# SILICON-29 NMR SPECTRA OF *tert*-BUTYLDIMETHYLSILYL AND TRIMETHYLSILYL DERIVATIVES OF SOME NON-RIGID DIOLS

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$^{29}$Si NMR spectra of trimethylsilyl (TMS) and *tert*-butyldimethylsilyl (TBDMS) derivatives of selected diols were measured under standardized conditions (*i.e.*, in diluted $CDCl_3$ solutions). Application of the recently reported correlation between the chemical shifts in TMS and TBDMS derivatives revealed considerable and systematic deviations which exceeded experimental errors and error estimates from the correlation. Two possible explanations of the deviations are considered: interaction between the two bulky substituent groups and invalidity of the reported correlation for simple hydroxy derivatives. An independent study of analogous derivatives of monohydroxy compounds has shown that the linear correlation holds but the slope and intercept are significantly different from those reported previously on the basis of a study of amino acid derivatives. The data obtained for the diol derivatives fit the new correlation very well and no indication of an interaction between the bulky TBDMS groups was noticed. However, deviations do occur in branched diol derivatives in which branching reduces accessibility of the oxygen atoms surface to associate with proton donors. The largest deviation was found when intramolecular hydrogen bond was formed.

**Key words:** NMR; Silicon-29 NMR; Trimethylsilyl derivatives; *tert*-Butyldimethylsilyl derivatives; Diols.

While trimethylsilylation (TMS) has been extensively used for a number of purposes since 1950's, *tert*-butyldimethylsilyl (TBDMS) group has been introduced by Corey and Venkateswarlu[1] only in 1972. Since then the bulkier and hydrolytically more stable *tert*-butyldimethylsilyl group has become the most popular silicon protecting group in synthetic chemistry[2,3]. Despite that little has been reported on NMR properties of the compounds containing TBDMS group, the data being usually hidden in experimental parts of synthetic publications. Only Ralph[4] has initiated a limited $^{29}$Si NMR study in an attempt to analyze polyhydroxy compounds contained in lignin. The lack of suitable data for comparison has become acute in our study of $^{29}$Si NMR spectra of TBDMS derivatives of amino acids[5], which was supposed to be a useful alternative of $^{29}$Si tagging[6] based on TMS derivatives of amino acids, which proved to be rather unstable[7].

The studies of $^{29}$Si NMR spectra of TMS (ref.[7]) and TBDMS (ref.[5]) derivatives of amino acids produced a surprisingly good correlation ($r$ = 0.999 for 20 data points) between the $^{29}$Si chemical shifts in the two classes of compounds measured under identical standard conditions[6]. The correlation was surprisingly good in the sense that it involved both O- and N-bonded silicon atoms and covered a large chemical shift range from 8.1 to 25.8 ppm (for TBDMS groups). The correlation could be used to predict chemical shifts of *e.g.* TBDMS derivatives from the known shifts in TMS derivatives with an estimated error of 0.11 ppm. Such accuracy suggested that a study of $^{29}$Si NMR spectra of disilylated diols could reveal interactions between the bulky groups as deviations from the correlation. It is the goal of the present work to demonstrate that the correlation could be applied to diol derivatives with no steric interaction between the bulky groups.

## EXPERIMENTAL

TBDMS derivatives of alcohols and diols were prepared by Corey's procedure[1]. A flask was charged successively with dry alcohol (0.4–1.0 g), *tert*-butyldimethylchlorosilane (TBDMSCl, 1.2 mol per 1 mol of OH), imidazole (2.5 mol per 1 mol OH), and dry dimethylformamide (DMF, 1–2 ml). The reaction mixture was stirred at 50–70 °C under dry inert atmosphere for *ca* 1.5–2 h, cooled to room temperature and the product was extracted into dry ether. Pure TBDMS derivative was obtained by fractional distillation.

Two different procedures were used for preparation of TMS derivatives of alcohols.

