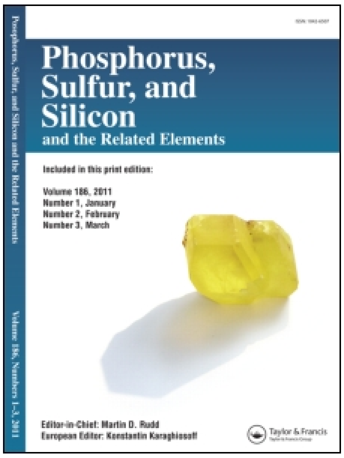

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SPIN LOCK VERSUS INEPT AND DEPT POLARIZATION TRANSFER FOR ^{29}Si NMR SPECTROSCOPY

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The ^{29}Si NMR spectra of a variety of silicon compounds were recorded with prior polarization transfer via spin locking of the protons. The results were compared with the traditional INEPT and DEPT protocols, and it is shown that, under optimized conditions, spin lock polarization transfer yields ^{29}Si NMR spectra with an increase in signal to noise ratio by a factor of 1.6 in the average. The advantages and disadvantages of the methods employed are discussed.

Key words: ^{29}Si NMR spectroscopy, polarization, techniques, INEPT, DEPT, spin lock.

INTRODUCTION

Insensitive NMR nuclei with a low gyromagnetic ratio γ and a low natural abundance, such as ^{15}N, ^{13}C or ^{29}Si, can best be detected if they are polarized via the bound protons. For ^{13}C, one usually uses only the NOE effect obtained by proton broad band decoupling, which yields, due to the γ_H/γ_C ratio, at best a factor of 3. For editing purposes, polarization schemes such as INEPT[1] and DEPT[2] are being used, which result in a theoretical enhancement of 4, although this is reached only for optimal conditions.

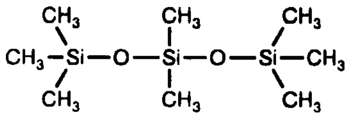
^{29}Si spectra are obtained with a DEPT[3] or INEPT[4] polarization transfer, since here, the γ_H/γ_{Si} ratio is much higher and, due to the negative γ_{Si} value, the NOE effect can reduce the signal to noise ratio. The relative performance of the two sequences for ^{29}Si NMR was thoroughly compared by West and coworkers.[3]

For various methods of ^{1}H NMR spectroscopy, the spin lock technique has gained considerable application in the last decade. Best known pulse schemes are the TOCSY[5] and ROESY[6] sequences, which by now, form routine standard procedures in many laboratories. Heteronuclear applications of these techniques are rare in high resolution NMR, whereas for solids, spin lock polarization transfer forms the heart of the CP/MAS technique.[7] Nevertheless, very recently, a number of reports demonstrated that spin locks can be applied for the ^{1}H, ^{13}C case in solution, spin lock and discuss the relative merits of this technique.[8] Two early papers on the use of spinlock fields for ^{29}Si NMR demonstrated the principal possibility of this technique in the liquid state.[9,10]

In principle, signal enhancement via spin lock polarization or INEPT polarization should yield similar results under optimized conditions.[11] Such optimized conditions are only defined for a two or three spin system. It was shown, however, that in practical experimental situations the spin lock technique may have advantages. Especially for quaternary carbon atoms, the spin lock technique was claimed to be superior.[11] Since the silicon nucleus is nearly always "quaternary" in organosilicon compounds, bearing no directly bound protons, we thought it worthwhile to investigate whether in practice spin lock polarization techniques significantly improve the signal to noise ratio in ^{29}Si NMR spectroscopy, and report here our findings for a variety of silicon compounds.

RESULTS AND DISCUSSION

Seven different siloxanes have been chosen for this investigation. Octamethyltri- and decamethyltetrasiloxane, (**1**) and (**2**), serve as standards for small linear silicon compounds, in tetraphenyltetramethyltrisiloxane (**3**) some methyl groups were interchanged with phenyl groups in order to see whether aromatic residues behave differently. Whereas **1**–**3** have Q_1 and Q_2 silicon sites, methyltris(trimethylsiloxy)silane (**4**) has three Q_1 Si Atoms and one Q_3 Si atom with three oxygen neighbours. Tris(trimethylsiloxy)silane (**5**) serves as a reference compound for directly and remotely bound hydrogens. One linear and one branched polydimethylsiloxane, (**6**) and (**7**), were selected to check the method for practical applications. The measurements were performed in 25% $CDCl_3$ solutions. The three radiofrequency methods employed are given with the necessary details in Figure 1.



