Tetra(alkynyl)silanes, a 3,6-Disila-triyne, a 3,6,9-Trisila-tetrayne, a 1,3,4,6-Tetrasiladiyne, and Bis(trimethylstannyl)ethyne. Molecular Structures and Solid-state NMR Studies

Bernd Wrackmeyer[a], Ezzat Khan[a,b], Amin Badshah[a,c], Elias Molla[a,d], Peter Thoma[a], Oleg L. Tok[a], Wolfgang Milius[e], Rhett Kempe[a], and Jürgen Senker[e]

[a] Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany
[b] Department of Chemistry University of Malakand, Chakdara, Dir(Lower), N.W.F.P., Pakistan
[c] Department of Chemistry, Quaid I Azam University, Islamabad, Pakistan
[d] Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh
[e] Anorganische Chemie I, Universität Bayreuth, 95440 Bayreuth, Germany

Reprint requests to Prof. Dr. B. Wrackmeyer. E-mail: b.wrack@uni-bayreuth.de

Z. Naturforsch. **2010**, *65b,* 119 – 127; received November 27, 2009

The molecular structures of three alkynylsilanes, tetrakis(ethynyl-*p*-tolyl)silane, 3,3,6,6,-tetramethyl-3,6-disila-triyne, 3,3,6,6,9,9,-hexamethyl-3,6,9-trisila-tetrayne, and of bis(trimethylstannyl)-ethyne have been determined by X-ray diffraction. The same alkynylsilanes, and in addition 1,2-bis(trimethylsilylethynyl)-1,1,2,2-tetramethyldisliane, were studied by solid-state ^{13}C and ^{29}Si MAS NMR spectroscopy. The results of these measurements were compared with crystallographic evidence and also with relevant solution-state NMR data.

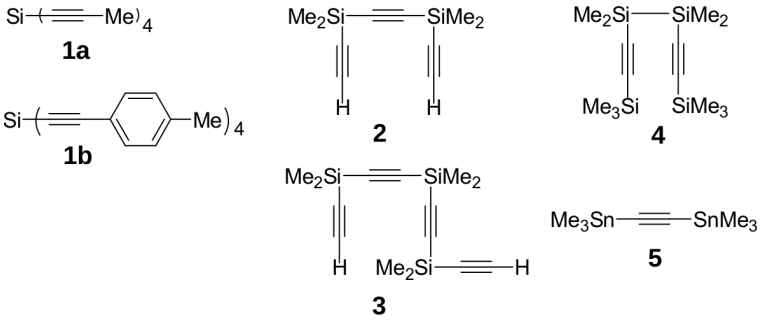
Key words: Alkynes, Silanes, Organotin Compounds, NMR, X-Ray

Introduction

Alkynylsilanes are useful starting materials in organic and organometallic synthesis [1 – 3]. Some alkynylsilanes are commercially available, and many examples can be readily prepared by conventional methods, starting from the respective chlorosilanes. Similarly, alkynylstannanes also deserve attention, although they are somewhat more difficult to prepare and to handle owing to the greater reactivity of the Sn–C bonds, when compared with Si–C bonds. The molecular structures of several alkynylsilanes have already been reported [4 – 8], and in some cases solid-state ^{13}C and ^{29}Si NMR measurements have been carried out [9 – 11]. There are also studies on solid alkynylstannanes both by X-ray diffraction [12 – 14] and by solid-state ^{13}C and ^{119}Sn NMR [9, 10, 12]. In the present work, we report on three further examples of molecular structures of alkynylsilanes (**1b**, **2**, **3**) and combine this information with that from solid-state ^{13}C and ^{29}Si NMR spectroscopy for **1** – **4** (Scheme 1). In addition, the molecular structure of bis(trimethystannyl)ethyne (**5**) has been determined which complements the thorough ^{13}C and ^{119}Sn NMR spectroscopic study of the same molecule [9, 10].

Results and Discussion

The tetraalkynylsilane **1b** was prepared in the usual way [15] by the reaction of $SiCl_4$ with four equivalents



Scheme 1. Alkynylsilanes and bis(trimethylstannyl)ethyne, studied here.

of the alkynyllithium reagent. The triyne **2** [16] and the tetrayne **3** [17] were obtained *via* stepwise procedures as reported. The disilane derivative **4** was obtained from the reaction of 1,2-dichlorotetramethyldisilane with two equivalents of trimethylsilylethynyllithium. Bis(trimethylstannyl)ethyne (**5**) was prepared from the reaction of Li_2C_2 with two equivalents of Me_3SnCl as described [18]. Recently, we have reported that a modification of the work-up procedure also affords the useful trimethylstannylethyne as a side product in moderate yield [19].

*X-Ray structural studies of the alkynylsilanes **1b**, **2**, **3**, and of bis(trimethylstannyl)ethyne (**5**)*

The molecular structures of the alkynylsilanes **1b**, **2**, **3**, and of bis(trimethylstannyl)ethyne (**5**) are shown in the Figs. 1, 2, 3, and 4, respectively. Apparently intermolecular interactions appear to be weak or negligible in all cases. All distances and angles are in the expected range [4 – 8].

In all cases, the surroundings of the silicon and tin atoms correspond to slightly distorted tetrahedra. Expectedly, the distortion is small in **1b**, mainly due to the slight difference in the orientation of the aryl groups (see, however, the solid-state ^{13}C NMR spectra in Fig. 6). There is a center of inversion in the triyne **2** which is absent in the tetrayne **4**, and this has consequences for the solid-state ^{13}C and ^{29}Si NMR spectra of the latter (*vide infra*). It should be noted that the optimized geometries in the gas phase of **2** and **3**, calculated [20] at the B3LYP/6-311+G(d,p) level of theory (Fig. 5), show different conformations as far as the mutual orientation of the alkynyl groups is concerned. Therefore, it can be assumed that the packing in the crystal lattice is affected significantly by the type of alkynyl moieties. In the case of **2**, the solid-state ^{13}C NMR spectrum (*vide infra*) indicates the presence of a second modification. Finally, the X-ray diffraction study of **5** shows that there is a center of inversion which answers one question left open in previous solid-state NMR studies of this compound [9, 10].

