

¹³C Fourier-Transform N.M.R. Study of Trimethyl(penta-1,3-diynyl)silane

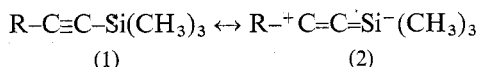
Milton T. W. Hearn

MRC Immunopathology Research Group, Medical School,
P.O. Box 913, Dunedin, New Zealand.

Abstract

The natural-abundance carbon-13 chemical shifts of trimethyl(penta-1,3-diynyl)silane and related compounds have been measured. The effect on the shieldings of the acetylenic carbons by the trimethylsilyl substituent at C1 is discussed.

Recently, evidence in support of significant (p→d)π bonding or equivalent electronic interaction between bonded carbon and silicon atoms in aryl alkynylsilanes (1; R = phenyl, 1,3-phenylene) has been reported.^{1,2} Such interactions would involve ground state polarization with net electron migration from the triple bond to the silicon atom through such resonance forms as structure (2). In conjugated enynylsilanes and diynylsilanes the intriguing possibility arises for more extended polarization and delocalization. Since ¹³C chemical shift data have proved a valuable adjunct to other techniques for providing insight into intramolecular changes in electron density (for a compendium, see³), we have examined the ¹³C n.m.r. spectra of trimethyl(penta-1,3-diynyl)silane and a series of related compounds.



Results and Discussion

The spectral data for the various compounds are presented in Table 1. The resonance assignments are based on intensity data, off-resonance decoupling and multiplicity patterns, chemical shift theory³ and the observation that for alkynylsilanes the assignment of the acetylenic C1 and C2 carbons can be readily based¹ on the larger one-bond ¹³C_α-²⁹Si coupling seen for the higher field signal.

From Table 1, it is evident that conjugation of an olefinic group with a carbon-carbon triple bond results in the considerable β-desielding of the acetylenic carbon C1. This has also been recognized in several other studies.^{4,5} Also evident is the pronounced α-effect of the triple bond itself which results in the shielding of the

¹ Levy, G. C., White, D. M., and Cargioli, J. D., *J. Magn. Reson.*, 1972, **8**, 280.

² White, D. M., and Levy, G. C., *Macromolecules*, 1972, **5**, 526.

³ Stothers, J. B., 'Carbon-13 N.M.R. Spectroscopy' (Academic Press: New York 1972).

⁴ Zeisberg, R., and Bohlmann, F., *Chem. Ber.*, 1974, **107**, 3800.

⁵ Hearn, M. T. W., *J. Magn. Reson.*, 1976, **22**, in press.

substituents' α -carbon nuclei relative to the analogous alkane. It is interesting to note in both penta-1,3-diyne and hexa-2,4-diyne that the α -effect can also operate through an sp-carbon atom since introduction of a second triple bond has a similar shielding effect on the adjoining sp-carbon. The conclusion that the effect of a triple bond at the neighbouring α -position is broadly independent of the hybridization of the α -carbon is supported by data recently obtained⁶ for acetylenic aldehydes, nitriles and conjugated α,β -unsaturated esters. The interior sp-hybridized carbons in penta-1,3-diyne and hexa-2,4-diyne are moved upfield by *c.* 14 ppm from their positions in the corresponding monoalkyne. This value is in good agreement with the data reported⁷ for similar carbon nuclei in octa-3,5-diyne and dodeca-5,7-diyne.

Table 1. Carbon-13 chemical shifts of penta-1,3-diyne and related compounds

In ppm downfield from Me₄Si

Compound	C1	C2	C3	C4	C5
MeCH ₂ CH ₂ CH ₂ Me ^A	13.7	22.6	34.5	22.6	13.7
HC≡CCH ₂ CH ₂ Me	68.2	83.6	20.1	22.1	13.1
(Z)-HC≡CCH=CHMe	82.1	80.3	109.4	140.3	15.9
(E)-HC≡CCH=CHMe	75.8	82.5	110.1	141.3	18.6
HC≡CC≡CMe	64.7	68.8	65.4	74.4	3.9
(Z)-Me ₃ SiC≡CCH=CHMe	100.0	103.0	111.4	141.0	17.3
(E)-Me ₃ SiC≡CCH=CHMe	92.2	104.0	110.9	140.8	18.6
Me ₃ SiC≡CC≡CMe	82.7	89.2	65.4	76.0	4.5
MeC≡CC≡CMe	4.0	72.2	64.9	—	—
Me ₃ SiC≡CC≡CSiMe ₃	86.0	88.7	—	—	—

^A Grant, D. M., and Paul, E. G., *J. Am. Chem. Soc.*, 1964, **86**, 2984.

