CONFORMATION OF CYCLIC POLYSILANE IN THE SOLID STATE AS STUDIED BY VARIABLE-TEMPERATURE $^{29}$Si CP/ MAS NMR

TOSHIO TAKAYAMA
Department of Applied Chemistry, Faculty of Technology, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221 (Japan)

SHINJI ANDO and ISAO ANDO
Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152 (Japan)

(Received 30 May 1989)

ABSTRACT

The $^{29}$Si cross-polarization/magic-angle spinning (CP/MAS) spectra of a cyclic polysilane, decaphenylpentasilane (DPPS), which has a five-membered Si ring puckered in an envelope form ($C_5$ symmetry) and a half-chair form ($C_2$ symmetry), were measured in the solid state over a wide temperature range, in order to obtain information about their conformational behaviour. In addition, the quantum-chemical calculation of the $^{29}$Si shielding constant was done in order to understand clearly the observed $^{29}$Si-NMR behaviour and to be able to discuss the conformational behaviour. From these results, it was found that DPPS mainly takes an envelope form at low temperature (ca 153 K) and takes a half-chair form at high temperature (ca 393 K). The effect of the ring current due to the phenyl group is discussed.

INTRODUCTION

It has been demonstrated that $^{13}$C cross-polarization/magic-angle spinning (CP/MAS) NMR spectroscopy is a very powerful tool in the structural analysis of polymers in the solid state [1]. This is because $^{13}$C chemical shifts are considerably displaced, depending on characteristic conformations in the solid state. Such situations also occur in the case of the $^{29}$Si nucleus considered here. Despite its usefulness, there have been few systematic studies of the $^{29}$Si CP/MAS NMR spectra of polysilanes [2–4]. Most of the CP/MAS NMR experiments carried out to date have been done only at room temperature, but variable temperature (VT) CP/MAS NMR experiments provide more useful information about the conformational change and dynamics such as chemical exchange.

The aim of the present work was to measure the $^{29}$Si CP/MAS NMR spectra
of a cyclic polysilane cyclic decaphenylpentasilane (DPPS) which has a five-membered Si ring puckered in an envelope form or a half-chair form, in the solid state over a wide temperature range, and to discuss the chemical-shift behaviour of the backbone Si atoms which arises from conformational isomerism. In order to be able to give a more detailed discussion of the above experimental results, the $^{29}$Si chemical shifts of the backbone Si atoms were calculated by means of the finite perturbation theory (FPT) within the CNDO/2 MO framework.

EXPERIMENTAL

Materials

DPPS was prepared by a method similar to that used by Hengge and Markez [5]. Dry toluene (28 ml) and sodium (2.0 g, 0.084 mol) were added to a reaction flask equipped with a stirrer and an Ar inlet, and the stirred mixture was heated to gentle reflux. Diphenyldichlorosilane (10.1 g, 0.04 mol) was added dropwise at a rate which maintained vigorous refluxing. After all the diphenyldichlorosilane had been added, the mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature and quenched with ethanol (5 ml) and water (50 ml). The insoluble polymer fraction was separated by filtration. The toluene layer was separated, washed with water, and dried. The solvent was then evaporated to give a white solid consisting of the crude DPPS. The residue was dissolved in THF (8 ml) and a mixture of methanol (50 ml) and 2-propanol (50 ml) was added slowly to the THF solution with stirring in order to precipitate the purified DPPS. In this method, DPPS is obtained in 85% yield, but only traces of insoluble material and waxy solid are formed. The result leads us to conclude that the thermodynamically favoured product in the $(\text{Ph}_2\text{Si})_n$ series is a five-membered ring compound. The cyclic compound is apparently of a monomodal lower molecular weight distribution as determined from the gel permeation chromatography (GPC 150-C Module with spectrograde THF as eluent and polystyrene as standard) elution profile.

NMR measurement

The $^{29}$Si VT-CP/MAS NMR spectra were recorded over the temperature range $-120^\circ\text{C}$ (153 K) to $120^\circ\text{C}$ (393 K) at 53.54 MHz using a JEOL GX270 spectrometer equipped with a variable-temperature CP-MAS accessory. The sample was contained in a cylindrical-type rotor and spun at 4–5 kHz. The contact time was 5 ms and the repetition time 20 s. The spectral width and number of data points were 10 kHz and 8 k, respectively. The spectra were usually accumulated 100–200 times in order to achieve a reasonable signal-to-noise ratio. The $^{29}$Si chemical shifts were calibrated indirectly through the $^{29}$Si
peak of polydimethylsilane and were converted to the exact value relative to
tetramethylsilane (TMS). The variable-temperature control was used for all
probe temperatures at which measurements were taken.

