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Two-dimensional silicon-29 inadequate as a structural tool for branched and dendritic polysilanes

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Abstract

The 2D silicon-29-silicon-29 INADEQUATE experiment provides connectivity information in systems whose skeleton is composed entirely of Si–Si bonds. We have developed this method to confirm the structure of the first generation dendritic polysilane $[(Me_3Si)_2SiMeSiMe_2]_3SiMe$. The 2D spectrum demonstrates connectivity for each of the three Si–Si bonds in the molecule. This method should be generally useful for dendritic and branched polysilanes. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Polysilanes emerged as a major subdiscipline of organosilicon chemistry during the 1980s, as synthetic methods were developed to link silicon atoms in long chains [1]. These materials have been examined out of interest in their semiconductor, photoconductor, thermochromic, and third-order nonlinear optical properties. Reported structures were almost entirely linear or cyclic, although more complex examples, involving cross-linking or branching, have been reported [2]. During the last 2 years, considerable interest has arisen in polysilanes that possess branched [3] or dendritic [4] structures. It is hoped that these molecules will have enhanced electronic properties and better stability.

Linear polysilanes, like their organic polymer analogues, contain a distribution of molecular weights. The new branched and dendritic polysilanes in contrast are pure, monodispersed materials with a single molecular weight. To be classified as a branched polysilane, the material need have only a single branch point. as in $(Me_3Si)_3SiMe$, the simplest such methyl-substituted structure. To be classified as a dendritic polysilane, the material must have a silicon core and either three or four wings that contain at least one branching point, as in $[(Me_3Si)_2SiMe]_3SiMe$, the simplest such methyl-substituted structure. We have given a shorthand designation of **1302** to this latter molecule [5], in which the first digit indicates that it is a first generation dendrimer (only one branching point other than the core), the second digit that there are three wings, the third digit that there are no spacer groups between the core and the branching point, and the fourth digit that the wings contain 2-fold branching.

It became clear to us early in this program that characterization would be an increasing problem as more complex molecules were prepared. Consequently, we sought to obtain X-ray crystal structures of our dendritic molecules to avoid ambiguity [5]. Even some of the smaller molecules, however, failed to crystallize, and we anticipate that crystals will be increasingly more difficult to obtain with higher generations because of the larger number of side chains that can produce

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disorder. The ^1H and ^{13}C spectra of these materials are unremarkable for the most part, as the peaks tend to cluster in a tight group close to the resonance of TMS. Only ^{29}Si NMR spectroscopy proved to be of fundamental use, as the variously substituted silicon atoms often fell in well separated spectral regions [5]. Nonetheless, standard 1D NMR methods lack definitive information on connectivity.

We report herein that the silicon–silicon 2D-INADEQUATE experiment is uniquely suited to unravel the structures of branched and dendritic polysilanes in solution. The 2D-INADEQUATE experiment originally was developed to provide information about carbon–carbon connectivities [6]. The experiment selects double quantum coherences, thereby eliminating all of the information in the ^{13}C spectrum that arises from carbon atoms uncoupled to other carbon atoms. In the 2D display, the horizontal axis is the normal ^{13}C chemical shift, and the unconventional vertical axis is the sum of the chemical shifts of two coupled carbons. Carbon–carbon connectivities are revealed by relating appropriate 2D peaks.

The 1D silicon–silicon INADEQUATE experiment dates back to the work of West et al. in 1987 [7] and has been exploited widely to measure $J(^{29}Si–^{29}Si)$, as for example in the work of West [8] and of Hengge [9]. The 1D experiment deletes single quantum coherences and permits measurement of coupling between two dilute nuclei, but it does not provide connectivity information except by matching values of coupling constants. This is a risky process, either for carbon–carbon connectivities in saturated hydrocarbons or silicon–silicon connectivities in polysilanes, because of the similarity of values. Duddeck and Dietrich [10] have noted that the $^1J(^{13}C–^{13}C)$ in cyclooctanol all fall in the small range of 34.2–34.5 Hz, except for $^1J(C1–C2)$. Thus determination of C–C, and presumably Si–Si, connectivities is not feasible by the 1D INADEQUATE experiment. In contrast, the 2D INADEQUATE experiment through double quantum filtering automatically provides atom–atom connectivity via a COSY-like 2D display.