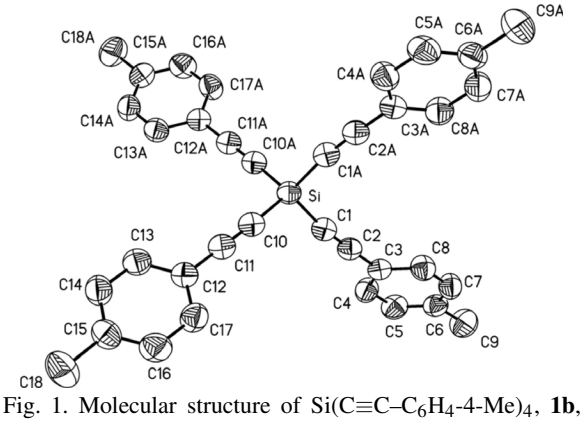


Fig. 1. Molecular structure of $Si(C{\equiv}C{-}C_6H_4\text{-}4\text{-}Me)_4$, **1b**, in the solid state (ORTEP, 40 % probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (pm) and angles (deg): Si–C1 181.5(2), C1–C2 120.3(3), C2–C3 143.2(3), C3–C4 138.9(3), C3–C8 138.6(3); C1–Si–C10 110.8(9), C2–C1–Si 172.4(19), C1–C2–C3 177.7(2), C4–C3–C8 117.8(2).

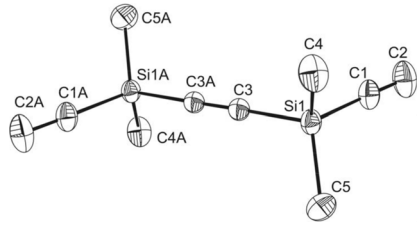


Fig. 2. Molecular structure of the triyne **2** in the solid state (ORTEP, 40 % probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (pm) and angles (deg): Si1–C1 182.90(13), Si1–C3 183.20(12), C1–C2 118.2(2), C3–C3 120.4(2); C1–Si1–C3 106.66(6), C1–Si1–C5 109.95(8), C3–Si1–C5 108.70(6), C1–Si1–C4 109.29(7), C3–Si1–C4 109.19(6), C5–Si1–C4 112.86(9), C2–C1–Si1 178.73(15), C3–C3–Si1 178.82(13).

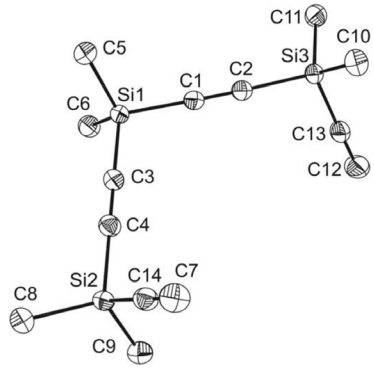


Fig. 3. Molecular structure of the tetrayne **3** in the solid state (ORTEP, 40 % probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (pm) and angles (deg): Si1–C1 183.93(15), Si1–C3 184.06(15), Si2–C14 183.96(16), Si2–C4 183.97(15), Si3–C13 183.80(17), Si3–C2 184.39(16), C1–C2 120.8(2), C3–C4 120.5(2), C7–C14 118.3(2), C12–C13 118.0(2); C1–Si1–C3 106.73(6), C14–Si2–C4 105.92(8), C13–Si3–C2 106.16(8), C2–C1–Si1 178.97(12), C1–C2–Si3 178.01(13), C4–C3–Si1 178.16(13), C3–C4–Si2 177.97(13), C12–C13–Si3 178.59(15), C7–C14–Si2 179.14(14); C13–Si3–Si1–C3 60.2, C14–Si2–Si1–C1 57.2.

Table 1. ^{13}C and ^{29}Si NMR data of alkynylsilanes **1** – **4** in solution and in the solid state.

	δ^{13}C (≡C)	δ^{13}C (Si–C≡)	δ^{13}C (R)	δ^{29}Si
1a	104,7	78.6	4.5 (Me)	−95.1
solid:	108.0, 106.2 105.6, 105.2	78.5, 77.7 77.1, 76.6	5.9, 5.5, 4.6, 4.4 (Me)	−97.6
1b[a]	107.5	86.5	120.2(1), 133.3(2), 130.1(3), 141.0(4), 21.8 (Me) 118.6(1), 132 ± 1 (broad,2,3), 140.2(4),	−93.8
solid:	109.7	85.7	22,7 (Me)	−92.7
2	94.6(1)	86.1(2), 110.6(4)	−0.2 ($SiMe_2$)	−40.7
solid:	98.4(1)	84.5(2) 110.9(4)	1.2, 0.4 ($SiMe_2$)	−40.0
3	94.8(1)	86.4(2) 110.8(4), 111.1(5) 88.6(2,10)	0.0 ($Si(3)Me_2$), −0.1 ($Si(6)Me_2$)	−39.9(3) −41.0(6)
solid:	98.5 97.0 (1,11)	113.5, 112.3 111.1, 110.4 (4,5,7,8)	1.3, 1.0, 0.5, 0.0, −0.5 ($Si(3,6)Me_2$)	−38.9, −39.3(3) −41.4(6)
4[b]		111.9 (C–$SiMe_2$) 117.1 (C–$SiMe_3$)	0.0 ($SiMe_3$), −2.9 ($SiMe_2$)	−18.9 ($SiMe_3$) −37.8 ($SiMe_2$)
solid:		114.5 119.3, 119.4	3.3 ($SiMe_3$), 0.6, 0.2, −0.1, −0.4 ($SiMe_2$)	−18.9, −19.1 ($SiMe_3$) −38.0, −38.1 ($SiMe_2$)

[a] Measured in [D_8]THF; $^1J(^{29}Si,^{13}C)$ = 128.9 Hz, $^2J(^{29}Si,^{13}C)$ = 26.5 Hz; [b] ^{13}C NMR data given in ref. [1d] without assignment; measured here in C_6D_6, and the assignment is based on the coupling constants, as follows: $^1J(^{29}Si(Me_2),^{13}C\equiv)$ = 69.6 Hz, $^2J(^{29}Si(Me_3),^{13}C\equiv)$ = 12.5 Hz, $^1J(^{29}Si(Me_3),^{13}C\equiv)$ = 77.8 Hz, $^2J(^{29}Si(Me_2),^{13}C\equiv)$ = 10.5 Hz, $^1J(^{29}Si(Me_2),^{13}C(Me))$ = 49.8 Hz, $^1J(^{29}Si(Me_2),^{13}C(Me))$ = 56.3 Hz.

