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^{29}Si NMR Spectra of *tert*-Butyldimethylsilylated Alcohols

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^{29}Si NMR spectra of a series of *tert*-butyldimethylsilyl derivatives of simple alcohols were measured under standard conditions in chloroform-*d*. The chemical shifts are linearly related to those in analogous trimethylsilyl derivatives. The correlation is very good ($r = 0.998$, $n = 24$) but significantly different from the correlation which holds for derivatives of amino acids (including both Si—N and Si—O silicon atoms) despite that the two correlations cover approximately the same range of chemical shifts. The quality of the correlation now reported (error estimate $\pm$ 0.19 ppm) is such that it should allow the detection of specific interactions that might occur in the case of silylated polyols. The observed chemical shifts are affected by polar effects and by sterically controlled association with the solvent (chloroform), but other factors are not excluded.

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INTRODUCTION

Following the suggestion of Ralph[1] that the ^{29}Si chemical shifts in hydrolytically more stable *tert*-butyldimethylsilyl derivatives, δ(TBDMS), can be predicted from the shifts in less stable but more frequently studied trimethylsilyl derivatives, δ(TMS), we have recently described[2] a linear correlation holding between the chemical shifts in these derivatives of amino acids. The linear correlation found is extremely good [the range of ^{29}Si chemical shifts covered is 20 ppm, correlation coefficient $r = 0.999$ for 20 data points with standard error of the estimate of $\pm$0.11 ppm for δ(TBDMS)] and, what is more surprising, the same correlation holds irrespective whether the silicon atom is bonded to oxygen (R—COOSi) or nitrogen (R—NH—Si) atom. The low error estimate suggested that the correlation could be used not only to predict the chemical shifts but also to detect specific (e.g. steric) interactions as deviations from the correlation when both (TMS and TBDMS) derivatives are measured. When testing this assumption on diol derivatives, deviations considerably exceeding the error of estimate were observed in compounds in which no specific interactions were likely to occur (linear non-rigid α,ω-diols).[3] Since all the calculated chemical shifts were larger than those found experimentally, the correlation employed becomes suspect as a cause of the systematic error and a more appropriate correlation for alcohol derivatives was sought. The results are described here.

EXPERIMENTAL

TBDMS derivatives were prepared according to Corey's procedure.[4] A flask was charged successively with 0.4–1 g of dry alcohol, *tert*-butyldimethylchlorosilane (TBDMSCl, 1.2 mol per mole OH), imidazole (2.5 mol per mole OH), and dry dimethylformamide (DMF) (1–2 ml). The reaction mixture was stirred at 50–70 °C under a dry, inert gas atmosphere for *ca.*, 1.5–2 h, cooled to room temperature and the product was extracted into dry diethyl ether. Pure TBDMS derivatives were obtained by fractional distillation.

NMR spectra were measured in dry chloroform-*d* solutions containing 1% (v/v) of hexamethyldisilane (HMDSS) as a secondary reference. The concentration of the sample in the measured solution was reduced until the ^{13}C chemical shift of HMDSS was $\delta = -2.48 \pm 0.02$, relative to the central line of the solvent at 76.99 pm (see Ref. 5 for details of this standard procedure). All the NMR spectral measurements were performed on a Varian UNITY-200 spectrometer (operating at 50.3 MHz for ^{13}C and at 39.7 MHz for ^{29}Si NMR measurements), using the standard software version vnmr 3.2 (APT and INEPT pulse sequences). The spectra were recorded at 23 $\pm$ 1 °C.

^{29}Si NMR spectra were measured by the INEPT with the pulse sequence optimized[5] for TMS derivatives, i.e. for coupling to nine protons and a coupling

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constant of 6.5 Hz. The signal loss relative to a properly optimized experiment for the TBDMS derivatives was negligible.[6] Acquisition (1.0 s) was followed by a relaxation delay of 5 s. During the acquisition period, WALTZ decoupling was used and FID data (8K) were sampled for the spectral width of 4000 Hz. Zero filling to 32K and mild exponential broadening were used in the data processing.

The ^{29}Si $\pi/2$ pulses were a maximum of 17 μs long whereas the ^{1}H $\pi/2$ pulses were 10 μs in a 5 mm switchable probe. The ^{29}Si spectra were referenced to the line of HMDSS at $\delta = -19.79$. The ^{13}C NMR spectra were measured using a spectral width of 16 000 Hz. WALTZ decoupling was applied both during acquisition (1 s) and relaxation delay (2–5 s). Zero filling to 64K and 1–3 Hz line broadening were used in data processing. All compounds were identified by their ^{1}H and ^{13}C NMR spectra.