*A*) Larger scale preparations were performed by refluxing 10–20 g of alcohol with HMDS (hexamethyldisilazane, 1.25 mol per 1 mol OH) until the evolution of ammonia ceased (about 2 days) followed by fractional distillation.

*B*) Small scale derivatizations were carried out by stirring *ca* 0.5 g of alcohol with a silylating reagent (*N,O*-bis(trimethylsilyl)acetamide, BSA, trimethylsilyldiethylamine, TMSDMA, trimethylsilyldimethylamine, TMSDEA, chosen to maximize boiling point difference, 1.3 mol per 1 mol OH) under dry inert gas at 60–80 °C for 2 h. Pure TMS derivatives were isolated by fractional distillation.

NMR spectra were measured in dry $CDCl_3$ 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 ± 0.02, relative to the central line of the solvent at 76.99 ppm (see ref.[6] for the 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 standard software (APT and INEPT pulse sequences). The spectra were recorded in the temperature range 22–24 °C. The $^{29}$Si NMR spectra were measured by the INEPT with the pulse sequence optimized[6] for TMS derivatives, *i.e.*, for coupling to 9 protons and coupling constant of 6.5 Hz. The signal loss in the case of TBDMS derivatives was negligible[8]. Acquisition (1.0 s) was followed by a relaxation delay of 5 s. During the acquisition period WALTZ decoupling was used and FID data (8 K) were sampled for the spectral width of 4 000 Hz. Zero filling to 32 K and a mild exponential broadening were used in the data processing. The $^{29}$Si $\pi/2$ pulses were at the maximum 17 μs long whereas $^{1}$H $\pi/2$ 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 64 K and 1–3 Hz line broadening were used in data processing. The $^{29}$Si lines of diol derivatives were assigned by de-

scribed[8] variants of SPINEPTR (ref.[9]), selective INEPT and selective decoupling[10]. These methods were also used in the determination of the silylation site in a monosilylated diol. Long-range $^{29}Si$-$^{1}H$ coupling constants were determined either from 1D spectra or selective 2D *J*-resolved spectra[10].

The diastereoisomers of butane-2,3-diol and its derivatives were identified by a comparison of the spectra of the mixtures with the spectra of an authentic *R,R* diastereoisomer (Aldrich). All compounds were identified by their $^{1}H$ and $^{13}C$ NMR spectra; the latter being reported here for all compounds studied. For the identification of coupling constants in compounds with two diastereotopic $CH_2$ protons the protons are labelled a and b. The proton a resonates at a lower magnetic field. The two protons differ substantially in their coupling constants.

Solvent accessible surface (*A*) was calculated for oxygen atoms exactly as described previously[12,13].

The isolated compounds and their $^{13}C$ NMR chemical shifts are as follows:

1,10-Bis(trimethylsilyloxy)decane: 62.73 ($CH_2O$); 32.73, 29.56, 29.42, 25.82 ($CH_2$); –0.46 ($CH_3Si$).

1,10-Bis(*tert*-butyldimethylsilyloxy)decane: 63.33 ($CH_2O$); 32.89, 29.59, 29.43, 25.80 ($CH_2$); 25.99 ($CH_3C$); 18.39 (C); –5.25 ($CH_3Si$).

1,5-Bis(trimethylsilyloxy)pentane: 62.58 ($CH_2O$); 32.50, 22.10 ($CH_2$); –0.48 ($CH_3Si$).

1,5-Bis(*tert*-butyldimethylsilyloxy)pentane: 63.21 ($CH_2O$); 32.67, 22.14 ($CH_2$); 25.98 ($CH_3$); 18.37 (C); –5.28 ($CH_3Si$).

1,4-Bis(trimethylsilyloxy)butane: 62.44 ($CH_2O$); 29.10 ($CH_2$); –0.48 ($CH_3Si$).

1,4-Bis(*tert*-butyldimethylsilyloxy)butane: 63.11 ($CH_2O$); 29.33 ($CH_2$); 25.97 ($CH_3$); 18.35 (C); –5.27 ($CH_3Si$).

