

ROUTINE USE OF INEPT TECHNIQUE FOR MEASUREMENTS OF ^{29}Si NMR SPECTRA OF TRIMETHYLSILYL DERIVATIVES

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Low sensitivity of ^{29}Si NMR, slow ^{29}Si relaxation, and negative Overhauser effect severely limit practical applications of ^{29}Si NMR. The need for the large amount of the sample or of spectrometer time is dramatically reduced if the spectra can be recorded by INEPT technique. It is shown that a standard set of acquisition parameters allows routine measurements of proton decoupled ^{29}Si NMR spectra by INEPT technique in trimethylsilyl derivatives of organic compounds with unknown structure. The INEPT technique makes measurements of ^{29}Si chemical shifts from as little as 20 μmol of compound practical.

Low sensitivity of silicon — 29 to NMR detection¹ has been the major problem in analytical applications of ^{29}Si NMR. These applications are based on a strong dependence of ^{29}Si chemical shift on structural effects in compounds containing $(\text{CH}_3)_3\text{SiO}-$ or $(\text{CH}_3)_3\text{SiN}$ groups^{2,3}. Despite that such groups are easily introduced into functional organic compounds by simple trimethylsilylation⁴, the analytical potential of the method could be exploited until recently only if a relatively large amount of the parent compound with unknown structure was available.

Analytical applications require recording of proton decoupled ^{29}Si NMR spectra. In addition to the inherently low sensitivity of ^{29}Si , efficiency of recording decoupled spectra is further reduced by negative nuclear Overhauser effect (NOE, due to negative magnetogyric ratio of ^{29}Si nucleus γ_{Si}) and by usually slow relaxation of ^{29}Si nucleus. Two techniques are now in general use⁵ for overcoming these factors in pulsed Fourier transform NMR: *i*) the use of relaxation reagents and *ii*) gated proton decoupling. Addition of a relaxation reagent to the sample is feared because the reagents are not necessarily inert and shiftless and, also, the sample is contaminated with the added reagent. Therefore, gated proton decoupling is preferable for samples of unknown structure, but that technique removes only the effect of negative NOE; the measuring time is still long since the problem of slow relaxation remains.

Recent advances in NMR instrumentation has made possible the introduction of sophisticated methods for sensitivity enhancements. They all are based on a transfer of the large proton polarization to nuclei with low magnetogyric ratio through the scalar spin-spin coupling. Since the optimum use of these enhancement techniques requires knowledge of the coupling constant the techniques are not thought to be suitable for routine applications when the coupling constants and line multiplicity are not known. However, we shall show here, that some of the enhancement methods can be applied on a routine basis to trimethylsilyl derivatives of compounds with unknown structure. The use of these techniques, even not under the optimum conditions, leads to considerable shortening of measuring time and dramatically expands the range of possible analytical applications of ^{29}Si NMR.

Three of the so far described polarization transfer methods allow FID acquisition with proton decoupling and are not critically sensitive to coupling constant estimates. The methods, usually known by their acronyms, are: INEPT, insensitive nuclei enhanced by polarization transfer⁶⁻⁹, PREP, population redistribution for enhancement with proton decoupling¹⁰, and DEPT, distortionless enhancement by polarization transfer¹¹. We have chosen to try for the routine applications the INEPT technique since the corresponding pulse sequence is simpler and less sensitive to erroneous estimate of coupling constant than the PREP technique; the DEPT method was not known at the onset of our work. The results obtained here for INEPT can be extended to the DEPT technique which is in some respects¹² even superior to INEPT.

RESULTS

The INEPT pulse sequence used here (Fig. 1) incorporates all the developments described in refs⁶⁻⁹ including the appropriate phase cycling. The equilibration time, t_{eq} , assures relaxation of protons, which is usually much faster than that of silicon. The optimum polarization transfer time, t_{pt} , is⁶⁻⁹

$$t_{pt} = 1/(2J), \quad (1)$$

where J is the value of the spin-spin coupling constant employed in the polarization transfer. The optimum refocusing time, t_{ref} , is^{13,14}

$$t_{ref} = \arcsin(n)^{-0.5}/(\pi J) \quad (2)$$

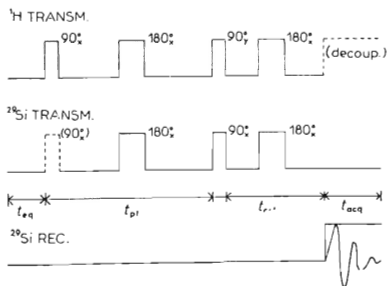


FIG. 1

The pulse scheme for INEPT. (The flip angle of the pulse is given above the pulse in degrees, the index indicates the phase. The distances and lengths are not to scale. The first dashed ^{29}Si pulse was not used here)

(n is the number of coupled protons). Under optimum conditions (*i.e.* when the times t_{pt} and t_{ref} are determined from the known value of J) the decoupled INEPT spectrum is enhanced by the factor¹⁴

$$E_{dopt} = (\gamma_H/\gamma_{Si}) n^{0.5} (1 - 1/n)^{0.5(n-1)}. \quad (3)$$

In trimethylsilyl derivatives the two-bond spin-spin couplings $^2J(^{29}\text{Si}-\text{C}-^1\text{H})$ can be used for polarization transfer as already demonstrated for the case of hexamethyl disiloxane¹⁵. Then, the number of coupled protons $n = 9$ and $E_{dopt} = 9.4$, *i.e.* INEPT gives almost tenfold increase in signal intensity over „normal” recording with the same number of scans. The achieved enhancement per unit of time is even larger as faster proton relaxation allows to use t_{eq} shorter than the delay necessarily for ^{29}Si relaxation in „normal” measurements. In our experiments t_{eq} varied between 1–4 seconds depending on the molecular weight and sample viscosity.

