# SILICON-29 NMR SPECTRA OF TRIMETHYLSILYLATED ALCOHOLS

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<sup>29</sup>Si NMR spectra of trimethylsilyl (TMS) derivatives of 26 simple alcohols were measured under standardized conditions (*i.e.*, in sufficiently diluted deuteriochloroform solutions). Due to association with the solvent the chemical shifts are in almost all cases larger than those reported earlier for different solutions. This observation is in agreement with the proposed mechanism of steric effects as being due to sterically controlled association with the solvent. The use of chloroform as a solvent enhances steric effects but at the same time it can reduce small differences due to polar effects in closely related compounds. In the studied class of compounds the gross dependence of the chemical shift on polar effects is not substantially affected by the change of the solvent.

Key words: <sup>29</sup>Si NMR; Trimethylsilyl derivatives; Alcohols; Polar effects; Steric effects.

Studies of <sup>29</sup>Si NMR spectra of trimethylsilyl<sup>1</sup> (TMS) and *tert*-butyldimethylsilyl<sup>2</sup> (TBDMS) derivatives of amino acids produced excellent correlation (r = 0.999 for 20 data points) between the <sup>29</sup>Si chemical shifts in the two classes of compounds measured under identical conditions<sup>3</sup>. The correlation was surprisingly good in the sense that it involved both O- and N-bonded silicon atoms and covered a large range of the chemical shifts ( $\delta$ (TBDMS) 8.1 to 25.8 ppm). Application of this correlation to chemical shifts in disilyl derivatives of diols showed, however, large deviations even in cases where no interaction between the two bulky groups was possible<sup>4</sup>. In order to find the cause of these deviations, we decided to remeasure chemical shifts of TMS derivatives of simple alcohols under the conditions (diluted deuteriochlorofom solutions) now considered standard. Similar reinvestigation of TMS derivatives of several adamantanols<sup>5</sup> and steroid alcohols<sup>6</sup> has allowed simple interpretation of the results in terms of sterically controlled association with the solvent. In the present paper we report <sup>29</sup>Si chemical shifts of TMS derivatives of simple alcohols (and phenol) and compare them with the values reported earlier under not so well defined experimental conditions.

### EXPERIMENTAL

Two different procedures were used for preparation of TMS derivatives of alcohols. (1) Larger-scale preparations were performed by refluxing 10–20 g of alcohol with hexamethyldisilazane (HMDS,

1.25 mol per 1 mol OH) until evolution of ammonia ceased (about 2 days) followed by fractional distillation. (2) Small-scale derivatizations were carried out by stirring *ca* 0.5 g of alcohol with sily-lating reagent (bis(trimethylsilyl)acetamide, BSA, *N*-(trimethylsilyl)dimethylamine, TMSDMA, and *N*-(trimethylsilyl)diethylamine, TMSDEA, chosen to maximize boiling point differences (1.3 mol per 1 mol OH) under dry nitrogen at 60–80 °C for 2 h. Pure TMS derivatives were isolated by fractional distillation.

The NMR spectra were measured in dry deuteriochlorofom 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 <sup>13</sup>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.<sup>3</sup> 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 <sup>13</sup>C and at 39.7 MHz for <sup>29</sup>Si NMR measurements), using the standard software (APT and INEPT pulse sequences) *vnmr* 3.2. The spectra were recorded in the temperature range 22–24 °C. The <sup>29</sup>Si NMR spectra were measured by the INEPT with the pulse sequence optimized<sup>3</sup> for TMS derivatives, *i.e.*, for coupling to 9 protons and coupling constant of 6.5 Hz. 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 <sup>29</sup>Si  $\pi/2$  pulses were at maximum 17 µs long whereas <sup>1</sup>H  $\pi/2$  were 10 µs in a 5 mm switchable probe. The <sup>29</sup>Si spectra were referenced to the line of HMDSS at  $\delta = -19.79$ . The <sup>13</sup>C NMR spectra were measured using the 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.

Solvent accessible surface (A) was calculated for oxygen atoms and probe diameter of 100 pm exactly as described previously<sup>6</sup> for A (10) and geometry optimization.

#### **RESULTS AND DISCUSSION**

The <sup>29</sup>Si NMR experimental results are summarized in Table I. As Figs 1 and 2 illustrate, the already discussed<sup>7</sup> dependences of the chemical shift on Taft polar  $\sigma^*$  constants of substituents R and on the atomic charges on the silicon atoms, Q(Si), are not substantially affected by the change in the experimental conditions.

With the single exception of the phenol derivative (which is more complex because of additional effects due to magnetic anisotropy and formation of CT complex with chloroform), all the <sup>29</sup>Si chemical shifts measured under standard conditions (*i.e.*, new data) are larger than those reported earlier which were measured essentially in neat liquids. The difference by far exceeds the estimated errors of the measurements (estimated previously<sup>7</sup> to be  $\pm 0.3$  ppm and  $\pm 0.02$  ppm here)\*. This finding is in full agreement with our earlier observations on adamantanol<sup>5</sup> and steroid alcohol<sup>6</sup> derivatives and

<sup>\*</sup> The difference observed for hexamethyldisiloxane deserves special attention. This compounds is still sometimes used as a reference despite the fact that already the compilation of Marsmann<sup>8</sup> listed for it a number of chemical shift values ranging from 4.0 to 7.2. Obviously, this chemical shift is subject to a number of influences (concentration, solvent, and temperature) and the compound should not be used as a secondary reference.