1,3-Bis(trimethylsilyloxy)propane: 59.17 ($CH_2O$); 35.53 ($CH_2$); –0.51 ($CH_3Si$).

1,3-Bis(*tert*-butyldimethylsilyloxy)propane: 59.68 ($CH_2O$); 35.92 ($CH_2$); 25.94 ($CH_3$); 18.32 (C); –5.35 ($CH_3Si$).

1,2-Bis(trimethylsilyloxy)ethane: 63.88 ($CH_2O$); –0.43 ($CH_3Si$).

1,2-Bis(*tert*-butyldimethylsilyloxy)ethane: 64.66 ($CH_2O$); 25.96 ($CH_3$); 18.42 (C); –5.26 ($CH_3Si$).

1-Butoxy-2-trimethylsilyloxyethane: 72.04, 71.17, 62.05 ($CH_2O$); 31.77, 19.29 ($CH_2$); 13.91 ($CH_3$); –0.41 ($CH_3Si$).

1-Butoxy-2-(*tert*-butyldimethylsilyloxy)ethane: 72.15, 71.19, 62.75 ($CH_2O$); 31.83, 19.27 ($CH_2$); 25.92, 13.91 ($CH_3$); 18.37 (C); –5.26 ($CH_3Si$).

1,2-Bis(trimethylsiloxy)propane: 69.13 (CHO); 68.28 ($CH_2$); 20.41 ($CH_3$); 0.20 ($CH_3Si$); –0.47 ($CH_3Si$).

1,2-Bis(*tert*-butyldimethylsilyloxy)propane: 69.44 (CHO); 69.00 ($CH_2O$); 25.98, 25.89 ($CH_3$); 18.39, 18.20 (C); –4.57, –4.73, –5.27, –5.36 ($CH_3Si$).

1,3-Bis(trimethylsilyloxy)butane: 65.29 (CH); 59.35 ($CH_2$); 42.34 ($CH_2$); 24.03 ($CH_3$); 0.22, –0.50 ($CH_3Si$).

1,3-Bis(*tert*-butyldimethylsilyloxy)butane: 65.50 (CHO); 60.18 ($CH_2O$); 42.82 ($CH_2$); 25.98, 25.93 ($CH_3C$); 24.05 ($CH_3$); 18.29, 18.12 (C); –4.37, –4.80, –5.30 ($CH_3Si$).

(2*R*,3*R*)-2,3-Bis(trimethylsilyloxy)butane: 72.09 (CH); 18.18 ($CH_3$); 0.25 ($CH_3Si$).

(2*R*,3*R*)-2,3-Bis(*tert*-butyldimethylsilyloxy)butane: 71.36 (CH); 25.87 ($CH_3C$); 18.10 ($CH_3$); 18.06 (C); –4.34 ($CH_3Si$).

(2*R*,3*S*)-2,3-Bis(trimethylsilyloxy)butane: 73.04 (CH); 20.05 ($CH_3$); 0.23 ($CH_3Si$).

(2*R*,3*S*)-2,3-Bis(*tert*-butyldimethylsilyloxy)butane: 73.32 (CH); 25.93 ($CH_3C$); 20.17 ($CH_3$); 16.32 (C); –4.62 ($CH_3Si$).

2,4-Bis(trimethylsilyloxy)-2-methylpentane: 73.35 (CHO); 65.90 (CO); 54.09 ($CH_2$); 31.74, 29.63, 25.57 ($CH_3$); 2.64, 0.50 ($CH_3Si$).

2,4-Bis(*tert*-butyldimethylsilyloxy)-2-methylpentane: 73.05 (CO); 66.12 (CH); 54.76 ($CH_2$); 31.76, 29.57 ($CH_3$); 25.97, 25.88 ($CH_3C$); 18.05 (C); –3.82, –4.52 ($CH_3Si$).

4-Trimethylsilyloxy-2-methylpentan-2-ol: 70.25 (CO); 67.77 (CHO); 49.95 ($CH_2$); 31.20, 27.86, 24.75 ($CH_3$); 0.58 ($CH_3Si$).

