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CARBON-13 CHEMICAL SHIFTS OF SUBSTITUTED t-BUTYLBENZENES, PHENYLTRIMETHYLSILANES AND PHENYLTRIMETHYLGERMANES

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Summary

Carbon-13 NMR chemical shifts are reported for three series of Group IV aromatics p-$XC_6H_4Y(CH_3)_3$ where Y = C, Si and Ge. The shifts for the C(1), C(2), CH_3 and C(α) carbons correlate with the substituent parameters σ_I and σ_R^0, and the slopes of the CH_3 correlations suggest roughly equal transmitting abilities for carbon and silicon. For a given substituent X, the shift of the C(1) carbon varies in the order C > Ge > Si expected from electronegativity considerations. The other ring carbon atoms experience smaller changes corresponding to their respective positions *ortho*, *para*, and *meta* to Y. The shifts of the C(4) and C(2, 6) carbons vary Si > Ge > C, in agreement (for X = $N(CH_3)_2$) with atomic charge values from published CNDO/2 calculations for carbon and silicon which indicate that while silicon exerts an electron-releasing effect through the σ-framework, there is a net π-withdrawal registered at the C(4) and C(2. 6) carbon atoms relative to Y = C.

Introduction

Although the bonding between an aromatic ring and the Group IV elements has been the subject of numerous investigations, the nature of this bonding and, in particular, its variation with the Group IV element, remain a matter for speculation [1, 2]. The direct relationship between NMR spectral parameters and the electronic effect of substituents in aromatic systems makes this technique an especially valuable probe of the metal—aromatic ring interaction. Indeed, proton shifts [3, 4] and ^{13}C—H coupling constants [5, 6] in aryltrimethylsilanes, as well as proton shifts and ^{13}C—H and ^{29}Si—H coupling constants in phenyl-, phenylmethyl-, and phenyldimethyl-silanes [7] have been interpreted in this way. Since *para*-^{13}C chemical shifts are known to be sensitive to variations in electron density [8] in aromatic compounds, we have undertaken and report here the results of a study of the ^{13}C spectra of a series of *para*-substituted t-butylbenzenes, phenyltrimethylsilanes, and phenyltrimethylgermanes.

Experimental

Compounds

Substituted t-butylbenzenes [9], aryltrimethylsilanes [5], and aryltrimethylgermanes [5] were available from previous investigations. *p*-t-Butylphenyltrimethyl germane was prepared by addition of trimethylbromogermane to the Grignard reagent obtained from *p*-bromo-t-butylbenzene in THF; m.p. 76.5—77° (recryst. abs. C_2H_5OH). (Anal. found: C, 61.68; H, 9.08. $C_{13}H_{22}Ge$ calcd.: C, 62.25; H, 8.79%.)

NMR parameters

Natural abundance, proton noise-decoupled ^{13}C NMR spectra were recorded at 25.14 MHz in the Fourier transform mode as described previously [10]. Carbon chemical shifts (ppm) were measured relative to internal tetramethylsilane (TMS). Solution concentrations were 50% (vol/vol or wt/vol) in spectroquality grade CCl_4. A resolution of ± 0.03 ppm was achieved using 16384 (16K) data points and sampling frequency of 12500 s^{-1}. Normally, 500 pulses were collected for each compound.

Assignments of aromatic carbons in the three series were based on additivity relationships [11], assuming a carbon chemical shift of 128.5 ppm for benzene. Ring carbons of phenyltrimethylsilane [12] and t-butylbenzene [13] have been previously assigned.

Regression analyses

Three-parameter analyses were obtained with the Biomedical Computer Program, Stepwise Regression, BMD02R.

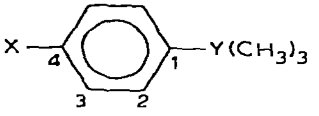
Results and discussion

The ^{13}C chemical shifts are presented in Table 1, and the parameters of a least squares analysis of the relationship between the shifts and the substituent constants σ_I and σ_R^0 [14] are given in Table 2. The correlation coefficients and standard deviations given in Table 2 indicate that eqn. 1 provides a satisfactory fit

$$\delta = \rho_I \sigma_I + \rho_R \sigma_R^0 + C \qquad (1)$$

for the shifts of the C(1), C(2), CH_3, and C(α) carbons. The correlation coefficients obtained with field and resonance (*F* and *R*) values [15] were similar. The relative values of ρ_I and ρ_R at C(1) reflect the high dependence of the *para*-carbon shifts on the π-electron density. The negative slope for ρ_R at C(2), the carbon *meta* to the X substituent, is noteworthy and has been discussed in terms of π-polarization effects by Reynolds et al. [16], for the styrene system. The relative ρ_I, ρ_R values for the methyl carbons indicate that substituent effects are transmitted to this carbon to roughly the same degree by inductive and resonance

TABLE 1. CARBON-13 CHEMICAL SHIFTS (± 0.03 ppm) OF



(Y = C, Si, Ge)[a]

