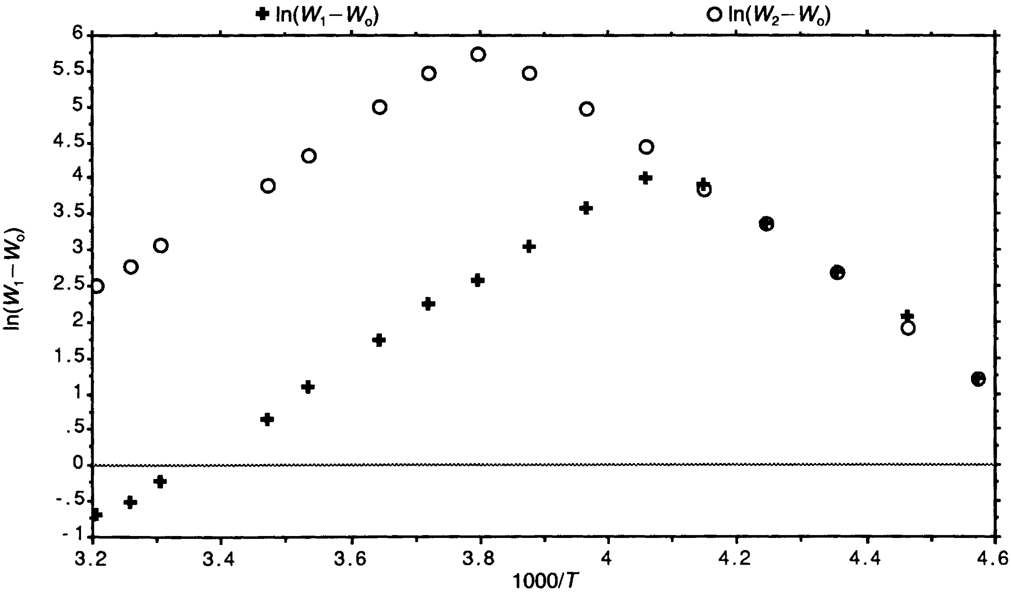

Fig. 2. The motionally broadened linewidth (W-W_0 in Hz) observed in ^1H-decoupled 75.4 MHz ^{13}C NMR spectra of *trans*-1,4-dichlorocyclohexane in acetone at different temperatures (T in K) [ln(W-W_0) versus 1000/T].

at 200 K and at room temperature. The 200 K spectrum contains peaks from both conformers, with the *ee* conformer being dominant as first found by Wood and Woo.[13] The ^{13}C chemical shifts (50.3 MHz, TMS) at 200 K are: *ee*: δ 58.1 (C-1), 37.0 (C-2); *aa*: 59.9 (C-1), 28.2 (C-2).

The ^{13}C NMR spectrum contains two sets of peaks that coalesce at different temperatures. At 75.4 MHz the C-1 peaks coalesce at about 245 K and the C-2 peaks at about 265 K. As the chemical shift differences are relatively large (C-1: 131.9 Hz; C-2: 670.2 Hz at 220 K) the spectra are motionally broadened from about 220 K to 320 K, i.e. information about the motion can be obtained from the spectra in a 100° temperature range.

The ring inversion *aa* ⇔ *ee* makes C-1 and C-2 in each molecule change between two sites with different chemical shifts. The complete band shape of such an uncoupled two-site exchange is known exactly analytically.[12] We have not performed a complete band-shape analysis, but measured the line width of the motionally broadened peaks at different temperatures (see Fig. 2).

Below the coalescence temperature the extra line-broadening, $W\text{-}W_0$, due to motion in the major peak is given by:

$$W\text{-}W_0 = p_a/(\tau\pi) \qquad (1)$$

(the linewidth of the minor peak is given by the same equation, but with p_e in stead of p_a).

Above coalescence, the extra line-broadening, $W\text{-}W_0$, due to motion is given by:

$$W\text{-}W_0 = 4\pi p_a p_e \Delta\nu^2\tau \qquad (2)$$

Here, W_0 is the linewidth without inversion, p_x the mole fraction of the xx conformer, $1/\tau$ the inversion frequency and $\Delta\nu$ the chemical shift (in Hz) averaged out by the inversion.[12] The rate constants and the inversion frequency are related through:

$$\tau = p_a/k_e = p_e/k_a \qquad (3)$$

Here, k_e is the rate constant for the *ee* to *aa* conversion, and k_a the rate constant for the reverse process.

