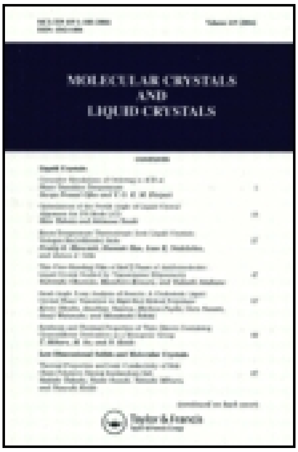

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Condis Crystals of Small Molecules. IV. Solid State NMR of Cyclododecamethylhexasilane

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Condis Crystals of Small Molecules. IV. Solid State NMR of Cyclododecamethylhexasilane

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Motion in the crystalline and plastic-crystalline phases of cyclododecamethylhexasilane has been analyzed by cross-polarization solid-state ^{13}C and ^{29}Si nuclear magnetic resonance under magic angle spinning (CP MAS NMR). It was found that even below the transition temperature to the plastic crystalline state large scale motion is possible without increase in disorder (entropy). The type of motion is described as a jump-like roto-reptation. Rate constants and activation energies are evaluated. The changes observed in the NMR spectra could be quantitatively reproduced with the kinetic parameters.

Keywords: cyclododecamethylhexasilane, solid state NMR, condis state, plastic crystal, roto-reptation, crystal

INTRODUCTION

In the first part of this series of publications[1-3] it was suggested that liquid crystals and plastic crystals of molecules capable of conformational isomerism possess similar conformational disorder and motion as in the liquid state.[1] On the example of linear bis(octyloxybenzal)phenylenediamine (OOBPD) it was then shown[2] that it is not only possible to have a stepwise freezing of the motion and disorder of the melt to nematic and various smectic phases, but also to continue this stepwise freezing through several condis states.[4] The latter have lost the translational disorder and mobility of the liquid crystals, but maintain still various degrees of conformational disorder and mobility. On the examples of several cyclosilanes it was next shown by thermal analysis through entropy and heat capacity discussions that conformational freedom must exist also in the plastic crystal phases of these molecules.[3]

In the meantime, many small and large molecule condis-crystals have been analyzed using literature data with respect to their state of disorder and motion.[5] The condis state could be shown to be particularly common for thermotropic and am-

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phiphilic liquid crystals of sufficiently flexible molecules. Similarly, it was shown to be prevalent as a state between melt and crystal of larger alkane rings.

In this paper motion of cyclododecamethylhexasilane $[Si(CH_3)_2\text{-}]_6$, abbreviated as $M_{12}Si_6$, in the crystal and plastic crystal state will be illuminated on the basis of ^{13}C and ^{29}Si CP/MAS solid state NMR. The thermal analysis of $M_{12}Si_6$ was carried out before and showed the following transitions[3]:

$$\text{Crystal} \underset{47.4\ \text{J/(Kmol)}}{\overset{352\ \text{K},T_d}{\rightleftarrows}} \text{Plastic Crystal} \underset{7.9\ \text{J/(Kmol)}}{\overset{529\ \text{K},T_i}{\rightleftarrows}} \text{Melt} \qquad (1)$$

Analysis of the crystal heat capacity below T_d indicated no entropy contributions beyond those from vibrations and possibly a beginning of hindered rotation, i.e. there is no low temperature entropic defect contributions.

The crystal structure at room temperature was reported to be rather loosely packed, monoclinic (A2/a) with four molecules per unit cell on symmetry sites $\bar{1}$.[6] At the transition temperature T_d the crystal structure changes to the FCC-lattice, typical for plastic crystals.[7] Proton-NMR relaxation times and spectral second-moment measurements as a function of temperature revealed[8] that rotation of the CH_3-groups about the C_3 axis is already possible between 100 and 200 K with an activation energy of 5.5 kJ/mol (from T_1-, T_{1p}- and T_{1D}-relaxation times). The second moment of the spectrum is in this temperature range narrowed from the rigid value of 28 ± 3 G^2 to 6.8 ± 0.5 G^2. At about 300 K, i.e. about 50 K below T_d, one finds a reduction of the second moment of the spectrum from 6.8 G^2 to about 1.0 G^2 and a change in the activation energies to about 42 kJ/mol. The authors suggested that such low value of the second moment could be rationalized only by rotation about the axis of the molecule normal to the molecular plane, coupled with ring-inversions. In solution, ^1H-NMR of $M_{12}Si_6$ gives a single sharp line, that was originally followed down to 180 K[3,9] and could in the meantime also be shown to remain a single sharp line in ^{13}C-NMR down to 130 K,[7] indicative of high intrinsic, intramolecular mobility. Any rigidity of the ring above 130 K must thus be linked to intermolecular interactions. The new solid state MAS ^{13}C and ^{29}Si NMR data will permit a more detailed description of the motion and can resolve some of the above, seemingly conflicting evidence obtained by the different analysis methods.