To date, no silicon–silicon 2D-INADEQUATE experiment has been reported, presumably because heretofore there was no compelling reason for applications to simple cyclic and linear oligosilanes and polysilanes. In polydispersed polysilanes, the mixtures of species render the information unusable under any circumstances. The method becomes applicable, however, to monostructural branched and dendritic polysilanes. First, pure species are involved. Second, the desired structural information is in fact Si–Si connectivities: core to spacers, core to branches, spacers to branches, and branches to termini.

For these reasons we have explored the previously unknown silicon–silicon 2D-INADEQUATE experiment. We report herein its successful application to the molecule $[(Me_3Si)_2SiMeSiMe_2]_3SiMe$. In our shorthand designation, this molecule is **1312** a first generation dendrimer with three wings connected to the core, one spacer dimethylsilyl group between the core and the branching point, and 2-fold branching after the spacer. We reported this molecule in our original study [5], but it failed to crystallize and no X-ray structure was reported. Consequently, we felt that its structure proof was incomplete. We sought further information by examination of silicon–silicon connectivities through 2D experiments.

2. Results and discussion

Three experiments were carried out at 600 MHz: (1) the simple 1D ^{29}Si spectrum for determination of ^{29}Si chemical shifts; (2) the 1D Si–Si INADEQUATE spectrum for the determination of Si–Si coupling constants, and (3) the novel Si–Si 2D-INADEQUATE spectrum for determination of connectivities. From the 1D spectrum, the ^{29}Si chemical shifts were found to be δ −61.9 for the core silicon, −26.1 for the spacer silicons, −76.3 for the branching silicons, and −7.5 for the peripheral (terminal) silicons. These values follow the same pattern as reported previously for an impure sample of this material [5], but differ by several Hz. The current values should be considered definitive.

From the 1D-INADEQUATE experiment for **1312** (Fig. 1), we were able to measure only two of the three Si–Si coupling constants. The value for Si(core)–Si(spacer) is 47.9 Hz, and the value for Si(branch)–Si(terminal) is 60.7 Hz. These were measured respectively from the core (δ −61.9) and terminal (δ −7.5) signals. The experiment failed for the spacer and branching silicons, both of which have two couplings. Our instrumental setup apparently was insufficient to resolve cases with two couplings due to peak overlap. This result suggests a potentially serious limitation to the 1D-INADEQUATE experiment.

Fig. 2 displays the 2D-INADEQUATE spectrum for **1312**. It is noted that we were successful in obtaining a complete Si–Si 2D-INADEQUATE experiment for **1312** even when the 1D experiment failed to yield all the Si–Si coupling constants. The 2D variant not only provides more useful information, but it may be more accessible in some cases. Viewed from the horizontal axis, silicons attached to only one other silicon display a single peak above its resonance position, whereas those attached to two other silicons display two peaks above their respective resonance positions. In the latter case, ascending vertically from any resonance position on the horizontal axis to one of the peaks, moving horizontally until another peak is encountered, and descending back to the horizontal axis links the chemical shifts of any pair of bonded silicons.