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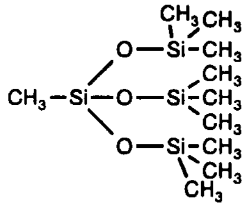

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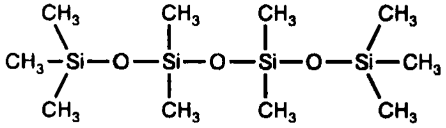

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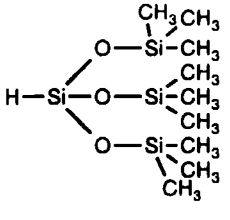

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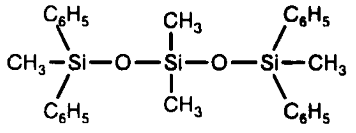

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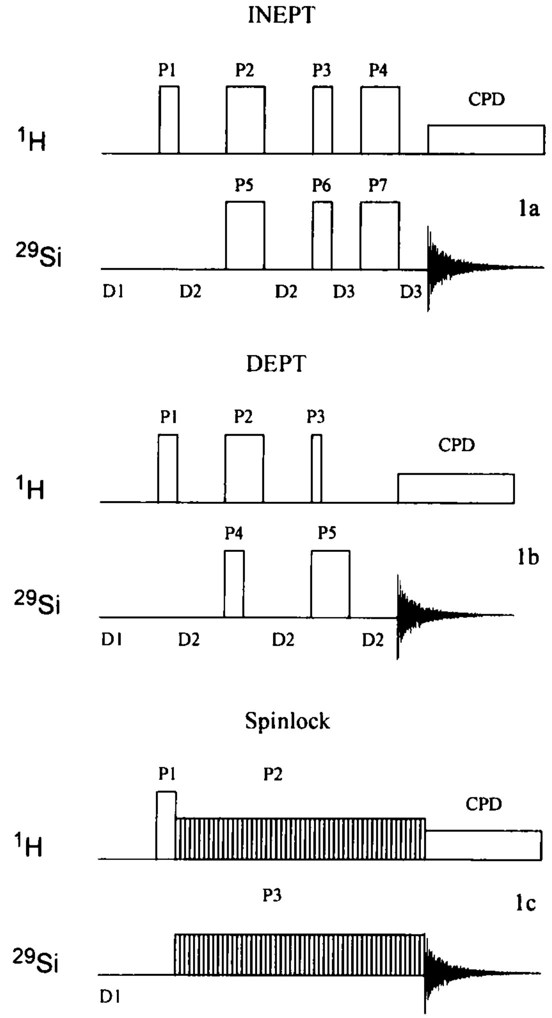

FIGURE 1 Pulse sequences used for polarization. (1a) INEPT technique, narrow bars represent 90° pulses, broad bars represent 180° pulses, phase programs as given in the original literature, D1 relaxation delay, D2 = $1/4J(\mathrm{Si,H})$, D3 refocusing delay, to be optimized, CPD: composite pulse decoupling using WALTZ16. (1b) DEPT technique, symbols used as in (1a), P3: adjustable decoupler pulse to be optimized corresponding to the number of protons. (1c) p1: 90° proton pulse, phase program $-y$, y; WALTZ16 spin lock on both channels, phase program x, $-x$, typical duration of 100 ms at individual pulse length of 50 μs of the attenuated 90° pulses.

For the INEPT protocol, two pulses have to be calibrated, the forward 90° transmitter pulse for ^{29}Si and the 90° ^{1}H decoupler pulse. This is standard routine for most NMR laboratories. There are two delay times within the refocused INEPT method. The first should be set to $1/4J(\mathrm{Si,H})$ and is, in our experience, rather insensitive with regard to the performance of the sequence, missetting by ± 1 ms does not severely affect the signal to noise ratio. Typically, a value of 10–30 Hz was chosen. The correct choice for the second refocusing delay proved to be most important, and should be optimized for the compound or class of compounds chosen. Empirically, we found that, under our conditions, a refocusing delay of 8–24 ms gave the best results for most compounds, misadjustment by ±0.1 ms drastically reduces signal to noise ratio. Thus, the INEPT method proved to be very sensitive to misadjustments.

For the DEPT protocol, the same number of RF pulses have to be determined and the first refocusing delay behaves similarly as in the INEPT technique. Contrary to INEPT, the second delay is replaced by the adjustable pulse angle of the decoupler pulse, which is usually set to 45° for all multiplicities in ^{13}C NMR spectroscopy, for ^{29}Si NMR it can be adjusted to the number of coupled protons using an equation given by West.[3] As seen from the figure, and pointed out by West,[3] DEPT uses three delay times d2, for small coupling constants, therefore, relaxation of the ^{29}Si magnetization within the sequence can diminish signal to noise.

