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^{29}Si-double-quantum coherence spectroscopy (INADEQUATE). An efficient method for the structure elucidation of silicon frameworks

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Abstract

The application of the INADEQUATE pulse sequence (both in the one-dimensional and two-dimensional cases) has been extended to study of silicon frameworks. The value of this method for structure elucidation and the determination of ^{29}Si–^{29}Si-coupling constants is illustrated for four cyclosilanes.

Introduction

In the course of our research on cyclopolysilanes [1–4] we have synthesized a number of polycyclic derivatives. The structures of such complex silicon frameworks can often only be determined by the X-ray diffraction. This is a costly and time-consuming procedure and moreover serious difficulties often arise in preparing suitable single crystals.

It occurred to us that ^{29}Si double quantum coherence spectroscopy might provide an alternative way of determining structure of larger polysilanes. The INADEQUATE-pulse sequence is already much used for the structure elucidation of organic molecules. (An excellent review has recently been presented by Buddrus and Bauer [5].) There have been a few attempts to apply double-quantum coherence spectroscopy to nuclei other than ^{13}C. Baker et al. [6] have described the determination of structures of some heteropolytungstate derivatives by two-dimensional ^{183}W-INADEQUATE spectroscopy. Lipmaa et al. [7] used a selective heteronuclear INADEQUATE experiment for the determination of Si–C connectivities, but this involves a special procedure which cannot be performed with a standard spectrometer configuration.

Up to now the double-quantum coherence spectroscopy has not been used for silicon frameworks. In double-quantum coherence spectroscopy the silicon nucleus is almost ten times as sensitive as the ^{13}C nucleus because of the natural abundance of ^{29}Si (4.7% compared with ^{13}C 1.1%). Disadvantages are the long $T1$ relaxation times and the negative nuclear-Overhauser-effect (NOE) of the ^{29}Si nuclei. In practice this means that very long recording times are necessary if a relaxation reagent such as $Cr(acac)_3$ can not be used.

Experimental

In order to reduce the negative NOE on silicon the standard pulse sequences are modified by switching on the broadband noise decoupler shortly before the acquisition time (the "gated decoupling" technique).

Pulse sequence of the 1D-INADEQUATE-experiment [8]. ^{29}Si: $90°(P1) - \tau - 180°(P2) - \tau - 90°(P1) - D1 - 90°(P3) - D2 - \text{FID}(P4) - RD$. The broadband noise decoupler is switched on at the beginning of the delay $D2$.

The value of τ is optimized for one bond ^{29}Si–^{29}Si-coupling constants and is calculated from the formula $\tau = (4\ {}^1J(\text{SiSi}))^{-1}$. In the period 2τ the single quantum coherence is separated from the double-quantum coherence. The delay $D1$ is simply a switching delay of 3 μs. The last 90°-pulse transforms the double-quantum coherence into observable magnetization. $D2$ is the so called "ring-down delay"; $D2$ should be set as short as possible in order to guarantee total decoupling on one hand and the reduction of the NOE on the other hand. The phase cycles $P1$, $P2$, $P3$ and $P4$ are set as quoted in the literature [8].

Because the first three pulses represent a "spin-echo-experiment" the ^{29}Si–^{1}H-couplings are also refocused and therefore no signal attenuation arises. In spite of the use of gated decoupling, in certain cases there is some reduction in the signal intensities caused by the negative NOE, especially if too long a $D2$ delay has been chosen. The best results are obtained with a $D2$ set between 40 and 60 μs but must be optimized in each case; the values we cite are appropriate for our Bruker MSL 300 spectrometer at moderate decoupling power.

Pulse sequence of the 2D-experiment (symmetrized form) [9,10]. ^{29}Si: $90°(P1) - \tau - 180°(P2) - \tau - 90°(P1) - T1 - 135°(P3)T1 - D2 - \text{FID}(P4) - \text{R}D$.

The decoupler is also switched on at the beginning of $D2$. The meanings of τ, $D2$, $P1$, $P2$, $P3$ and $P4$ are the same as in the one-dimensional experiment, as described above. $T1$ is the incremented delay (evolution period) to generate the double-quantum frequencies. For the symmetrized form used here the double-quantum frequency is given by the equation:

$$\nu_{\text{DQ}} = \nu_x/2$$

where ν_x means the resonance frequency of the corresponding single-quantum coherence. The advantages of this method are a sensitivity enhancement and a reduction in the size of the data matrix.

Because the Si–H long range couplings begin to develop in the first $T1$-period they are noticeable in the $2D$-spectra. In the case of the permethylated silicon cycles investigated, and generally for FID's of a size of 4k data points (sweep widths 4000 to 6000 Hz) no marked rise of the line widths at half height is observed, but there is a decrease in both sensitivity and resolution, though for most practical cases this can be neglected. For a good signal to noise ratio the accumulation of 160 FID's per row is sufficient (30% solutions in C_6D_6).