X[b]	Y	C(1)	C(2)	C(3)	C(4)	CH_3	C(α)
p $N(CH_3)_2$	C	139.02	125.46	112.85	148.48	31.65	33.61
	Si	125.20	134.11	112.13	150.84	−0.72	
	Ge	127.17	133.31	112.36	149.12	−1.58	
p OCH_3	C	142.65	125.83	113.40	157.47	31.57	33.87
	Si	130.62	134.44	113.60	160.46	−0.90	
	Ge	132.49	133.88	113.84	160.09	−1.68	
p t-C_4H_9	C	147.41	124.69	124.69	147.41	31.43	34.03
	Si	136.26	133.15	124.55	151.15	−1.02	
	Ge	138.23	132.59	124.67	150.52	−1.82	
p-CH_3	C	147.61	124.88	128.65	134.07	31.47	34.16
	Si	137.87	133.18	128.48	136.21	−0.99	
	Ge	138.25	132.78	128.73	137.30	−1.77	
p $Si(CH_3)_3$	Si	140.17	132.33	132.33	140.17	−1.18	
H[c]	C	150.48	124.91	127.93	125.29	31.38	34.45
	Si	139.70	133.02	127.58	128.59	−1.12	
p Cl	C	149.03	126.38	128.08	131.35	31.27	34.28
	Si	138.04	134.33	127.89	135.16	−1.19	
	Ge	140.27	134.07	128.17	134.66	−1.82	
p-Br	C	149.49	126.79	131.00	119.26	31.16	34.27
	Si	138.53	134.59	130.83	123.60	−1.25	
p NO_2	C	158.36	126.05	123.07	146.06	30.95	35.22

[a] 50% (vol/vol or wt/vol) in CCl_4. Relative to internal TMS. Positive values denote decreasing shielding.
[b] Listed in order of increasing Hammett σ-constant. [c] The *C*(4) chemical shift in neat phenyltrimethylsilane has been recorded as 128.3 ppm [22] and for all carbons in the fourth group phenyltrimethyl derivatives as THF solutions [23]. Carbon-13 shifts have also been recorded for the 4-substituted styrenes [16].

TABLE 2. CARBON CHEMICAL SHIFT REGRESSION ANALYSIS PARAMETERS

	Y	C(1)	C(2)	C(3)	C(4)	CH_3	C(α)
ρ_I[a]	C	7.58	2.60	−2.56	10.05	−0.56	0.67
	Si	9.58	2.50	13.24	−26.09	−0.58	
	Ge	11.62	2.47	7.34	−5.13	−0.23	
ρ_R[a]	C	22.04	−1.12	21.90	−27.99	−0.62	1.76
	Si	28.05	−2.01	39.96	−50.92	−0.90	
	Ge	28.78	−0.83	45.77	−49.30	−0.50	
C[a]	C	150.35	124.9	128.5	129.4	31.4	34.4
	Si	140.0	132.9	130.85	132.9	−1.1	
	Ge	141.8	132.8	134.4	130.1	−1.83	
r[b]	C	0.999	0.913	0.668	0.464	0.981	0.989
	Si	0.991	0.982	0.962	0.808	0.991	
	Ge	0.998	0.996	0.986	0.802	0.998	
S[c]	C	0.26	0.36	6.9	14	0.058	0.092
	Si	0.92	0.20	2.7	9.2	0.031	
	Ge	0.68	0.086	2.6	12	0.013	
n[d,e]	C = 7, Si = 7, Ge = 4						

[a] Parameters of the equation. $\delta = \rho_I\sigma_I + \rho_R\sigma_R^0 + C_0$ [b] Multiple correlation coefficient. [c] Standard deviation of residuals. [d] Number of compounds. [e] Lack of σ_R^0 value for t-C_4H_9 excludes this derivative from regression analysis.

effects. The signs of ρ_I and ρ_R for CH_3 indicate, however, an inverse dependence of the chemical shift on the electronic nature of the substituent (the greater the electron-withdrawing effect of the substituent the greater the upfield shift). The same phenomenon has been observed at the α-carbon in phenyl vinyl ethers and sulfides [17], styrenes [16], 1-arylpropynes [18], and 1-arylpropenes [18].

The similar values of ρ_I and ρ_R for the methyl carbons of the t-butylbenzenes and phenyltrimethylsilanes are indicative of the similar transmitting abilities of carbon and silicon reported earlier [5]. The larger absolute value of ρ_R for silicon may reflect a somewhat greater transmission of resonance effects by this atom. (The smaller number of compounds for germanium precludes meaningful comparisons with this atom.)

The ρ-values of the methylcarbons in $Y(CH_3)_3$ reflect the limited ability of Y to transmit the electrical effect of the substituent, X, to the trimethyl system. The variations in electronic effect as Y is changed are likewise transmitted through the molecule, but in the reverse direction, and can be measured in series of compounds in which X is held fixed and Y is varied from carbon to tin. The C(1), C(4) and methyl-carbon chemical shifts are summarized in Table 3 for four substituents X which bear methyl groups. Data for C(α) are included for the X = t-butyl cases, and tin data* are included for completeness from a previous study [10].

