# $^{29}$Si AND $^{13}$C NMR SPECTRA OF (E)-β-SUBSTITUTED 3-METHOXY-4-TRIMETHYLSILOXYSTYRENES

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NMR spectra of eleven (E)-β-substituted 3-methoxy-4-trimethylsiloxy-styrenes were measured under standard conditions that approach those of infinite dilution. The sensitivity of $^{29}$Si chemical shifts to the nature of (E)-β-substituent is high, in comparison with 4-substituted 2-methoxy-trimethylsiloxybenzenes the insertion of a CH═CH bridge between the substituent and the benzene ring reduces the sensitivity by a factor of 1·5 only.

In the course of our studies of NMR spectra of trimethylsilylated lignins and their models[1-5] we have measured $^{29}$Si NMR spectra of title compounds which show surprisingly high sensitivity to substitution. Because of synthetic difficulties we are not in a position to expand the series of investigated substituents into a complete basic set[6] that would allow dual substituent parameter (DSP) analysis of substituent effect transmission. However, the data presented here will serve later[7] in a test of the recently advanced theory of remote substituent effects on $^{29}$Si shielding[8].

## EXPERIMENTAL

The investigated compounds were all prepared by trimethylsilylation of the corresponding phenol derivatives. With the exception of the compounds listed below the parent phenols were either of commercial origin or prepared by the procedures compiled in ref.[9].4-Hydroxy-3-methoxy-styryl bromide was prepared from ferulic acid according to ref.[10]. Nitrile of ferulic acid was prepared by alkali-catalyzed condensation of vanillin with cyanoacetic acid according to a standard procedure. 4-Hydroxy-3-methoxystyryl methyl ketone was prepared by condensation of vanillin with acetone according to Nisbet[11]. 4-Trimethylsiloxy-3-methoxystyrene was tri-methylsilylated using a 100% excess of trimethylsilyldiethylamine for 30 min at ambient temperature. The product was purified by distillation in vacuo. Trimethylsilylation, product purification of other compounds as well as the spectral measurements were carried out exactly as described previously[4]. The relevant features of NMR measurements were: the samples were dissolved in deuteriochloroform containing 2% of hexamethyldisilane (HMDSS). The $^{13}$C NMR spectra were referenced to the central line of the solvent ($\delta = 76·99$) and the samples were diluted by this solvent until $^{13}$C chemical shift of HMDSS reached the value $\delta = -2·48 \pm 0·02$. The $^{29}$Si NMR spectra were referenced to the line of HMDSS ($\delta = -19·79$).

The $^{13}$C chemical shifts were assigned according to the described substituent effects in (E)--β-substituted styrenes[12,13], and 2-methoxytrimethylsiloxybenzenes[4] and the results of selective heteronuclear INADEQUATE experiments performed on trimethylsilylated ferulic acid (compound V)[14]. This procedure allowed unambiguous assignment of the lines due to substituted aromatic carbons (C-1, C-3, and C-4). Olefinic α carbon (C-α) was assigned to the intense line in the region of substituted aromatic carbon lines (which have lower intensity because of absence of nuclear Overhauser effect). Other line assignments were considerably less reliable and for that reason are not given here.

In correlating the chemical shifts with substituent constants we have used values recommended by Exner[15] for olefinic groups we employed the constants given in the compilation of Hansch and Leo[16]. The simple linear correlations that wi 1 be mentioned are given as illustrations of factors affecting the chemical shifts in question. They should not be taken as the best possible correlations. Values of the correlation coefficients are given here as r; n denotes the number of data points used in the correlation.

## RESULTS AND DISCUSSION

The experimental results for compounds I—XI listed below are gathered in Table I.

TABLE I

$^{29}$Si and $^{13}$C NMR chemical shifts[a] in compounds I—XI

| Compd. | $^{29}$Si | $^{13}$C | | | | | |
|--------|-----------|----------|----------|----------|----------|--------|--------|
| | | C-1 | C-3 | C-4 | C-α | OMe | MeSi |
| I | 20·93 | 131·71 | 150·89 | 144·58 | 136·62 | 55·46 | 0·30 |
| II | 20·72 | 132·07 | 150·81 | 143·61 | 130·70 | 55·39 | 0·27 |
| III | 20·82[b] | 131·08 | 150·84 | 144·26 | 130·70 | 55·43 | 0·33[c] |
| IV | 20·94 | 131·73 | 150·98 | 144·27 | 126·93 | 55·52 | 0·35 |
| V | 21·27 | 130·00 | 151·01 | 145·01 | 136·89 | 55·48 | 0·30 |
| VI[d] | 21·63[e] | 128·40 | 150·78 | 146·70 | 145·01 | — | 0·12[f] |
| VII | 21·76 | 128·34 | 151·05 | 147·01 | 144·86 | 55·40 | 0·33 |
| VIII | 22·19 | 128·03 | 151·26 | 148·04 | 152·91 | 55·50 | 0·37 |
| IX | 21·86 | 128·31 | 151·14 | 147·28 | 143·55 | 55·42 | 0·32 |
| X | 22·22 | 127·51 | 151·25 | 147·86 | 150·35 | 55·53 | 0·34 |
| XI | 22·61 | 123·77 | 151·41 | 148·96 | 139·34 | 55·54 | 0·36 |

[a] Chemical shifts in δ-scale, approximate error ±0·02 ppm; [b] other line at $\delta(CH_2OSi) = 18·85$; [c] other line at $\delta = 0·30$; [d] data taken from ref.[14]; [e] other line at $\delta(COOSi) = 23·58$; [f] other line at $\delta = -0·38$.