A way of overcoming this problem involves the application of a 180°-proton pulse at the same time as the 135°-^{29}Si-pulse. This proton-pulse leads to a refocusing of the Si–H-couplings. As the experiment shows, this results in a slight increase in sensitivity and resolution, and this procedure thus represents the method of choice.

All the spectra were recorded in 10 mm tubes with a Bruker MSL 300 spectrometer operating at 59.627 MHz for ^{29}Si. The compounds were dissolved in 2 ml of C_6D_6. The relaxation reagent $Cr(acac)_3$ (30 mg) was added to all samples, reducing the relaxation times of all ^{29}Si-nuclei to such an extent that a relaxation delay of 3 s was sufficient for all measurements. Chemical shifts are relative to external TMS. The accuracy of the determined ^{29}Si–^{29}Si-coupling constants is estimated to be better than ± 0.4 Hz.

Results

The efficiency of ^{29}Si-INADEQUATE-spectroscopy has been demonstrated for four known cyclosilanes namely:

(a) Trimethylsilylnonamethylcyclopentasilane, Si_5Me_9–$SiMe_3$.
(b) Dimethylsilylnonamethylcyclopentasilane, Si_5Me_9–$SiMe_2H$.
(c) Bis(undecamethylcyclohexasilanyl), $(Si_6Me_{11})_2$.
(d) Bis(undecamethylcyclohexasilanyl)dimethylsilane, $(Si_6Me_{11})_2SiMe_2$.

The chemical shifts and the ^{29}Si–^{29}Si-coupling constants (determined from the 1D-INADEQUATE-spectra) are summarized in Table 1.

Figure 1 shows the 1D-INADEQUATE-spectrum of $(Si_6Me_{11})_2SiMe_2$. If all the ^{29}Si–^{29}Si couplings can be determined the structure of a compound easily can be derived. Sometimes, when resonance frequencies are very close to one another, overlapping or extinguishing (both satellite signals are in antiphase) of single signals might occur, so that, not all couplings can be determined. In such cases the 2D-INADEQUATE -experiment, whose most serious disadvantage is the rather

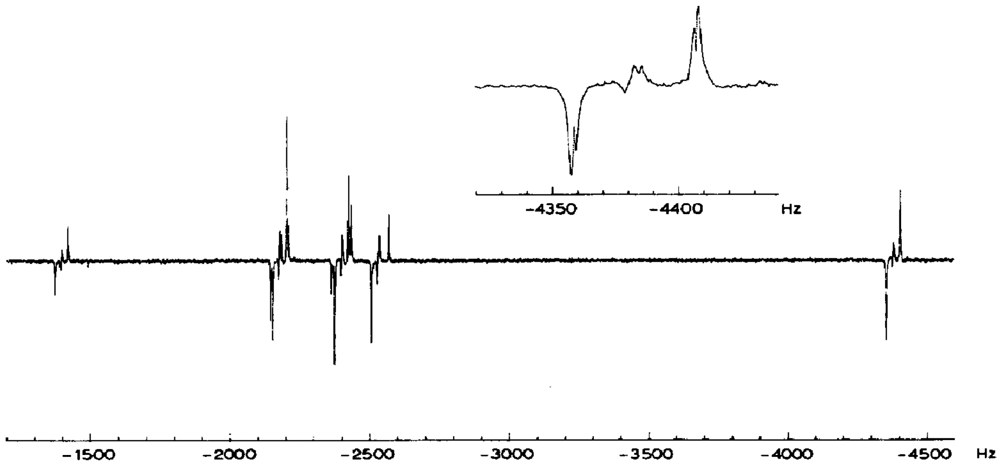
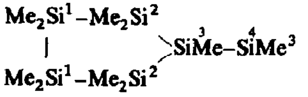
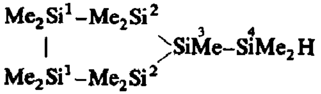
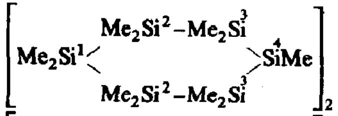
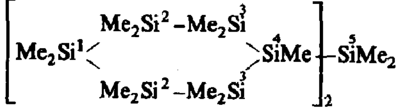


Fig. 1. 1D-INADEQUATE spectrum of $(Si_6Me_{11})_2SiMe_2$; 500 mg silane in 2 ml C_6D_6, 30 mg $Cr(acac)_3$ added; *T* 333 K; 6400 FID's accumulated; gentle exponential multiplication; insert shows the couplings at Si(4) in an expanded scale.