EXPERIMENTAL

All NMR analyses were done with a Bruker CPX 300 Fourier Pulse Spectrometer. The magnetic field-strength of 7.4 T resulted in ^{13}C and ^{29}Si resonances at 75.47 and 59.63 MHz, respectively. Data collection, Fourier transformation and treatment of spectra was carried out with an Aspect 2000 computer with software supplied by Bruker. Line-shape analysis was accomplished with an IBM computer (System 9000), coupled via an RS-232 interface.

The sample was placed in a double-bearing, magic-angle spinning (MAS) holder made of Al_2O_3. The frequency of rotation was 2.5 kHz. Cross-polarization (CP) at the Hartmann-Hahn condition took 3.1 μs and 4.3 μs for ^{13}C and ^{29}Si for the 90° pulses.

Temperature was handled by a Bruker VT-100 controller by conditioning the nitrogen needed for spinning. The temperature sensor was 1–2 cm from the sample. From experience in solution-NMR with the same controller, where it was possible to measure temperature additionally in the center of the probe, the error in the MAS experiments was estimated to be about ± 1 K.

The 90° pulse and homogenization of the magnetic field was calibrated with adamantane. Line-widths at room-temperature were less than 4 Hz.

The pulse sequence chosen was:

$$[90°_{+x}, \text{CP, Trigger, D0}, 90°_{+x}, \text{CP, Trigger, D0}]_n$$

where CP represents the pulse-sequence of the cross-polarization to increase the signal-to-noise ratio (with a 90° pulse equal to 3.1 μs for ^{13}C spectra and 43 μs for ^{29}Si and a contact time of 3.5 ms), D0 is the time for relaxation of the probe, and n is the number of repetitions. Successively the phase of the pulse exciting the spectrum was shifted by 180° to eliminate disturbances.[10] The free induction decay (FID) signal was then added with alternating sign to the computer. For the two-dimensional experiment the proper sequence of three 90° pulses was added to obtain the spectra after Fourier transformation of the FID relative to t_1 and t_2, as shown in Figure 2, below.[7,11]

The synthesis of the $M_{12}Si_6$ sample followed closely the method reported in the literature.[12] Details of the thermal characterization were reported in Reference 3.

RESULTS

Example scans of the ^{13}C and ^{29}Si NMR spectra of $M_{12}Si_6$ at different temperatures are shown in Figure 1. At low temperature the ^{13}C spectrum shows six, well-resolved lines that coalese at higher temperature. At 282 K, 70 K below T_d, a single, averaged signal is recorded. At T_d, which is variable with crystallization conditions[3] the sharp single line of the plastic crystal appears. The ^{29}Si spectrum shows analogous changes, just that the low temperature spectrum contains only three lines. Clearly, both spectra indicate attainment of large-scale motion below T_d. Details about this motion could be extracted from an analysis of the line shape to be described below.

Figure 2 represents the two-dimensional spectra at 190 K, in the rigid temperature range (—CH_3 rotation only); at 240 K, a temperature where already significant spin exchange occurs, and 285 K where the exchange is fast, but the sample is still at a temperature below the transition into the plastic state (T_d).

Figures 3 and 4 show the constancy of the centers of the ^{13}C and ^{29}Si resonance lines with temperature respectively. This constancy is taken as a check of the validity of the line-width analysis. Figures 5 and 6 are the Arrhenius diagrams line-widths and rate constants for the ^{13}C and ^{29}Si experiments, respectively. The derived activation energies are listed in the figures.

