

ASSIGNMENT TECHNIQUES FOR ^{29}Si NMR CHEMICAL SHIFTS IN PERTRIMETHYLSILYLATED PRODUCTS. TESTS OF EMPIRICAL ASSIGNMENT RULES BY A MODIFIED ^{29}Si INDOR

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A modification of the ^{29}Si INDOR technique is described that monitors instead of the usual $\text{Si}(\text{CH}_3)_3$ proton line the line of CH_nXSi ($n = 1, 2$; $\text{X} = \text{O}, \text{S}, \text{NH}$) protons while the ^{29}Si NMR spectrum is being scanned. Though less sensitive and accurate than the routine INDOR, the modified method permits assignment of ^{29}Si chemical shifts providing that the CH_n proton lines in ^1H NMR spectrum are well separated and assigned. The modified INDOR is used here to assign the ^{29}Si chemical shifts in pertrimethylsilylated 1,6-anhydro- β -D-glucopyranose (1) and methyl β -D-xylopyranoside (2). The values of chemical shifts determined by this technique agree with those determined by standard ^{29}Si NMR methods but the assignment suggested for 1 on empirical grounds previously must be partially revised, the empirical assignment in the spectrum of 2 (based on additivity rule) is fully confirmed.

Applications of ^{29}Si NMR to analysis of trimethylsilylated products is limited to rather trivial determination of the number of different trimethylsilyl groups in the molecule unless the ^{29}Si chemical shifts can be assigned to individual trimethylsilyl groups. Techniques presently employed for ^{29}Si NMR measurements^{1,2} (INDOR, pulsed Fourier transform NMR with gated decoupling, INEPT, and DEPT) do not lend themselves easily for the assignment purposes as they aim at high sensitivity. The high sensitivity is achieved by irradiation of trimethylsilyl proton lines which are not sensitive to molecular structure³. Though the low sensitivity of trimethylsilyl proton chemical shifts and coupling constants is of advantage for routine measurements⁴ of ^{29}Si chemical shifts by polarization transfer techniques like INEPT or DEPT it renders the assignment (and, sometimes, resolution) of these proton lines practically impossible and thus precludes assignment of the silicon-29 lines through shift correlation.

In trimethylsilylated products containing $\text{CH}_n\text{—X—Si}(\text{CH}_3)_3$ moiety the CH_nX ($n = 1, 2$; $\text{X} = \text{O}, \text{S}, \text{NH}$ etc.) protons are structurally sensitive and their lines can be

assigned by various techniques. As they have non-zero spin-spin coupling with the silicon nucleus, the assigned proton lines can yield the assignment for the silicon lines. Selective polarization transfer from the CHX instead from $\text{Si}(\text{CH}_3)_3$ protons reduces the sensitivity of INEPT or DEPT techniques by a factor of 1.87 (for proton decoupled spectra)^{5,6} and monitoring CH proton line instead of $\text{Si}(\text{CH}_3)_3$ proton line in the INDOR technique reduces the sensitivity by a factor of 9 at least. On the other hand small values of $^3J(^1\text{H}-\text{C}-\text{X}-^{29}\text{Si})$ coupling constants and their structural sensitivity together with strong coupling between CH_nX protons and other protons in the molecule cause considerable difficulties for such applications of INEPT or DEPT pulse sequences⁷ so the modified INDOR technique appears to be the method of choice when continuous wave spectrometer is available. In the present paper we will describe the method and its application to two pertrimethylsilylated monosaccharide derivatives: 1,6-anhydro- β -D-glucopyranose (1) and methyl β -D-xylopyranoside (2). These two derivatives were chosen because their ^{29}Si NMR lines had been assigned earlier according to two different empirical assignment rules^{8,9}; the INDOR assignment will provide the first test of the empirical rules^{8,9}.