The solvent accessible surface (A) was calculated for oxygen atoms and a probe diameter of 100 pm (including geometry optimization) exactly as described previously for $A(10)$;[7] Del Re atomic charges (Q) were calculated as in Ref. 8.

RESULTS AND DISCUSSION

The measured ^{29}Si chemical shifts, δ(TBDMS), are summarized in Table 1, where the shifts for the related TMS derivatives, δ(TMS), measured under identical conditions,[9] and polar σ^* constants of the substituent R are also given. As expected, there is an excellent linear correlation between the two ^{29}Si chemical shifts:

$$\delta(\text{TBDMS}) = 1.422 + 0.9899\ \delta(\text{TMS})$$

with correlation coefficient $r = 0.998$ for 24 data points and standard error of the estimate of ± 0.19 ppm. This correlation for alcohol derivatives confirms the trend found in amino acid derivatives [i.e. in related pairs of derivatives δ(TBDMS) is always larger than δ(TMS) and δ(TBDMS) increases with increasing δ(TMS) values], but the numerical coefficients in the two correlations are significantly (at the 95% significance level) different. As is apparent from Fig. 1, the older correlation always predicts larger values of δ(TBDMS) than found experimentally, despite the fact that the two correlations cover essentially the same range of δ values.

There is an obvious dependence of δ(TBDMS) on polar effects (Fig. 2) but the functional form is unclear; certainly other factors also contribute to the observed chemical shifts. The most notable deviation from the common trend is the chemical shift in the *tert*-butyl derivative $(CH_3)_3COSi(CH_3)_2C(CH_3)_3$. Similar deviations in TMS derivatives have been ascribed[10] to steric effects. The mechanism recently proposed for these steric effects in TMS derivatives,[7,11] i.e. steric hindrance to association with the solvent's proton, is in accord with the observed deviation (the observed chemical shift is lower than one would expect on the basis of a polar σ^* constant; Fig. 2). Moreover, this interpretation is in agreement with the trend in the series methyl, ethyl, isopropyl and *tert*-butyl derivatives. In this series the substituent effect of a γ-methyl group on the ^{29}Si chemical shift is essentially the same for the first two methyl

Table 1. ^{29}Si chemical shifts of TBDMS and TMS derivatives of alcohols ROH and polar σ* constants of R groups[a]

R	δ(TBDMS) exp.	δ(TMS) exp.	δ(TBDMS) calc.	Δ (exp. − calc.)	σ*(R)
CH_3—	21.02	19.64	20.86	0.16	0.000
CH_3CH_2—	18.52	17.09	18.34	0.18	−0.100
$CH_3CH_2CH_2$—	18.37	17.06	18.31	0.06	−0.115
$CH_3(CH_2)_3$—	18.27	17.00	18.25	0.02	−0.130
$(CH_3)_2CH$—	16.11	14.71	15.98	0.13	−0.190
c—C_6H_{11}—	15.91	14.57	15.84	0.07	−0.150
$(CH_3)_3C$—	8.60	7.62	8.97	−0.37	−0.300
$Cl(CH_2)_2$—	20.97	19.81	21.03	−0.06	0.385
$Cl(CH_2)_3$—	19.59	18.36	19.60	−0.01	0.140
$Cl(CH_2)_4$—	18.92	17.61	18.85	0.07	0.050
$Cl(CH_2)_6$—	18.51	17.27	18.52	−0.01	0.006
Cl_2CHCH_2—	22.58	21.55	22.75	−0.17	0.693
CCl_3CH_2—	23.40	22.73	23.92	−0.52	0.946
$C_6H_5CH_2$—	20.47	19.08	20.31	0.16	0.215
CH_2=CH—CH_2—	20.26	18.90	20.13	0.13	0.170
$BrCH_2CH_2$—	20.88	19.70	20.92	−0.04	0.360
$CH_3CH_2(CH_3)CH$—	15.95	14.78	16.05	−0.10	−0.210
$H_3CO(CH_2)_2$—	20.04	18.74	19.97	0.07	0.240
$(CH_3)_3CCH_2$—	17.42	16.37	17.63	−0.21	−0.165
$(CH_3)_3SiCH_2$—	19.62	18.40	19.64	−0.02	−0.260
$(CH_3)_3Si(CH_2)_2$—	17.98	16.32	17.58	0.40	−0.093
$(CH_3)_3Si(CH_2)_3$—	18.32	16.97	18.22	0.10	0.033
$(CH_3)_3Si(CH_2)_4$—	18.29	17.02	18.27	0.02	−0.012
C_6H_5—	20.61	19.43	20.66	−0.05	0.600

[a] Chemical shifts in δ scale; estimated precision of experimental values ±0.02 ppm; chemical shifts δ(TMS) were taken from Ref. 9; chemical shifts $\delta(\text{TBDMS})_{calc}$ were calculated according to the correlation given in the text with a standard error of the estimate ±0.18 ppm, values of σ^* constants were taken from Ref. 10.

