PROXIMITY EFFECTS IN ^{29}Si, ^{13}C, AND ^{1}H NMR SPECTRA OF *ortho* SUBSTITUTED PHENOXYTRIMETHYLSILANES

Jan Schraml[a], Václav Chvalovský[a], Harald Jancke[b], Peter Koehler[b], Mikhail F. Larin[c], Vadim A. Pestunovich[c] and Mikhail G. Voronkov[c]

[a] *Institute of Chemical Process Fundamentals,*
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol, Czechoslovakia
[b] *Central Institute of Physical Chemistry,*
Academy of Sciences of G.D.R., 1199 Berlin, G.D.R. and
[c] *Irkutsk Institute of Organic Chemistry,*
Siberian Division of Academy of Sciences of the U.S.S.R., 664033 Irkutsk, U.S.S.R

NMR Spectra of eight *ortho* substituted phenoxytrimethylsilanes, 2-X-C$_6$H$_4$-OSi(CH$_3$)$_3$ (X = Cl, Br, OCH$_3$, NH$_2$, NO$_2$, OSi(CH$_3$)$_3$, CH$_3$, and H), are reported. In contrast to analogous *ortho* substituted methoxybenzenes the ^{13}C chemical shifts of C-2 and C-6 aromatic carbons do not exhibit consistent trends indicating different conformational preferences in the trimethylsiloxybenzenes. Under the influence of the *ortho* substituents the nuclei of OSi(CH$_3$)$_3$ group (^{29}Si, ^{13}C, and ^{1}H) are deshielded; compounds with X = CH$_3$ (and H) appear anomalous in this respect. It is argued that this proximity effect is not due to an interaction involving terminal methyl groups but involves the oxygen atom of the OSi(CH$_3$)$_3$ group; it is most likely due to an interaction with unshared electrons of the *ortho* substituent.

In a limited study of NMR spectra of bis(trimethylsiloxy)benzenes[1] the contribution of electronic effects to the shielding of ^{29}Si and ^{13}C nuclei of the trimethylsiloxy group could not be evaluated and the whole difference between the shifts in the *ortho* and *para* isomers was attributed to steric effects. It was suggested[1] that the observed deshielding steric effect was not due to an interaction of the terminal methyl groups (as in bis(trimethylsilyl)benzenes[2]) but to an interaction that involved either one or both oxygen atoms. Similar steric effects were subsequently observed in the spectra of disubstituted adamantanes[3,4] in which the two groups bonded to saturated carbon skeleton interacted through the two oxygen atoms.

The aim of our investigation was (i) to determine to what extent is the observed ortho deshielding of ^{29}Si nuclei general (ii) to separate steric effects from other factors contributing to the observed shift, and (iii) to suggest possible mechanism for this steric effect.

Currently available technical means permit NMR measurements at lower concentrations and achieve higher precision than that used in our study of *para* and

meta substituted phenoxytrimethylsilanes[5]. However, we present with a considerable delay the results which were obtained several years ago under the experimental conditions identical with those employed earlier[5]. It is worth mentioning in this context that the spectra of *ortho* substituted trimethylsiloxybenzenes have not yet been reported and, also, our recent study of diluted solutions of bis(trimethylsiloxy)-adamantanes[6] has fully supported the conclusions reached much earlier on the basis of measurements in concentrated solutions[4].

EXPERIMENTAL

Preparation and physical properties of the studied compounds were described elsewhere[7]. Detailed description of the NMR measurements was given earlier[5], so only the most relevant features are repeated here.

