

PROXIMITY AND CONFORMATION EFFECTS IN ^{29}Si AND ^{13}C NMR SPECTRA OF Di-*Ortho* SUBSTITUTED TRIMETHYLSILOXYBENZENES

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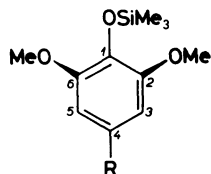
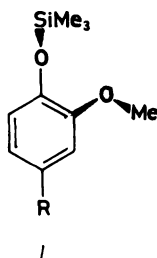
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^{29}Si and ^{13}C NMR spectra of five 4-substituted 2,6-dimethoxytrimethylsilyloxybenzenes were studied with the aim to elucidate the nature of the deshielding proximity effects observed in the spectra of *ortho* substituted trimethylsilyloxybenzenes. The sensitivity of ^{29}Si chemical shifts to *para* substitution is in the studied compounds essentially the same as in mono *ortho* methoxytrimethylsilyloxybenzenes. The deshielding proximity effect of the "second" methoxy group is somewhat smaller than that of the "first" group. The present results indicate that the two methoxy groups assume coplanar conformations with the benzene ring and are turned away from the trimethylsilyloxy group which is not in the benzene plane. It is argued that in mono *ortho* methoxytrimethylsilyloxybenzenes the two substituent groups adopt the same conformations as in the compounds studied here.

In our recent studies of substituted trimethylsilyloxybenzenes¹⁻³ and *o*-methoxytrimethylsilyloxybenzenes³ we have suggested that the trimethylsilyloxy group takes preferentially a perpendicular conformation in which the O—Si bond is perpendicular to the plane of the benzene ring while the *ortho* positioned methoxy group assumes planar conformation with the methyl group turned away from the trimethylsilyloxy group.



// a, R = H

// b, R = Me

// c, R = CHO

// d, R = COOSiMe₃

// e, R = CH₂OSiMe₃

Me = CH₃

The arguments in support of this suggestion came from the substituent-induced chemical shifts (SCS) of aromatic carbons and methoxyl carbon chemical shift. The suggested conformations are also in agreement with the results of model CNDO/2 and MNDO calculations⁴, with the deshielding proximity effects observed on ¹³C and ²⁹Si chemical shifts in methoxy and trimethylsiloxy groups, respectively, and with very small effects observed on methyl groups of the trimethylsilyl group.

As a further test of these suggestions we have followed the example set by studies of methoxybenzenes⁵⁻⁷ and investigated NMR spectra of a few di-*ortho* substituted trimethylsiloxybenzenes, namely 4-substituted 2,6-dimethoxytrimethylsiloxybenzenes (*Ila-Ile*) in which the spatial bulkiness excludes possibility of coplanar conformation for the O—Si bond.

The results of this investigation are reported here.

EXPERIMENTAL

Sample Preparation

The studied trimethylsiloxy benzenes were prepared by trimethylsilylation of the corresponding substituted 2,6-dimethoxyphenols. Syringol (precursor to *Ila*) was a commercial product, syringal (precursor to *Ila*) was a commercial product, syringaldehyde (prec. *Ilc*) was prepared from vanillin (4-hydroxy-3-methoxy-benzaldehyde) according to Pepper et al.⁸. Precursors of *Ilb*, *Ild* and *Ile* were prepared from syringaldehyde by reduction or oxidation according to common procedures compiled by Zakis⁹.

The phenols were trimethylsilylated by bis(trimethylsilyl)acetamide (BSA) in 200% stoichiometric excess (in some cases in the presence of catalytic amounts of trimethylchlorosilane). The reaction mixture was kept shaking at 45–70°C for 10–60 min. Afterward the excess of silylation reagent and by-products were distilled off in vacuum (1.3–2.0 kPa, 50–80°C).

The trimethylsilylated products (20–50 mg) were dissolved in deuteriochloroform (0.7–1.2 ml) containing 2% (v/v) of hexamethyldisilane (HMDSS). The identity and purity of the samples were checked by ¹³C NMR spectroscopy and the chemical shift of HMDSS in the solution was determined. If the ¹³C chemical shift of HMDSS was smaller than $\delta = -2.50$ the sample was diluted until this chemical shift was $\delta = -2.48 \pm 0.02$. Under such conditions the ²⁹Si chemical shifts sufficiently closely approximate infinite dilution shifts.

NMR Measurements

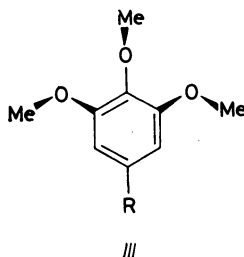
All the NMR spectra reported here were measured on a Varian XL-200 spectrometer operating at 39.7 and 50.3 MHz for ²⁹Si and ¹³C NMR, respectively. The spectrometer frequencies were locked to the deuterium signal of the solvent, the probe temperature was 23–25°C. ¹³C NMR spectra were measured using simple one pulse sequence (40° pulse flip angle, 1.0 s acquisition time, 1.0 s relaxation delay), spectral width of 16 kHz and 32 K memory for FID. The spectra were referenced to the central line of the solvent ($\delta = 76.99$). For the line assignment purposes also edited spectra were measured by APT pulse sequence¹⁰. The lines were assigned to aromatic carbon atoms on the basis of line intensity, APT spectra and known substituent effects¹¹. ²⁹Si NMR spectra were measured by the earlier described¹² variant of INEPT polarization transfer¹³ using acquisition time of 1.0 s, spectral width 4 kHz and 16 K of memory for FID.

with zero filling. The chemical shifts are given in the δ scale (relative to tetramethylsilane, TMS) through the use of a secondary reference (the line of HMDSS at $\delta = -19.79$).