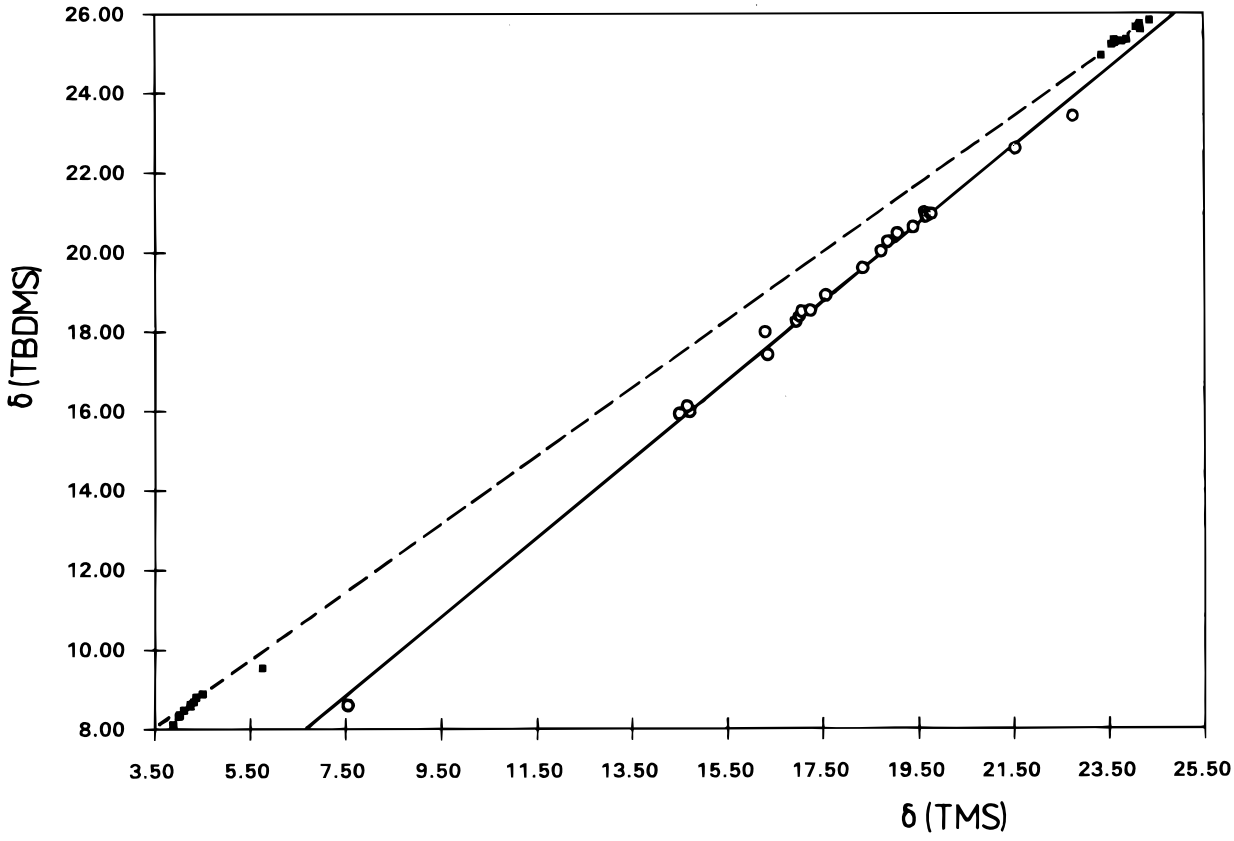

Figure 1. Correlation between δ(TBDMS) and δ(TMS) in (■) amino acid and (○) alcohol derivatives. Lines are the least-squares fits of data of amino acids (dashed line) and alcohols (solid line).

groups introduced (i.e. in ethyl and isopropyl derivatives, −2.5 ppm), but the introduction of the third methyl group to form the *tert*-butyl derivative has a markedly larger effect, −7.5 ppm.