Two independent methods were employed for ^{29}Si NMR measurements. Neat samples (with a drop of hexamethyldisiloxane, HMDSO) were measured using gated proton decoupling technique on a JEOL-PFT-100 spectrometer operating at 19·87 MHz. The line of HMDSO ($\delta = 6·66$) served as an internal reference. Carbon tetrachloride solutions (30%) were measured on a CW spectrometer Tesla BS 487C using ^{1}H $-$ (^{29}Si) INDOR method[8] with proton detection at 80 MHz. The same spectrometer and solutions were used for the measurement of ^{1}H NMR spectra. ^{13}C NMR spectra were measured in carbon tetrachloride solutions (10%) using the line of the solvent ($\delta = 96·00$) as an internal reference and hexadeuteriobenzene in a capillary to provide the lock signal. The spectra were recorded on a JEOL-PFT-100 spectrometer operating in pulse FT mode at 25·15 MHz with sweep width of 5 kHz and 8 K memory for FID accumulation.

The lines in the ^{13}C NMR spectra were assigned on the basis of their intensity and direct additivity rule. According to this rule the chemical shifts in substituted trimethylsiloxybenzenes are calculated by adding appropriate substituent chemical shifts (SCS) to the chemical shift of the corresponding carbon in the parent trimethylsiloxybenzene. The SCS values were taken from ref.[9]. In the few instances in which the difference in experimental or calculated shifts for two carbon nuclei was not significant, that assignment was chosen which resulted in smaller deviations of the calculated values from the experimental ones.

RESULTS AND DISCUSSION

The observed ^{1}H, ^{13}C, and ^{29}Si chemical shifts of trimethylsilyl groups and ^{13}C chemical shifts of aromatic carbon nuclei are collected in Table I. Also included are deviations of the observed shifts of aromatic carbons from the values calculated according to the direct additivity rule. For clarity, the chemical shifts of aromatic carbon nuclei and the nuclei of trimethylsilyl groups are discussed separately.

Aromatic Carbons

As in other *ortho* disubstituted benzenes[10] the observed chemical shifts of the substituted C-1 aromatic carbons deviate from the shifts calculated according to the

direct additivity rule (Table I) considerably more than in *para* or *meta* isomers[5]. Surprisingly, the deviations for the other substituted aromatic carbon (C-2) do not exceed the deviations of the other substituted carbons in the *meta* (C-3) or *para* (C-4) derivatives[5]. If the direct additivity is replaced by proportionality relationship of Lynch[11], the agreement between experimental and calculated shifts is improved as the relationship introduces two adjustable parameters. However, the agreement for C-1 carbons in *ortho* isomers remains worse than the corresponding fit for *meta* or *para* isomers[5].

It is illuminating to compare the present results with the recent studies of *ortho* substituted methoxybenzenes[12-16] (anisoles). According to a number of quantum

TABLE I

Chemical shifts in *ortho* substituted phenoxytrimethylsilanes[a] $2\text{-}X\text{-}C_6H_4\text{-}OSiMe_3$

Observed group		Substituent X							
		H	Cl	Br	CH_3	OCH_3	NH_2	NO_2	$OSiMe_3$
$SiMe_3$	Si[b]	17·72	21·11	20·91	17·38	18·47	19·39	23·92	18·90[c]
	Si[d]	18·00	e	21·10	17·60	e	e	24·00	19·24
	C[f]	0·26	0·31	0·33	0·46	0·46	0·36	0·22	0·26
	H[d]	0·231	e	0·290	0·230	e	e	0·319	0·275
C-1[f]		154·81	151·07	152·20	153·20	144·47	142·09	148·83	146·50[g]
	(—		−4·14	−6·01	−2·31	4·06	0·58	−1·18	−0·08)
C-2[f]		119·67	125·64	115·51	128·16	150·49	137·91	136·70	146·50[g]
	(—		−0·23	1·34	−0·41	−0·58	0·24	−2·97	−0·08)
C-3[f]		129·03	130·05	133·13	130·63	111·95	115·15	125·20	121·12[g]
	(—		0·62	0·70	0·90	−2·68	−0·58	0·97	0·32)
C-4[f]		121·07	121·90	122·40	121·02	121·36	121·85	122·38	121·79[g]
	(—		−0·47	−0·37	0·05	−0·71	−0·12	0·41	−0·41)
C-5[f]		129·03	126·99	127·88	126·27	120·78	117·82	133·06	121·79[g]
	(—		−0·14	0·45	0·14	−0·55	−1·41	−1·77	−0·41)
C-6[f]		119·67	120·78	120·41	118·40	120·78	118·26	120·93	121·12[g]
	(—		−0·20	−0·96	−1·17	0·11	−2·31	0·36	0·32)