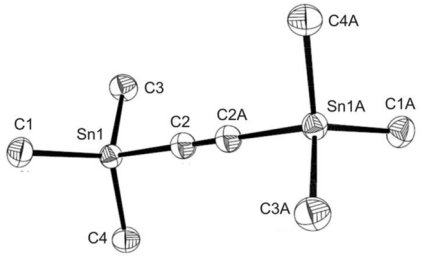


Fig. 4. Molecular structure of bis(trimethylstannyl)ethyne, **5**, in the solid state (ORTEP, 40 % probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (pm) and angles (deg): Sn1–C1 212.8(3), Sn1–C2 210.6(3), Sn1–C3 213.8(3), Sn1–C4 213.8(3), C2–C2A 120.2(6); C2–Sn1–C1 107.87(12), C2–Sn1–C3 106.31(12), C1–Sn–C3) 112.79(14), C1–Sn–C4 112.00(12), C3–Sn1–C4 111.03(13), C2–C2A–Sn 179.6(4).

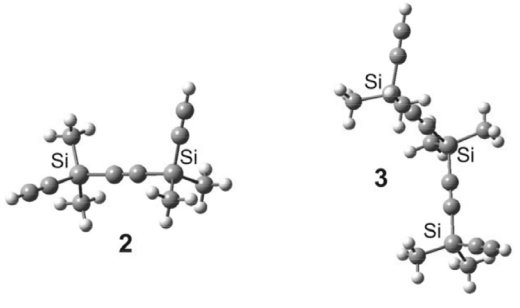


Fig. 5. Calculated [B3LYP/6-311+G(d,p)] and optimized gas-phase geometries of the triyne and the tetrayne, to be compared with the solid-state structures in Figs. 2 and 3.

Solid-state ^{13}C and ^{29}Si NMR spectroscopic studies

The ^{13}C and ^{29}Si chemical shifts of the compounds **1** – **4** measured in solution differ very little from those measured in the solid state (Table 1), indicating weak or negligible intermolecular interactions. This fact is now clearly established by the results of the X-ray diffraction studies also for the bis(trimethylstannyl)ethyne (**5**). The differences in ^{13}C and ^{29}Si nuclear shielding between liquid and solid state are most pronounced (a few ppm) for ^{13}C nuclei in peripheral positions, such as ≡C–H or SiMe groups, which is in support of different conformations preferred on average in solution when compared with the solid state.

The solid-state ^{13}C MAS NMR spectrum of **1b** (Fig. 6) is only consistent with the result of the X-ray diffraction by considering a fast exchange regime on the NMR time scale, in which reorientation of the aryl groups takes place, leading on average to four identical surroundings for the alkynyl carbon atoms as well

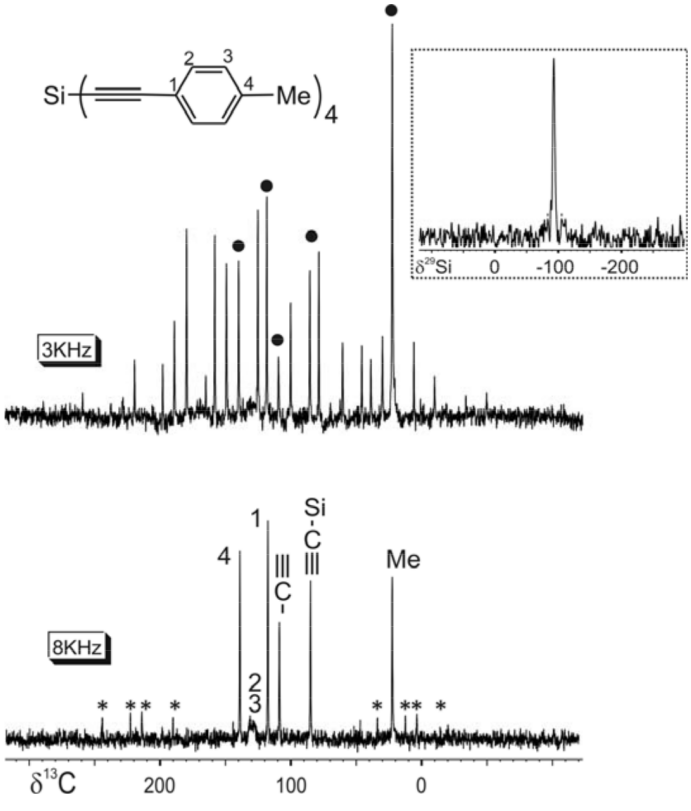


Fig. 6. Solid-state 75.1 MHz $^{13}C\{^1H\}$ MAS NMR spectra of **1b** (recycle delay 20 s; upper trace 1536 transients; lower trace 512 transients). The exchange-broadened $^{13}C^{2,3}$ NMR signals could only be observed at high spinning rates (lower trace). Rotational side bands (lower trace) are indicated by asterisks. At lower spinning rate (upper trace), only the fairly sharp ^{13}C NMR signals for alkynyl carbons, aryl carbons C^1, C^4 and CH_3 were readily observed together with the rotational side bands. The solid-state 59.6 MHz $^{29}Si\{^1H\}$ NMR spectrum of **1b** (insert; single pulse, recycle delay 20 s) is a fairly sharp line, even without MAS.

as the C^1, C^4 and CH_3 carbon atoms. The proposed rotation of the aryl groups is evident by inspection of the exchange-broadened $^{13}C^{2,3}$ NMR signals. In the case of **1a** which was studied previously, motional averaging was slow on the NMR time scale, and the four different propynyl groups, found by X-ray diffraction [8], were clearly distinguished in the solid-state ^{13}C NMR spectrum [11] (see also Table 1).

