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STERIC EFFECTS IN ^{29}Si AND ^{13}C NMR SPECTRA OF TRIMETHYLSILYL- AND ALKYL-SUBSTITUTED BENZENES

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Summary

^{29}Si and ^{13}C NMR spectra of trimethylsilylbenzenes substituted at different positions by methyl and trimethylsilyl groups were investigated with special reference to steric interactions between the *ortho*-substituents. The steric effects, as measured by ^{13}C and ^{29}Si chemical shifts, are generally smaller in trimethylsilyl- than in t-butyl-substituted compounds. Both nuclei follow the same general trends in the benzene derivatives.

Introduction

^{29}Si chemical shifts in compounds of the type $(CH_3)_3SiOR$ have been shown [1] to be sensitive to the nature and stereochemistry of the group R. Complexity and flexibility of the substituents R did not permit detailed evaluation of the steric effects on the silicon shielding. The recently synthesized poly(trimethylsilyl)benzenes [2] offered the possibility of studying such effects in compounds with a rigid skeleton. Also, as shown by Maciel et al. [3], the silicon shielding is only little affected (2.5 ppm is the overall variation) by electronic interactions in *meta*- and *para*-substituted trimethylsilylbenzenes, and it should be possible to observe comparatively pure steric effects in *ortho*-substituted trimethylsilylbenzenes. So far only two *ortho*-substituted trimethylsilylbenzenes (*o*-CH_3 and *o*-NO_2) have been measured by ^{29}Si NMR spectroscopy [3]. These compounds

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are also interesting for the study of steric effects on ^{13}C chemical shifts. The effects caused by bulky groups such as t-butyl are quite unusual [4—10], but have been little studied. A better understanding of steric effects in ^{13}C NMR is essential, because the ^{13}C method is accepted as one of the most useful methods for stereochemical studies [11].

Experimental

The observed carbon-13 and silicon-29 chemical shifts are summarized in Table 1.

The preparation and properties of the poly(trimethylsilyl)benzenes have been published [2,13]. The sources of the other compounds are indicated in papers dealing with studies of phenyl- and benzyl-silanes by ^{13}C and ^{29}Si NMR [14,15].

The ^{13}C and ^{29}Si NMR spectra were recorded at 15.09 MHz and 11.92 MHz in the Fourier transform mode. Silicon chemical shifts were measured with respect to internal hexamethyldisiloxane (chemical shift from internal TMS 6.6 ppm) and carbon chemical shifts with respect to internal cyclohexane (chemical shift from internal TMS 27.5 ppm) or internal CCl_4 (chemical shift from internal TMS 96.7 ppm), the latter also served as solvent for the compounds VII to XI. Carbon chemical shifts of *p*-trimethylsilyltoluene (IV) were measured from external TMS [15].

The problem of assigning ^{29}Si chemical shifts arises in compounds VIII and XI, see Table 1. In the first case the signal at —4.6 ppm obviously belongs to the 4-trimethylsilyl group (compare with the compounds VI and VII), but assignment of the other two signals to 1- and 2-trimethylsilyl groups is difficult, although closeness of one remaining shift to that in IX leads to the tentative assignment given in Table 1. In the second compound (XI) it is logical (by comparison with compound X) to assign the signal at —6.2 ppm to the 4-trimethylsilyl group.

The assignment of carbon chemical shifts to C-2 or C-3 in trimethylsilylbenzene (I) is based on the well-known fact that *meta*-carbon shifts in substituted benzenes vary insignificantly [16]; our results agree well with those of Doddrell et al. [17]. Assignment of the ring carbon atoms in compounds III, IV, VI and VII is justified by the very general applicability of simple additivity relationships for the *meta*- and *para*-substituted benzenes [11,16], see Table 2. The substituted ring carbon atoms in II, X and XI are assigned through selective double resonance experiments, in V and IX on the basis of signal intensities. The remaining carbon atoms in XI are assigned by comparison with X, and in VIII by comparison with I and V (see ref. 16). The assignment of unsubstituted carbon atoms in II and V is made by preserving the order of chemical shifts indicated by the additivity rule; such a method is reasonable, especially as applied to the shift intervals and general trends, except for the assignment of atoms C-3 and C-4 in II, for which the additivity rule gives very close values (see Table 2). The silylmethyl carbon signals in VIII and XI are easily assigned by comparison with other compounds in the series, except for the signals at 2.1 and 2.0 ppm in VIII that are too close for an unambiguous assignment.

