Ultrahigh Resolution ^{29}Si N.M.R. Spectroscopy: Natural Abundance Studies of Oxygen-18/16 Isotope Effects on ^{29}Si Nuclear Shielding

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$^{18/16}O$ Isotope effects on ^{29}Si chemical shifts have been measured in various organosilanes for the first time; their magnitude depends on the nature of the Si–O chemical bond, particularly, on the extent of d_π–p_π conjugation.

$^{18/16}O$ Isotope effects on ^{13}C,[1] ^{15}N,[2] and ^{31}P[3] chemical shifts ($^1\Delta$) have been widely exploited in biosynthetic investigations[4] and studies of reaction mechanisms,[5] because they allow the determination of the site and degree of isotopic substitution in the molecule. On the other hand these effects are sensitive to various structural parameters, such as bond length, bond order, and stretching force constants, which makes them useful for investigations of the electronic structure of molecules.[6] Although $^{18/16}O$ isotope effects on the ^{29}Si chemical shift can be used in a similar manner, their values had not been determined until recently. This can be explained in part by the necessity for the compounds to be isotopically enriched in ^{18}O, but the situation has now improved. Recently, we have shown[7] that under ultrahigh resolution conditions $^{18/16}O$ isotope effects can be measured in ^{29}Si n.m.r. spectra at the natural ^{18}O level of *ca.* 0.2% (Figure 1). Here we report the first systematic study of such effects on ^{29}Si nuclear shielding in the series of organosilicon compounds.

The observed $^1\Delta^{18/16}O$ (^{29}Si) values (Table 1) are smaller than the analogous effects in ^{13}C n.m.r. spectra [for example, 35 p.p.b. in Me_3COH, 15 p.p.b. in $C(OR)_4$].[6] This is in contrast with the wider range of chemical shifts and greater mass factor in the case of ^{29}Si, implying larger isotopic effects in ^{29}Si spectra.[4,6]

This contradiction can be explained by at least two reasons. Firstly, this anomaly provides evidence of the difference in nature of Si–O and C–O chemical bonds, in agreement with the concept of d_π–p_π conjugation between the lone electron pairs of oxygen and the vacant d-orbitals of the silicon atom in organosilicon compounds.[8] This is further supported by the fact that the diminishing d_π–p_π interaction (a rise in Si–O bond polarity) for Me_3SiOR derivatives in the series $R = NR_2 > Alk > SiR_3 > Ph$ (caused by the increase in concurrent conjugation between the lone electron pairs of the oxygen atom and substituent R) results in a systematic increase in $^1\Delta$ $^{18/16}O(^{29}Si)$. Secondly, the values $^1\Delta$ $^{18/16}O(^{29}Si)$ exhibit a strong dependence on the nature of substituents at the silicon atom. An increase in their electronegativity causes a dramatic decrease in the $^1\Delta$ $^{18/16}O(^{29}Si)$ values. A parallel increase in

Table 1. ^{29}Si N.m.r. parameters of various organosilanes.[a]

N	Compound	$^1\Delta$ $^{18/16}O$	$^1J\,(^{29}Si–^{13}C)$	$\delta\,(^{29}Si)$/ p.p.m.
1	Me_3SiOPh	28.5	59.74	18.8
2	$Me_3SiOSiMe_3$[b]	26.2	59.62	6.9
3	$(Me_3SiO)_2SiMe_2$[c]			
	$SiMe_3$	25.6	59.70	6.7
	$SiMe_2$	16.6	74.43	−21.3
4	Me_3SiOBu^t	25.2	59.19	6.4
5	Me_3SiOMe[d]	23.1	59.06	17.9
6	$Me_3SiONHSiMe_3$[b,e]			
	OSi	21.8	59.47	20.9
	NSi	—	59.69	10.9
7	$(Me_2SiO)_4$	17.3	75.58	−19.6
8	$Me_2Si(OMe)_2$[f]	15.2	73.73	−1.7
9	$MeSi(OMe)_3$[9]	7.5	97.15	−40.1
10	$Si(OMe)_4$[h]	4.0	—	−78.6
11	$Si(OEt)_4$[b,i]	4.6	—	−82.3

