NMR Spectroscopy of Tetra(propyn-1-yl)silane in the Solid State and in Solution

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The crystal structure of tetra(propyn-1-yl)silane, $Si(C\equiv C\text{-}Me)_4$ **1**, has revealed a completely asymmetric molecule (point group C_1). Since this finding concerns a single crystal, the bulk material of **1** was studied by solid-state ^{29}Si and ^{13}C MAS NMR. This confirmed the result of the X-ray analysis, and by comparison with previous NMR measurements of the tin analogue **1(Sn)** it is concluded that **1** and **1(Sn)** must have very similar solid-state structures which are in contrast to those known for other tetra(alkyn-1-yl)silicon and -tin compounds. The NMR data set of **1** in solution was completed by determination of the magnitude of coupling constants $^1J(^{13}C,^{13}C)$.

Key words: Alkynes, Silane, NMR, Solid State

Tetra(propyn-1-yl)silane, $Si(C\equiv C\text{-}Me)_4$ **1**, is an apparently simple, highly symmetrical molecule. The presence of reactive $Si\text{-}C\equiv$ and $C\equiv C$ bonds makes it an attractive target for various transformations [1 – 3]. In contrast to many other polyalkynides. compound **1** is remarkably stable, can be handled in air, prepared in high yield and stored for prolonged time without decomposition; in solution, it survives heating at 110 °C for several days. The NMR data set in solution [1,4] leaves no doubt, as to be expected, that at least on average the expected T_d symmetry prevails. However, the recent observation of IR linear dichroism (LD) for **1** in nematic liquid crystal phases [5] indicates that this high molecular symmetry breaks down readily as a result of weak anisotropic interactions. Also recently, the crystal structure of **1** has revealed that the asymmetric unit contains only a single type of molecule which, however, is completely unsymmetrical (point group

C_1) [6]. In order to investigate the structural properties of the bulk material of **1**, we have measured now the solid-state ^{29}Si and ^{13}C MAS NMR spectra, and we have also completed the NMR data set for solutions of **1** by determining the coupling constants $^1J(^{13}C,^{13}C)$.

Experimental Section

The compound $Si(C\equiv C\text{-}Me)_4$ **1** was prepared as described [1], and its purity was checked by ^1H, ^{13}C and ^{29}Si NMR spectroscopy in solution (Bruker ARX 250 spectrometer). The coupling constants $J(^{13}C,^{13}C)$ in solution were measured by using the refocused INEPT pulse sequence [7], based on $^1J(^{13}C,^1H)$ and on $^{2,3}J(^{13}C,^1H)$. The solid state ^{13}C and ^{29}Si MAS NMR spectra were measured using a Bruker Avance 500 spectrometer equipped with a double-bearing probe for standard 4 mm ZrO_2 rotors. Isotropic chemical shifts are given relative to Me_4Si, using adamantane ($\delta^{13}C$) and Q_8M_8 ($\delta^{29}Si$) as secondary external references for solid state NMR measurements. These compounds also served for setting up the optimum conditions for resolution, ^1H decoupling and cross polarisation (with variable amplitude [8]).

Results and Discussion

Table 1 lists the solid and solution state NMR data of the silane **1** and of its tin analogue **1(Sn)** [9,10] for comparison, and solid state ^{29}Si and ^{13}C NMR spectra of **1** are shown in the Figures 1 and 2, respectively. In agreement with the crystal structure of **1**, there is only a single crystallographic silicon site in the bulk material of **1**, and all propynyl groups are different (point group C_1), ruling out potential polymorphism under standard conditions.

The shape of the static solid state ^{29}Si NMR signal reminds of an axially symmetric shielding tensor which indicates the problem to relate molecular symmetry and the shielding tensor [9]. The information on molecular symmetry in the solid is gained much more reliably by the comparison of the ^{13}C NMR data with the crystal structure. Nevertheless, the ^{29}Si NMR signal in Fig. 1 can be used to estimate the chemical shift anisotropy $\Delta\sigma(^{29}Si) \approx 10$ ppm, which is much larger than in the case of $Si(C\equiv C\text{-}SiMe_3)_4$ (≤ 3 ppm [9]), for which the crystal structure [11] indicates point group C_s. It has been pointed out that $\Delta\sigma^{119}Sn$ of **1(Sn)** is also much greater than for other tetra(alkyn-1-yl)tin compounds [9]. Since the molecule **1(Sn)** must have C_1 symmetry in the solid state [9], the same as **1**,

	δ^{29}Si/δ^{119}Sn	δ^{13}C(Me)	δ^{13}C(Si-C≡)/(Sn-C≡)	δ^{13}C(≡C-)
Si(C≡C-Me)$_4$	Solution: −95.1	Solution: 4.5[a]	Solution: 78.6[b]	Solution: 104.7[c]
1	Solid: −97.6	Solid: 5.9, 5.5,	Solid: 78.5, 77.7,	Solid: 108.0, 106.2,
	$\Delta\sigma$(Si) ≈ 10 ppm	4.6, 4.4	77.1, 76.6	105.6, 105.2
Sn(C≡C-Me)$_4$	Solution: −345.3	Solution: 5.0	Solution: 75.2	Solution: 107.5
1(Sn)	Solid: −354.5	Solid: 6.3, 6.1,	Solid: 78.9, 78.0,	Solid: 111.8, 109.4,
	$\Delta\sigma$(Sn) ≈ 60 ppm	5.8, 5.1	77.3, 76.9	109.0, 109.0

Table 1. ^{1}H, ^{13}C, and ^{29}Si NMR data of Si(C≡C-Me)$_4$ **1** in solution and in the solid state, and data of **1(Sn)** [9, 10] for comparison.

