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Nuclear Magnetic Resonance Studies of the Bonding in Aryltrimethylsilanes and Germanes, Aryldimethylphosphines and Arsines, and Arylmethylsulfides

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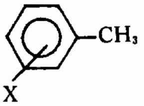
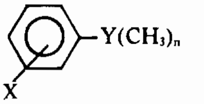
Methyl chemical shifts and ^{13}C–H coupling constants were measured for the title compounds. Reasonably good ($r > 0.9$) linear correlations between chemical shifts and Hammett σ-constants were found for all series, and the relative slopes of these lines were interpreted in terms of the mode of transmission of substituent effects to the methyl site. The effects of the $Si(CH_3)_3$, $Ge(CH_3)_3$, $P(CH_3)_2$, $As(CH_3)_2$, and SCH_3 groups on the methyl chemical shifts and coupling constants of toluenes, anisoles, and dimethylanilines were also determined and related to the electronic nature of these groups.

Introduction

We have recently reported the existence of a linear relationship between methyl ^{13}C–H coupling constants and Hammett σ-constants in systems of types I and II, where Y equals C($n=3$), N($n=2$), and O($n=1$).[1]



I



II

We have suggested furthermore that the slope of such relations are indicative of the ability of Y to transmit the electrical effects of X to the methyl group. The transmitting ability of Y is, in turn, related to such factors as its size, polarizability, electronegativity, and the nature of Y-aromatic bond.

We have now extended this study to include the third and fourth row elements, examining series of substituted aromatic silanes (II, Y=Si, $n=3$), germanes (II, Y=Ge, $n=3$), phosphines (II, Y=P, $n=2$), arsines (II, Y=As, $n=2$), and sulfides (II, Y=S, $n=1$), It was hoped that the J–σ and/or δ–σ relationships, if indeed they do exist in these series, would shed some light upon the relative transmittivities of Si, Ge, P, As, and S and upon the nature of the organometallic-aromatic bond.

Experimental Section

Syntheses. Aryltrimethylsilanes were obtained by the reaction of trimethylchlorosilane and the appropriate Grignard or lithium[2] reagents in diethyl ether, followed by hydrolysis, ether extraction, and fractionation. Boiling points or melting points and refractive indices for these compounds were found to be: *p*–Cl, bp 110-112° (24 mm), n_D^{20} 1.5097 (lit.[3] bp 119-120° (50 mm), n_D^{20} 1.5128); *p*–Br, bp 120.5-121.0° (32 mm), n_D^{25} 1.5306 (lit.[3] bp 146-148° (50 mm), n_D^{20} 1.5128); *p*–H, bp 74° (20 mm), n_D^{20} 1.4898 (lit.[4] bp 168° (747 mm), n_D^{20} 1.4908); *p*–CH_3, bp 90-91° (20 mm), n_D^{20} 1.4920 (lit.[5] bp 192° (745 mm), n_D^{20} 1.4915); *p*–*t*–C_4H_9, mp 75-76° (lit.[6] mp 78°); *p*–OCH_3, bp 123° (31 mm), n_D^{20} 1.5124 (lit.[7] bp 222.5-223.0°, n_D^{20} 1.5020); *m*–OCH_3, bp 116-118° (24 mm), n_D^{20} 1.5016 (lit.[5] bp 216° (751 mm), n_D^{20} 1.5020); *p*–$N(CH_3)_2$, bp 66° (0.8 mm), n_D^{20} 1.5412 (lit.[8] bp 252-253°, n_D^{20} 1.5338); *p*–OC_2H_5 (*via.* Grignard), bp 100.5-102° (8 mm), n_D^{23} 1.4915. *Anal.* Calcd for $C_{11}H_{18}OSi$: C, 68.0; H, 9.28. Found: C, 67.90; H, 9.63.