According to the molecular structure of **2** in the crystal, the solid-state ^{29}Si and ^{13}C MAS NMR spectra (Fig. 7) should be simple, showing one and five signals, respectively. However, in addition to the expected signals, there are three ^{13}C NMR signals of minor intensity in the alkynyl range as marked. Therefore, in the bulk material of **2**, a small amount of a second modification is most likely present, of which the ^{29}Si and $^{13}C(SiMe_2)$ NMR signals are not resolved.

Solid-state ^{13}C and ^{29}Si MAS NMR spectra of the tetrayne **3** (Fig. 8) are in perfect agreement with the results from X-ray diffraction. Except of the methyl groups linked to the central silicon atom, and the alkynyl carbon atoms $C^{2,10}$, all other ^{13}C NMR signals are clearly resolved. The absence of a mirror plane or a center of inversion in solid **3** is also illustrated by two different ^{29}Si NMR signals for $Si^{3,9}$ in addition to the signal for Si^6.

In the case of the disilane derivative **4**, attempts failed to obtain suitable single crystals for X-ray diffraction. However, the solid-state ^{13}C (Fig. 9) and ^{29}Si (Fig. 10) MAS NMR spectra of the microcrystalline material could be measured. The different ^{13}C NMR signals for the alkynyl carbons and for all methyl groups at the disilane unit clearly indicate the absence of a mirror plane or a center of inversion in the solid-state molecular structure of **4**. Different $^{13}C(SiMe_3)$ signals were not resolved. In addition to expectedly small differences in the chemical shifts of the $SiMe_3$ groups (see the ^{29}Si NMR spectrum in Fig. 10), these ^{13}C NMR signals may be slightly exchange-broadened by $2\pi/3$ propeller jumps [9, 10]. The assignment of the alkynyl ^{13}C NMR signals was based on the solution-state ^{13}C NMR spectra. The solid-state ^{29}Si MAS NMR spectrum measured at high spinning rate shows two resolved pairs of signals for the $SiMe_3$ and $SiMe_2$ groups, consistent with the ^{13}C NMR spectra. At low spinning rate, the

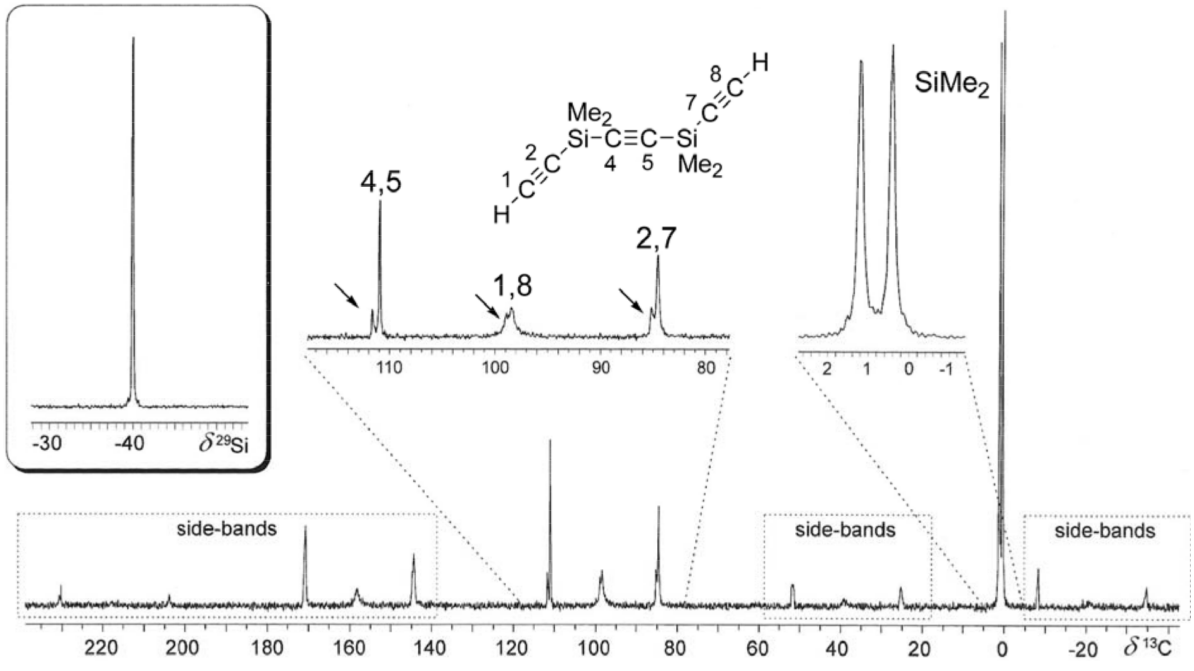


Fig. 7. Solid-state 100.6 MHz $^{13}C\{^1H\}$ and 79.5 MHz $^{29}Si\{^1H\}$ MAS NMR spectra of the triyne **2** (recycle delay 8 s; 64 transients for ^{13}C and 26 transients for ^{29}Si).