4-*tert*-Butyldimethylsilyloxy-2-methylpentan-2-ol: 70.30 (CHO); 68.10 (CO); 50.03 ($CH_2$); 31.20, 27.73, 24.96 ($CH_3$); 25.80, 25.56 ($CH_3C$); 17.80 (C); –2.49 ($CH_3Si$).

## RESULTS AND DISCUSSION

The $^{29}Si$ NMR experimental data are summarized in Table I, $^{13}C$ NMR chemical shifts are given in Experimental for each of the compounds studied.

As expected, the $^{29}Si$ chemical shifts of both TMS and TBDMS groups in the derivatives of linear diols reach the values found for the derivatives of simple alcohols as the distance between the two oxygen atoms sufficiently increases. For example, the chemical shifts in TMS and TBDMS derivatives of decane-1,10-diol differ from those in butanol derivatives[13] by +0.03 and +0.08 ppm, respectively. Shortening of the alkyl chain increases these differences (*e.g.*, the maximum shift differences are found[13] between ethanediol and ethanol derivatives, +0.29 and +0.22 ppm, respectively). This trend and the sign of the differences are in agreement with the reported dependence of these shifts upon polar effects[13,14] (electronegative substituents R on the oxygen atom cause deshielding of the silicon atom in the R–O–$SiR'_3$, moiety if the substituents on the silicon atom R′ are alkyl groups) and with the different polar effects of $(CH_3)_3SiO$ groups and hydrogen atoms.

Branching has similar effects on $^{29}Si$ chemical shifts in TMS and TBDMS derivatives, its effects are in agreement with the trends observed for other nuclei, *e.g.*, for $^{13}C$ chemical shifts. Thus, branching at carbon α to the oxygen atom has a larger effect (about –2 ppm) than branching at β position (about –0.5 ppm).

Even for the shortest $–(CH_2)_n–$ chain, substitution on one of the oxygen atoms has little effect on the $^{29}Si$ chemical shift of the silicon atom on the other oxygen atom. This observation follows from comparison of chemical shifts in 1,2-bis(trimethylsilyloxy)ethane (18.52), 1-butoxy-2-trimethylsilyloxyethane (18.56) and 2-trimethylsilyloxy-1-methoxyethane (18.79) (ref.[13]). Violation of this rule will be discussed later in connection with intramolecular hydrogen bond in a monosilylated diol.

The chemical shifts reported here exhibit large deviations from the described[6] correlation between the shifts in the two classes (TMS and TBDMS) of derivatives. These deviations are expressed in Table I as differences Δ between the observed experimental chemical shift and the shifts calculated for the TBDMS derivatives according to the correlation[6]. In most cases (including derivatives of both linear and branched diols), the deviations are about 10 times larger than the error estimate due to the correlation (±0.11 ppm) (ref.[6]) and since they are all negative they suggest some systematic error. In view of the above discussion of the shifts in linear diols fitting the general trends, it seems most probable that the large deviations are due to the correlation employed. This observation

TABLE I
$^{29}$Si NMR chemical shifts (in δ scale, estimated accuracy ±0.02 ppm)