Aryltrimethylgermanes were synthesized by procedures analogous to those used for the silanes, reacting trimethylbromogermane[9] with the appropriate Grignard or lithium reagent. Boiling points and refractive indices for these derivatives were as follows: *p*–Cl, bp 120-123° (28 mm), n_D^{25} 1.5211 (lit.[10] bp 108-114° (12 mm), n_D^{26} 1.5241); *p*–H, bp 85-87° (23 mm), n_D^{20} 1.5053 (lit.[11] bp 182-184° (760 mm), n_D^{25} 1.5045); *p*–OCH_3, bp 125-127° (21 mm), n_D^{25} 1.5155 (lit.[12] n_D^{25} 1.5158); *p*–CH_3 (Grignard), bp 120-122° (26 mm), n_D^{20} 1.5065. *Anal.* Calcd for $C_{10}H_{16}Ge$: C, 57.53; H,

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7.67; Ge, 34.80. Found: C, 58.27; H, 8.22; Ge, 34.23. *p*–C_2H_5 (Grignard), bp 112-115° (20 mm), n_D^{25} 1.5035. *Anal.* Calcd for $C_{11}H_{18}Ge$: C, 59.29; H, 8.08; Ge, 32.61. Found: C,60.16; H, 7.91; Ge, 31.53. *m*–CH_3 (Grignard), bp 108-110° (30 mm), n_D^{25} 1.5090. *Anal.* Calcd for $C_{10}H_{16}Ge$: C, 57.53; H, 7.67. Found: C, 58.67; H, 7.86. *m*–OCH_3 (Grignard), bp 126-127° (28 mm), n_D^{23} 1.5149. *Anal.* Calcd for $C_{10}H_{16}GeO$: C, 53.43; H, 7.12. Found: C, 53.65; H, 7.28. *p*–N-$(CH_3)_2$(lithium), bp 149-150° (16 mm), n_D^{23} 1.5483. *Anal.* Calcd for $C_{11}H_{19}GeN$: C, 55.55; H, 7.99; N, 5.89. Found: C, 55.78; H, 8.07; N, 6.02.

Aryldimethylphosphines were prepared by the treatment of the appropriate phosphonous dichlorides with excess commercial CH_3MgCl in THF. *Phenylphosphonous dichloride* was commercially available.[13] *p–Chlorophenyl-*, p*–tolyl-*, and p*–bromophenylphosphonous dichlorides* were prepared from chlorobenzene, toluene, and bromobenzene, respectively, under the modified Friedel-Crafts conditions described by Buchner and Lockhart.[14] Boiling points for these compounds were found to be: *p*–Cl, 117-120° (2 mm) (lit.[15] 82-83° (2 mm)); *p*–CH_3, 133-36° (28 mm) (lit.[14] 135 (30 mm)); and *p*–Br, 154-60° (20 mm) (lit.[16] 144° (18 mm)). *p–Methoxy* and p*–ethoxyphenylphosphonous dichlorides* were prepared by the method of Gefter.[17] Fractionation of the crude *p*–OC_2H_5 compound gave a colorless liquid, bq 123-26° (0.35 mm) (lit.[18] 266°); the crude *p*–OCH_3 compound was methylated without further purification. *N,N–dimethyl-* and *N,N–diethylanilylphosphonous* dichlorides were prepared in low yields by the method of Viout.[19] The crude products were methylated without further purification. The boiling points of the *aryldimethylphosphines* were found to be: *p*–$N(CH_3)_2$, 95-98° (1 mm) (lit.[20] 265° (760 mm)); *p*–OCH_3, 117-19° (28 mm) (lit.[21] no bp reported). *Anal.* Calcd for $C_9H_{13}OP$: C, 64.21; H, 7.81. Found: C, 63.09; H, 7.15; *p*–CH_3, 116-19° (40 mm) (lit.[22] 93-95° (12 mm), 210° (760 mm)); *p*–H, 84-86° (26 mm) (lit.[23] 82° (20 mm)); and *p*–Br, 135-37° (28 mm) (lit.[21] 99° (17.5 mm)).