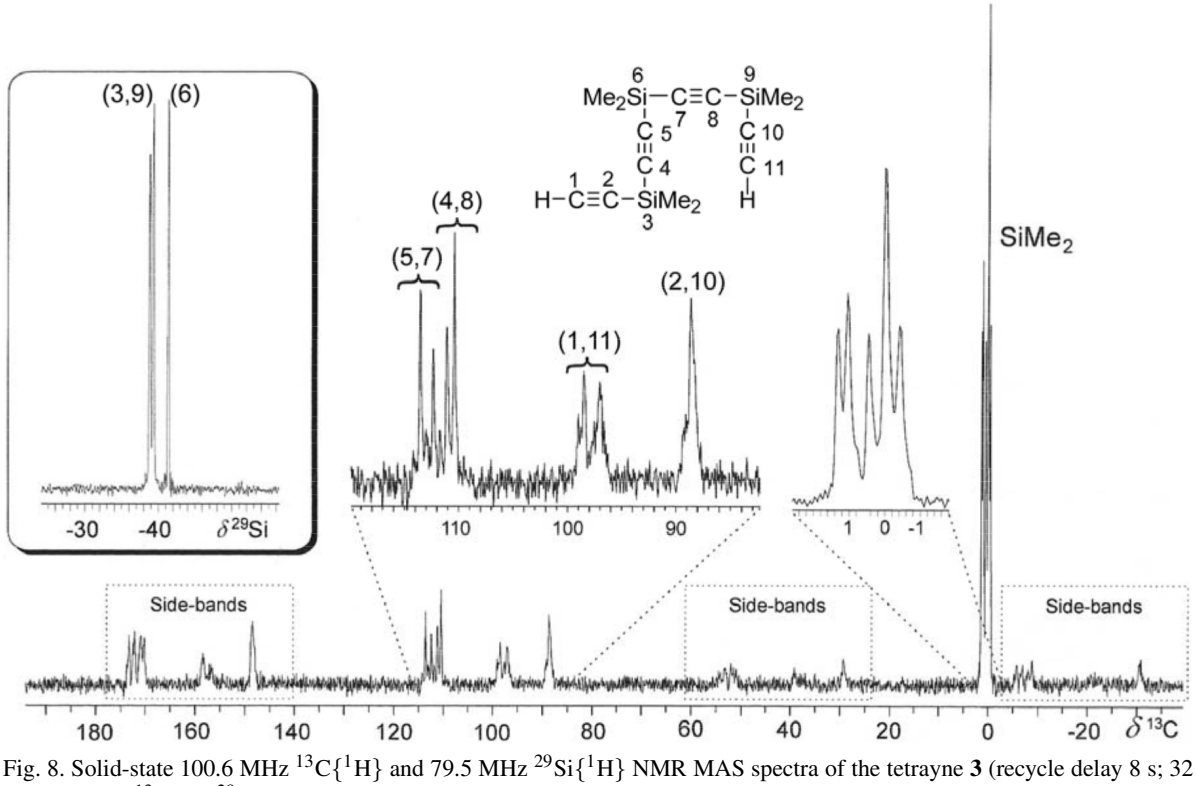


Fig. 8. Solid-state 100.6 MHz $^{13}C\{^1H\}$ and 79.5 MHz $^{29}Si\{^1H\}$ NMR MAS spectra of the tetrayne **3** (recycle delay 8 s; 32 transients for ^{13}C and ^{29}Si). Rotational side bands (rotation 6 kHz) are indicated.

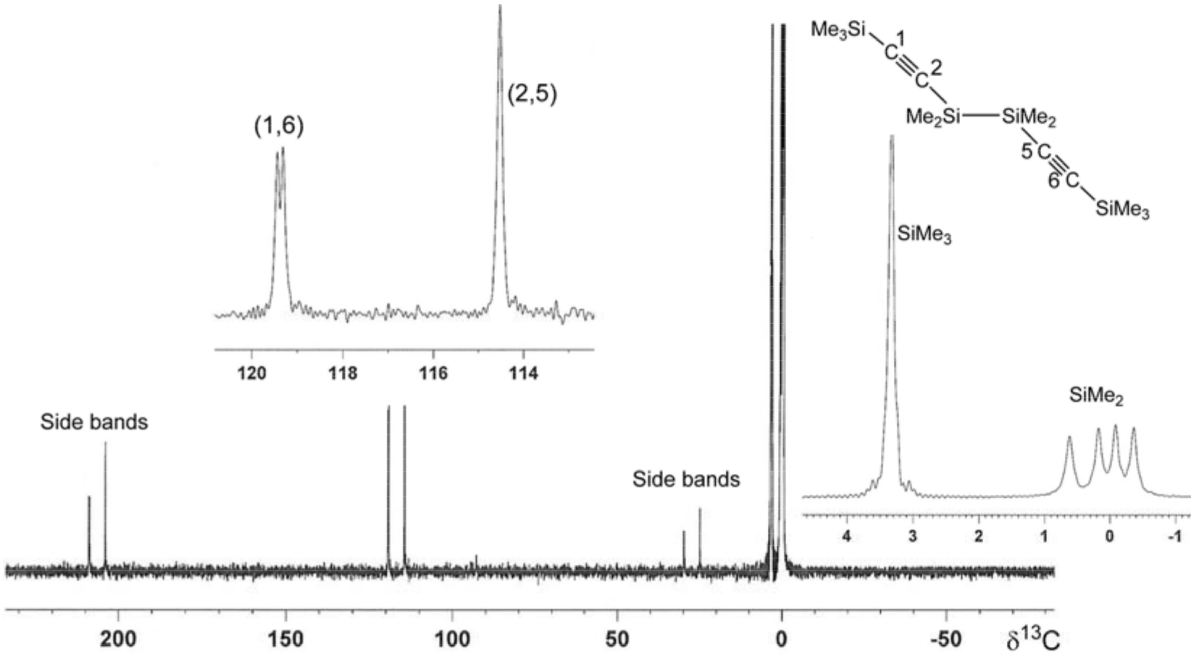


Fig. 9. Solid-state 100.5 MHz $^{13}C\{^1H\}$ NMR spectrum of the disilane derivative **4** (recycle delay 10 s; 492 transients; rotation 9 kHz).

