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 **$^{29}\text{Si}$  AND  $^{13}\text{C}$  NMR SPECTRA OF SOME SUBSTITUTED  
BIS(TRIMETHYLSILOXY)BENZENES**Jan SCHRAML<sup>a</sup>, Robert BREŽNÝ<sup>b</sup>, Jan ČERMÁK<sup>a</sup> and Václav CHVALOVSKÝ<sup>a</sup><sup>a</sup> *Institute of Chemical Process Fundamentals,**Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát and*<sup>b</sup> *Faculty of Chemical Technology, Slovak Technical University, 812 37 Bratislava*

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NMR spectra of a few 4-substituted 1,2-bis(trimethylsiloxy)benzenes and positional isomers of bis(trimethylsiloxy)benzene were measured under standard conditions that approach those of infinite dilution. Under these conditions somewhat smaller values of steric or proximity deshielding effects on  $^{29}\text{Si}$  chemical shifts are found but the trends established earlier are confirmed; the deshielding effect of the "second" *ortho* positioned trimethylsiloxy group in a tris(trimethylsiloxy)benzene derivative on  $^{29}\text{Si}$  chemical shift is somewhat smaller. Also, overcrowding of three trimethylsiloxy groups probably drives the outer groups to assume, at least for a part of their time, coplanar conformation which is not encountered in bis(trimethylsiloxy)-derivatives. The sensitivity of  $^{29}\text{Si}$  chemical shifts to *para* substitution is in 1,2-bis(trimethylsiloxy)benzenes equal to that in 2-methoxytrimethylsiloxybenzenes.

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In connection with our studies of *ortho* substituted trimethylsiloxybenzenes<sup>1</sup> we have investigated a series of 4-substituted 2-methoxytrimethylsiloxybenzenes<sup>2</sup> which model structures encountered in important applications of  $^{29}\text{Si}$  NMR to analysis of lignins<sup>3-5</sup>. The results of these studies lead to the conclusion that the trimethylsiloxy (TMSO) group is for most of its time in a conformation in which the O—Si bond is perpendicular to the benzene ring plane and the *ortho* positioned methoxy group is in a coplanar conformation with the methyl group turned away from the TMSO group. These findings were later confirmed in a study of 2,6-dimethoxytrimethylsiloxybenzenes<sup>6</sup> in which the two *ortho* positioned methoxy groups do not allow the TMSO group to assume coplanar conformation. Proximity deshielding effects that were observed both in  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR spectra of these compounds could be explained by an interaction of the oxygen atom of the TMSO group with the unshared electrons of the *ortho* substituent(s).

Since this conformational behavior of TMSO groups on benzene ring is so markedly different from that of methoxy groups deduced by the same means<sup>7-11</sup> from the  $^{13}\text{C}$  NMR spectra of methoxybenzenes, we have undertaken the present limited study of several derivatives of bis(trimethylsiloxy)benzenes with the aim to establish whether the TMSO groups behave in these compounds as they do in mono

trimethylsilyloxybenzenes or whether they behave more like the methoxy groups in polymethoxybenzenes<sup>7-11</sup>.

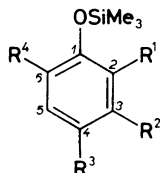
### EXPERIMENTAL

The parent compounds for trimethylsilylation were of commercial origin except for 1,2-dihydroxy-4-methylbenzene and 3,4-dihydroxyacetophenon. The former compound was prepared from vanilin in two steps. Thus, vanilin was demethylated by aluminium chloride in dichloromethane<sup>12</sup> to yield 3,4-dihydroxybenzaldehyde, which was then reduced by catalytic hydrogenation in methanol over palladium on charcoal by a standard procedure. 3,4-Dihydroxyacetophenon was prepared by reaction of 1,2-dihydroxybenzene with acetic acid in polyphosphoric acid in a way described by Nakazawa<sup>13</sup>. Trimethylsilylation, product purification and spectral measurements were carried out exactly as described previously<sup>2</sup>. For convenience the most significant features of NMR measurements are briefly repeated here: the samples were dissolved in deuteriochloroform containing 2% of hexamethyldisilane (HMDSS). The <sup>13</sup>C NMR spectra were referenced to the central line of the solvent ( $\delta = 76.99$ ) and the samples were diluted by this solvent until <sup>13</sup>C chemical shift of HMDSS reached the value  $\delta = -2.48 \pm 0.02$ . The <sup>29</sup>Si NMR spectra were referenced to the line of HMDSS ( $\delta = -19.79$ ).

The chemical shifts of the aromatic carbons were also calculated according to the direct additivity rule using the substituent-induced chemical shift (SCS) values derived for the TMSO group earlier<sup>2</sup> and the SCS values of the other substituents measured under comparable conditions<sup>14</sup>.