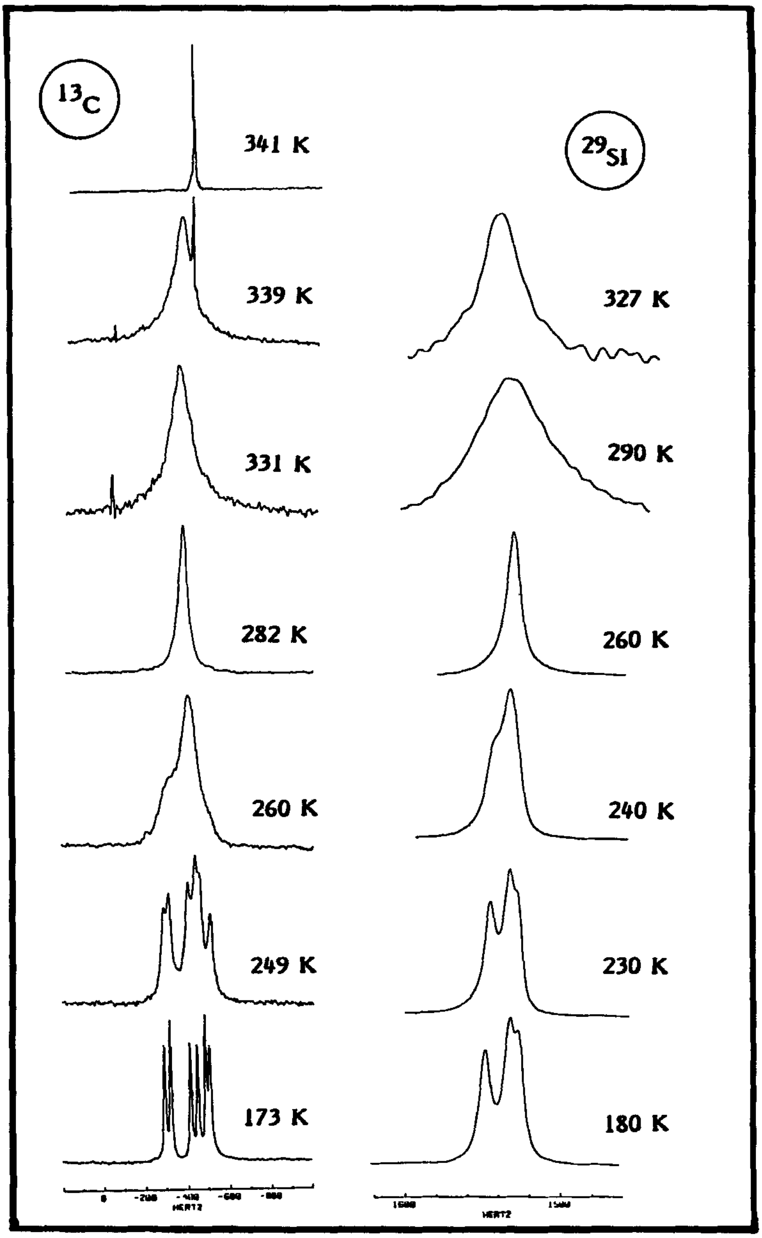

FIGURE 1 CP/MAS NMR spectra of $M_{12}Si_6$ at different temperatures. Rotation at 2.5 kHz, D0 5–10 s, n = 10–30, contact time 3.5 ms. (a) ^{13}C-spectra; (b) ^{29}Si-spectra. Linewidth of the signals at low temperature for ^{13}C are 11.9, 11.4, 11.2, 11.2, 11.3, and 12.5 Hz, for ^{29}Si 7.6, 7.3 and 8.2 Hz, respectively, from low to high field. All lines show equal population.