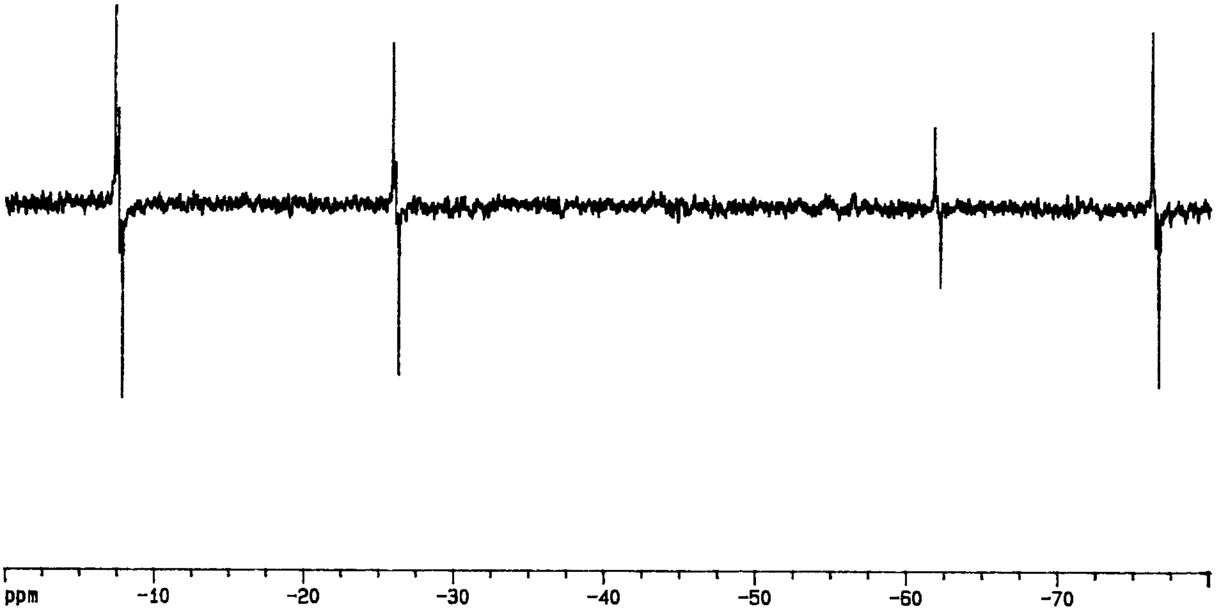

Fig. 1. The silicon–silicon 1D-INADEQUATE spectrum of $[(Me_3Si)_2SiMeSiMe_2]_3SiMe$.

The spectrum for example is analyzed by the series of horizontal and vertical lines displayed in Fig. 2. Beginning with the left peak above the terminal silicon at δ −7.5, the horizontal line leads to the right to a connectivity at δ −76.3, the branching silicon. The vertical line moves up to the second peak for the branching silicon, and the horizontal line leads left to its second connectivity at δ −26.1 with the spacer silicon. The vertical line moves down to the second peak for the spacer silicon, and the horizontal line leads to the right to its second connectivity at δ −61.9 with the core silicon. As this silicon has no further connectivities, the analysis ends at this point. The connectivity analysis confirms the structure as **1312**.

This experiment should be general for branched and dendritic polysilanes. High sensitivity is required. We used 600 rather than 400 MHz not for improved disper-