[a] All the values are in δ scale estimated error ±0·05 ppm; Si, H, and C denote ^{29}Si, ^1H and ^{13}C chemical shifts, respectively, in the indicated group. Me stands for CH_3. Phenyl carbon atoms are numbered starting from the carbon bearing the trimethylsiloxy group. The lines in parenthesis give deviations from additivity $\Delta = \delta_{exp.} - \delta_{calc.}$. [b] In neat samples; [c] in 50% carbon tetrachloride solution; [d] in 30% carbon tetrachloride solutions, indirect measurements of ^{29}Si NMR spectra; [e] not measured; [f] in 10% carbon tetrachloride solutions; [g] in 30% deuteriochloroform solution.

chemical calculations[17], including the CNDO/2 level of approximation[17,18], the planar conformers of anisole have the lowest energy. At room temperature rapid interconversion between the two coplanar rotamers takes place in solutions[12]. Introduction of an *ortho* substituent prevents the interconversion around the O—C-1 bond, the methoxy group is turned away from the substituent and executes only restricted rotation around the O—CH$_3$ bond in the plane of the aromatic ring[13,19]. In a such restricted conformation the measured properties are no longer dynamic averages between the two coplanar conformers and, hence, the SCS values are different for the two *ortho* carbons in C-2 and C-6 positions which are *trans* and *cis* to the methyl group, respectively. Neglecting this difference, as it is done in applying the direct additivity in the usual way, leads to systematic errors. This is why the calculated shifts are in *ortho* substituted anisoles consistently at higher and lower fields for the C-2 and C-6 positions, respectively, than the experimental values[12,14].

There are at least two (complementary) interpretations of the observed consistency in the signs of the deviations. According to the lines of interpretation of γ-effects in ^{13}C NMR spectroscopy, the fact that the methoxy group spends most of its time in the vicinity of *cis* C-6 position in *ortho* substituted anisoles leads to increased crowding at this position (as compared with the unsubstituted anisole) and hence to increased shielding of C-6 carbon; analogously the opposite is true for the C-2 carbon. According to calculations of charge densities[19,20] the total charge density is about 0·02 electrons higher at *cis* than at *trans ortho* carbon in the planar anisole conformer. Using the approximate correlation between the ^{13}C chemical shifts of aromatic carbons and the total charge density[21], the calculated difference in charge density corresponds to the *cis* C-6 carbon being shielded by about 4 ppm more than the *ortho* C-2 carbon. This value is in good agreement with experimentally determined[12] SCS values of methoxy group for C-2 and C-6 positions in *ortho* substituted anisoles which differ by 7·6 ppm in the correct direction. Interpretation in the terms of electron density also successfully accounts for ^{17}O NMR chemical shifts in *ortho* substituted methoxybenzenes[13]. Turning the methoxy group away from the plane of the benzene ring increases the charge on the oxygen and hence shifts its [17]O signal upfield.

According to CNDO/2 calculations for phenoxysilanes[5] the conformers which have the C—O—Si plane perpendicular to the benzene ring are energetically favoured over the coplanar species. Also, according to molecular models coplanar rotamers with the Si—O bond in the plane of the benzene ring exhibit even more acute crowding in the *ortho* positions of trimethylsiloxybenzene than encountered in these positions in the coplanar rotamers of anisole. One may assume that introduction of an *ortho* substituent affects dynamic averaging between perpendicular rotamers less than between coplanar rotamers. Under this assumption we can understand why the additivity of SCS is satisfied better in *ortho* substituted trimethylsiloxybenzenes than