TABLE 1

^{29}Si AND ^{13}C NMR CHEMICAL SHIFTS IN TRIMETHYLSILYL- AND ALKYL-SUBSTITUTED BENZENES [a]

Compound	Substituents in benzene ring	$\delta(^{29}Si)$ (ppm) from internal TMS	$\delta(^{13}C)$ (ppm) from internal TMS							
			C-1	C-2	C-3	C-4	C-5	C-6	SiMe$_3$	Other carbon atoms
I	1-SiMe$_3$	−4.7	140.2	133.6	128.1	129.2	128.1	133.6	−0.5	
II	1-SiMe$_3$, 2-Me	−5.1	138.0	143.1	129.5 [b]	130.1 [b]	125.4	134.6	0.5	23.4
III	1-SiMe$_3$, 3-Me	−4.9	140.0	134.3	136.8	130.0	128.1	130.8	−0.4	22.0
IV	1-SiMe$_3$, 4-Me [c]	−4.76 [d]	135.8	132.7	128.1	137.4	128.1	132.7	−1.1	21.2
V	1,2-(SiMe$_3$)$_2$	−4.1	145.7	145.7	135.4	128.0	128.0	135.4	2.0	
VI	1,3-(SiMe$_3$)$_2$	−4.7	139.1	138.4	139.1	134.2	127.5	134.2	−0.7	
VII	1,4-(SiMe$_3$)$_2$	−4.7	140.6	132.8	132.8	140.6	132.8	132.8	−0.9	
VIII	1,2,4-(SiMe$_3$)$_3$	−3.6(1-Si) [b] −4.1(2-Si) −4.6(4-Si)	[e]	[e]	140.1	139.2	133.1	134.7	2.1; 2.0 −0.7(4-SiMe$_3$)	
IX	1,2,4,5-(SiMe$_3$)$_4$	−3.4	144.2	144.2	141.7	144.2	144.2	141.7	2.1	
X	1,4-(SiMe$_3$)$_2$,2,5-Me$_2$	−5.4	138.8	139.3	136.0	138.8	139.3	136.0	0.5	23.1
XI	1,4-(SiMe$_3$)$_2$,2-Me, 5-i-Pr	−5.0(1-Si) −6.2(4-Si)	139.0	139.5	135.8	137.9	151.0	131.0	0.6(1-SiMe$_3$) 1.2(4-SiMe$_3$)	23.1(2-Me) 25.5; 33.9(CH)

[a] Low field shifts positive (±0.1 ppm). [b] Tentative assignment. [c] Carbon-13 chemical shifts are measured from external TMS (see ref. 15). [d] Ref. 3. [e] Lines could not be detected because of the limited quantity of compound available.