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TABLE I

<sup>29</sup>Si chemical shifts,  $\delta$ , in trimethylsilylated alcohols R–O–Si(CH<sub>3</sub>)<sub>3</sub>, Taft polar  $\sigma^*$  constants of substituent R and net atomic charges on the silicon atom, Q(Si)

R	δ( <sup>29</sup> Si)			$\sigma^{*^a}$	$O(Si) . 10^{3a}$
	old <sup>a</sup>	new	new - old		~~ /
CH <sub>3</sub>	17.20	19.64	2.44	0.000	229.39
CH <sub>3</sub> CH <sub>2</sub>	14.53	17.09	2.56	-0.100	229.12
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	13.80	17.06	3.26	-0.115	229.10
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	14.00	17.00	3.00	-0.130	229.10
(CH <sub>3</sub> ) <sub>2</sub> CH	12.12	14.71	2.59	-0.190	228.91
c-C <sub>6</sub> H <sub>11</sub>	12.70	14.57	1.87	-0.150	_
(CH <sub>3</sub> ) <sub>3</sub> C	6.20	7.62	1.42	-0.300	228.75
$Cl(CH_2)_2$	18.36	19.81	1.45	0.385	229.46
Cl(CH <sub>2</sub> ) <sub>3</sub>	16.70	18.36	1.66	0.140	229.15
Cl(CH <sub>2</sub> ) <sub>4</sub>	16.10	17.61	1.51	0.050	229.10
Cl(CH <sub>2</sub> ) <sub>6</sub>	14.30	17.27	2.97	0.006	229.10
Cl <sub>2</sub> CHCH <sub>2</sub>	20.65	21.55	0.90	0.693	229.77
CCl <sub>3</sub> CH <sub>2</sub>	21.75	22.73	0.98	0.946	230.04
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	17.40	19.08	1.68	0.215	_
CH2=CHCH2	16.59	18.90	2.31	0.170	_
BrCH <sub>2</sub> CH <sub>2</sub>	18.29	19.70	1.41	0.360	229.50
CH <sub>3</sub> CH <sub>2</sub> (CH <sub>3</sub> )CH	-	14.78	-	-0.210	_
H <sub>3</sub> CO(CH <sub>2</sub> ) <sub>2</sub>	16.25	18.74	2.49	0.240	229.25
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub>	14.10	16.37	2.27	-0.165	229.08
$(CH_3)_3C(CH_2)_2$	15.60	17.16	1.56	-0.059	229.10
(CH <sub>3</sub> ) <sub>3</sub> Si	6.83	7.34	0.51	-0.810	228.76
(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub>	16.10	18.40	2.30	-0.260	229.88
(CH <sub>3</sub> ) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub>	13.10	16.32	3.22	-0.093	229.18
(CH <sub>3</sub> ) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub>	-	16.97	-	0.033	229.11
$(CH_3)_3Si(CH_2)_4$	13.90	17.02	3.12	-0.012	229.10
C <sub>6</sub> H <sub>5</sub>	19.62	19.43	-0.19	0.600	-

<sup>*a*</sup> Values taken from ref.<sup>7</sup>.

with the theory proposed. In detail, however, the picture is more complex owing to larger variability of the structure of compounds studied here.

The observed chemical shift is a weighted average of the chemical shifts in the free compound and in its associate complex with chloroform. The chemical shift  $\delta$  in the complex is larger than that in the free compound. The populations of the complex and







Fig. 2

<sup>29</sup>Si chemical shift dependences on the net atomic charge on the silicon atom Q(Si) for new ( $\bullet$ ) and old ( $\bigcirc$ ) data

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the free compound are given by the concentration and association constant which we take as proportional to the basicity of oxygen atom and its surface accessible for association with the solvent. In a series of closely related alcohol derivatives, one could assume that either the oxygen basicity does not vary appreciably (*e.g.*, in secondary steroid alcohols<sup>6</sup>) or that it can be approximated by atomic net charge Q(O) on the oxygen atom. Thus, in the series methyl, ethyl, isopropyl, and *tert*-butyl derivatives the solvent-accessible surface A decreases as intuitively expected in the series 4.39, 3.20, 1.94, and 1.44 ( $10^4 \text{ pm}^2$ ), respectively, while the net charge on the oxygen atom becomes more negative in the series -0.33843, -0.34259, -0.34571, and -0.34814 e, respectively. Obviously, in this short series, the solvent mediated steric effects are, at least partially, compensated by the increase in the basicity of oxygen. The large changes in the chemical shifts when going from primary to secondary, and further to tertiary alcohol derivatives appear to be governed by the charge on the silicon atom (Fig. 2).

These results point to a drawback of using the standard conditions. When inductive effects increase the basicity of oxygen and at the same time, decrease the positive charge on the silicon atom, association with chlorofom decreases the overall sensitivity of <sup>29</sup>Si chemical shifts to such inductive effects.

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