Aryldimethylarsines were prepared through a four-step scheme starting with the appropriate aromatic amine. The amine was diazotized to form the fluoborate salt,[24] which was converted to the arsonic acid by means of a Sandmeyer-type reaction with As_2O_3, NaOH, and CuCl.[25] Reduction of the arsonic acid with SO_2 in conc. HCl[26] afforded the dichloroarsines, which were methylated with CH_3MgCl in THF. Melting points for the *arsonic acids* were found to be: *p*–OC_2H_5, 250-55°; *p*–OCH_3, 264-74°; *p*–CH_3, 322-39° (lit.[27] 300° dec., 355°); *m*–CH_3, 145-50° (lit.[27a] 150°); *m*–OCH_3, 327-33° subl.; m–Cl, 305-10°; and *m*–Br, 162-70°. Commercial samples of benzenearsonic acid and *p*–chlorophenylarsonic acid were used. Boiling points and analytical data for the aryldimethylarsines were found to be: *p*–OCH_3, 120-25° (28 mm), *Anal.* Calcd. for $C_9H_{13}OAs$: C, 50.95; H, 6.19. Found: C, 51.37; H, 6.18; *p*–CH_3 100-10° (28 mm) (lit.[28] 220° (760 mm)); m–CH_3, 87-89° (28 mm). *Anal.* Calcd for $C_9H_{13}As$: C, 55.11; H, 6.69. Found: C, 54.81; H, 6.87; *p*–H, 85-90° (25 mm) (lit.[29] 200° (760 mm)); *m*–OCH_3, 80-90° (28 mm) (lit.[30] 123-24° (15 mm)); *m*–Cl, 155-58° (28 mm). *Anal.* Calcd for $C_8H_{10}ClAs$: C, 44.39; H, 4.66. Found: C, 45.01; H, 4.83.

Arylmethyl sulfides were obtained by treatment of the appropriate commercially-available mercaptans in basic methanol with methyl iodide. Boiling or melting points for these sulfides were found to be: *p*–OCH_3, bp 115-17° (40 mm) (lit.[31] bp 99-100° (4 mm)); *p*–CH_3, bp 96° (20 mm) (lit.[32] bp 104-105° (20 mm)); *m*–CH_3, 101-3° (28 mm) (lit[33] bp 107° (50 mm)); *p*–*t*–C_4H_9, mp 31-3°, bp 133-7° (28 mm). *Anal.* Calcd for $C_{11}H_{16}S$: C, 73.26; H, 8.96. Found: C, 73.02; H, 8.85; *p*–Cl, bp 118-20° (19 mm) (lit.[34] bp 160° (760 mm); *p*–Br, mp 35-6° (lit.[35] 37.5°); and *p*–NO_2, mp 68-70° (lit.[36] 67°, 71-2°).

The n.m.r. and i.r. spectra of all compounds were consistent with the proposed structures.

N.m.r. Parameters. Coupling constants were determined by standard side-banding techniques on a Varian A-60D n.m.r. spectrometer with Hewlett-Packard Model 200 CD audiooscillator and Model 522B electronic counter. The probe temperature was 38 ± 2°. Recorded values are averages of at least five traces at 50-cps sweep width (500 sec sweep time) and are believed accurate to within ±0.2 cps. Solution concentrations were 30% (vol:vol or wt:vol) in all cases.

Chemical shifts were measured relative to internal TMS at 100 cps sweep width (500 sec sweep time) at concentrations of 1%. Recorded values are averages of three traces and are believed accurate to ±0.3 cps.

Solvents used were spectroquality grade CCl_4, spectroquality grade $CHCl_3$ (shaken three times with alumina to remove ethanol), chemical grade CH_2Cl_2 (dried over $CaSO_4$ and distilled), chemical grade C_6H_6 (dried over sodium and distilled), and chemical grade DMSO (dried over $CaSO_4$ and distilled).

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Table I. Methyl ^{13}C–H Coupling Constants (±0.2Hz)

X	 Si(CH$_3$)$_3$	 Ge(CH$_3$)$_3$	 P(CH$_3$)$_2$	 As(CH$_3$)$_2$	 SCH$_3$
	CCl$_4$	CCl$_4$	C$_6$H$_6$	CCl$_4$	CCl$_4$
p-NO$_2$					140.7
p-Cl	119.3	125.9	128.6		139.4
m-Cl				132.4	
p-Br	119.1		128.7		139.6
m-Br					
H	119.2	125.4	128.5	132.2	139.2
p-CH$_3$	119.1	125.5	128.2	132.3	139.1
m-CH$_3$		125.5		132.0	139.1
p-C$_2$H$_5$		125.4			
p-*t*-C$_4$H$_9$	119.2				139.1
p-OCH$_3$	119.1	125.6	128.1	131.9	139.1
m-OCH$_3$	119.1	125.5		132.0	
p-OC$_2$H$_5$			127.8	132.0	
p-N(CH$_3$)$_2$	118.9	124.9	128.0		138.9