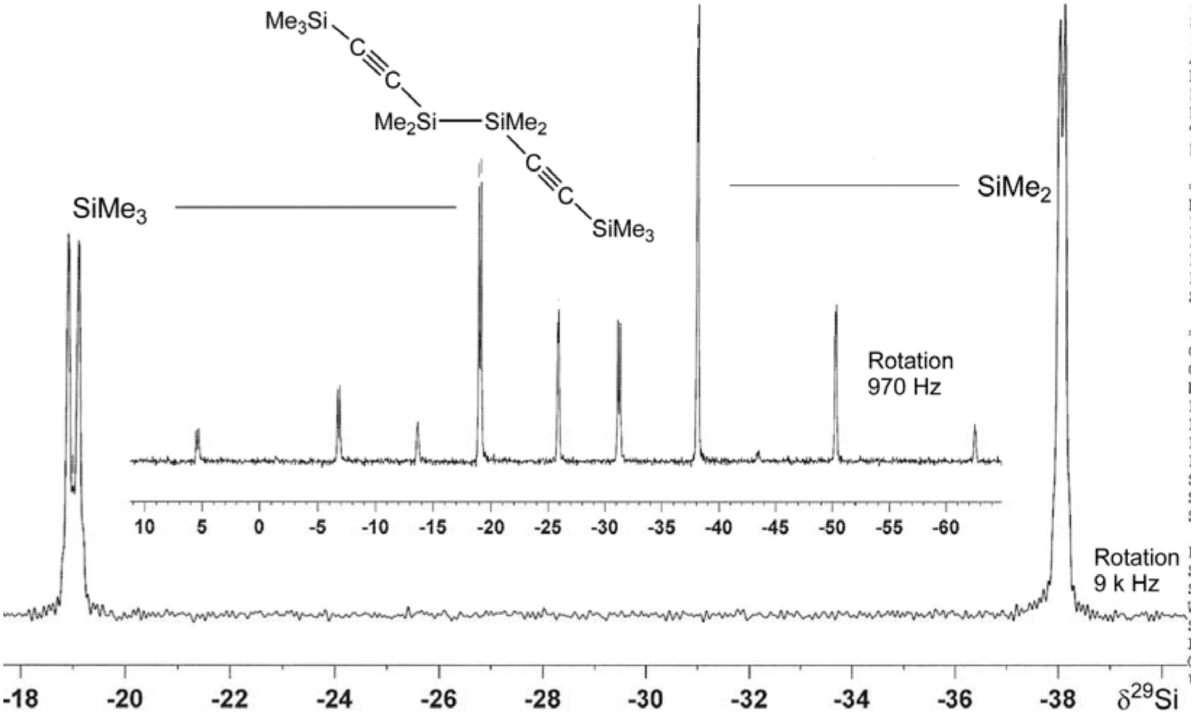


Fig. 10. Solid-state 79.5 MHz $^{29}Si\{^1H\}$ NMR spectrum of the disilane derivative **4** measured at different spinning rates (recycle delay 8 s; 32 transients). At a spinning rate of 970 Hz the rotational side bands become visible, and their pattern is consistent with non-axially symmetric ($SiMe_2$) and close to axially symmetric ($SiMe_3$) ^{29}Si shielding tensors.

Table 2. Crystallographic data of the alkynylsilanes **1b**, **2**, **3** and of bis(trimethylstannyl)ethyne (**5**).

	1b	**2**	**3**	**5**
Formula	$C_{36}H_{28}Si$	$C_8H_{14}Si_2$	$C_{14}H_{20}Si_3$	$C_6H_{18}Sn_2$
Crystal	needle	prism	prism	prism
Dimensions, mm^3	$0.93 \times 0.14 \times 0.14$	$0.60 \times 0.50 \times 0.50$	$0.66 \times 028 \times 0.09$	$0.36 \times 0.23 \times 0.11$
T, K	133(2)	193(2)	193(2)	133(2)
Crystal system	tetragonal	trigonal	monoclinic	monoclinic
Space group	$I4_1/a$	$R\bar{3}$	$P2_1/n$	$P2_1/c$
Lattice parameters				
a, pm	1966.5(2)	1612.1(2)	1635.2(5)	913.3(2)
b, pm	1966.5(2)	1612.1(2)	553.9(5)	559.3(1)
c, pm	729.00(11)	1253.3(2)	1958.9(5)	1221.7(3)
α, deg	90	90	90	90
β, deg	90	90	103.4(5)	97.49(2)
γ, deg	90	120	90	90
Z	4	9	4	2
μ, mm^{-1} (MoK_α)	0.1	0.2	0.3	4
Diffractometer	— Stoe IPDS II; MoK_α, λ = 71.073; graphite monochromator —			
Absorption correction	none[a]	none[a]	numerical	numerical
ϑ range, deg	2.1 – 35.7	2.18 – 26.8	1.47 – 26	1.18 – 26
Reflections collected	17538	10922	22889	2192
Independ. refl. [$I \geq 2\sigma(I)$]	1000	1158	2705	1166
Refined parameters	85	83	234	49
$wR2/R1[I \geq 2\sigma(I)]$	0.112 / 0.051	0.076 / 0.075	0.099 / 0.030	0.041 / 0.017
Max. / min. resid. electron density, e $pm^{-3} \times 10^{-6}$	0.19 / −0.27	0.23 / −0.15	0.14 / −0.31	0.55 / −0.39

[a] Absorption corrections did not improve the parameter set.

rotational side bands expectedly indicate ^{29}Si shielding tensor patterns typical of a non-axial symmetry of the $SiMe_2$ groups and close to axial symmetry for the $SiMe_3$ groups.

Conclusions

Crystallographic evidence and solid-state ^{13}C and ^{29}Si MAS NMR results are in good agreement for alkynylsilanes. Dynamic processes such as reorientation of aryl groups are mirrored by exchange-broadened ^{13}C NMR signals. Furthermore, the solid-state NMR spectra indicate the presence of modifications so far not readily apparent from single crystal X-ray diffraction studies, as shown in the case of the triyne **2**. The crystal structure study of bis(trimethylstannyl)ethyne (**5**) has answered the question left open after temperature-dependent solid-state ^{13}C and ^{119}Sn MAS NMR investigations [9, 10], the results of which are in perfect agreement with the particular inversion symmetry of this molecule.

Experimental Section

Starting materials and measurements

The preparations and all handling of samples were carried out under an inert atmosphere (Ar), and carefully oven-dried glassware, and dry solvents were used throughout. ^{n}BuLi in hexane (1.6 M), 1-ethynyl-4-methylbenzene, ethynyltrimethylsilane, $SiCl_4$, and $Me_4Si_2Cl_2$ were commercial products. The 3,3,6,6,-tetramethyl-3,6-disila-triyne (**2**) [16], 3,3,6,6,9,9-hexamethyl-3,6,9-trisila-tetrayne (**3**) [17], and bis(trimethylstannyl)ethyne (**5**) [18] were prepared adopting the literature procedures. Single crystals of **2** and **3** were collected after slow sublimation at ambient temperature. Single crystals of **5** were grown from concentrated hexane solutions at ambient temperature. Solution-state NMR measurements were carried out in $[D_8]$THF (**1b**) and C_2DCl_2 (**4**) in 5 mm o.d. tubes at 296 ± 1 K: Varian Inova 300 or 400 MHz and Bruker ARX 250 spectrometer for ^1H, ^{13}C, and ^{29}Si NMR; chemical shifts are given with respect to Me_4Si [δ^1H $[D_7]$THF/C_6D_5H = 1.73, 7.15; $\delta^{13}C$ ($[D_8]$THF/C_6D_6) = 25.4/128.0; $\delta^{29}Si$ = 0 for $\Xi(^{29}Si)$ = 19.867184 MHz]. Chemical shifts δ^1H are given to $\pm$0.04 ppm, $\delta^{13}C$ and $\delta^{29}Si$ to $\pm$0.1 ppm. Solid-state ^{13}C and ^{29}Si NMR spectra were measured at ambient temperature with Bruker Avance II 300 and Bruker Avance 400 spectrometers, using 4 mm zirconia rotors in double-bearing probe heads. All MAS spectra were measured with variable amplitude cross polarization (VACP) [21], and the SPINAL pulse sequence [22] was used to achieve efficient ^1H decoupling. EI-MS spectra: Finnigan MAT 8500 spectrometer (ionisation energy 70 eV) with direct inlet. The *m/z* data refer to the isotopes ^1H, ^{12}C, and ^{28}Si. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