Calculation of $^{29}$Si-NMR chemical shifts

The calculations were performed employing the FPT-CNDO/2 MO method
[6-8] on two equilibrium forms; namely, the envelope and half-chair form of
Si$_5$H$_{10}$ as the model cyclic polysilane for the Si backbone of DPPS. The values
used in the calculation for the Si–Si and Si–H bond lengths were 2.40 and 1.48
Å, respectively, and the values of the Si–Si–Si and H–Si–H bond angles used
were 108° and 109.47°, respectively [9]. All calculations were carried out using
a FACOM VP-30 computer (Computer Centre of Kanagawa University) and
a HITAC M-280H computer (Tokyo Institute of Technology).

RESULTS AND DISCUSSION

The $^{29}$Si CP/MAS NMR spectra of DPPS at various temperatures are shown
in Fig. 1. It was found that as the temperature varied, the spectral patterns
changed considerably because large shifts were seen in the individual peaks
constituting the spectrum. The spectrum consists of five peaks corresponding
to the five backbone Si atoms. Each peak was numbered as shown in Fig. 1. In
order to clarify the chemical-shift behaviour of each peak, the chemical-shift
values were plotted against temperature (Fig. 2). Peaks 1, 3 and 5 moved about
2 ppm downfield as the temperature was increased from 153 to 393 K, but peaks
2 and 4 are independent of temperature. The large downfield shifts of peaks 1,
3 and 5 lead to the above-mentioned large spectral change.

Such a large spectral change is associated with the structural change in DPPS
in the solid state. A five-membered ring compound generally takes two non-
planar forms with two kinds of conformers: the envelope and half-chair forms
as determined by electron diffraction where the envelope form has a single Si
atom out of the plane formed by the remaining four Si atoms, and the half-
chair form has three adjacent Si atoms in a plane and the other two adjacent
Si atoms twisted so that one is as much above the plane as the other is below
(Fig. 3) [10-12]. As predicted from the results of the VT-$^{29}$Si CP/MAS spectra,
we consider that DPPS in the solid state undergoes a fast transition (puckering)
between the envelope form and the half-chair form in the NMR time
scale at the appropriate temperature. Such puckering may decrease the ring
strain in the cyclopentasilane ring. With regard to which of the conformations
is the most stable at low temperature, according to an X-ray diffraction study,
DPPS takes predominantly the envelope form at room temperature [13] and
at high temperature the predominant structure is probably the half-chair form.

On the basis of such a view of the structure, we assigned the five peaks cor-
Fig 1. The $^{29}\text{Si}$ CP/MAS NMR spectra of decaphenylpentasilane at temperatures from 153 to 393 K. The peaks are numbered.

Fig 2. Temperature dependence of the observed $^{29}\text{Si}$ CP/MAS NMR chemical shifts in decaphenylpentasilane. The numbers refer to the peaks in Fig 1.

responding to the five backbone Si atoms. In the envelope form, the Si(1) and Si(3), and Si(2) and Si(5) peaks may appear at the same or similar positions because of the symmetry of the molecule. For this reason the spectrum should separate into the three groups of peaks. As expected from such a consideration, the spectrum at low temperature is constituted by three peaks. From the peak intensity, peak 4 may be assigned to the Si(4) atom. However, the other Si atoms and the spectrum of the half-chair form cannot be assigned easily. The FPT CNDO/2 calculation of the $^{29}\text{Si}$ chemical shifts provide useful information about the peak assignments of the $^{29}\text{Si}$ atoms. The $^{29}\text{Si}$ nuclear shieldings of Si$_5$H$_{10}$ for the envelope form, calculated using FPT-CNDO/2 MO theory as a function of the dihedral angle $\psi$ [Si(1)Si(3)–Si(5)Si(4)], together with the observed $^{29}\text{Si}$ chemical shifts of DPPS at 153 K, are given in Table 1. Note that the calculated chemical shift ($\sigma$) is a nuclear shielding constant and so the
negative sign indicates deshielding. On the other hand, the negative sign of the observed chemical shift ($\delta$) indicates shielding. Therefore, the relative difference in the calculated chemical shifts should be compared with the observed chemical shifts. As can be seen from the data in Table 1, the calculated shieldings of the backbone Si atoms in Si$_8$H$_{10}$ shift downfield in the Si atom order $3<1<2<5<4$ during the change of $\psi$ from $6^\circ$ to $14^\circ$. The Si atom 4 peak, corresponding to a single carbon atom out of the plane of the other four atoms, moves downfield the most. This is in agreement with the above-mentioned assignment. The observed peaks of the remaining Si atoms can be assigned on the basis of the calculated shielding, as shown in Table 1.