We see by combining Eqns. (1) and (3) that we obtain k_e directly from the extra line-broadening observed below the coalescence temperature [$k_e = (W\text{-}W_0)\pi$]. To use all the data, however, we have to separate the chemical shift, the conformer mole fraction and the rate constant. We will return to this separation elsewhere. Here, we will only report on the analysis of the low-temperature data.

Table 1. The ^{1}H spin-lattice relaxation time (T_1 in s) and linewidth ($\Delta\nu$ in kHz) for solid *trans*-1,4-dichlorocyclohexane (high-temperature phase) at different temperatures (T in K).

T	T_1	ΔN
273	3.5	22.7
278	3.9	22.3
284	4.6	21.6
291	5.4	20.2
295	5.6	19.8
305	6.5	18.3
315	7.5	16.8
325	8.3	15.8
335	9.2	15.0
345	10.1	14.9
355	10.6	14.2
365	10.9	13.7
370	11.0	13.4

The conformer mole fraction has been determined at low temperature from the ^{1}H and ^{13}C spectra. At 220 K we find the mole fraction of *aa* conformer to be 0.281(3). This corresponds to $\Delta_r G^{\circ}_{aa\text{-}ee} = 1.72(3)$ kJ mol^{-1}. According to the Eyring theory of absolute reaction rates, the rate constant k_e is given by:

$$k_e = p_a/\tau = (kT/h)\exp(-\Delta G^{\ddagger}/(RT))$$

$$= (kT/h)\exp(\Delta S^{\ddagger}/R)\exp(-\Delta H^{\ddagger}/(RT)) \qquad (4)$$

By linear regression of the low temperature data we obtain:

$$\Delta H^{\ddagger} = 48.8(8)\ \text{kJ mol}^{-1} \qquad \Delta S^{\ddagger} = 1(2)\text{J K}^{-1}$$

The high-resolution ^{13}C NMR spectrum (^{1}H-decoupled MAS spectrum) of solid DCC at room temperature, also shown in Fig. 1, shows peaks at the chemical shifts expected from the solution spectra for both conformers [*ee*: δ 59.6 (C-1), 37.5 (C-2); *aa*: 59.6 (C-1), 27.1 (C-2)]. From the relative areas of the C-2 peaks we estimate the concentration of the *aa* conformer to be about

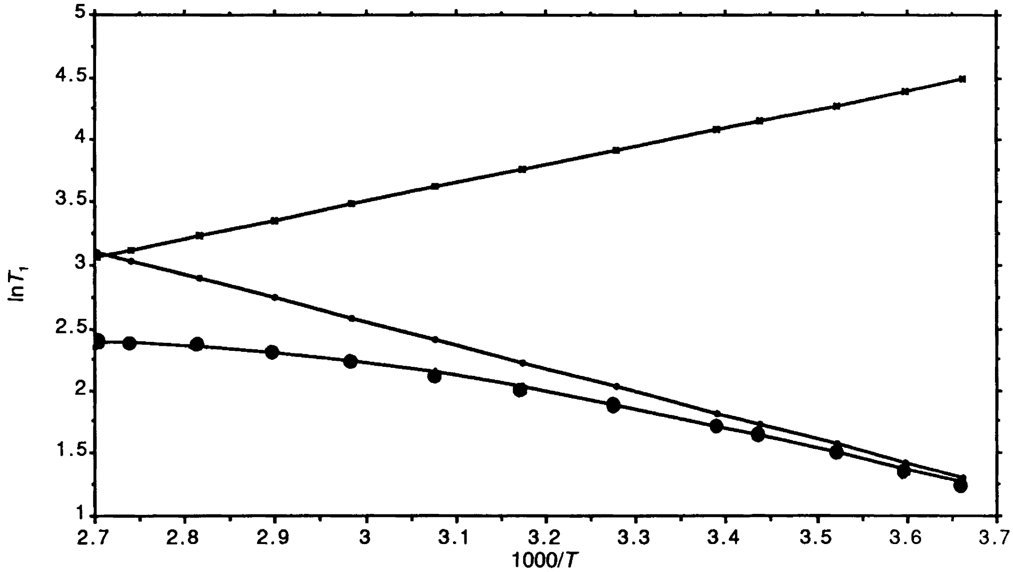

Fig. 3. The observed (●) and calculated ^{1}H spin-lattice relaxation time (T_1in s) of the solid high-temperature phase of *trans*-1,4-dichlorocyclohexane as a function of temperature (T in K) (lnT_1 versus 1000/T). The two straight lines are the calculated T_1 for the two processes contributing to the spin-lattice relaxation ($1/T_1 = 1/T_{11} + 1/T_{12}$).

