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Preliminary communication

Organosilicon compounds
CVIII*. Carbon-13 and silicon-29 NMR spectra of phenyl- and benzyl-substituted silanes

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SUMMARY

^{29}Si and ^{13}C NMR chemical shifts in Si-substituted phenyl- and benzylsilanes are determined and intercorrelated.

It was recently shown[2] that the electronic interactions between a benzene ring and MR_3 or CH_2MR_3 substituents are usefully studied by methods which do not involve the need for other ring substituents acting as a probe. ^{13}C and ^{29}Si NMR spectra meet this requirement, furthermore aromatic carbon-13 chemical shifts correlate with structural parameters[3]. For this reason the data presented in Table 1 were obtained using the spectrometer and experimental techniques previously described[6,7].

Unfortunately, the latest and apparently best correlations[8] cannot be applied to our results without reservation because they were obtained under experimental conditions (10 mol % solutions) not attainable in our laboratories at present. The average value of the apparently constant difference $\Delta\delta(C_p)$ between the chemical shifts in $C_6H_5CH_2X$ and C_6H_5X (−6.02 ppm) corresponds[8] (±20% error due to solvent effects[8]) to the total charge density in $C_6H_5CH_2X$ compounds being shifted by 0.02 units to more negative values compared with C_6H_5X compounds for the same X. Similarly, the σ^+ constants are 0.5 units more negative for CH_2X groups as compared with X groups. These findings agree well

* For part CVII see ref. 1.

TABLE 1

CARBON-13 AND SILICON-29 NMR DATA FOR BENZYL–, PHENYL- AND METHYLSILANES AND σ_p VALUES OF VARIOUS SILYL GROUPS [a]

	$C_6H_5CH_2X$		C_6H_5X		CH_3X					
Substituent X	$\delta(C_p)$ [g]	$\delta(Si)$	$\delta(C_p)$ [g]	$\delta(Si)$	$\delta(Si)$	$\Delta_0\delta(Si)$ [b]	$\Delta_I\delta(Si)$ [c]	$\Delta\delta(C_p)$ [d]	$\sigma_p(DM)$ [e]	$\sigma_p(NMR)$ [f]
$SiMe_3$	123.1	0.4	128.3	−5.1	0.0 [h]	0.4	5.5	−5.2	−0.05	0.06
$SiMe_2Cl$	124.1	26.6			29.9	−3.3			0.30	0.15
$SiMeCl_2$	125.3	26.9	131.0	17.9	31.8	−4.9	9.0	−5.7	0.41	0.42
$SiCl_3$	126.0	7.2	132.8	−0.8	12.2	−5.0	8.0	−6.8	0.43	0.37
$SiMe_2(OEt)$	123.4	11.7	129.0	5.1	13.5	−1.8	6.6	−5.6	(0.12) [i]	(0.10) [i]
$SiMe(OEt)_2$	123.6	−11.9	128.8	−20.2	−6.1	−5.8	8.3	−5.2	(0.18) [i]	(0.15) [i]
$Si(OEt)_3$	123.6	−52.7	129.5	−59.4	−44.5	−8.2	6.7	−5.9	(0.19) [i]	(0.10) [i]
$SiMe_2F$	124.1	27.4	130.1	19.8	(30.5) [j]	(−3.1)	7.6	−6.0	0.23	0.15
$SiMeF_2$	124.6	−2.9	131.5	−12.4	(4.5) [j]	(−7.4)	9.5	−6.9	0.40	0.28
SiF_3	125.8	−64.2	132.7	−73.2	[k]		9.0	−6.9	0.51	0.51
SiH_3	124.9	−56.0	129.4	−59.9	[k]		3.9	−4.5	0.07	0.10

[a] ^{13}C and ^{29}Si chemical shifts were measured at 15.09 and 11.91 MHz, resp. in neat liquids relative to external tetramethylsilane. The shifts are given in δ scale, *i.e.* in ppm units with positive values corresponding to lower shielding, the maximum error ±0.3 ppm. ^{13}C chemical shift of benzene is 128.1 ppm in this scale. [b] Substituent effect of C_6H_5 group determined as $\Delta_0\delta(Si) = \delta(Si)(C_6H_5CH_2X) - \delta(Si)(CH_3X)$. [c] $\Delta_I\delta(Si) = \delta(Si)(C_6H_5CH_2X) - \delta(Si)(C_6H_5X)$. [d] $\Delta\delta(C_p) = \delta(C_p)(C_6H_5CH_2X) - \delta(C_p)(C_6H_5X)$. [e] σ_p values determined from dipole moments of *p*-$CH_3C_6H_4X$ in ref. 4. [f] σ_p values determined from NMR $J(^{13}C–^1H)$ couplings in *p*-$CH_3C_6H_4X$ in ref. 4. [g] ^{13}C chemical shift of carbon in *para*-position to the substituent. [h] Reference compound. [i] Value for analogous methoxy derivative. [j] Taken from ref. 5. [k] Not available.

with the established (see *e.g.* ref.2) electron-accepting properties of SiR_3 groups and electron-releasing ability of CH_2SiR_3 groups and with the charges calculated by Nagy *et al.*[9,10] The present data show an interesting linear correlation between $\delta(Si)(C_6H_5CH_2X)$ and $\delta(Si)(C_6H_5X)$ characterized by unit slope and correlation coefficient of 0.999 (ten data points). This and other correlations involving $\delta(C_p)$ and σ^+ or σ_p constants will be discussed in a forthcoming paper.

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