The spin lock technique requires more calibrations in advance. As for INEPT, the 90° decoupler pulse has to be determined, and, in addition, an attenuated ^{1}H pulse has to be calibrated to fulfill the Hartmann Hahn condition with an attenuated ^{29}Si pulse, which must also be calibrated. On most spectrometers, furthermore,

TABLE I

Relative signal to noise ratios of ^{29}Si NMR signal with different polarization techniques, normalized to the Q_1 site

Substance	Experiment	Q_1	Q_2/Q_3
Octamethyltrisiloxane	INEPT	1.00	0.48
(1)	Spinlock	2.00	0.95
DEPT optimized for Q1	DEPT	0.98	0.43
DEPT optimized for Q2	DEPT	0.64	0.42
Decamethyltrisiloxane	INEPT	1.00	0.91
(2)	Spinlock	1.13	1.06
DEPT optimized for Q1	DEPT	0.91	0.51
DEPT optimized for Q2	DEPT	0.62	0.52
Tetramethyltetraphenyl-	INEPT	1.00	0.69
trisiloxane	Spinlock	1.19	0.75
(3)	DEPT	0.52	0.40
Methyltris(trimethylsiloxy)-	INEPT	1.00	0.37
silane	Spinlock	2.25	0.57
(4) optimized for Q1 (^2J)	DEPT	2.06	0.63
Methyltris(trimethyl-	INEPT	0.26	0.49
siloxy)silane	Spinlock	1.96	0.65
(4) optimized for Q3 (^2J)	DEPT	0.69	0.92
Tris(trimethylsiloxy)silane	INEPT	1.00	0.31
	Spinlock	2.50	2.15
(5) optimized for Q1 (^2J)	DEPT	0.91	0.05
Tris(trimethylsiloxy)silane	INEPT	-----	2.59
	Spinlock	-----	0.39
(5) optimized for Q3 (^1J)	DEPT	-----	2.20
linear Polydimethylsiloxane	INEPT	1.00	0.83
(6)	Spinlock	1.92	1.48
DEPT optimized for Q1	DEPT	1.10	0.67
DEPT optimized for Q2	DEPT	1.08	0.73
branched	INEPT	-----	1.00
Polydimethlylsiloxane	Spinlock	-----	1.39
(7)	DEPT	-----	0.85

the phase difference between hard and attenuated ^{1}H pulses has to be taken into account. Thus, it must be determined and appropriately adjusted. For the actual measurement, the only parameter is the spin lock length, which should be set to approximately 1/*J*(Si,H), and which is, in our experience rather insensitive to misadjustment. Care must be taken that the spin lock is present for all silicon sites of different chemical shifts which, in practical applications, can easily be met. The spin lock technique often yields a moderate heating of the sample, this is however, for silicon compounds, not of importance. Thus, from an experimental point of view, the DEPT and INEPT methods require less preparation, INEPT and DEPT, however, are more sensitive to false parameters.

The results are given in Table I. The signal to noise ratios are normalized for the Q_1 site with the INEPT method. They demonstrate a general, although modest advantage of the spin lock technique for the case of ^{29}Si NMR spectroscopy. We are not able to draw structural conclusions from the table, phenyl and methyl substitution, polymer and monomer, Q_1 and Q_2 sites behave similarly within the limits of error, although it is not possible to optimize in one experiment for both sites. The DEPT technique gives comparable results with INEPT in the silicon case, however, both INEPT and DEPT require careful optimization of either the refocusing delay or the pulse angle of the last decoupler pulse. This optimization is not as elaborate for the spin lock technique.

Interesting is the comparison between **4** and **5**, because in **5** there is one proton directly bound to one silicon atom, thus a simultaneous optimization for both the Q_1 and the Q_3 sites is totally impossible. Nevertheless, if the polarization experiments are carried out with ^{1}J(Si,H), the spin lock technique still gives a very good signal to noise ratio for the Q_3 site in **5**, probably working via ^{4}J(Si,H) for the Q_1 site. On the other hand, if the polarization experiments are carried out via ^{1}J(Si,H) the spin lock technique fails, as predicted, probably due to the power requirements.

EXPERIMENTAL

The measurements were performed on a Bruker AMX 500 spectrometer at 300 K using 25% solutions in $CDCl_3$. A broadband probe head in inverse geometry was used, the multinuclear coil was tuned to ^{29}Si at 99.36 Mhz. For the spin lock (WALTZ16)[12] a rf field strength of 5000 Hz, corresponding to a 90° pulse of 50 μs for both ^{1}H and ^{29}Si at attenuations of 16 dB and 21 dB respectively, was used in all cases. All spectra were taken for 32 K data points using relaxation delays of 30 s and 4 scans for each FID. δ_{Si} values are referenced to external TMS.

All pulses (hard and attenuated) were calibrated using TMS. The ^{1}H pulses were adjusted as forward pulses; the phase difference between hard and attenuated ^{1}H pulses was determined. Final calibration of the ^{1}H decoupler pulses was taken directly with the samples.

CONCLUSION

We have shown in this work that the spin lock technique offers modest advantages for routine ^{29}Si NMR spectroscopy, its implementation in service laboratories, however, requires somewhat more preparation compared with the INEPT or DEPT protocol. We feel that after the initial adjustments have been performed, the use of the spin lock techniques pays off, since the method is less prone to minor miscalibrations.

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