| Compound | Assignment | Experimental | | Calculated for R = TBDMS | | | |
|---|---|---|---|---|---|---|---|
| | | R = TMS | R = TBDMS | as acid[a] | Δ[b] | as alcohol[c] | Δ[d] |
| **Linear diols** | | | | | | | |
| RO–$(CH_2)_{10}$–OR | | 17.03 | 18.35 | 19.55 | –1.20 | 18.28 | 0.07 |
| RO–$(CH_2)_5$–OR | | 17.16 | 18.37 | 19.66 | –1.29 | 18.41 | –0.04 |
| RO–$(CH_2)_4$–OR | | 17.18 | 18.43 | 19.68 | –1.25 | 18.43 | 0.00 |
| RO–$(CH_2)_3$–OR | | 17.43 | 18.67 | 19.89 | –1.22 | 18.68 | –0.01 |
| RO–$(CH_2)_2$–OR | | 18.52 | 19.75 | 20.83 | –1.08 | 19.75 | 0.00 |
| $CH_3(CH_2)_3O$–$(CH_2)_2$–OR | | 18.56 | 19.91 | 20.86 | –0.95 | 19.79 | 0.12 |
| **Branched-chain diols** | | | | | | | |
| RO–$CH_2$–$CH(CH_3)$–OR | $CH_2OR$[e] | 18.00 | 19.23 | 20.38 | –1.15 | 19.24 | –0.01 |
| | CHOR[e] | 16.24 | 17.60 | 18.87 | –1.27 | 17.50 | 0.10 |
| RO–$CH_2$–$CH_2$–$CH(CH_3)$–OR | $CH_2OR$[e] | 17.10 | 18.46 | 19.61 | –1.15 | 18.35 | 0.11 |
| | CHOR[e] | 15.26 | 16.47 | 18.03 | –1.56 | 16.53 | –0.06 |
| (*R*,*R*)-RO–$CH(CH_3)$–$CH(CH_3)$–OR | [f] | 15.53 | 16.59 | 18.26 | –1.67 | 16.80 | –0.21 |
| (*R*,*S*)-RO–$CH(CH_3)$–$CH(CH_3)$–OR | [f] | 16.02 | 16.91 | 18.68 | –1.77 | 17.28 | –0.37 |
| RO–$C(CH_3)_2$–$CH_2CH(CH_3)$OR | COR[e] | 7.37[g] | 9.06[h] | 11.24 | –2.17 | 8.72 | 0.34 |
| | CHOR[e] | 14.34[i] | 15.42[j] | 17.24 | –1.79 | 15.62 | –0.20 |
| | CHOR[e] | 17.55[k] | 19.62[l] | 20.00 | –0.38 | 18.79 | 0.83 |

[a] The value calculated from the equation δ(TBDMS) = 0.8597 δ(TMS) + 4.908 found[5] for amino acid derivatives. [b] The difference Δ = δ(exp) – δ(calc) in ppm, the shift calculated as for acid derivatives. [c] The value calculated from the equation δ(TBDMS) = 0.9899 δ(TMS) + 1.422 found[11] for alcohol derivatives. [d] The difference Δ = δ(exp) – δ(calc) in ppm, the shift calculated as for alcohol derivatives. [e] Assignment. [f] Configuration of the compound. [g] Coupling $^4J(^{29}Si\text{-}C^1H_2a)$ = 0.6 Hz. [h] Coupling $^4J(^{29}Si\text{-}C^1H_2a)$ < 0.5 Hz. [i] Couplings $^4J(^{29}Si\text{-}C^1H_2b)$ = 0.5 Hz; $^3J(^{29}Si\text{-}C^1H)$ = 3.05 Hz. [j] Coupling $^3J(^{29}Si\text{-}C^1H)$ = 2.2 Hz, $^4J(^{29}Si\text{-}C^1H_2)$ not observable. [k] Coupling $^4J(^{29}Si\text{-}C^1H_2b)$ = 1.6 Hz, $^3J(^{29}Si\text{-}C^1H)$ = 1.9 Hz. [i] Coupling $^3J(^{29}Si\text{-}C^1H)$ = 1.7 Hz, $^4J(^{29}Si\text{-}C^1H_2b)$ = 1.2 Hz, $^4J(^{29}Si\text{-}C^1H_2a)$ not observable.

has triggered an independent study of TMS and TBDMS derivatives of simple alcohols which is reported elswhere[13]. The study of derivatives of 24 alcohols yielded correlation

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

(with correlation coefficient 0.998 and error estimate ±0.19 ppm) which is significantly different (on 90% significance level) from the correlation reported earlier for amino acid derivatives[6]. The chemical shifts predicted according to this correlation and their differences from the experimental values are given in the last two columns of Table I.