in anisoles (standard deviations being in trimethylsiloxybenzenes 1·3, 0·5, 0·5, 0·2, 0·4, and 0·4 ppm for carbons C-1, C-2, C-3, C-4, C-5, and C-6, respectively, which are values about three times smaller than the corresponding values in anisoles[12]). Also, in agreement with this interpretation and in contrast to the situation in anisoles, the signs of the small deviations from additivity for C-2 and C-6 carbons of tri-methylsiloxybenzenes do not show any consistent trend. This distinction becomes even more apparent when one compares C-2 and C-6 carbon shifts due to O-methyla-tion[15] with those due to O-trimethylsilylation of phenols (which can be calculated from the present data and the data on the corresponding *ortho* substituted phenols[15]). For C-2 carbon O-methylation and O-tirmethylsilylation shifts are of the same sign (upfield, though of considerably different magnitudes) but for C-6 carbon the methy-lation shifts are upfield while trimethylsilylation shifts are downfield. The difference in the calculated optimum conformations for methyl and silyl phenylethers can, at least partially, account for the reported difference in the ^{17}O NMR shielding between tert-butyl and trimethylsilyl phenylethers that was originally assigned only to lower electronegativity of silicon as compared to carbon[22].

Due to an "*ortho* effect" in *ortho* substituted benzenes successful linear correla-tions of aromatic carbon chemical shifts with Hammett-type substituent parameters require multiple regressions[23,24]. Since our limited set of data did not warrant such an approach[24] we tried limited linear correlation with semi-empirical Q param-eter that was especially designed to cope with the "*ortho* effect"[23]. Similarly as in *ortho* substituted phenols[25] the chemical shifts of C-1, C-2, and C-3 correlate reason-ably well with the Q parameters of the substituents. In the correlation of δ(C-1) vs Q notable deviations occure for substituents H and CH_3 (both having the chemical shift larger than predicted by approximately 4 ppm), which are the only two substi-tuents studied with no unshared electron pairs.

Trimethylsilyl Group

In all the instances in which two values are available for [29]Si chemical shift, the value obtained by indirect method from carbon tetrachloride solution is by 0·1 − 0·3 ppm larger than the value obtained directly from the neat sample. Since the two sets of values correlate very well $(\delta(\text{neat}) = 1·030.\delta(\text{CCl}_4) − 0·005;\ r = 0·9997,\ n = 5)$ we shall limit our discussion ot the data from neat samples as that set is more com-plete.

In the *meta* substituted phenoxytrimethylsilanes the silicon-29 chemical shifts are about the same as in the *para* isomers[5]. In the studied *ortho* isomers such rela-tionship (Fig. 1) holds only for the methyl derivatives, and, of course, for parent compounds $(X = H)$. In all the remaining *ortho* substituted compounds the silicon is shielded by about 1·5 ppm less than in the corresponding *para* isomer. This "proximity shift" of [29]Si is accompanied by similar (deshielding) but smaller shifts

of ^{13}C $(0.1-0.3$ ppm$)$ and ^1H $(0.00-0.05$ ppm$)$ nuclei of the $Si(CH_3)_3$ group when going from the *para* to *ortho* isomer.

Generality of this observation confirms the earlier suggestion[1] that the steric effect observed in ^{29}Si chemical shift in *o*-bis(trimethylsiloxy)benzene is not due to the interaction between the terminal methyl groups of the two substituents. However, it does not exclude the possibility of the steric effect being due to an interaction of the *ortho* substituent with the methyl groups of the trimethylsiloxy group being observed. Considering this posibility we note that though there is a linear correlation between ^{29}Si and ^1H chemical shifts $(\delta(Si) = 66.87.\delta(H) + 1.78$; $r = 0.954$, $n = 5)$ the methyl carbon shifts do not linearly correlate with ^1H shifts. This fact and the very small ranges of both ^1H and ^{13}C $(0.08$ and 0.24 ppm, respectively$)$ as compared with the range of 6.5 ppm of ^{29}Si chemical shifts make this mechanism most unlikely. Also, as we failed to find any simple correlation between the ^{29}Si chemical shifts and parameters of the *ortho* substituents, it seems unlikely that the proximity effect is governed by an electronic interaction transmitted through the bonds. We cannot exclude, however, operation of electric field effect the evaluation of which is difficult for *ortho* substituted benzenes.
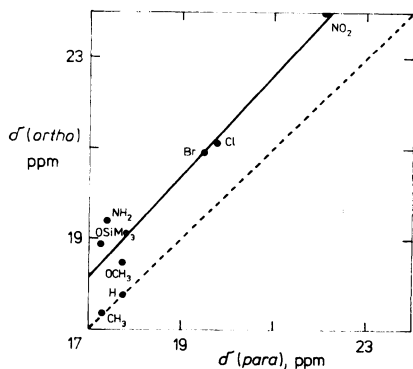