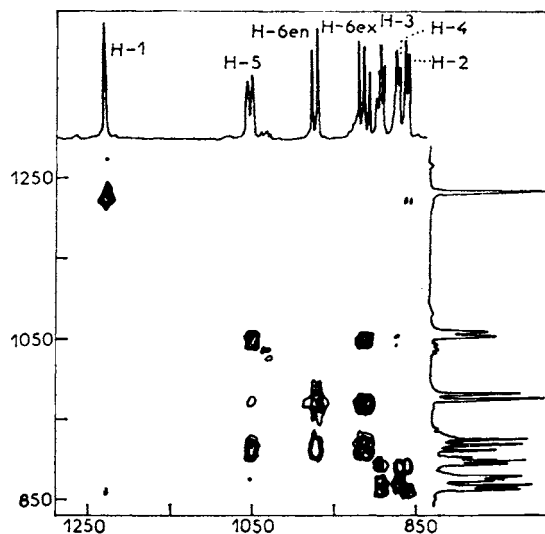


FIG. 1

Contour plot of homonuclear chemical shift correlated two-dimensional ^1H NMR spectrum and ordinary ^1H NMR spectrum of 1 in deuteriochloroform solution at 200 MHz. (The proton labeling on the top refers both to one dimensional spectrum and to the dia-peaks in the 2D NMR spectrum, the protons are labeled by the ordinal numbers of their skeletal carbon atoms)

RESULTS AND DISCUSSION

Before the assignment of ^{29}Si lines by INDOR technique can be attempted the ^1H NMR spectra of the CH_nX protons must be assigned unequivocally. The assignment of the proton spectra of compound *1* was derived from the two-dimensional homonuclear chemical shift correlated NMR spectrum shown in Fig. 1. The assignment is straightforward; starting from the highest frequency singlet line which is obviously¹⁰ due to H-1 proton we proceed through the only cross-peak to the dia-peak of H-2 proton. The only other cross-peak of proton H-2 is that with the H-3 proton and it brings us to the H-3 dia-peak and so on until the full assignment is obtained. ^1H NMR spectrum of compound *2* was assigned through a series of homonuclear double resonance experiments described earlier¹¹, the spectrum with the indicated assignment is shown in Fig. 2.

As the INDOR experiments must be carried on a cw spectrometer we could use only a spectrometer operating at 80 MHz (for protons) and hence the multiplets of H-2, H-3, and H-4 protons were not so well separated as in Figs 1 and 2 (200 MHz) but the separation was sufficient to ensure selective monitoring of CH—O proton signal intensity. The INDOR spectra of *1* obtained when monitoring H-2, H-3, and H-4 intensities are shown in Fig. 3. In comparison with the usual INDOR

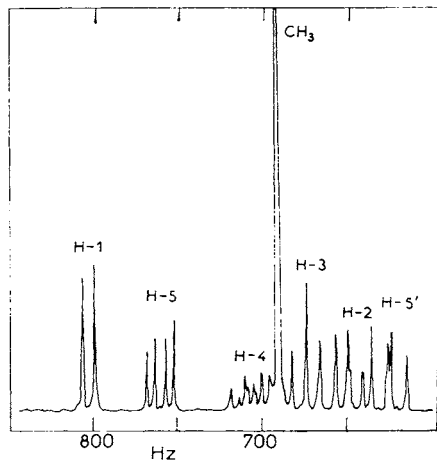


FIG. 2

^1H NMR spectrum of *2* in deuteriochloroform at 200 MHz. (For the explanation of proton labeling see Fig. 1)

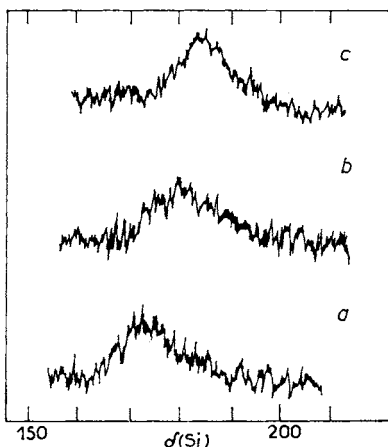


FIG. 3

^{29}Si INDOR spectra of *1* in deuteriochloroform. Trace *a* H-3 proton monitored, trace *b* proton H-4 monitored and trace *c* H-2 proton monitored