### RESULTS AND DISCUSSION

Table I summarizes the experimental results for compounds *I*–*VIII*.



Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
<i>I</i>	H	H	H	H
<i>II</i>	TMSO	H	H	H
<i>III</i>	H	TMSO	H	H
<i>IV</i>	H	H	TMSO	H
<i>V</i>	TMSO	H	Me	H
<i>VI</i>	TMSO	H	CO-TMSO	H
<i>VII</i>	TMSO	H	CO-Me	H
<i>VIII</i>	TMSO	H	CO-TMSO	TMSO

The NMR based arguments for coplanar conformation of methoxy groups in methoxybenzenes rest essentially on systematic and consistent deviations,  $\Delta$ , of experi-

TABLE I  
 $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR chemical shifts<sup>a</sup> in compounds I–VIII

Compound	$^{29}\text{Si}$	$^{13}\text{C}$						
		C-1	C-2	C-3	C-4	C-5	C-6	MeSi
I	19.29	155.16	120.07	129.39	121.41	129.39	120.07	0.17
II	20.26	146.58 (-0.34)	146.58 (-0.34)	121.11 <sup>b</sup> (-0.04)	121.80 <sup>b</sup> (-0.69)	121.80 <sup>b</sup> (-0.69)	121.11 <sup>b</sup> (-0.04)	0.32
III	19.50	156.12	112.25	156.12	113.46	135.43	113.46	0.19
IV	19.12	149.39	120.53	120.53	149.39	120.53	120.53	0.15
V	19.94 <sup>c</sup>	144.13 (0.26)	146.13 (-0.70)	121.86 (0.02)	131.34 (-0.73)	122.21 (-0.97)	120.67 (-0.39)	0.34 <sup>c</sup>
VI	21.69 <sup>d</sup>	151.25 (-0.09)	146.29 (-0.54)	122.70 (0.38)	123.94 <sup>e</sup> (-0.69)	124.57 (-0.91)	120.34 (-0.72)	0.30 <sup>f</sup>
VII	21.91 <sup>g</sup>	151.52 (-0.07)	146.56 (-0.27)	120.83 <sup>b</sup> (-0.47)	131.54 (0.36)	123.24 <sup>b</sup> (0.60)	120.32 <sup>b</sup> (-0.74)	0.30 <sup>c</sup>
VIII	22.45 <sup>f</sup>	143.48 (0.47)	147.55 (0.18)	115.75 (-0.05)	123.69 (-1.33 <sup>e</sup> )	115.75 (-0.58)	147.55 (0.36) <sup>j</sup>	0.64 <sup>i</sup>

<sup>a</sup> Chemical shifts in  $\delta$  – scale, approximate error  $\pm 0.02$  ppm. Lines in parentheses give deviations,  $\Delta$ , of experimental values  $\delta_{\text{exp}}$  from the shifts calculated according to the additivity rule,  $\Delta = \delta_{\text{exp}} - \delta_{\text{calc}}$ . <sup>b</sup> Assignments in the row can be interchanged. <sup>c</sup> Accidentally single line. <sup>d</sup> Other lines  $\delta(\text{Si-2}) = 21.32$  and  $\delta(\text{SiOOC}) = 24.06$ , assigned according to ref.<sup>15</sup>. <sup>e</sup> Possibly in error due to an impurity. <sup>f</sup> Other line with lower intensity at  $\delta = -0.15$  is due to ester group, ref.<sup>15</sup>. <sup>g</sup> Assignment uncertain, the other line at  $\delta = 21.53$ . <sup>h</sup> Other lines at  $\delta(\text{Si-2,6}) = 21.25$  and  $\delta(\text{SiOOC}) = 23.97$  assigned according to ref.<sup>15</sup>. <sup>i</sup> Other lines at  $\delta = 0.26(2)$  and  $-0.21$ . <sup>j</sup> The values of  $\delta_{\text{calc}}$  used for evaluation  $\Delta$  were calculated from the chemical shifts in the compound VI and SCS values of TMSO group.

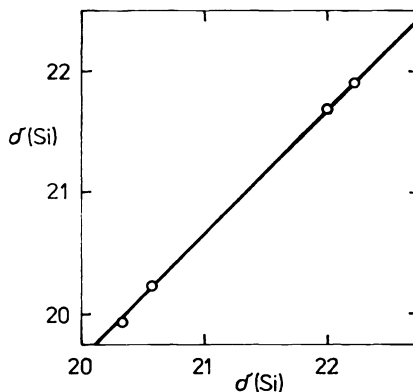


FIG. 1  
 Correlation of  $\delta(^{29}\text{Si})$  in 4-substituted 2,3-bis(trimethylsiloxy)benzenes vs  $\delta(^{29}\text{Si})$  in 4-substituted 1-methoxytrimethylsiloxybenzenes<sup>2</sup>