FIG. 1

Correlation between ^{29}Si chemical shifts in *ortho* and *para* isomers of substituted phenoxytrimethylsilanes (the dashed line corresponds to the relation $\delta(ortho) = \delta(para)$; the solid line is the least-square fit of the data points $\delta(ortho) = 1.11 \delta(para) - 0.78$; $r = 0.987$, $n = 5)$
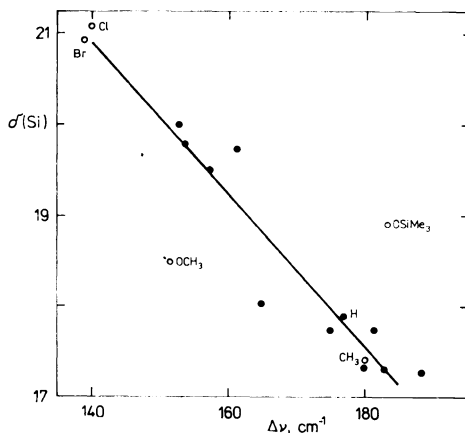
FIG. 2

Correlation between ^{29}Si chemical shifts, $\delta(Si)$, and relative basicity, $\Delta\nu$ (the full points and the solid correlation line correspond to *meta* and *para* isomers, data taken from ref.[5], the open points correspond to *ortho* substituted phenoxytrimethylsilanes)

Recalling that there is no proximity effect in the *ortho* methyl derivative although the van der Waals volume of the methyl group is intermediate between those of chlorine and bromine which both exhibit the proximity effect of about 1·4 ppm, we are lead to suggest that the mechanisms responsible for the *ortho* deshielding effect involves the oxygen atom of the trimethylsiloxy group on one side and unshared electron pair(s) of the *ortho* substituent on the other. Analogous interactions between two oxygen atoms were proposed to account for the steric effects in bis-(trimethylsiloxy)adamantanes[3,4,6]. The dependence of ^{29}Si chemical shifts in mono- and bis(trimethylsiloxy)cycloalkenes[26,27] on the ring size was interpreted by invoking steric inhibition of resonance[27,28]. The interpretation of proximity effect can, when adopted to cycloalkenes, account for the difference in the shielding in mono- and bis(trimethylsiloxy) derivatives.

Accepting interaction between unshared electron pairs of the *ortho* substituent with the oxygen atom of the trimethylsiloxy group as the mechanism of the proximity effect, one would expect to find correlations between observables associated with the Si—O—C-1 moiety. Though proximity of the *ortho* substituent lowers both the relative basicity of oxygen and the silicon shielding, the change is along the regression line (Fig. 2) only for chloro, bromo, and methyl derivatives. The ^{13}C chemical shifts of C-1 carbons do not correlate with the basicity and, also, we do not see any simple correlation between ^{13}C and ^{29}Si chemical shifts in this moiety. Apparently, the detailed mechanism of the interaction depends on the nature of the *ortho* substituent.