Results and discussion

The silicon chemical shift in trimethylsilylbenzene is very little affected by methyl or trimethylsilyl groups in the *meta*- or *para*-positions (see Table 1, compounds I, III, IV, VI, VII). More significant shifts are induced by the same substituents in the *ortho*-position, so that the interval of silicon shifts in the compounds studied increases about tenfold to about 2 ppm. Such increase of the silicon substituent effects can hardly be attributed exclusively to the electronic influence of the *ortho*-positioned groups, although in this case the direction of the substituent effects (upfield for *o*-Me and downfield for *o*-$SiMe_3$) corresponds to the electronic nature of these substituents. Comparison of silicon chemical shift in the trimethylsilyl group with that of the quaternary carbon atom in t-butyl group shows good parallelism, i.e. downfield differential shifts in the *ortho*-disubstituted benzenes [4]. The silylmethyl carbons are always deshielded by *ortho*-methyl, -isopropyl and -trimethylsilyl groups, as are the methyl carbons in sterically crowded t-butyl groups [4—9]. Finally, methyl carbons in the *ortho*-position to the trimethylsilyl groups are always deshielded in comparison with toluene (about 2 ppm), as a result of the 1,5-interaction [4,10,11,23].

The most important arguments for steric interaction between the *ortho*-substituents are based on deviations from additivity of the ring carbon chemical shifts [11,16]. When in the *meta*- and *para*-derivatives of trimethylsilylbenzene the methyl and trimethylsilyl groups act upon the ring carbon chemical shifts practically independently (deviations from additivity are as a rule smaller than 0.7 ppm, see Table 2), then in *ortho*-substituted compounds deviations of more than 1 ppm are usual, and reach 3.8 ppm in the tetrasubstituted compound IX. Especially characteristic are differences between the sums of deviations (see Table 2). The study of the relationship between the deviations from additivity and the positions of the corresponding ring carbon atoms is complicated, because we have no data available about the real geometrical structure of the compounds studied. On intuitive grounds, using molecular models and data for standard bond lengths and bond angles [18] and Van der Waals radii [19], the steric strain should increase in the order II→V→IX (see Table 1). The same order corresponds to an increase in the sum of deviations from additivity in Table 2 (6→6.8→13.2 ppm). This method of estimating the magnitude of steric strain also gives a high value for compound X, but the unexpectedly low value for compound XI underlines the limitations of this approach when the symmetry of substituents is changed.

Bulky substituents can cause very significant deformations of the ring. The carbon analog of compound IX (1,2,4,5-tetra-t-butylbenzene has been studied by X-rays [20]. It was found that mutual repulsions of *ortho*-t-butyl groups lead to substantial bond angle deformations of the benzene ring, especially at the unsubstituted positions, where the internal bond angles increase to 129.5°. Unfortunately, we have no carbon chemical shift data for this compound, but in durene, a compound of closely similar symmetry, in which the internal bond angles by unsubstituted carbons are also increased [21], deviations from additivity of the corresponding carbon shifts are positive (Δ for C-3,6 +1.7 [16]), i.e. these carbon atoms are deshielded. Because similar deformations are highly likely in silicon analogs, large positive deviations from additivity for C-3 and C-6 carbon atoms in compound IX (see Table 2) may be a result of the increased internal

TABLE 2

^{13}C NMR CHEMICAL SHIFTS CALCULATED FOR THE AROMATIC CARBON ATOMS ON THE BASIS OF ADDITIVITY RULE AND THE DIFFERENCES FROM THE EXPERIMENTAL VALUES [a, b]

Compound	C-1		C-2		C-3		C-4		C-5		C-6		$\sum_{i=1}^{6} \lvert\Delta_i\rvert$ (ppm)
	calcd.	Δ_1	calcd.	Δ_2	calcd.	Δ_3	calcd.	Δ_4	calcd.	Δ_5	calcd.	Δ_6	
II	141.0	−3.0	142.8	+0.3	128.9	+0.6 [c]	129.2	+0.9 [c]	125.2	+0.2	133.6	+1.0	6.0
III	140.2	−0.2	134.4	−0.1	137.3	−0.5	130.0	0.0	128.1	0.0	130.7	+0.1	0.9
IV	136.5	−0.7	132.8	−0.1	128.1	0.0	137.5	−0.1	128.1	0.0	132.8	−0.1	1.0
V	145.3	+0.4	145.3	+0.4	133.2	+2.2	128.8	−0.8	128.8	−0.8	133.2	+2.2	6.8
VI	139.8	−0.7	138.7	−0.3	139.8	−0.7	134.3	−0.1	127.7	−0.2	134.3	−0.1	2.1
VII	140.9	−0.3	133.2	−0.4	133.2	−0.4	140.9	−0.3	133.2	−0.4	133.2	−0.4	2.2
VIII	146.0	[d]	144.9	[d]	138.3	+1.8	140.5	−1.3	133.9	−0.8	132.8	+1.9	
IX	145.6	−1.4	145.6	−1.4	137.9	+3.8	145.6	−1.4	145.6	−1.4	137.9	+3.8	13.2
X	141.7	−2.9	139.5	−0.2	134.0	+2.0	141.7	−2.9	139.5	−0.2	134.0	+2.0	10.2
XI	141.7	−2.7	139.9	−0.4	134.0	+1.8	138.9	−1.0	150.4	+0.6	131.2	−0.2	6.7