mental aromatic carbon chemical shifts from the shifts predicted according to the direct additivity of substituent effects. Chemical shifts of aromatic *ortho* carbons *cis* to the methyl group are smaller and those that are *trans* (refs<sup>7-11</sup>) are larger than the calculated values. In the derivatives with two *ortho* positioned trimethylsiloxy groups (i.e. in compounds *II*, *V*, *VI* and *VII*) we do not find such trends for C-1 and C-3 aromatic carbons (i.e. positive  $\Delta$  for C-1 and negative for C-3). However, deviations found for carbons C-1 and C-5 which are *ortho* to TMSO group in the compound *VIII* have such signs. Perhaps, overcrowding in this compound turns the two outer TMSO groups toward the benzene plane.

The proximity deshielding effects on <sup>29</sup>Si and <sup>13</sup>C chemical shifts of TMSO group in benzene derivatives were first reported for *ortho* substitution by TMSO group<sup>16</sup>; later, this effect was found<sup>1</sup> to be a general feature of *ortho* substituents containing unshared electrons. The reported values<sup>1,16</sup> were, however, obtained from concentrated solutions. The present data, which approximate infinite dilution shifts in deuteriochloroform, yield values of the proximity deshielding effects of TMSO group that are for <sup>29</sup>Si chemical shifts somewhat smaller (1.1 ppm, as the average of the difference between the shifts in *II* and *IV* and in *II* and *I*) and for <sup>13</sup>C chemical shift essentially the same (0.16 ppm) as the values found in the concentrated solutions<sup>16</sup> for this group. Analogous comparison of the chemical shifts in compounds *VIII* and *VI* provides estimates of the proximity effects of the "second" *ortho* TMSO group. The effects are also deshielding (0.8 and 0.3 ppm for <sup>29</sup>Si and <sup>13</sup>C chemical shifts, respectively) but according to their relative magnitude we cannot exclude the possibility of a contribution from an interaction of terminal methyl groups that was not observed in mono *ortho* substituted trimethylsiloxybenzenes<sup>1,2,16</sup>.

Though the available data are limited, it is apparent from Fig. 1 that the <sup>29</sup>Si chemical shifts in 4-substituted 1,2-bis(trimethylsiloxy)benzenes and in the corresponding 2-methoxytrimethylsiloxybenzenes exhibit approximately the same sensitivity to substitution.

#### REFERENCES

1. Schraml J., Chvalovský V., Jancke H., Koehler P., Larin M. F., Pestunovich V. A., Voronkov M. G.: Collect. Czech. Chem. Commun. 55, 2019 (1990).
2. Schraml J., Kvičalová M., Chvalovský V., Elder T., Brežný R.: Magn. Reson. Chem., in press.
3. Brežný R., Schraml J.: Holzforschung 41, 283 (1987).
4. Brežný R., Schraml J., Kvičalová M., Zelený J., Chvalovský V.: Holzforschung 39, 297 (1985).
5. Brežný R., Schraml J., Čermák J., Micko M. M., Paszner L.: Tappi, in press.
6. Schraml J., Brežný R., Čermák J.: Collect. Czech. Chem. Commun. 55, 2027 (1990).
7. Dhami K. S., Stothers J. B.: Can. J. Chem. 44, 2855 (1966).
8. Jardon P. W., Vickery E. H., Pahler L. F., Pouramady N., Mains G. J., Eisenbraun E. J.: J. Org. Chem. 49, 2130 (1984).
9. Fujita M., Yamada M., Nakajima S., Kawai K., Nagai M.: Chem. Pharm. Bull. 32, 2622 (1984).

10. Biekofsky R. R., Pomilio A. B., Contreras R. H., de Kowalevski D. G., Facelli J. C.: *Magn. Reson. Chem.* 27, 158 (1989).
11. Wysocki M. A., Jardon P. W., Mains G. J., Eisenbraun E. J., Boykin D. W.: *Magn. Reson. Chem.* 25, 331 (1987).
12. Prager R. H., Tan Y. T.: *Tetrahedron Lett.* 1967, 3661.
13. Nakazawa K.: *J. Pharmacol. Soc. Jpn.* 74, 836 (1954).
14. Bromilow J., Brownlee R. T. C., Craik D. J., Sadek M.: *Mag. Reson. Chem.* 24, 862 (1986).
15. Schraml J., Past J., Puskar J., Pehk T., Lippmaa E., Brežný R.: *Collect. Czech. Chem. Commun.* 52, 1985 (1987).
16. Schraml J., Chvalovský V., Jancke H., Engelhardt G.: *Org. Magn. Reson.* 9, 237 (1977).

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