The spectra of *IId* were assigned exactly by selective heteronuclear INADEQATE method¹⁴ in a different solution.

RESULTS AND DISCUSSION

The experimental results for compounds *IId*–*IIf* are summarized in Table I. The chemical shifts of methoxyl carbons around $\delta = 55.8$ indicate coplanar conformation of the methoxy groups in which the carbon atoms lie most of their time in the plane of the benzene ring; methoxy groups in perpendicular conformations have chemical shifts by 4–8 ppm larger^{5,7,15,16}. Substitution of the hydrogen atom at the C-6 position in 4-substituted 2-methoxytrimethylsiloxybenzenes *I* to form the corresponding compounds *II* causes $+0.44 \pm 0.03$ ppm downfield shift of the methoxyl carbon line, independently of the nature of the substituent R at C-4. This deshielding effect is about three times larger than the effect of similar *meta* substitution in methoxybenzene¹⁷ but it is somewhat smaller than the $+0.57$ ppm effect seen for analogous substitution in *ortho*-dimethoxybenzene to form 1,2,3-trimethoxybenzene⁶. In solution, the last mentioned compound takes predominately the form described by the formula¹⁸ *III*.



with the outer methoxy groups in coplanar conformations and both turned away from the central methoxy group which assumes the perpendicular conformation; their ¹³C chemical shifts being $\delta = 55.8$ and 59.9 , respectively⁶.

Extending the validity of correlation between methoxyl carbon chemical shift and substituent parameters that holds for *ortho* substituted methoxybenzenes¹⁹ we estimate that replacing the central methoxy group in *III* by trimethylsiloxy group can change the chemical shift of the outer methoxyl carbons by -0.1 ppm at maximum, i.e. to $\delta = 55.7$. The experimental value, $\delta = 55.87$, is in good agreement with the prediction and so it confirms the assumption that the compounds *II* and *III* have analogous conformations.

Further support to the proposed conformation of methoxy groups comes from asymmetry of substituent-induced chemical shifts (SCS) of aromatic carbons. Sub-

tracting from the chemical shifts of aromatic C-1 and C-5 carbons of *II* the corresponding shifts in compounds *I* with the same substituent R we get the SCS values for *ortho* positions due to the „second” methoxy group. In all five compounds both SCS values are negative but the substituent shift at C-5 position is 4–7 ppm larger than that at C-1. This is again in agreement with the proposed conformations and with the observation that aromatic carbons in *syn* position to the methyl group are shielded more than in anisole whereas the opposite behavior is observed at *anti* positions in *ortho* substituted methoxybenzenes^{5,6,20}.

TABLE I
Chemical shifts^a in 4-substituted 2,6-dimethoxytrimethylsiloxybenzenes *IIa–IIe*

Compound	²⁹ Si	¹³ C					
		C-1	C-2 C-6	C-3 C-5	C-4	OMe	MeSi
<i>IIa</i>	21.48	134.21	151.81	105.28	120.71	55.87	0.35
<i>IIb</i>	21.19	131.75 ^b	151.31	106.07	130.40 ^b	55.84	0.31
<i>IIc</i>	23.40	135.41 ^b	151.94	106.75	129.53 ^b	55.98	0.45
<i>IId</i>	22.83 ^c	138.82	151.13	107.32	123.64	55.90	0.37
<i>IIe</i>	21.46 ^d	135.45 ^b	151.50	103.86	133.57 ^b	55.88	0.35

^a All the values of chemical shifts are in the δ scale, estimated error ± 0.02 ppm. Me denotes methyl group, aromatic carbons are numbered according to the formula *II*. ^b The assignment of the lines can be interchanged. ^c Signal at $\delta = 24.55$ is due to the substituent at C-4. ^d Signal at $\delta = 18.97$ is due to the substituent at C-4.

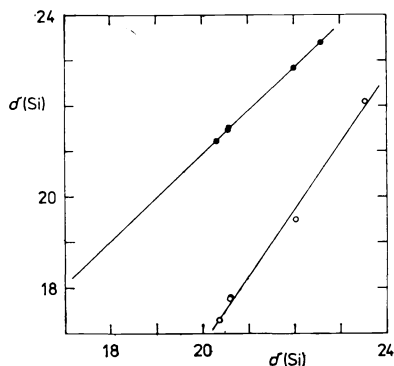


FIG. 1
Plot of ²⁹Si chemical shifts in *II* (full points) and in *IV* (open points) against ²⁹Si chemical shifts in *I* (the straight lines are least-square fits of the data points shown)

In the limited series of compounds *II* the ^{29}Si chemical shifts exhibit about the same sensitivity to *para* substitution as in compounds *I*, which is somewhat lower than that in *para* substituted trimethylsiloxybenzenes (*IV*), $\text{R}-\text{C}_6\text{H}_4-\text{OSiMe}_3$ (ref.¹, compare the slopes in Fig. 1).

The difference between the ^{29}Si chemical shifts in the corresponding compounds *II* and *I* is 0.86 ± 0.03 ppm. This difference represents proximity effect due to the "second" methoxy group. The effect is of the same sign (deshielding) but smaller than the proximity effect of the "first" methoxy group ($1.43-3.04$ ppm depending on substituent R)³. (Analogous proximity effect on methyl carbon shift is very small, 0.05 ppm.)

All these observations lead us to conclude that the conformation of the trimethylsiloxy group is essentially the same in the two classes of compounds *II* and *I*. Since, for steric reasons, the trimethylsiloxy group in compounds *II* cannot take coplanar conformation with the O—Si bond in the plane of the benzene ring, also compounds *I* have the trimethylsiloxy group predominantly in perpendicular conformation as suggested previously².

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