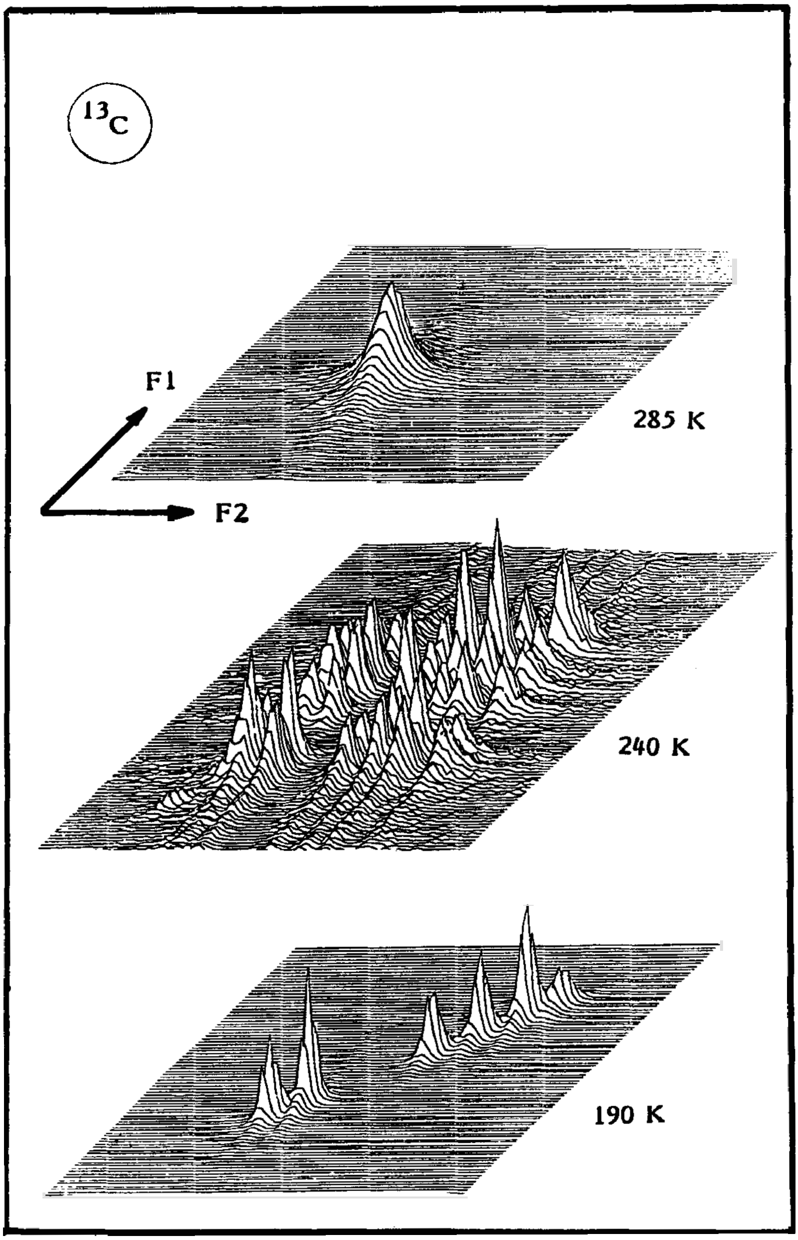

FIGURE 2 Two-dimensional ^{13}C NMR spectra at 190, 240, and 285 K. The axis F_1 represents the Fourier transformation with respect to time t_1; F_2, with respect to t_2.

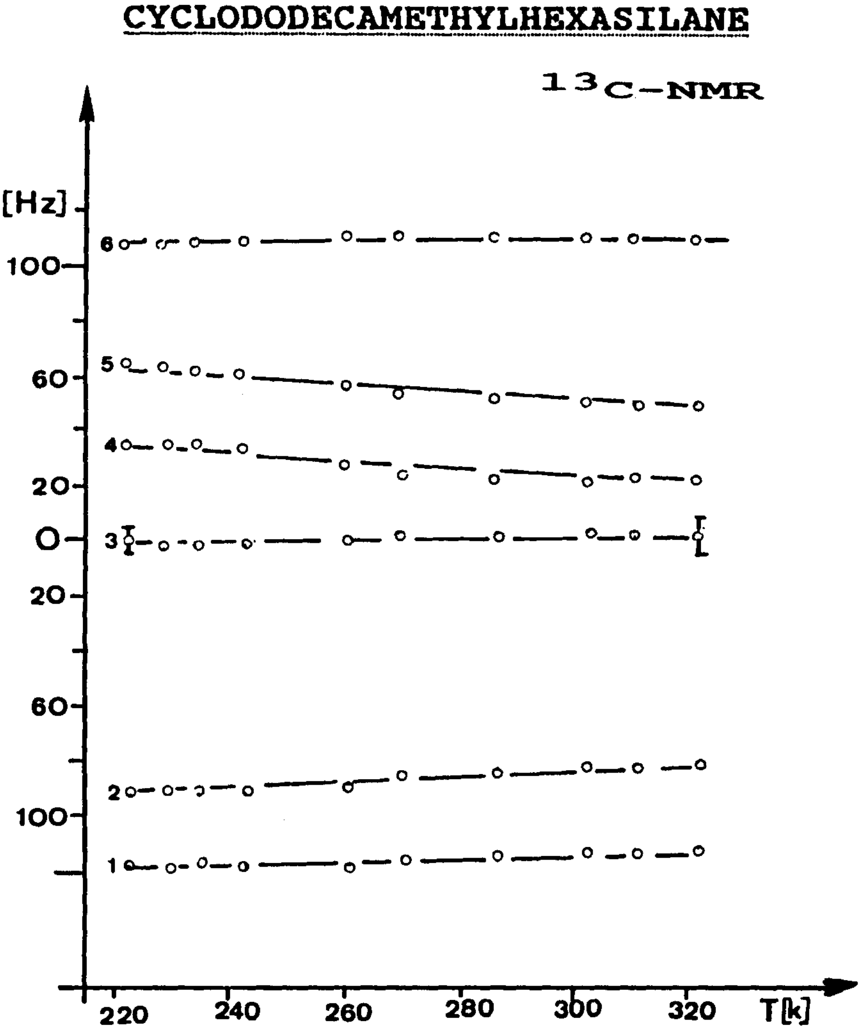

FIGURE 3 Shift of the resonance-lines of the ^{13}C spectrum as a function of temperature.