In agreement with general trends[17] the chemical shifts of aromatic carbons (C-3) *meta* to the varied substituent show little changes with substitution, their overall variation is 0·8 ppm. The chemical shifts of *ipso* (C-1) and *para* (C-4) carbons
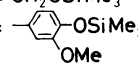
$$H \underset{\alpha}{\overset{}{C}} = \underset{\beta}{\overset{}{C}} \overset{R}{\underset{H}{}}$$

Me₃SiO — OMe
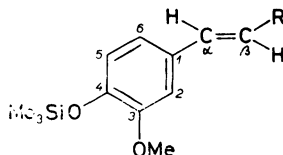
| | |
|---|---|
| *I*, R = H | *VI*, R = COOSiMe₃ |
| *II*, R = Me | *VII*, R = COOMe |
| *III*, R = CH₂OSiMe₃ | *VIII*, R = CHO |
| *IV*, R = ⟨benzene ring⟩—OSiMe₃ OMe | *IX*, R = COMe |
| | *X*, R = CN |
| *V*, R = Br | *XI*, R = NO₂ |
| **Me = CH₃** | |

exhibit much stronger and opposite dependences on $\sigma_p^0$ constant of substituent R ($\delta$(C-1) = 131·63 − 7·631$\sigma_p^0$, $r$ = −0·952, $n$ = 11; $\delta$(C-4) = 144·29 + 5·790$\sigma_p^0$, $r$ = = −0·965, $n$ = 11). The dependence of C-$\alpha$ on substituent parameters is more complex. It should be also noted that the chemical shift $\delta$(C-4) shows an excellent linear correlation with the ²⁹Si chemical shift ($r$ = 0·992; $n$ = 11) which might provide a clue in the analysis of substituent effect transmission mechanism.

The chemical shifts of methoxyl carbons fall into the region in which chemical shifts of other *ortho* substituted methoxybenzenes are found[18-21]. It is generally accepted that the chemical shifts of the methoxyl carbon in the vicinity of $\delta$ = 55
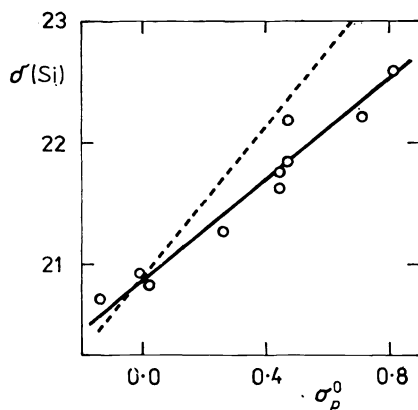


Fig. 1

Linear correlation between $\delta$(²⁹Si) in (*E*)-β--substituted 3-methoxy-4-trimethylsiloxy-styrenes and $\sigma_p^0$ constants of substituent R. (Solid line is the least-squares fit of all data points, dashed line is analogous correlation that holds in 4-substituted 2-methoxytri-methylsiloxybenzenes)

indicate coplanar conformation in which all the heavy atoms of the methoxy group lie in the plane of the benzene ring and the methyl group is *anti* to the *ortho* substituent. Such conformations of methoxy groups were found in other substituted 2-methoxytrimethylsiloxybenzenes[4,5].

Recently we have described a good linear correlation that holds between $\delta(^{29}\text{Si})$ and $\sigma_p^o(R)$ in 4-substituted 2-methoxytrimethylsiloxybenzenes[4]. Using the inverse correlation to estimate $\sigma_p^o$ values from the $^{29}\text{Si}$ chemical shifts listed in Table I we obtain values, $\sigma_p^o = 0.05$ for $-CH=CH-CH_3$ and $\sigma_p^o = 0.54$ for $-CH=CH-NO_2$ and values between these two extremes for other $-CH=CH-R$ substituents employed here. Obviously, this range of values is not realistic (e.g. Hansch and Leo[16] give values $\sigma_p^o = -0.04$ and $0.26$ for these two substituents, resp.); some other, more efficient, mechanism of substituent effect transmission is operating in the $(E)$-$\beta$-substituted styrenes *I*. The $^{29}\text{Si}$ chemical shifts of Table I, however, correlate linearly rather well with the $\sigma_p^o$ constant of the substituent R (Fig. 1, $r = 0.974$; $n = 11$). The slope in this correlation is 1·5-times smaller than the slope found for the analogous correlation in 4-substituted 2-methoxytrimethyl-siloxybenzenes[4], the difference in the two slopes is significant on 90% confidence level.

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