[a] $^1J(≡^{13}C,^{13}C(Me)) = 62.7$ Hz; $^3J(^{29}Si-C≡C-^{13}C) = 1.0$ Hz; [b] $^1J(^{29}Si-^{13}C≡) = 127.0$ Hz;
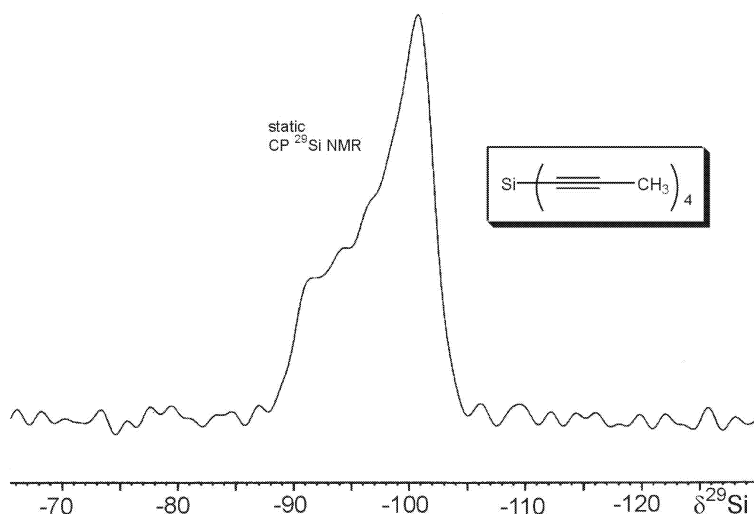[c] $^1J(^{13}C≡^{13}C) = 141.0$ Hz; $^2J(^{29}Si-C≡^{13}C) = 26.5$ Hz.

Fig. 1. 99.4 MHz static CP ^{29}Si NMR spectrum of tetra(propyn-1-yl)silane **1** (128 transients; repetition delay 15 s; $\pi/2(^1$H) 3.5 μs), indicating a chemical shift anisotropy $\Delta\sigma(^{29}$Si) of ca. 10 ppm. For the spinning sample, a single signal was observed with the isotropic chemical shift δ^{29}Si = −97.6 (to be compared with −95.1 in C$_6$D$_6$ solution).
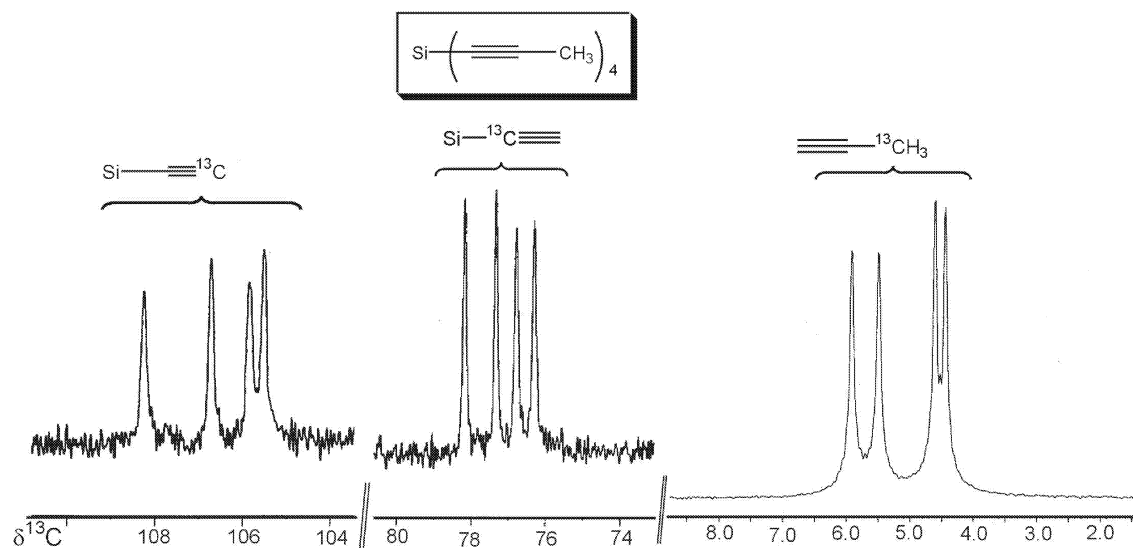