DISCUSSION AND INTERPRETATION

The most surprising observation from Figure 1 when compared to the transition temperatures of Equation (1) is that large-scale motion is possible below T_d, in the solid state, without discontinuous increase in entropy (disorder). Such motion has been observed before in other organic crystals, but has in the past found little attention. Such motion may involve: molecular rotations as found, for example, in adamantane, cyclopropane, cyclohexane, and benzene; conformational motion, as found, for example, in the $—CH_3$, $—O—CH_3$, and $—CH_2—CH_3$ motion in crystals of liquid-crystal-forming molecules; translation, as illustrated by diffusion

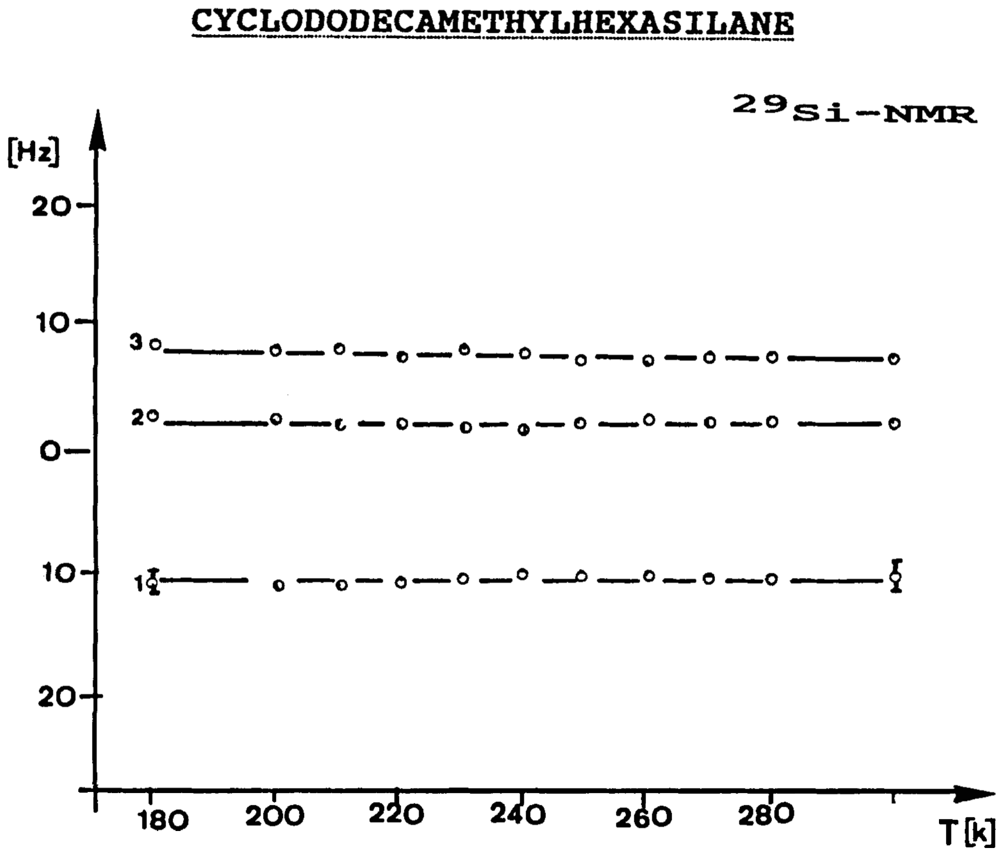

FIGURE 4 Shift of the resonance-lines of the ^{29}Si spectrum as a function of temperature.

of cyclic alkanes in the plastic crystalline state; and, finally, also combined rotation or translation and conformational motion as documented by the rotoreptation in cyclobutane and cyclodecane. The listed examples are taken from the review of conformational motion and disorder given in Reference 5 with over 400 literature citations. The first discussion of the possibility of such large-amplitude motion without disorder was seemingly given by Darmon and Brot in 1967.[13] It was shown that such motion must be jump-like and between positions of identical symmetry. In this case there would then be no entropy change, and structure determinations by X-ray diffraction or IR-analysis would also show little record of the intermediate states.