[a] The shielding contributions for Me and i-Pr groups are taken from ref. 12. [b] $\Delta = \delta_{exp} - \delta_{calcd}$ ppm. [c] Tentative assignment. [d] Lines could not be detected because of the limited quantity of compound available.

bond angles in these positions. The same situation is found in other *ortho*-substituted compounds II, V, VIII and X, where Δ-values for the unsubstituted ring carbon atoms C-3 and C-6 are also relatively large and positive. Of course, non-bonded interactions (depending on symmetry and nature of substituents, see compound XI in Table 2), must also be important for the ring carbon chemical shifts. For example, the short distance between the methyl group and the ring hydrogen atom in durene [21] must lead to polarization of the C—H bonds [22] and shield the unsubstituted aromatic carbon atom in the *ortho*-position to the methyl group, i.e. act in the opposite direction.

High carbon chemical shifts in the substituted positions must be influenced in a complex way, and deviations from additivity for these positions, although mostly negative in our compounds, are difficult to understand. So, in *o*-trimethylsilyltoluene (II), the deviations from additivity for the substituted carbon atoms are very different and in *o*-bis(trimethylsilyl)benzene (V) the corresponding Δ-values for C-1,2 are surprisingly small.

It is interesting to compare the chemical shifts and steric effects in *o*-bis(trimethylsilyl)benzene (V in Tables 1 and 2) and *o*-di-t-butylbenzene [4]. In both cases *ortho*-positions to the substituted carbons (C-3,6) show the largest positive deviations from additivity, but in *o*-di-t-butylbenzene this deviation is more than twice that in the silicon compound (4.92 ppm vs. 2.2 ppm). Considerably larger in the carbon analog are also the Δ-values for the substituted carbons (1.44 ppm vs. 0.4 ppm). As a result, the sum of deviations from additivity for *o*-di-t-butylbenzene is 14.3 ppm, much larger than 6.8 ppm for *o*-bis(trimethylsilyl)benzene. Moreover, larger deviations from additivity for the ring carbon atoms parallel larger shift effects for the substituent nuclei: in *o*-di-t-butylbenzene the methyl carbon and quaternary carbon atoms are shifted downfield from the corresponding resonances in t-butylbenzene by 3.85 and 3.28 ppm [4], in *o*-bis(trimethyl)-benzene these increments are 2.5 ppm for the methyl carbon and 0.6 ppm for silicon.

Unfortunately, only the methyl carbon chemical shift is available for *o*-t-butyltoluene [23], but comparison of *o*-trimethylsilyltoluene chemical shift data with these of *o*-xylene [4] shows no large differences in steric effects. Summarizing these data, it is difficult to see a stronger steric strain in the silicon analogs. Indeed, the increased length of the Si—C bonds (in comparison with C—C bonds) does not appear to lead to increased steric effects in the chemical shifts, although the trimethylsilyl group is certainly more bulky than the t-butyl group [24].