The $\psi$ dependence of the calculated shieldings was also considered. It can be said that as the amplitude of puckering of Si$_8$H$_{10}$ (that is $\psi$) is increased, the chemical shift for all the backbone Si atoms moves downfield. The chemical shift changes for Si(2), Si(4) and Si(5) atoms are larger than those for the other atoms. For convenience, the calculated nuclear shieldings were converted with respect to the Si(3) atom. As can be seen, the calculated results at $\psi=11^\circ$ and $12^\circ$ agree well with the observed ones. This may support the experimental finding from an X-ray diffraction study [13] that DPPS takes the envelope form at low temperature. Furthermore, it can be said that the assignment of the backbone Si atoms can be reasonably done by using the FPT-CNDO/2 calculation.

With regard to the $^{29}$Si chemical shifts for the half-chair form, the calculated $^{29}$Si nuclear shieldings of Si$_8$H$_{10}$ with this form as a function of the dihedral angles $\psi_1$ [Si(3)Si(1)–Si(2)Si(4)] and $\psi_2$ [Si(2)Si(1)–Si(3)Si(5)] and the observed $^{29}$Si chemical shifts of DPPS at 393 K are given in Table 2. The calculated chemical shifts of the backbone Si Atoms of Si$_8$H$_{10}$ shift downfield in the Si atom order $1\simeq 2\simeq 3<4<5$, being $11^\circ$ at $\psi_1$ and varying in the range $1-5^\circ$ for $\psi_2$. The value of $\psi_1$ obtained from the calculated results of the envelope form was used. It is found that Si atoms 4 and 5 largely shift downfield with increasing $\psi_2$, but Si atoms 1, 2 and 3 are almost independent of $\psi_2$. The values of $\psi_1=11^\circ$ and $\psi_2=3^\circ$ agree reasonably well with the observed ones at 393 K. The calculations show that the chemical shifts of the Si(1) and Si(3) atoms, and of the Si(4) and Si(5) atoms, respectively, are very similar to each other. This trend explains well the observed spectral features. Therefore, from
the above results, it can be said that at low temperature the envelope form is predominant and at high temperature the half-chair form is predominant. At intermediate temperature there is rapid transition between the envelope and half-chair forms and so the ring conformation between the envelope and half-chair forms occurs as reported by Parkanyi et al. [13] It appears that the overall trend for the conformation dependence of the observed $^{29}$Si chemical shifts in DPPS can be explained qualitatively by the present calculations.

We will now discuss the effects of the ring current of the phenyl group on the $^{29}$Si chemical shifts of the backbone Si atoms in DPPS. For convenience, the planar form and the dihedral angles between the phenyl planes in the SiPh$_2$ moieties (1, 2, 3 and 4) were set at 90° and those for the SiPh$_2$ moiety (5) were

<table>
<thead>
<tr>
<th>$\psi$ (°)</th>
<th>Si atom</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>315 21</td>
<td>315 25</td>
<td>315 09</td>
<td>315 17</td>
<td>315 13</td>
<td></td>
</tr>
<tr>
<td>(0.12)</td>
<td>(0.16)</td>
<td>(0.0)</td>
<td>(0.08)</td>
<td>(0.04)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>315 61</td>
<td>316 88</td>
<td>315 35</td>
<td>317 81</td>
<td>316 89</td>
<td></td>
</tr>
<tr>
<td>(0.26)</td>
<td>(1.53)</td>
<td>(0.0)</td>
<td>(2.46)</td>
<td>(1.54)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>315 71</td>
<td>317 42</td>
<td>315 44</td>
<td>318 74</td>
<td>317 48</td>
<td></td>
</tr>
<tr>
<td>(0.27)</td>
<td>(1.98)</td>
<td>(0.0)</td>
<td>(3.30)</td>
<td>(2.04)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>315 83</td>
<td>318 02</td>
<td>315 53</td>
<td>319 79</td>
<td>318 14</td>
<td></td>
</tr>
<tr>
<td>(0.30)</td>
<td>(2.49)</td>
<td>(0.0)</td>
<td>(4.26)</td>
<td>(2.61)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>315 97</td>
<td>318 68</td>
<td>315 64</td>
<td>320 93</td>
<td>318 87</td>
<td></td>
</tr>
<tr>
<td>(0.33)</td>
<td>(3.04)</td>
<td>(0.0)</td>
<td>(5.29)</td>
<td>(3.23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>316 13</td>
<td>319 39</td>
<td>315 75</td>
<td>322 17</td>
<td>319 66</td>
<td></td>
</tr>
<tr>
<td>(0.38)</td>
<td>(3.64)</td>
<td>(0.0)</td>
<td>(6.42)</td>
<td>(3.91)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>316 24</td>
<td>320 04</td>
<td>315 83</td>
<td>323 40</td>
<td>320 43</td>
<td></td>
</tr>
<tr>
<td>(0.41)</td>
<td>(4.21)</td>
<td>(0.0)</td>
<td>(7.57)</td>
<td>(4.60)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>316 42</td>
<td>320 83</td>
<td>315 97</td>
<td>324 78</td>
<td>321 33</td>
<td></td>
</tr>
<tr>
<td>(0.45)</td>
<td>(4.86)</td>
<td>(0.0)</td>
<td>(8.81)</td>
<td>(5.36)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>316 62</td>
<td>321 65</td>
<td>316 12</td>
<td>326 23</td>
<td>322 28</td>
<td></td>
</tr>
<tr>
<td>(0.50)</td>
<td>(5.53)</td>
<td>(0.0)</td>
<td>(10.11)</td>
<td>(6.16)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>316 84</td>
<td>322 50</td>
<td>316 29</td>
<td>327 74</td>
<td>323 28</td>
<td></td>
</tr>
<tr>
<td>(0.55)</td>
<td>(6.21)</td>
<td>(0.0)</td>
<td>(11.45)</td>
<td>(6.99)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \delta_{dihedral} = (0.9)\frac{4.4}{4.0}\frac{8.1}{5.2} \]