Synthesis of tetraalkyn-1-ylsilane ***1b***

Tetrachlorosilane (3 mL; 10 mmol) was added slowly at low temperature (−78 °C) to a suspension of Li–C≡C–C_6H_4-4-Me (39.4 mmol) in 75 mL of hexane. The reaction mixture was allowed to warm to r. t., heated to reflux for 2 h and stirred for further 10 h at r. t. The solid materials were separated and washed with an excess of toluene. The toluene fractions were collected, and all volatiles were removed in a vacuum. The solid residue left was mainly the product **1b** (3.8 g, 77 %). It was washed with hexane and dissolved in THF. Needle-like crystals (m. p. > 263 °C, decomp.) suitable for X-ray structural analysis were grown from concentrated THF solutions at r. t. – ^{1}H NMR (400 MHz) data: δ = 2.4, 7.3, 7.6 (s, m, m, 28H, 4-Me-C_6H_4).

Synthesis of 1,3,4,6-tetrasiladiyne ***4***

A solution of 1,2-dichloro-tetramethyldisilane (4.14 g, 35.3 mmol) in hexane (20 mL) was added at room temperature within 15 min to a suspension of freshly prepared trimethylsilylethynyllithium (71 mmol) in hexane (300 mL). The mixture was heated at reflux for 12 h, insoluble materials were filtered off, and the solvent was removed in a vacuum to leave a colorless powder. After recrystallization from pentane at −20 °C, the pure disilane derivative **4** was obtained (m. p. 36 – 38 °C; 6.8 g, 62 %). – ^{1}H NMR (250 MHz in C_6D_6): δ = 0.24 (s, 12H, $SiMe_2$), 0.02 (s, 18H, $SiMe_3$). – EI-MS (70 eV): *m/z* = 310 (10) $[M]^+$, 295 (28) $[M–15]^+$, 73 (100) $[SiMe_3]^+$.

X-Ray structure analyses of compounds ***1b, 2, 3,*** *and* ***5***

The X-ray crystal structural analyses of **1b**, **2**, **3**, and **5** were carried out at 133(2) K (**1b**), 193(2) K (**2**, **3**) on single crystals selected in perfluorinated oil [23] at r. t., using a Stoe IPDS II (MoK_α radiation, λ = 71.069 pm) system equipped with an Oxford Cryostream low-temperature unit. Structure solutions and refinement were accomplished using SIR97 [24], SHELXL-97 [25], and WINGX [26]. Pertinent data are given in Table 2. Since the solid-state NMR spectra of **1b** were measured at r. t. and showed dynamic processes, the X-ray diffraction of **1b** was repeated at r. t. (Stoe IPDS I) with a single crystal sealed in a Lindemann capillary. The results were essentially identical with those obtained at 133 K.

CCDC 753787 (**1b**), 753788 (**2**), 753789 (**3**), and 753790 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. E. K. and A. B. thank the DAAD and HEC (Pakistan), and E. M. the Alexander-von-Humboldt Stiftung for fellowships.

[1] a) T. Hiyama, A. Mori, *Science of Synthesis* **2002**, *4*, 647; b) B. Wrackmeyer, *Coord. Chem. Rev*. **1995**, *145*, 125; c) B. Wrackmeyer, *Heteroatom Chem*. **2006**, *17*, 188; d) H. Sakurai, Y. Nakadaira, A. Hosomi, Y. Eriyama, C. Kabuto. *J. Am. Chem. Soc.* **1983**, *105*, 3359; e) K. Tamao, S. Yamaguchi, M. Shiro, *J. Am. Chem. Soc*. **1994**, *116*, 11715; f) E. Khan, B. Wrackmeyer, R. Kempe, *Eur. J. Inorg. Chem.* **2008**, 5367; g) E. Khan, R. Kempe, B. Wrackmeyer, *Appl. Organomet. Chem*. **2009**, *23*, 124; h) E. Khan, S. Bayer, R. Kempe, B. Wrackmeyer, *Eur. J. Inorg. Chem.* **2009**. 4416.

[2] a) K. Uchida, K. Utimoto, H. Nozaki, *Tetrahedron* **1977**, *33*, 2987; b) J. A. Soderquist, B. Santiago, *Tetrahedron Lett*. **1990**, *31*, 5113; c) G. A. Molander, *J. Org. Chem*. **1983**, *48*, 5409; d) H. Lang, M. Weinmann, L. Zsolnai, *J. Organomet. Chem*. **1996**, *522*, 277; e) T. Beweries, V. V. Burlakov, S. Peitz, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, *Organometallics* **2008**, *27*, 3954; f) P.-M. Pellny, N. Peulecke, V. V. Burlakov, W. Baumann, A. Spannenberg, U. Rosenthal, *Organometallics* **2000**, *19*, 1198; g) N. Peulecke, A. Ohff, P. Kosse, A. Tillack, A. Spannenberg, R. Kempe, W. Baumann, V. V. Burlakov, U. Rosenthal, *Chem. Eur. J.* **1998**, *4*, 1852; h) H. Werner, M. Baum, D. Schneider, B. Windmüller, *Organometallics* **1994**, *13*, 1089.