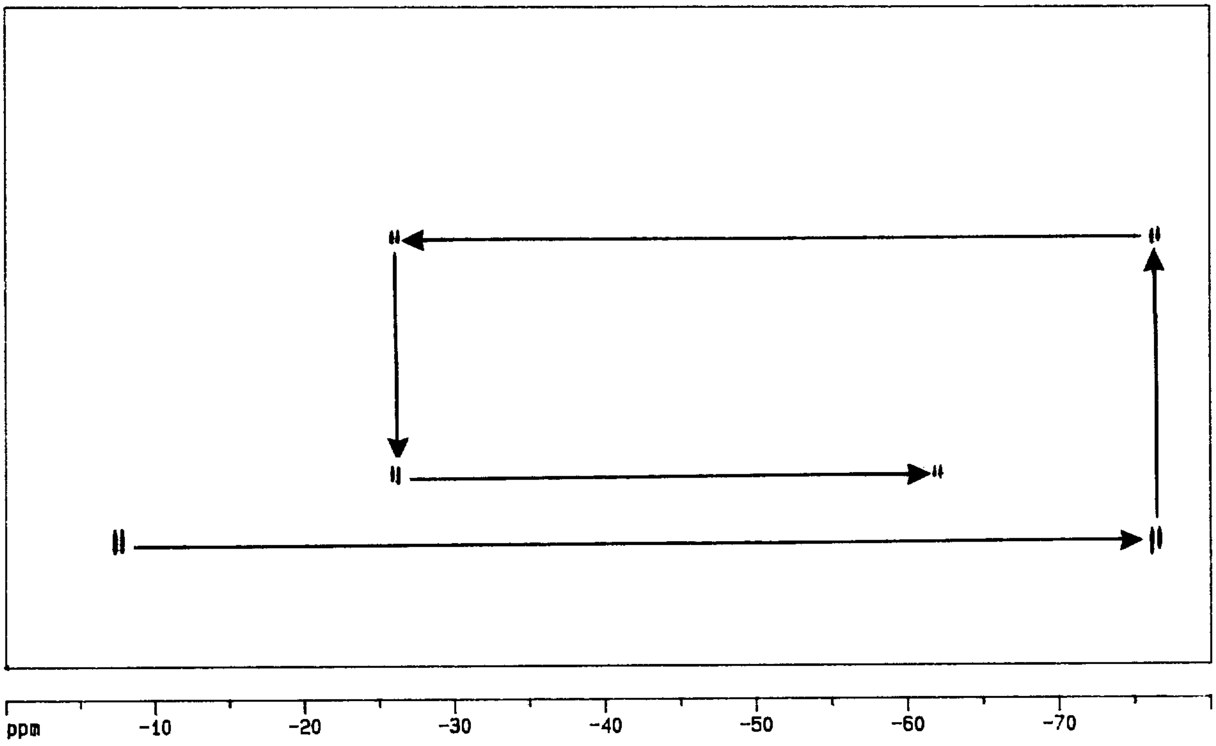

Fig. 2. The silicon–silicon 2D-INADEQUATE spectrum of $[(Me_3Si)_2SiMeSiMe_2]_3SiMe$.

sion but for optimal sensitivity. The experiment required ≈4 days on the spectrometer. Such a time is not excessive compared with the time required for X-ray crystallographic analysis. Moreover, the 2D-INADEQUATE method does not require crystalline or even solid materials. We believe that it provides the most direct and general approach to the structural analysis of these families of materials.

3. Experimental section

*3.1. 2,6 Bis(trimethylsilyl)-4-[2′-(trimethylsilyl)-1′,1′,2′,3′,3′,3′-hexamethyltrisilyl]-1,1,1,2,3,3,4,5,5,6,7,7,7,-tridecamethylheptasilane (**1312**)*

A 250 ml three-necked flask was charged with methyltris(trimethylsilyl)silane (5.0 g, 19.13 mmol), methyllithium (13.95 ml, 21 mmol), and 75 ml of THF. The solution was stirred for 2 days, and the solvent, THF, was exchanged for pentane. Excess methyllithium precipitated and was removed to leave a pentane solution of the silyllithium reagent, $(Me_3Si)_2SiMeLi$. Methyltris(chlorodimethylsilyl)silane [5] (1.09 g, 3.39 mmol) in 50 ml of pentane was added slowly to the silyllithium reagent in pentane. The mixture was stirred overnight and then washed with 150 ml of H_2O. The aqueous layer was extracted with ether (2 × 40 ml), and the combined organic layers were dried ($NaSO_4$). The solvent was removed, and 5.6 g of a clear, yellow oil was dissolved in acetone to yield 0.7 g of white crystals. The product was purified by sublimation at 100°C and 2 mm of Hg to give 0.53 g (20%): m.p. 139–141°C; ^1H NMR ($CDCl_3$) δ 0.37 (spacer), δ 0.34 (core), δ 0.18 (branch), δ 0.15 (terminal; ^{13}C NMR ($CDCl_3$) δ 2.22 (spacer), δ 1.60 (terminal), δ -5.44 (core), δ -9.46 (branch); MS *m/z* 785.28 (M^+, 9), 769 (8), 595 (53), 537 (55), 522 (100), 247 (75), 173 (82), 131 (45).

3.2. INADEQUATE experiments

The NMR experiments were carried out on a 600 MHz Bruker instrument. The ^{29}Si spectra were obtained at 119.225 MHz with inverse gated ^1H decoupling during acquisition. The 1D pulse sequence was $90°\text{-}\Delta_1\text{-}180° = \Delta_1\text{-}90°\Delta_2\text{-}90°$-acquire, in which $\Delta_1 = 4.1$ ms and $\Delta_2 = 3$ μs. The 2D pulse sequence was $90°\text{-}\Delta\text{-}180°\text{-}\Delta\text{-}90° = t_1\text{-}90°$-acquire, in which $\Delta = 4.1$ ms.

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