*The numbers in parentheses are the calculated chemical shifts converted with respect to the atom
*3 The positive sign indicates a downfield shift
*4 Dihedral angle of Si(1)Si(3)−Si(5)Si(4)
*5 Observed values at 153 K
TABLE 2

The calculated $^{29}\text{Si}$ chemical shifts (in ppm) of Si$_5$H$_{10}$ as a function of the dihedral angles $\phi_1$ and $\phi_2$ and the observed $^{29}\text{Si}$ chemical shift of DPPS.

<table>
<thead>
<tr>
<th>$\phi_1$ (°)</th>
<th>$\phi_2$ (°)</th>
<th>Si atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>(11.05)</td>
<td>(1.22)</td>
<td>(0.0)</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>-315.48</td>
</tr>
<tr>
<td>(11.09)</td>
<td>(1.22)</td>
<td>(0.0)</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>-315.61</td>
</tr>
<tr>
<td>(11.12)</td>
<td>(1.19)</td>
<td>(0.0)</td>
</tr>
<tr>
<td>11</td>
<td>4</td>
<td>-315.75</td>
</tr>
<tr>
<td>(11.21)</td>
<td>(1.16)</td>
<td>(0.0)</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>-315.85</td>
</tr>
<tr>
<td>(11.30)</td>
<td>(1.12)</td>
<td>(0.0)</td>
</tr>
</tbody>
</table>

$\delta_{\text{obsd}}$

(10 24 00 60 57)

*The numbers in parentheses are the calculated chemical shifts converted with respect to atom 3.

The positive sign means indicates a downfield shift.

$^b$Dihedral angle of S13-S1(1)-S1(2)-S1(4).

$^c$Dihedral angle of S1(2)-S1(1)-S1(3)-S1(5).

$^d$Observed values at 393 K.

set at 45° (Fig. 4). Ring currents produced by neighbouring phenyl groups of the first, second, and third SiPh$_2$ moieties were estimated for each Si atom along the main chain. The Johnson–Bovey table [14] was used to estimate the
ring-current effect. The calculated chemical shifts (δ) due to the ring current for the Si atoms in the planar DPPS were 2.2, 2.4, 2.5, 2.4 and 2.3 ppm downfield shift for Si atoms 1, 2, 3, 4 and 5, respectively. The phenyl rings produce large ring-current shifts in each Si atom. However, the maximum difference in ring-current shifts between the Si atoms is smaller than 0.3 ppm. The ring-current effects in the envelope and the half-chair forms seem to be very similar to that of the planar form; the SiPh₂ moieties lie in a five-membered ring and so the ring-current effects on each Si atom tend to be of similar magnitude. Therefore, the ring-current effects make only a relatively minor contribution as compared with the backbone-conformation effects.

Finally, it can be concluded that variable-temperature ²⁹Si-CP/MAS NMR confirms that DPPS is mainly in the envelope form at low temperatures and is mainly in the half-chair form at high temperatures. The FPT-CNDO/2 MO calculation shows that the chemical shift is significant.

REFERENCES

1 See, for example, (a) C A Fyfe, Solid State NMR for Chemists, C F C Press, Guelph, Canada, 1983
(b) R A Komoroski (Ed.), High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk, VCH Publishers, Deerfield Beach, FL, 1986
2 R K Harris, K Metcalfe and E Hengge, Polyhedron, 4 (1985) 1319
3 F C Schilling, F A Bovey, A J Lovinger and J M Zegler, Macromolecules, 19 (1986) 2663
5 E Hengge and H Marketz, Monatsch Chern, 100 (1969) 890
6 I Ando, A Nishihoka and M Kondo, J Magn Reson, 21 (1976) 429
8 T Takayama and I Ando, Bull Chem Soc Jpn, 60 (1987) 3125
14 C E Johnson, Jr and F A Bovey, J Chem Phys, 29 (1958) 1012