The introduction of the trimethylsilyl group at C1 in penta-1,3-diyne results in a downfield shift of the α - and β -acetylenic carbons (C1 and C2) by 18.0 and 20.4 ppm respectively. The shift difference between the α - and β -carbons is larger than that observed between the same carbons in butadiyne-1,4-diylbis(trimethylsilane). The chemical shifts of the remaining carbon nuclei are however very similar to the corresponding carbons in the trimethylsilyl-unsubstituted counterpart. A similar pattern can be seen in the related (Z)- and (E)-trimethyl(pentenynyl)silanes in which the α - and β -acetylenic carbons experience considerable downfield shifts whilst the olefinic carbon nuclei remain essentially unperturbed. The substantial deshielding of the β -acetylenic carbon C2 in these compounds can be accommodated by invoking an electron withdrawal from the π -orbitals of the triple bond to the empty d-orbitals of the silicon atom which can be represented by the ground state resonance contributinal form (2; R = CH₃C≡C, CH₃CH=CH). A further consequence of the trimethylsilyl group is the deshielding of the α -acetylenic carbon C1 by *c.* 18–20 ppm. A similar downfield shift, attributable to the composite effect of the inductive, neighbour anisotropic and intramolecular dispersion terms,⁸ but of smaller magnitude has been observed for the point of attachment carbon for both aryl-⁸ and vinyl-silanes.⁹ The similarity of the γ -, δ - and ϵ -carbons (C3, C4 and C5) for the parent and related

⁶ Hearn, M. T. W., *J. Chem. Soc., Perkin Trans. 2*, 1976, in press.

⁷ Dorman, D. E., Jautelat, M., and Roberts, J. D., *J. Org. Chem.*, 1973, **38**, 7026.

⁸ Maciel, G. E., and Natterstad, J. J., *J. Chem. Phys.*, 1965, **42**, 2427.

⁹ Maciel, G. E., *J. Phys. Chem.*, 1965, **69**, 1947.

substituted alkynylsilanes indicates that extensive polarization and further π -orbital delocalization over subsequent conjugating groups is unlikely. Such delocalization would result in considerable electronic perturbations of these more distant carbon atoms. If any significant electronic demands were made on the substituent then the C 4 resonance of trimethyl(penta-1,3-diynyl)silane would be substantially deshielded relative to the C 5 of hexa-2,4-diyne or C 4 of penta-1,3-diyne. However, only small downfield shifts of 3.8 or 1.6 ppm respectively are observed. In phenylacetylene there is similarly little electronic perturbation of the *para*-phenyl carbon on the introduction of the trimethylsilyl group at the ethynyl carbon.¹ These results are consistent with the conclusion that the silicon atom of the trimethylsilyl group induces (p \rightarrow d) π electronic interactions in directly bonded carbon-carbon triple bonds but this effect is poorly transmitted through more distant sp²- or sp-hybridized nuclei.

Experimental

The carbon-13 chemical shifts were measured under conditions of full proton decoupling on a Bruker HFX multinuclear spectrometer operating at 22.63 MHz. The compounds were measured as 25% (w/w) solutions in deuteriochloroform containing c. 5% Me₄Si (w/w). The data recorded thus are in ppm downfield from the carbon resonances of the internal tetramethylsilane and are thought to be accurate to ± 0.2 ppm. The compounds were prepared by well established methods¹⁰ and purified immediately prior to use.

Acknowledgments

M.T.W.H. acknowledges the award of an I.C.I. Fellowship, the support of the Medical Research Council of New Zealand and thanks Professor Sir Ewart Jones for his encouragement.

Manuscript received 12 March 1976

¹⁰ Hearn, M. T. W., Jones, E. R. H., and Thaller, V., unpublished data.