Obviously, the differences are within the expected error of estimate for all the linear and some of the branched diol derivatives. Larger differences are found only in the last 5 rows of Table I which comprise the most branched compounds studied here. Similar negative differences are, however, noticed in the source correlation[13] for branched compounds like *tert*-butyl alcohol derivatives. Negative differences (*i.e.*, the calculated shifts being larger than the experimental ones) are probably due to steric hindrance to association with the proton of the solvent. As described previously[11,12] such an association leads to higher chemical shift values. The different association capabilities of TMS and TBDMS derivatives are well ilustrated in Fig. 1 for association of 2-methylpentane-2,4-diol derivatives with phenol. The derived association constants ($K$ in mol dm$^{-3}$) roughly follow the order in solvent accessible surface ($A$ in $10^4$ pm$^2$) of the corresponding oxygen atoms. In TMS and TBDMS derivatives the $K$(CHOSi) values are 2.5 and 0.5, respectively, while the respective $A$(CHOSi) values are 0.6 and 0.1 and $K$(COSi) ones are 2.0 and 0.4, while the surfaces $A$(COSi) values are 0.1, and 0.0.

The large positive deviation in the monosilyl derivatives (the last line in Table I) is caused by intramolecular hydrogen bonds in these compounds as illustrated by (i) limited asso-

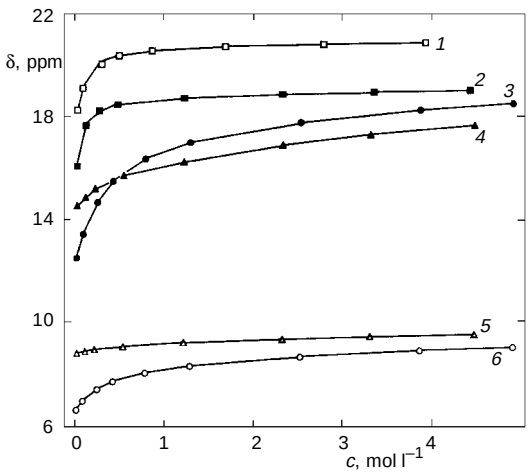
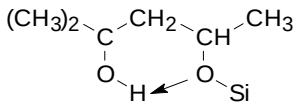



FIG. 1
Dependence of $^{29}$Si chemical shift δ (ppm) on the concentration $c$ (mol l$^{-1}$) of phenol added to carbon tetrachloride solutions of 4-*tert*-butyldimethylsiloxy-2-methylpentan-2-ol (*1*), 4-trimethylsilyloxy-2-methylpentan-2-ol (*2*), 2,4-bis(trimethylsilyloxy)-2-methylpentane (CHOSi *3*, COSi *6*), 2,4-bis-(*tert*-butyldimethylsilyloxy)-2-methylpentane (CHOSi *4*, COSi *5*)

ciation of both mono-TMS and mono-TBDMS derivatives with phenol (Fig. 1) and (ii) large downfield shifts of both TMS and TBDMS monosilyl derivatives relative to their disilyl counterparts (despite the insensitivity of the shifts to substitution on the other oxygen atom as discussed above). The calculated solvent accessible surface is 0.6 and 0.1 for the oxygen atom in the CH–O–Si moieties in these two compounds. The compounds can form a six-membered ring through the hydrogen bond formation. Since the hydroxy proton is much more acidic than the proton of chloroform, this hydrogen bond is stronger and shifts the $^{29}$Si resonance downfield more than the association with chloroform in the model compounds from which the correlation was derived. Hence, we observe the large positive differences between the experimental and calculated shifts.




The large shift due to intramolecular hydrogen bond observed in this case brings an important warning. In analyses of complicated mixtures of polyfunctional compounds utilizing $^{29}$Si NMR tagging technique in which the spectral lines can be assigned only by comparison with the tabulated chemical shifts the assignment can be in error if similar association (not necessarily intramolecular) occur due to *e.g.* incomplete silylation.

Summarizing – the correlation between (TMS) and (TBDMS) gives good prediction for the $^{29}$Si chemical shifts in the latter derivatives. The deviation exceeding the error of the estimate may indicate specific interactions.

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