The X-ray structure of $M_{12}Si_6$ at room temperature was suggested to be, in analogy to $H_{12}C_6$, a centro-symmetric, flattened chair-conformation (D_{3d}) with rather large deviations in the torsional angles from those knows from $H_{12}C_6$.[6] The spectra in Figure 1 reveals that at low temperature (below about 200 K) the ring conformation cannot be a chair-conformation. The chair-conformation would lead to only one ^{29}Si NMR signal and two ^{13}C signals. The other well-known confor-

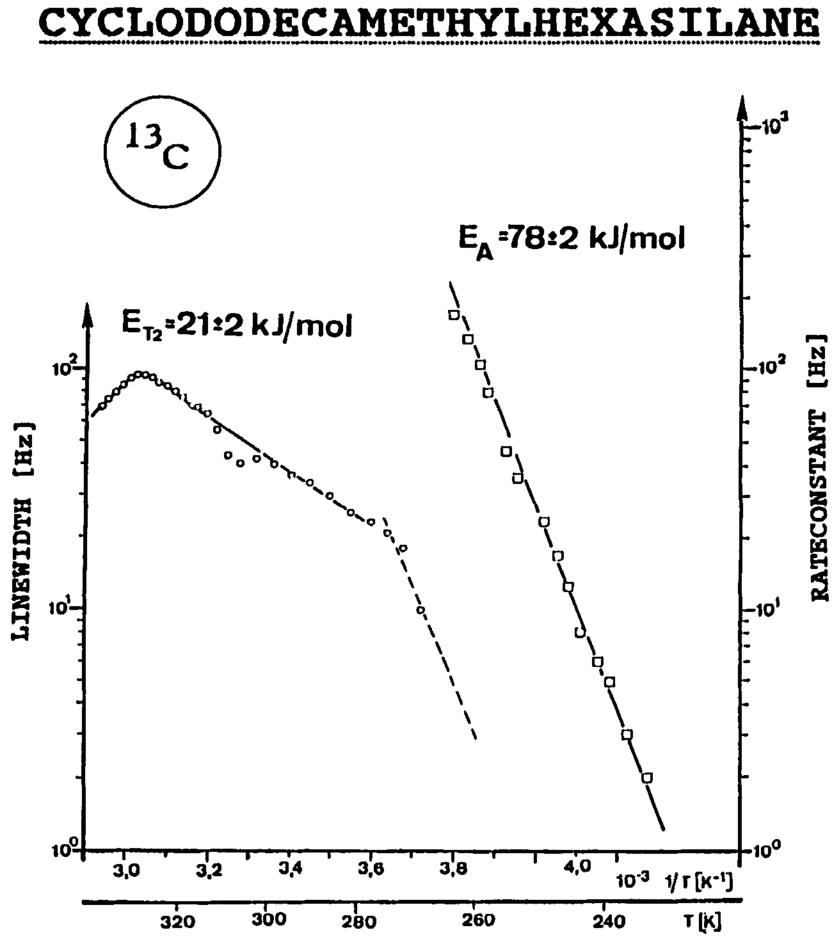

FIGURE 5 Arrhenius diagram of the rate constant for the exchange (^{13}C, right) and the T_2-minimum (left).

mation, the boat-form (C_{2v}) is also not in accord with Figure 1. It would call for two ^{29}Si NMR signals in the intensity ratio 1:2 and four ^{13}C signals in the ratio 2:2:1:1. Only a conformation similar to the twist-conformation of $H_{12}C_6$ (D_2) would correspond to the observed, equal-intensity three ^{29}Si and six ^{13}C resonances. The conformational energies of the different rotational isomers of $M_{12}Si_6$ are listed in Table I along with analogous data for $H_{12}Si_6$ and $H_{12}C_6$.[14,15] Although the cyclosilanes can be treated similar to the cycloalkanes and have the same low-energy chair conformation, the energy barriers between successive chair conformations and the energy differences to the twist and boat conformations are much smaller. The conversion sequence between the different conformational isomers is:

$$\text{chair} \rightleftarrows \text{activated state} \rightleftarrows \text{twist} \rightleftarrows \text{boat} \rightleftarrows \text{twist}, \tag{2}$$