[3] a) T. Takahashi, Z. Xi, Y. Obora, N. Suzuki, *J. Am. Chem. Soc*. **1995**, *117*, 2665; b) H. Ito, K. Arimoto, H. Sensui, A. Hosomi, *Tetrahedron Lett*. **1997**, *38*, 3977; c) T. Yu, X. Sun, C. Wang, L. Deng, Z. Xi, *Chem. Eur. J.* **2005**, *11*, 1895; d) Z. Xi, R. Fischer, R. Hara, W.-H. Sun, Y. Obora, N. Suzuki, K. Nakajima, *J. Am. Chem. Soc.* **1997**, *119*, 12842; e) J. Liu, S. Zhang, W.-X. Zhang, Z. Xi, *Organometallics* **2009**, *28*, 413; f) M. Zirngast, C. Marschner, J. Baumgartner, *Organometallics* **2006**, *25*, 4897.

[4] a) G. Dierker, J. Ugolotti, G. Kehr, R. Fröhlich, G. Erker, *Adv. Synth. Catal*. **2009**, *351*, 1080; b) C. Rüdinger, H. Beruda, H. Schmidbaur, *Z. Naturforsch*. **1994**, *49b*, 1348; c) H. Schmidbaur, J. Ebenhöch, G. Müller, *Z. Naturforsch.* **1988**, *43b*, 49; d) W.-Y. Wong, A. W.-M. Lee, C.-K. Wong, G.-L. Lu, H. Zhang, T. Mo, K.-T. Lam, *New. J. Chem*. **2002**, *26*, 354.

[5] a) C. Ackerhans, H. W. Roesky, D. Vidovic, J. Magull, *Eur. J. Inorg. Chem*. **2003**, 66; b) C. Mechtler, M. Zirngast, J. Baumgartner, C. Marschner, *Eur. J. In-*

org. Chem. **2004**, 3254; c) J. Liu, W.-X. Zhang, X. Guo, Z. Hou, Z. Xi, *Organometallics* **2007**, *26*, 6812.

[6] a) W.-Y. Wong, C.-K. Wong, G.-L. Lu, *J. Organomet. Chem*. **2003**, *671*, 27; b) W.-Y. Wong, C.-K. Wong, G.-L. Lu, K.-W. Cheah, J.-X. Shi, Z. Lin, *Dalton Trans*. **2002**, 4587; c) W.-Y. Wong, K.-H. Choi, G.-L. Lu, Z. Lin, *Organmetallics* **2002**, *21*, 4475; d) T. Kuhnen, M. Stradiotto, R. Ruffolo, D. Ulbrich, M. J. McGlinchey, M. A. Brook, *Organometallics* **1997**, *16*, 5048; e) W. A. Chalifoux, M. J. Ferguson, R. R. Tykwinski, *Eur. J. Org. Chem*. **2007**, 1001.

[7] a) B. Wrackmeyer, H. E. Maisel, J. Süß, W. Milius, *Z. Naturforsch*. **1996**, *51b*, 1320; b) B. Wrackmeyer, W. Milius, O. L. Tok, *Chem. Eur. J.* **2003**, *9*, 4732.

[8] B. Wrackmeyer, W. Milius, A. Badshah, *J. Organomet. Chem.* **2002**, *656*, 97.

[9] E. Klaus, A. Sebald, *Magn. Reson. Chem*. **1994**, *32*, 679.

[10] J. Kümmerlen, A. Sebald, E. Sendermann, *Organometallics* **1994**, *13*, 802.

[11] B. Wrackmeyer, O. L. Tok, A. Badshah, *Z. Naturforsch.* **2003**, *58b*, 809.

[12] B. Wrackmeyer, B. H. Kenner-Hofmann, W. Milius, P. Thoma, O. L. Tok, M. Herberhold, *Eur. J. Inorg. Chem*. **2006** 101.

[13] B. Wrackmeyer, G. Kehr, D. Wettinger, W. Milius, *Main Group Met. Chem*. **1993**, *16*, 445.

[14] B. Wrackmeyer, P. Thoma, R. Kempe, *Eur. J. Inorg. Chem.* **2009**, 1469.

[15] a) W. E. Davidsohn, M. C. Henry, *Chem. Rev.* **1967**, *67*, 73; b) L. Brandsma, *Preparative Acetylenic Chemistry* (2nd ed.), Elsevier, Amsterdam, **1988**; c) L. Brandsma, *Synthesis of Acetylenes, Allenes, and Cumulenes – Methods and Techniques*, Elsevier, Amsterdam, **2004**.

[16] B. Wrackmeyer, G. Kehr, J. Süß, E. Molla, *J. Organomet. Chem.* **1998**, *562*, 207.

[17] B. Wrackmeyer, G. Kehr, J. Süß, E. Molla, *J. Organomet. Chem.* **1999**, *577*, 82.

[18] B. Wrackmeyer in *Organometallic Syntheses* (Eds. R. B. King, J. J. Eisch), Vol. 4, Elsevier, New York **1988**, p. 559.

[19] B. Wrackmeyer, O. L. Tok, P. Thoma, *Arkivoc* **2008**, 6.

[20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN 03 (revision B.02), Gaussian, Inc., Pittsburgh PA, **2003**.

[21] a) O. B. Peersen, X. Wu, S. O. Smith, *J. Magn. Reson. A* **1994**, *106*, 127; b) G. Metz, X. Wu, S. O. Smith, *J. Magn. Reson. A* **1994**, *110*, 219; c) S. C. Shekar, A. Ramamoorthy, *Chem. Phys. Lett*. **2001**, *342*, 127.

[22] B. M. Fung, A. K. Khitrin, K. Ermolaev, *J. Magn. Reson*. **2000**, *142*, 97.

[23] T. Kottke, D. Stalke, *J. Appl. Cryst*. **1993**, *26*, 615.

[24] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. C. Moliterni, G. Polidori, R. Spagna, SIR97, A Program for the Automatic Solution of Crystal Structures by Direct Methods; see: *J. Appl. Crystallogr*. **1999**, *32*, 115.

[25] M. Sheldrick, SHELXL-97 (release 97-2), Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1998**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

[26] L. J. Farrugia, WINGX, A MS-Windows System of Programs for Solving, Refining and Analysing Single Crystal X-ray Diffraction Data for Small Molecules, University of Glasgow, Glasgow, Scotland (U.K.) **2005**. See also: L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.