Fig. 2. 125.8 MHz ^{13}C MAS (2730 Hz) NMR spectrum of **1** (variable amplitude cross polarisation; 1024 transients; repetition delay 15 s; $\pi/2(^1$H) 2.5 μs), showing the centre bands for the respective ^{13}C NMR signals. In each case, four ^{13}C signals are resolved, proving that all four propynyl groups are different.

all arguments (see Table 1) suggest that **1** and **1(Sn)** should have rather similar crystal structures, in contrast to the lead analogue **1(Pb)** which shows solid state NMR data typical of higher molecular symmetry [9].
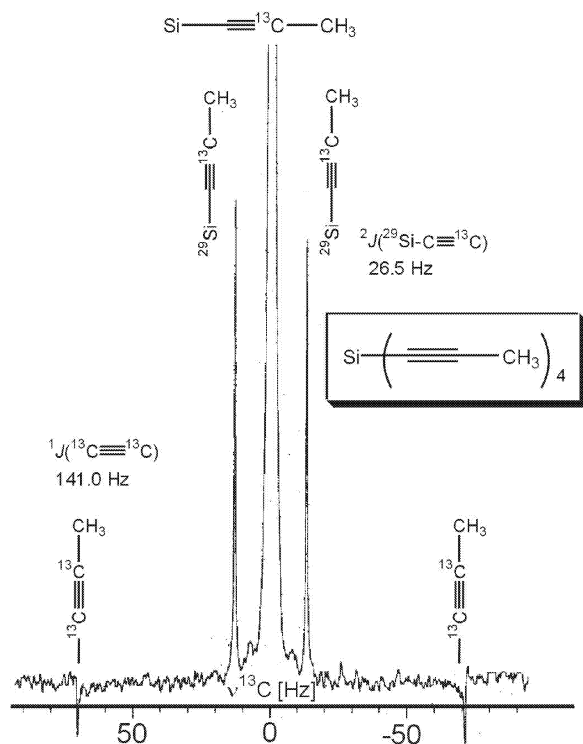
Fig. 3. 62.3 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **1** (saturated in CD$_2$Cl$_2$), showing the $\equiv^{13}$C-CH$_3$ signal (δ^{13}C = 104.7) recorded by using the refocused INEPT pulse sequence based on $^{2}J(\equiv^{13}$C,^{1}H(Me)) = 10 Hz (1600 transients, repetition time 2 s, acquisition time 3 s). The ^{13}C satellite signals possess a distorted phase (in contrast to the ^{29}Si satellites) since homonuclear couplings are not refocused in the INEPT pulse sequence. The intensities are also wrong, and the ^{13}C satellites belonging to $^{1}J(\equiv^{13}$C,^{13}C(Me)) are not visible at all under these conditions.

The determination of $^{1}J(^{13}$C,^{13}C) by the INADEQUATE pulse sequence [12] is straightforward as long as the relaxation times of the carbon atoms involved are not exceedingly long. In the case of molecules such as **1**, the T$_1(^{13}$C) values of the alkynyl ^{13}C nuclei are rather long (> 60 s, depending on the field strength). Therefore, the application of the refocused INEPT pulse sequence based on $^{2,3}J(^{13}$C,^{1}H(Me)) (in the order of 5 to 12 Hz) might provide the desired information more conveniently, since the fairly fast ^{1}H nuclear spin relaxation determines the repetition rate of the experiment. Figure 3 shows, that $^{1}J(^{13}$C$\equiv^{13}$C) can indeed be measured within reasonable time, although the phase of the ^{13}C satellite signals is distorted and their intensities are wrong. This is typical of the refocused INEPT pulse sequence, based on small long range coupling constants. Whereas the magnetisation belonging to heteronuclear couplings is perfectly refocused (see the ^{29}Si satellite signals), the magnetisation due to homonuclear ^{13}C-^{13}C coupling is not refocused and may even be completely eliminated in the course of the pulse sequence [*e. g.* satellites for $^{1}J(\equiv^{13}$C,^{13}C(Me)) = 62.7 Hz are missing in this experiment (Fig. 3)]. In contrast, these satellites were observed readily in the INEPT experiment for the CH$_3$ groups, based on $^{1}J(^{13}$C,^{1}H) ≈ 135 Hz. As the consequence of the large coupling constant $^{1}J(^{13}$C,^{1}H), the refocusing times are much shorter, and phase and intensity distortions of satellites due to homonuclear coupling do not pose a serious problem.

The magnitude of $^{1}J(^{13}$C$\equiv^{13}$C) (141 Hz) in **1** is increased when compared with monoalkyn-1-yl(trimethyl)silanes (*ca.* 130 Hz [13]) which indicates that the polar nature of the Si-C$\equiv$ bond is reduced. However, the influence of the electropositive silicon atom is still dominant, as one can see by comparison with $^{1}J(^{13}$C$\equiv$C) in ethyne (171.5 Hz). The magnitude of $^{1}J(\equiv^{13}$C,^{13}C(Me)) = 62.7 Hz is in the expected range [13, 14].

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