When the present text was completed we bacame aware of the studies by Zuckerman et al. [25,26] who investigated a series of substituted aryltrimethylstannyl derivatives. Our ^{13}C NMR results complement their observations (e.g. the carbons of trimethylstannyl groups are shielded by 2.57 ppm more in trimethylstannylbenzene than in *o*-bis(trimethylstannyl)benzene [25]), but they observed upfield shifts of ^{119}Sn resonances with steric compression [26].

References

1 J. Schraml, J. Pola, M. Černý, H. Jancke, G. Engelhardt and V. Chvalovský, Collect. Czech. Chem. Commun., 41 (1976) 360.

2 P. Bourgeois, R. Calas, E. Jousseaume and J. Gerval, J. Organometal. Chem., 84 (1975) 165.
3 R.L. Scholl, G.E. Maciel and W.K. Musker, J. Amer. Chem. Soc., 94 (1972) 6376.
4 E.L. Motell, D. Lauer and G.E. Maciel, J. Phys. Chem., 77 (1973) 1865.
5 A. Kiewiet, J. de Wit and W.D. Weringa, Org. Magn. Resonance, 6 (1974) 461.
6 P.P. Nicholas, C.J. Carman, A.R. Tarpley, Jr. and J.H. Goldstein, J. Phys. Chem., 76 (1972) 2877.
7 G.J. Abruscato, P.D. Ellis and T.T. Tidwell, J. Chem. Soc. Chem. Commun., (1972) 988.
8 J.W. de Haan and L.J.M. van de Ven, Org. Magn. Resonance, 5 (1973) 147.
9 D.G. Garratt and T.T. Tidwell, Org. Magn. Resonance, 6 (1974) 87.
10 J.G. Batchelor, J. Magn. Resonance, 18 (1975) 212.
11 N.K. Wilson and J.B. Stothers, in Topics in Stereochemistry, Vol. 8, Wiley-Interscience, New York, 1974, chapt. 1.
12 D. Lauer, E.L. Motell, D.D. Traficante and G.E. Maciel, J. Amer. Chem. Soc., 94 (1972) 5335.
13 M. Laguerre, J. Dunoguès, N. Duffaut and R. Calas, J. Organometal. Chem., 112 (1976) 49.
14 Nguyen-Duc-Chuy, V. Chvalovský, J. Schraml, M. Mägi and E. Lippmaa, Collect. Czech. Chem. Commun., 40 (1975) 875.
15 J. Schraml, V. Chvalovský, M. Mägi and E. Lippmaa, Collect. Czech. Chem. Commun., 40 (1975) 897.
16 J.B. Stothers, Carbon NMR Spectroscopy, Academic Press, New York and London, 1972, chap. 3 and
17 D. Doddrell, K.G. Lewis, C.E. Mulquiney, W. Adcock, W. Kitching and M. Bullpitt, Austral. J. Chem., 27 (1974) 417.
18 Tables of Interatomic Distances and Conformations in Molecules and Ions, The Chemical Society, London, 1958.
19 A. Bondi, J. Phys. Chem., 68 (1964) 441.
20 A. van Bruynsvoort, L. Eilermann, H. van der Meer and C.H. Stam, Tetrahedron Lett., (1968) 2527.
21 C.H. Stam, Acta Cryst. B, 28 (1972) 2630.
22 D.M. Grant and B.V. Cheeney, J. Amer. Chem. Soc., 89 (1967) 5315.
23 H. Pearson, J. Chem. Soc. Chem. Commun., (1975) 912.
24 M. Charton, J. Amer. Chem. Soc., 91 (1969) 615.
25 C.D. Schaeffer Jr. and J.J. Zuckerman, J. Organometal. Chem., 99 (1975) 407.
26 H.J. Kroth, H. Schumann, H.G. Kuivila, C.D. Schaeffer Jr. and J.J. Zuckerman, J. Amer. Chem. Soc., 97 (1975) 1754.