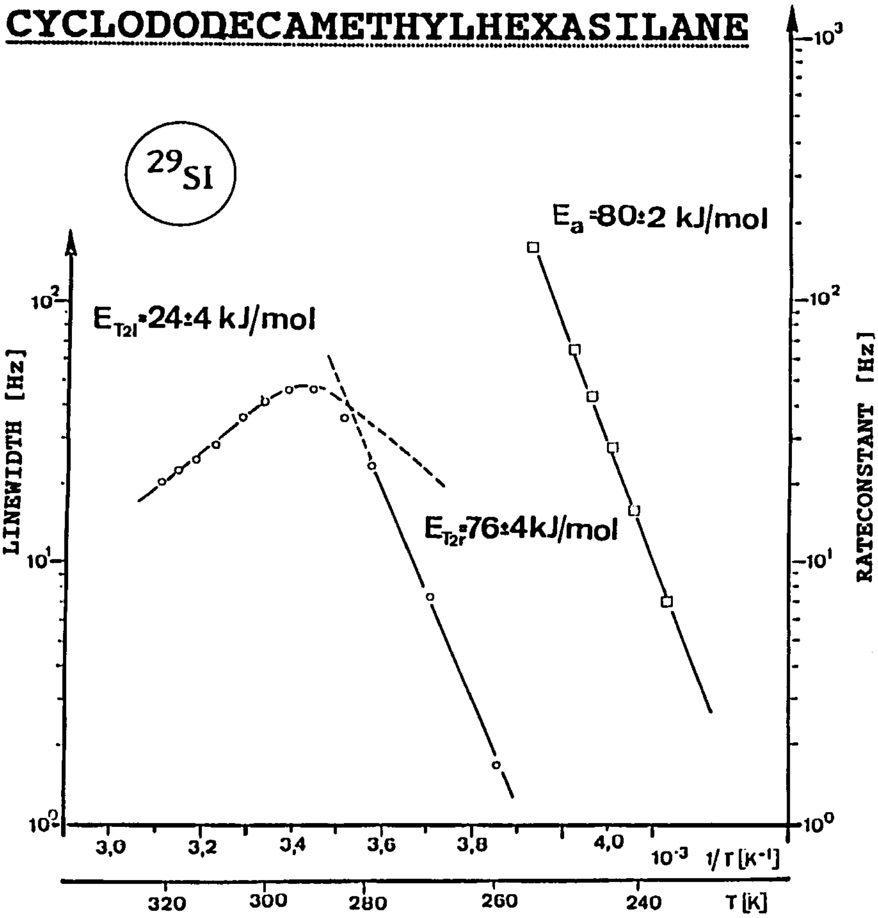

FIGURE 6 Arrhenius diagram of the rate constant for the exchange (^{29}Si, right) and the T_2-minimum (right).

with, in case of $M_{12}Si_6$, almost equal energy maxima for the activated state (C_2) and the boat conformation (C_{2v}). The low temperature conformation is thus neither in accord with the room-temperature X-ray data nor with the isolated-molecule energetics. The twist conformation must be forced by intermolecular energetics. One must predict then on cooling a continuous reduction of the crystal symmetry since the twist conformation does not permit placement of the motifs at point of $\bar{1}$ symmetry. A sharp crystal-crystal transition has, however not been observed. Similar, more or less continuous reductions in symmetry have been found for crystals of polyphenyls.[5] An indication of strong intermolecular effects in the crystal are also the observed shortest CH_3-separations of 0.398 nm in the crystal at room temperature.[6] This compares to 0.421 nm calculated for the isolated molecule.[15]

The motion that causes the coalescence of the multi-line NMR signals of Figure 1 to a single, relatively sharp line on heating to about 280 K is clearly an exchange process between all resonance signals with a single rate constant. The proof is the

TABLE I

Conformational energies in kJ/mol

	Chair (D_{3d})	Act. State (C_2)	Twist (D_2)	Boat (C_{2v})
Cyclohexane[a]	0	45.2	23.8	26.8
Cyclohexasilane[b]	0	17.3	8.2	9.7
Cyclododecamethylhexasilane[b]	0	17.2	9.8	16.0

[a] Data from Reference 14.
[b] Data from Reference 15.

two-dimensional NMR experiment illustrated in Figure 2. In Figure 2c, at 190 K, no exchange is detectable. The six different chemical surroundings of the ^{13}C nuclei are shown. In Figure 2b, at 240 K, considerable exchange takes place. The fact that each off-diagonal shows a signal indicates that exchange occurs between all chemical environments, i.e. each nucleus exchanges with each other in the motion under consideration. In Figure 2a exchange is so fast that only one signal results. Since the crystal structure is maintained (with a possible change in symmetry), a jump-like rotation is unlikely for $M_{12}Si_6$. To keep the rotation angle small for each jump it is likely that simultaneous with the rotation jump there is a conformation jump as observed in pseudorotation of gaseous $H_{12}C_6$. This combined rotation and conformation change was called roto-reptation.[5]

More information on the motion was extracted from line-position and shape. The population and basic half-widths of lines were determined from spectra between 173 and 231 K and are listed in the legend of Figure 1. Their fluctuations in this region were at most 0.4 Hz. The ^{29}Si spectrum between 180 to 210 K led to the data in the legend of Figure 1 with maximum fluctuations of 0.2 Hz. By fitting of the spectrum up to 260 K, respectively 236 K, the constancy of the position of the ^{13}C and ^{29}Si signals shown in Figures 2 and 3 could be proven. Beyond these temperatures the signal positions were then extrapolated. The resulting ^{13}C rate constants, shown in Figure 5 slowed significantly in their increase starting at 269 K, indicating the influence of a T_2-minimum process. For the analysis of the T_2-minimum process the rate constants were extrapolated past 260 K and the additional line-widths determined by increasing the basic line-width. The resulting activation energies are listed in the Figure. A similar analysis for ^{29}Si is shown in Figure 5. Good agreement is found for the activation energy E_a of the exchange rate-constant for both nuclei. For the left branch of the T_2-process agreement exists also in the activation energies of ^{13}C and ^{29}Si. The right branch must be broken into two parts as indicated. One part just beyond the maximum in line-width with a low activation energy corresponding to the left branch, and one, beginning at about 280 K, corresponds to the higher value of E_a. With the resulting rate constants and activation energies it was possible to calculate the spectra over the whole temperature range. The result is shown in Figure 7.