10 % in the solid at room temperature. Such a quantitative estimate from solid state MAS ^{13}C NMR spectra is known to be uncertain. The estimate must therefore be said to be in acceptable agreement with the estimate of Yoshino[3] (≈ 17 % at room temperature).

The ^{1}H spin-lattice relaxation time T_1 in the high-temperature phase, given in Table 1, can be interpreted on the basis of two types of motion, as shown in Fig. 3. At low temperature one process gives the dominant contribution to the relaxation, but as lnT_1 is not linear, another process contributes increasingly at higher temperatues. The data can be decomposed as shown in Fig. 3. The activation energy for the process dominating at low temperature is found to be 15.6(2) kJ mol^{-1}, and for the process dominating at high temperature 11.3(5) kJ mol^{-1}. The experimental spin-lattice relaxation rate in the whole temperature range is found to be given by:

$$1/T_1 = 2.80\times10^{-4}\, e^{15.6/(RT)} + 1.81e^{-11.3/(RT)} \qquad (5)$$

The slopes of the T_1 curves show that in the region around the phase transition we are on the high-temperature side of a T_1-minimum. At higher temperatures another, slower process contributes increasingly, and we are on the low-temperature side of another T_1-minimum. Owing to undercooling we can study the high-temperature phase about 20° below the transition temperature, but that is insufficient to locate the T_1-minimum. The T_1-minimum for the high-temperature process is also unavailable due to melting of the compound before the minimum is reached. Hence, because the T_1-minima have not been found we are unable to determine the absolute value of the correlation time of the motion from the T_1-data.

In the low-temperature phase T_1 is much longer. Down to 250 K we found T_1 to be about 180 s. The value of T_1 was constant within the experimental uncertainty (10 %) up to the phase transition temperature. The ^{1}H NMR spectrum of the low temperature phase consists of an approximately gaussian peak with a linewidth at half-height of about 60 kHz. The line-shape and linewidth are approximately independent of temperature up to the transition temperature.

The ^{1}H NMR spectrum of the high-temperature phase consists of a markedly narrower peak that becomes narrower as the temperature increases. At 263 K the linewidth is 24 kHz, and at higher temperatures it approaches a plateau with a linewidth of about 11 kHz (see Table 1). The line-shape is also approximately gaussian at low temperature, but deviates progressively at higher temperature. The curve is slightly asymmetric and not lorentzian (the small asymmetry could be due to an unresolved chemical shift anisotropy). The change in linewidth indicates that molecular motion partially averages out the inter-spin dipole-dipole coupling. From the temperature dependence we can derive the frequency of the molecular motion $1/\tau$ from the expression:[14]

$$1/\tau = 2\pi\Delta/tg\{\pi(\Delta^2 - \Delta_h^2)/[2(\Delta_l^2 - \Delta_h^2)]\} \qquad (6)$$

Δ_h is the limiting linewidth at high temperature (11 kHz) and Δ_l the low-temperature linewidth (assumed somewhat arbitrarily to be 40 kHz). We find that the derived values of τ define a straight line in an Arrhenius plot ($\ln\tau$ versus $1/T$; see Fig. 4). By linear regression we obtain:

$1/\tau = 1.5\times10^8\ e^{-\Delta E/(RT)}$
with $\Delta E = 12.6(4)$ kJ mol^{-1}

The obtained value of ΔE (and the pre-exponential factor) depends somewhat on the choice of the limiting linewidth at high and low temperature. The uncertainty is therefore larger than shown.

Discussion

The observation of C-2 peaks from both conformers in the solid at room temperature shows that the rate of interconversion between the two conformers is much smaller than the chemical shift difference of the methylene carbons of about 400 Hz. From the solution data we estimate that the interconversion rate in solution at room temperature will be about 60 kHz. The interconversion rate is therefore at least three orders of magnitude smaller in the solid than in solution.