Examination of these data reveals that the effect of the change in Y from carbon to silicon and the lower metalloids is registered, as expected, most strongly at the methyl-carbons and C(1) to which the atom Y is directly attached, and then less so at the C(2, 6) and C(4) carbons, and least at the C(3, 5) (see Table 1) positions which are respectively *ortho*, *para* and *meta* to Y in the ring. The shifts at the C(1) site vary in the order C > Ge > Si ≈ Sn, nicely consistent with the predictions of electronegativity. Little effect is seen at the methyl-carbon in the X substituent at which site the transmission is almost entirely attenuated. Some feeble electron release is also felt at the C(3, 5) (*meta*) carbons when carbon is exchanged for silicon, except in the X = OCH_3 cases.

The chemical shifts of the C(2, 6) (*ortho*) and C(4) (*para*) carbons change in the opposite direction, however, for all the substituents X studied. The demonstrated dependence of the C(4) carbon chemical shifts in aromatic systems on the total electronic effect of the substituent *para* to this site [8] leads to the conclusion that both the trimethylsilyl and trimethylgermyl groups exert a predominantly electron-withdrawing effect relative to the Y = C homologues in all cases studied. Moreover, since both silicon and germanium have lower electronegativities than carbon, the order of the C(4) shifts is probably determined by a predominant π-effect: that is, the removal of π-electron density by silicon outweighs its σ-donating effect at the C(4) site.

For the two *para*-substituted dimethylanilines in which Y = C and Si, the results of CNDO/2 calculations are now available [19]. It has recently been shown that carbon-13 chemical shifts of phenyl ring carbons in monosubstituted benzenes can be made to correlate with total charge densities derived from CNDO/2 or INDO SCF-MO calculations for all aromatic carbons [20]. Table 4 presents the differences observed in chemical shift at the ring and $Y(CH_3)_3$ methyl-carbon sites

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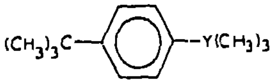
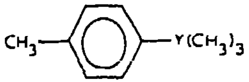
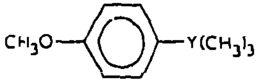
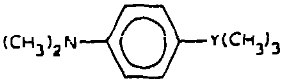
* The tin compounds except for the t-butyl derivative were studied as neat liquids, and the data are thus not strictly comparable.

TABLE 3

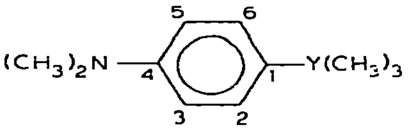
CARBON-13 CHEMICAL SHIFTS FOR SELECTED METHYL-CARBON-CONTAINING SUBSTITUENTS

													
Y	C-CH_3	C(α)	C(4)	C(1)	CH_3	C(4)	C(1)	O-CH_3	C(4)	C(1)	N-CH_3	C(4)	C(1)
C	31.43	34.03	147.41	147.41	20 74	134.07	147.61	54.52	157.17	142.65	40.62	148.48	139.02
Si	31.31	34.42	151.15	136.26	21.31	136.21	137.87	54.33	160.46	130.62	39.96	150.84	125.20
Ge	31.31	34 35	150.62	138.23	21.26	137.30	138.25	54.34	160 09	132.49	40.04	149.12	127.17
Sn[a]	31.29	34.28	150.64	137.59	21.29	137.29	137.58	54.37	160.27	131.68	39.78	150.52	126.02

[a] Tin derivatives run as neat liquids except for the t-butyl [10].

TABLE 4

CHANGES IN CARBON-13 CHEMICAL SHIFTS AND CNDO/2 NET ATOMIC CHARGES IN



(Y = C and Si[a])

	Y-CH$_3$	C(1)	C(2,6)	C(3,5)	C(4)
$\Delta\delta\,^{13}$C(Si—C) (ppm)	−32.37	−13.82	+8.65	−0.72	+2.36
CNDO/2 charges (Si—C) [b]					
Total	−0.184	−0.140	+0.083	−0.028	+0.033
$\Delta\sigma$		−0.144	+0.001	+0.003	−0.018
$\Delta\pi$		+0.004	+0.082	−0.031	+0.051

[a] Positive values denote decreased electron density. [b] Taken from ref 19.

along with the differences calculated in net atomic charges at the same sites from published CNDO/2 results as Y is changed from carbon to silicon. It can be seen that the direction of the change imposed by silicon substitution at Y predicted by the total excess charge densities on the atoms indicated is borne out by the experimental data in all cases, and that the magnitudes of the shifts in the order Y(CH$_3$)$_3$ > C(1) > C(2, 6) > C(4) > C(3, 5) correspond as well. The total charge densities give better agreement than do the π-densities, although both should be equivalent for consideration of the C(4) (*para*) position only. The carbon-13 chemical shift data reported here cannot serve to distinguish between a $(p \rightarrow d)\pi$ or a hyperconjugative σ—π interaction between the metalloid atoms and the aromatic ring, however [21].

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