A comparison of the rate constants for the exchange process between ^{13}C and ^{29}Si gives a factor three larger value for ^{29}Si. Such differences in rate-constants are possible when carrying out conformational inversions on models. A given Si-atom carries out its cycle more than once during the time a given C-atom is returning

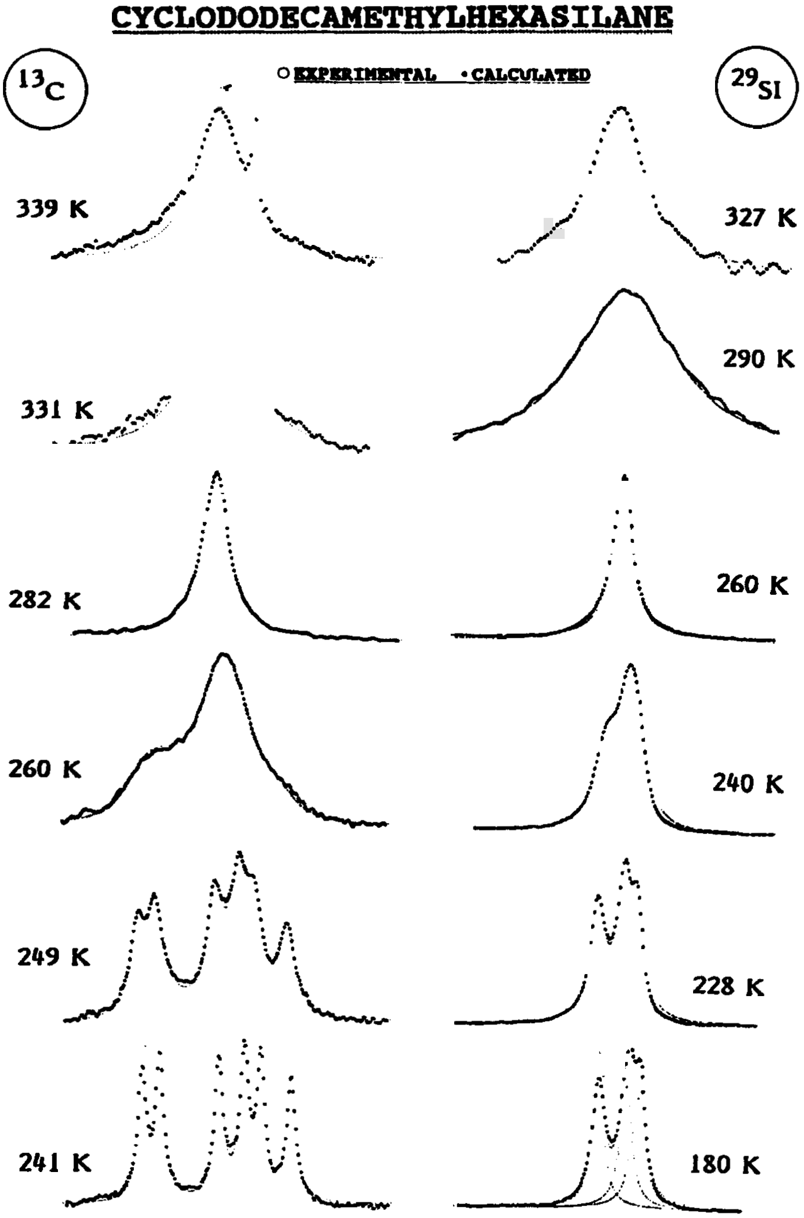

FIGURE 7 Superposition of calculated and measured spectra of Figure 1.

to its starting environment. The two maxima in Figures 4 and 5 that are separated by 40 K can be linked again to a double as fast motion for the Si-atoms.

CONCLUSIONS

The cyclic $M_{12}Si_6$ shows jump-like large amplitude motion below T_d. There must be a continuous loss of symmetry of the crystals on lowering the temperature to account for the low-temperature twist conformation. Maintenance of a crystal structure requires jump-like motion to be a roto-reptation. The derived activation energies and rate constants permit a full simulation of the spectra.

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