In the high-temperature phase the data indicate that two kinds of motion occur that partially average out the dipole-dipole coupling, making the ^{1}H-spectrum narrower and T_1 shorter. In the fastest process the molecules reorient at a rate

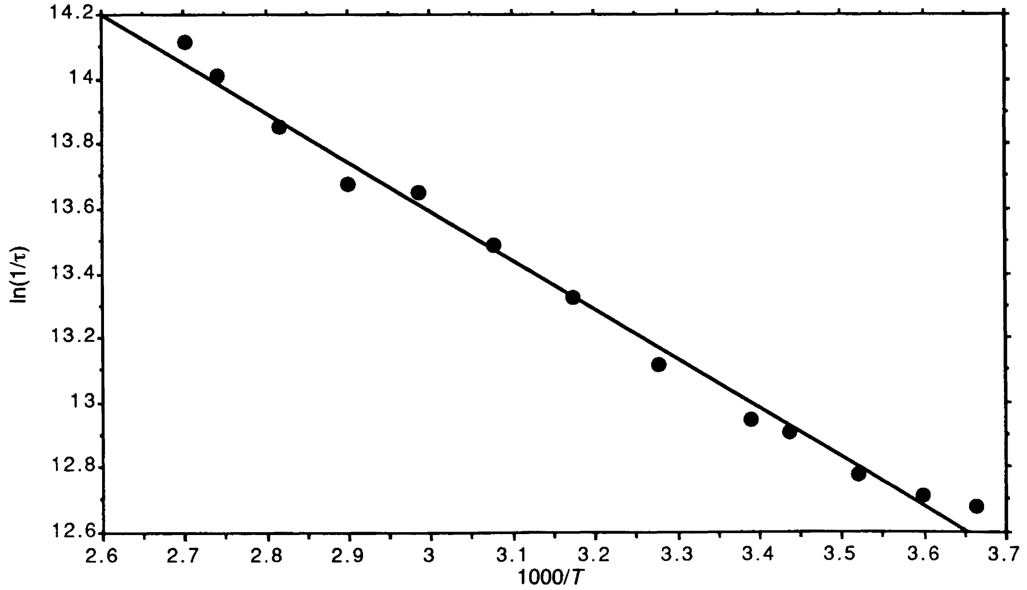

Fig. 4. The reorientation frequency ($1/\tau$ in Hz) of the *trans*-1,4-dichlorocyclohexane molecule derived from the measured linewidth of the ^{1}H NMR spectrum of the solid high-temperature phase as a function of temperature (T in K) [$\ln(1/\tau)$ versus $1000/T$].

Table 2. Activation parameters for cyclohexane and some chloro-substituted cyclohexane derivatives.

Compound	$\Delta H^{\neq}$ ((kJ/mol)	$\Delta S^{\neq}$ (J/K)	Ref.
Cyclohexane-d_{11}	44.8 (2)	9.1 (8)	11
1-Chlorocyclohexane	51.2 (6)	22 (2)	12
trans-1,2-Dichlorocyclohexane	41 (2)	13 (9)	15
trans-1,4-Dichlorocyclohexane	48.8 (8)	1 (2)	This work

which is faster than the resonance frequency (> 50 MHz).

The value of the activation energy derived from the temperature dependence of the linewidth (12.6 kJ mol^{-1}) is, within the experimental uncertainty, equal to the activation energy for the slow process derived form the T_1 data (11.3 kJ mol^{-1}). The observed values of the pre-exponential factors also show that it is the same process [as $T_1 = \omega^2\tau/(\Delta_l^2-\Delta_h^2)$ on the low temperature side of a T_1-minimum. Hence, $1/T_1 = 1.5\times10^{-8}(1/\tau)$]. We therefore conclude that it is the same process which is affecting the two NMR parameters.

The exact nature of the reorientational process cannot be determined from the NMR data. As the linewidth is not averaged to zero, both processes are probably rotation about a lattice site and not diffusion. To make progress, the information obtained here should be used in a new attempt to analyze the diffraction data.

The rate of interconversion between the two conformers in the solid is too low to contribute to the solid state ^{1}H spin-lattice relaxation or to affect the proton linewidth. It would be of interest to determine the amount of *aa* conformer at different temperatues. An attempt to do that will be made as soon as our new variable temperature MAS probe becomes operational.

The thermodynamic data for the chair-to-chair interconversion obtained for DCC in solution are similar to what has been found for cyclohexane and chloro-substituted cyclohexanes, as shown by the data in Table 2.

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