spectra ($(\text{CH}_3)_3\text{Si}$ proton line monitoring)^{12,13} the lines are broad, the fine structure due to methyl proton coupling is not well visible and the spectra have worse signal-to-noise ratio. All this deterioration of the quality of the spectra is due to the necessity to monitor the $\text{CH}-\text{O}$ proton line instead of the usual $(\text{CH}_3)_3\text{Si}$ line. However, even with these broad spectra the positions of maxima agree with the ^{29}Si chemical shifts determined either by the usual INDOR technique or by the pulsed FT NMR (refs^{8,9}) and the assignment is unambiguous. In deuteriochloroform solution, the silicon-29 chemical shifts at $\delta = 17.3$, 17.8 , and 18.3 in *1* belong to Si-3, Si-4, and Si-2, respectively. In the compound *2* Si-3, Si-4, and Si-2 resonate at $\delta = 18.6$, 18.9 , and 19.1 , respectively. (The silicon atoms are labeled by the number of the skeletal carbon atoms to which they are connected). These assignments are confirmed independently by another experimental method¹⁴ based on measurements of ^{29}Si satellites in ^{14}C NMR spectra.

Comparison with the published^{8,9} empirical assignments shows a full agreement in the case of compound *2* which confirms the assignment rule based on additivity of substituent effects. In the case of compound *1* the assignment of Si-3 lines agrees also with the empirical one based on Hammett-type correlation of the chemical shifts but the assignments of Si-2 and Si-4 lines are reversed. The two lines were assigned⁸ on the basis of comparison of the ^{29}Si NMR spectra of *1* and of 3,4-bis(trimethylsiloxy)-2-*O-p*-toluensulphonyl-1,6-anhydro- β -D-glucopyranose (*3*). One of the two lines in the spectrum of *3* was assigned to Si-3 on the basis of the Hammett-type dependence and hence the other line was due to Si-4. Since the Si-4 line in *3* had the same chemical shift ($\delta = 18.54$) as one of the remaining two lines in the spectrum of *1* ($\delta = 18.52$ and 17.78), the line with the same shift was assigned to the corresponding Si-4 silicon atom in the compound *1*. It remains to be determined whether the erroneous empirical assignment is caused by improper comparison of the spectra of *1* and *3* or by a failure of the correlation in the case of the compound *3*.

CONCLUSION

The results show that the described minor modification of INDOR technique gives reliable assignments for the ^{29}Si chemical shifts in pertrimethylsilylated products though at the expense of sensitivity and accuracy of chemical shift values. The technique can be applied only to compounds with CH_nXSi protons which have ^1H NMR lines sufficiently separated and assigned. Unfortunately, these are rather severe limitations as all new high-field spectrometers are designed for pulsed regime and not for continuous wave operation necessary for INDOR technique.

EXPERIMENTAL

Trimethylsilylation of the parent monosaccharides was carried out as described elsewhere^{8,11}. The samples were measured as 10–20% solutions in deuteriochloroform in 5 mm NMR tubes.

^1H NMR spectra used for the assignment (Figs 1 and 2) were measured on a Varian XL200 spectrometer operating at 200 MHz. Standard software provided by the manufacturer (H-1Z version) was employed for the measurement, calculations and plotting of 2D NMR spectra (HOMCOR pulse sequence, 1024×512 data points, pseudo-echo FID shaping in two dimensions, no data symmetrization).

^{29}Si INDOR spectra were recorded on a modified^{12,13} Tesla BS-387C spectrometer operating at 80 MHz for protons and at 15.9 MHz for ^{29}Si . In order to improve signal-to-noise ratio 100–150 spectral scans were accumulated using accumulator "Sigma". As the $^3J(^1\text{H}-\text{C}-\text{O}^{29}\text{Si})$ coupling constants were small (1–4 Hz) it was sufficient to monitor the CHO proton main resonance (and not a ^{29}Si satellite). Naturally, the decoupling power had to be sufficiently strong to decouple silicon from protons. Accuracy of the chemical shifts determined in this way is about ± 0.15 ppm (*i.e.* about an order of magnitude less than with the usual INDOR technique).

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