According to the proposed mechanism of the steric effect,[7] the observed chemical shift is a weighted average of the shifts in a free silyl derivative (lower δ value) and in its complex with chloroform (larger δ value). The relative population of the complex depends on the basicity of the oxygen atom in the silyl derivative and on the steric accessibility of the oxygen atom to the chloroform proton (deuterium). The steric accessibility

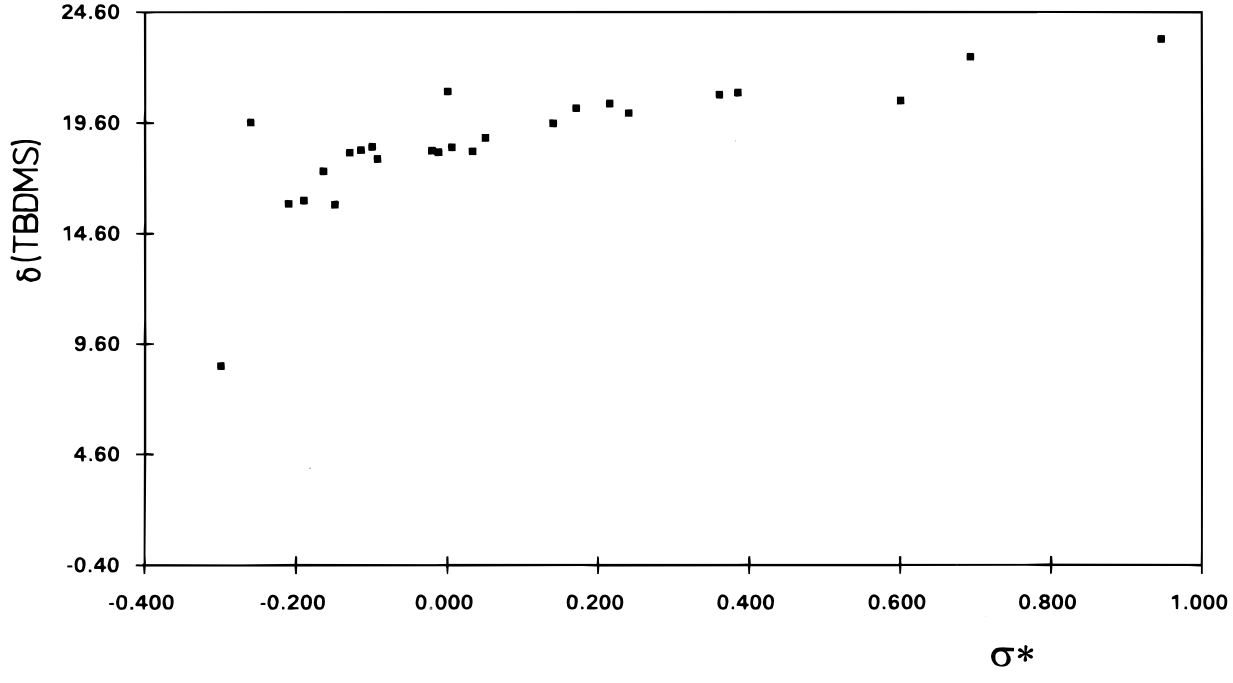

Figure 2. Dependence of δ(TBDMS) on Taft polar σ^* of the R group.

Table 2. *A* and *Q* values for the derivatives studied

Parameter	CH_3	CH_2CH_3	$CH(CH_3)_2$	$C(CH_3)_3$
A (10^4 pm^2)	2.20	0.83	0.50	0.04
Q ($\times 10^3$)	−343.7	−347.9	−351.0	−353.4

can be estimated by the so-called solvent-accessible surface A. For a rough estimate of relative changes in oxygen basicity, we can take the net atomic charge Q on oxygen. Then, the values calculated for the present series of derivatives are given in Table 2.

The solvent-accessible surface A of the oxygen atom in the *tert*-butyl derivative is only 2% of that calculated for the methyl derivative. Accordingly, the hydrogen-bonded complex of this derivative with chloroform, which has a larger chemical shift, is much less populated at equilibrium and hence we observe a lower average chemical shift value than would correspond to polar effects. The negative charge on oxygen is in the *tert*-butyl derivative increased by only 3% relative to the methyl derivative, which is most unlikely to compensate for the large decrease in accessibility. While the presence of the third methyl group makes any association very unlikely, the first two methyl groups reduce the solvent-accessible surface only to 38 and 22% of that in the methyl derivative. This decrease is also, at least partially, compensated by an increase in the negative charge on the oxygen atom. It is interesting that in TMS derivatives[9] the A values do not change as dramatically. While replacing the *tert*-butyl group of TBDMS by a methyl group to form the TMS derivative increases (as expected) A in the methyl derivative ($A = 4.39$) by a factor of 2 in the *tert*-butyl derivative ($A = 1.44$), the increase is 36-fold, so that in the latter compound A is only one third of that in the former compound. Of course, direct electronic effects on the ^{29}Si shielding also contribute to the observed chemical shift. However, in this short series the steric effects appear to determine the trend.

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