[a] ^{29}Si N.m.r. spectra were recorded at 71.55 MHz on a Bruker WM-360 spectrometer under ultrahigh resolution conditions as described earlier[7] for 80% solutions in C_6D_6 at 308 K in 10 mm sample tubes. The isotope effects ($^1\Delta$) are expressed in parts per billion (±0.1 p.p.b.). Positive value denotes an upfield shift for the nucleus bonded to the heavier isotope. Spin–spin couplings are in Hz (±0.01) and chemical shifts (δ) in p.p.m. (±0.1) relative to the internal standard Me_4Si. [b] Ref. 7. [c] $^2J(^{29}Si–^{29}Si)$ 1.32 Hz. [d] $^2J(^{29}Si–^{13}C)$ 1.77 Hz. [e] $^1\Delta(^{15/14}N)$ 14.2 p.p.b., $^3J(^{29}Si–^{29}Si)$ 2.45 Hz. [f] $^2J(^{29}Si–^{13}C)$ 1.77 Hz. [g] $^2J(^{29}Si–^{13}C)$ 1.32 Hz. [h] $^2J(^{29}Si–^{13}C)$ 1.10 Hz. [i] $^2J(^{29}Si–^{13}C)$ 1.10 Hz, $^3J(^{29}Si–^{13}C)$ 2.35 Hz.

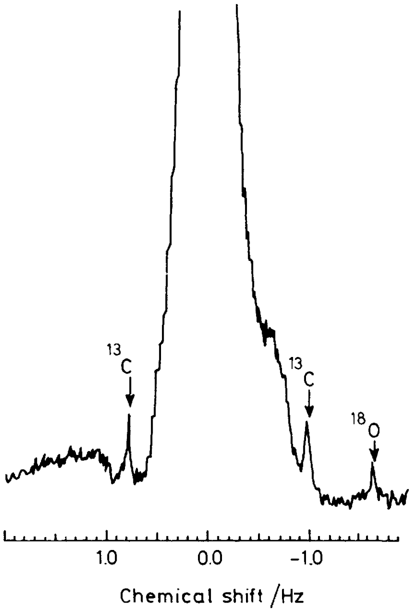

Figure 1. A region of ±2 Hz relative to the major resonance in the ultrahigh resolution ^{29}Si n.m.r. spectrum of Me_3SiOMe (with 20%, v/v, C_6D_6 in a 10 mm sample tube) acquired with the INEPT sequence and noise modulated broad-band proton decoupling on Bruker WM-360 spectrometer at 71.55 MHz and 303 K. ^{13}C and ^{18}O Satellites of the OMe group are visible. Number of scans 80, spectral width 300 Hz, acquisition time 27.3 s, 16 K data points acquired. The data were processed with 30 mHz Lorentzian narrowing plus GB = 0.4 and zero-filling into 128 K data points, which yielded a digital resolution of 4.5 mHz.

$^{1}J(^{29}Si-^{13}C)$ indicates that this may be due to the growth in s-character of the Si–O bond with increasing number of electronegative substituents at Si. At the same time enhanced shielding of the ^{29}Si nuclei in the same series suggests that the decrease in $^{1}\Delta$ can also be related to a greater positive charge on the silicon atom.[9]

It is noteworthy that $^{1}\Delta\ ^{18/16}O(^{29}Si)$ tends to increase with lengthening of the Si–O bond in compounds with the same substituents at oxygen: Me_3SiOMe (1.639 Å[10]), $MeSi(OMe)_3$ (1.632 Å[11]), $Si(OMe)_4$ (1.613 Å[12]).

Received, 2nd August 1988; Com. 8/03167C

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