REFERENCES

1. Schraml J., Chvalovský V., Jancke H., Engelhardt G.: Org. Magn. Reson. *9*, 237 (1977).
2. Schraml J., Chvalovský V., Mägi M., Lippmaa E., Calas R., Dunogues J., Bourgeois P.: J. Organomet. Chem. *120*, 41 (1976).
3. Schraml J., Včelák J., Chvalovský V., Engelhardt G., Jancke H., Vodička L., Hlavatý J.: Collect. Czech. Chem. Commun. *43*, 3179 (1978).
4. Schraml J., Jancke H., Engelhardt G., Vodička L., Hlavatý J.: Collect. Czech. Chem. Commun. *43*, 3192 (1978).
5. Schraml J., Ponec R., Chvalovský V., Engelhardt G., Jancke H., Kriegsmann H., Larin M. F. Pestunovich V. A., Voronkov M. G.: J. Organomet. Chem. *179*, 55 (1979).
6. Schraml J., Čermák J.: Collect. Czech. Chem. Commun. *55*, 452 (1990).
7. Koehler P., Geissler H., Jakoubková M., Dube G., Licth K., Kriegsmann H.: Z. Anorg. Allg. Chem. *440*, 183 (1978).
8. Larin M. F., Pestunovich V. A.: Tesla NMR Bull. *9*, 1 (1976).
9. Levy G. C., Nelson G. L.: *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists* p. 81. Wiley–Interscience, New York 1972.
10. Stothers J. B.: *Carbon-13 NMR Spectroscopy*, p. 196. Academic Press, New York 1972.
11. Lynch B. M.: Can. J. Chem. *55*, 541 (1977).
12. Biekofsky R. R., Pomilio A. B., Contreras R. H., de Kowalewski D. G., Facelli J. C.: Magn. Reson. Chem. *27*, 158 (1989).

13. Wysocki M. A., Jardon P. W., Mains G. J., Eisenbraun E. J., Boykin D. W.: Magn. Reson. Chem. *25*, 331 (1987).
14. Dhami K. S., Stothers J. B.: Can. J. Chem. *44*, 2855 (1966).
15. Fujita M., Nagai M., Inoure T.: Chem. Pharm. Bull. *30*, 1161 (1982).
16. Yoder C. H., Sheffy F. K., Howell R., Hess R. E., Pacala L., Schaeffer C. D. Jr., Zuckerman J. J.: J. Org. Chem. *41*, 1511 (1976).
17. Anderson III G. M., Kollman P. A., Domelsmith L. N., Houk K. N.: J. Am. Chem. Soc. *101*, 2344 (1979).
18. Tylli H.: Suom. Kemistiseuran Tied. *82*, 16 (1973).
19. Jardon P. W., Vickery E. H., Pahler L. F., Pourahmady N., Mains G. J., Eisenbraun E. J.: J. Org. Chem. *49*, 2130 (1984).
20. Eberhardt M. K., Chuchani G.: J. Org. Chem. *37*, 3654 (1972).
21. Nelson G. L., Levy G. C., Cargioli J. D.: J. Am. Chem. Soc. *94*, 3089 (1972).
22. Kalabin G. A., Kushnarev D. F., Valeyev R. B., Trofimov B. A., Fedotov M. A.: Org. Magn. Reson. *18*, 1 (1982).
23. Smith W. B., Proulx T. W.: Org. Magn. Reson. *8*, 567 (1976).
24. Johnels D., Edlund U., Grahn H., Hellberg S., Sjöström M., Wold S., Clementi S., Dunn III W. J.: J. Chem. Soc., Perkin Trans. 2, *1983*, 863.
25. Smith W. B., Proulx T. W.: Org. Magn. Reson. *8*, 205 (1976).
26. Schraml J., Šraga J., Hrnčiar P.: Org. Magn. Reson. *21*, 73 (1983).
27. Schraml J., Šraga J., Hrnčiar P.: Collect. Czech. Chem. Commun. *48*, 2937 (1983).
28. Schraml J., Šraga J., Hrnčiar P.: Collect. Czech. Chem. Commun. *48*, 3097 (1983).

Translated by the author (J.S.).