Table 1

^{29}Si-data

		Chemical shifts (ppm)	$^{1}J(^{29}Si-^{29}Si)$ (Hz)
	[a]	1: −40.9 3: −83.2 2: −36.1 4: −10.2	1,2: 61.1 2,3: 51.1 3,4: 62.5
	[b]	1: −41.0 3: −83.3 2: −36.2 4: −34.2	1,2: 61.6 2,3: 51.8 3,4: 60.5
	[c]	1: −42.6 3: −36.3 2: −39.6 4: −68.2	1,2: 61.4 2,3: 59.6 3,4: 51.1
	[d]	1: −42.5 4: −73.5 2: −40.3 5: −23.4 3: −36.6	1,2: 61.4 2,3: 59.8 3,4: 50.7 4,5: 46.3

[a] D2 40 μs, 900 mg, *T* 20 °C; Preparation Lit. 11. [b] D2 60 μs, 950 mg, *T* 20 °C; Preparation Lit. 12. [c] D2 50 μs, 650 mg, *T* 60 °C; Preparation Lit 1. [d] D2 60 μs, 500 mg, *T* 60 °C; Preparation Lit 1.

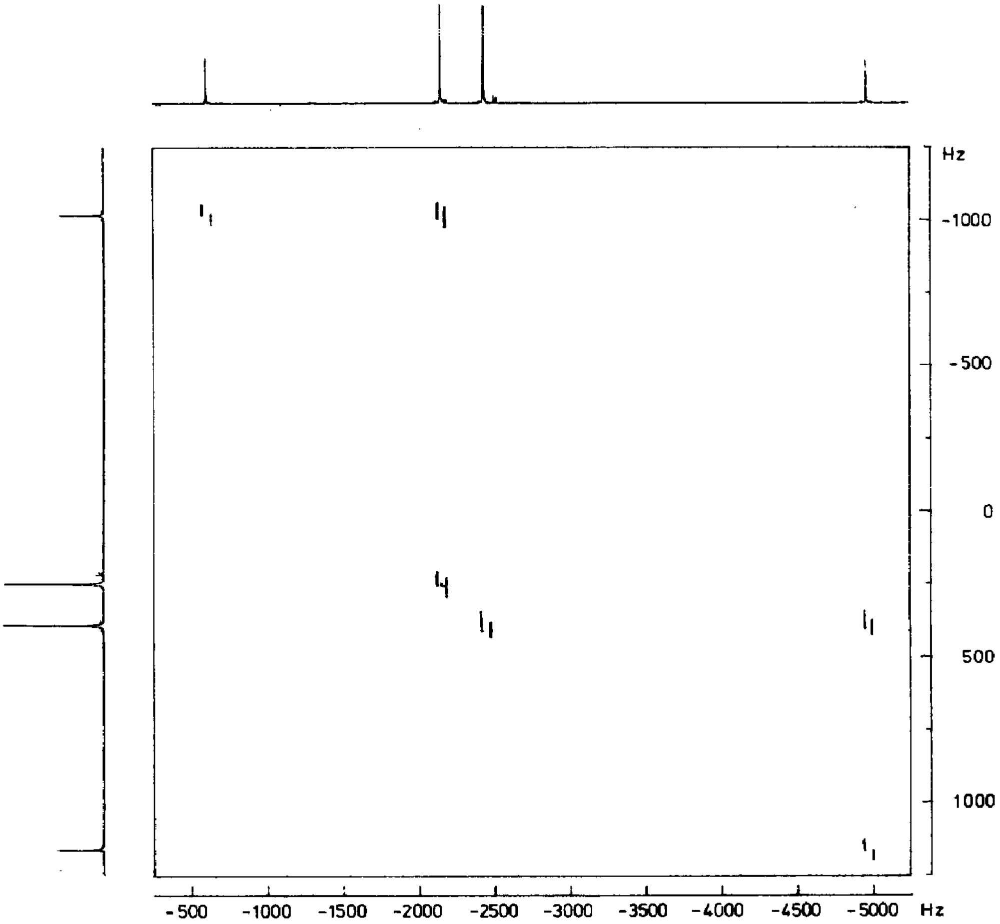


Fig. 2. 2D-INADEQUATE spectrum of Si_5Me_9–$SiMe_3$. 900 mg silane in 2 ml C_6D_6 containing 30 mg $Cr(acac)_3$; ^{29}Si–^1H-couplings refocused; 256 rows recorded, each 96 FID's accumulated; 4×4 K data matrix, spectral width in F1-dimension is 6000 Hz (2.9 Hz digital resolution); mild gaussian multiplication in both dimensions; 24 h performance time.

long recording time, provides the desired information about the structure. The applicability of the 2D-INADEQUATE technique to Si compounds is demonstrated by the spectrum of Si_5Me_9–$SiMe_3$ shown in Fig. 2, though we should mention that in this case all the required information can be obtained from the 1D-experiment.

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