Literature surveys^{16–19} of the reported $^2J(^{29}\text{Si}-\text{C}-^1\text{H})$ coupling constants indicate that they range from 6 to 9 Hz; lower values occurring only for silicon substituted by electropositive substituents, larger values are characteristic for silicon with two or more electronegative substituents. In $(\text{CH}_3)_3\text{SiO}$ and $(\text{CH}_3)_3\text{SiN}$ groups the couplings vary only within 6.5 to 7.5 Hz. In our routine applications we assume $J' = 6.7$ Hz which corresponds to $t_{pt} = 0.07463$ and $t_{ref} = 0.01614$ seconds.

Fig. 2 demonstrates the improvement in signal-to-noise ratio achieved by the INEPT technique. The two spectra were measured in the identical sample in the same total measuring time. The sample was 0.3M deuteriochloroform solution of hexamethyldisiloxane in which the two-bond coupling is $J = 6.7$ Hz (ref.²⁰), the enhancement factor found for the same number of scans is somewhat larger (10.2) than the theoretical value apparently due to the fact that „normal” measurements were not optimized. In other compounds in which the true coupling constant J differs from the assumed value J' , the enhancement factor is

$$E_d = n(\gamma_H/\gamma_{Si}) \cos(\pi \Delta/2) \sin(A + A \Delta) \cos^{n-1}(A + A \Delta), \quad (4)$$

where $\Delta = (J/J') - 1$ and $A = \arcsin(n)^{-0.5}$.

According to this equation the routine INEPT technique would yield spectra with signal to noise ratio worse than the “normal” technique only if the true coupling constant was either smaller than 2 Hz or larger than 12 Hz, which is far beyond the range of found values. We have also recorded good INEPT spectra of compounds in which the coupling constant could not be determined¹⁹ supposedly because of quadrupolar effects of nitrogen.

Typical routine INEPT enhancement for a compound with unknown values of coupling constants is shown in Fig. 3. The sample was 0.5 ml of 0.1M deuteriochloroform solution of 1,6-anhydro-2,3,4-tri-O-trimethylsilyl- β -D-glucopyranose, the total measuring time was 18 minutes. Simple calculation shows that using the same spectrometer and similar routine INEPT enhancement it would be feasible to measure ^{29}Si chemical shifts from as little as 20 μmol of the parent compound in 24 hours.

CONCLUSION

The results show that the INEPT technique can be used for routine measurements of ^{29}Si chemical shifts in trimethylsilyl derivatives of unknown structure. The routine application is possible because the technique is not critically dependent on the values of coupling constants and because the ^{29}Si lines in all trimethylsilyl derivatives have the same multiplicity and the coupling constants are not structurally sensitive. Similar conclusion would apply to the DEPT technique. With these methods ^{29}Si chemical shifts can be determined from as little as 20 μmol of compound and thus the two techniques remove the practical limitations for application of ^{29}Si NMR to organic analytical problems.

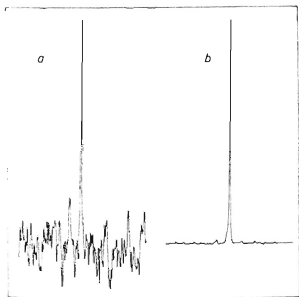


FIG. 2

The "normal" (a) and INEPT (b) ^{29}Si NMR spectra of hexamethyldisiloxane. (0.3M solution in deuteriochloroform, for the details see Experimental)

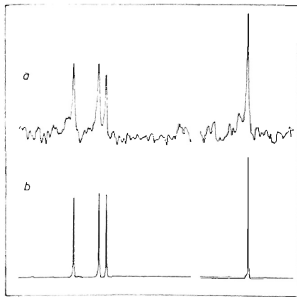


FIG. 3

The "normal" (a) the routine INEPT (b) ^{29}Si NMR spectra of 1,6-anhydro-2,3,4-tri-O-trimethylsilyl- β -D-glucopyranose. (0.1M solution in deuteriochloroform with 1% of hexamethyldisilane as a reference, for details see the text)

EXPERIMENTAL

All the spectra shown were obtained on a Varian XL-200 spectrometer operating at 200 MHz for proton and at 3.97 MHz for silicon with 5 mm broad band probe. The "normal" spectra were recorded using the standard S2PUL pulse sequence with gated proton decoupling to suppress the negative Overhauser effect. Delay of 15 s between successive pulses was used with flip angle of 30° and acquisition time 1 s. Spectral width 4 kHz and zero data filling of FID to 16 k of memory. Exponential weighting function was employed with line-broadening 1.6 Hz.

The INEPT spectra were measured with slightly modified standard pulse sequence provided by the manufacturer. The 90° observe pulse was 13 μ s, the 90° decoupler pulse was 63 μ s. The same data treatment as of "normal" spectra was utilized.

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