Table II. Methyl Chemical Shifts (±0.3Hz) in CCl$_4$, CHCl$_3$, DMSO

X		 Si(CH$_3$)$_3$			 Ge(CH$_3$)$_3$	
	CCl$_4$	CHCl$_3$	DMSO	CCl$_4$	CHCl$_3$	DMSO
p-NO$_2$						
p-Cl	15.0	16.1	14.6	22.3	22.4	21.8
m-Cl						
p-Br	15.0	15.2				
m-Br						
H	15.4	15.9	14.5	22.1	22.8	21.25
p-CH$_3$	13.8	14.8	12.9	20.7	21.7	19.9
m-CH$_3$				21.2	22.1	20.5
p-C$_2$H$_5$				20.8	21.9	
p-*t*-C$_4$H$_9$	14.2	15.1				
p-OCH$_3$	13.3	14.6	12.75	20.2	21.2	19.8
m-OCH$_3$	14.8	15.7	14.0	21.8	22.5	20.95
p-OC$_2$H$_5$	13.0	14.2	12.45			
p-N(CH$_3$)$_2$	12.0	13.4	10.9	18.7	20.2	17.7

X	 P(CH$_3$)$_2$	 As(CH$_3$)$_2$		 SCH$_3$	
	CHCl$_3$	CCl$_4$	CHCl$_3$	CCl$_4$	CHCl$_3$
p-NO$_2$				152.1	152.9
p-Cl	76.5, 79.3			145.5	147.5
m-Cl		71.8	7.26		
p-Br	76.0, 78.9			145.6	147.0
m-Br					
H	77.9, 80.5	70.0	72.1	145.9	148.4
p-CH$_3$	76.7, 79.2	68.2	70.8	143.8	147.0
m CH$_3$		69.2	71.5	144.6	147.6
p-C$_2$H$_5$					
p-*t*-C$_4$H$_9$				144.6	147.6
p-OCH$_3$	75.6, 78.2	67.9	70.2	142.6	145.8
m-OCH$_3$		70.1			
p-OC$_2$H$_5$	75.4, 78.0	67.6			
p-N(CH$_3$)$_2$				140.2	144.5

Results

The Y–CH$_3$ ^{13}C–H coupling constants and chemical shifts are presented in Tables I, II, and III. Coupling constants were measured in CCl$_4$; however, the fact that tertiary phosphines react violently with CCl$_4$[37] precluded its use as a solvent for this series and C$_6$H$_6$ was therefore employed. Chemical shifts were obtained in CCl$_4$, CHCl$_3$, and C$_6$H$_6$ for each series (phosphines were not analyzed in CCl$_4$). Chemical shifts of the silanes and germanes were also determined in DMSO.

The regression analysis parameters for J–σ and δ–σ plots are given in Tables IV and V. Parameters for the *t*–butylbenzenes, dimethylanilines, and anisoles are included for purposes of comparison. In all cases ordinary Hammett σ–constants[38] were used. Within some series coupling constants are quite similar and

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Table III. Methyl Chemical Shifts (±0.3Hz) in C_6H_6

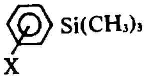
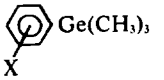
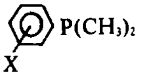
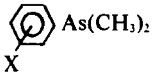
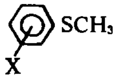
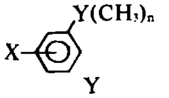
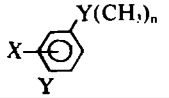
X	 Si(CH$_3$)$_3$	 Ge(CH$_3$)$_3$	 P(CH$_3$)$_2$	 As(CH$_3$)$_2$	 SCH$_3$
p-NO$_2$					102.4
p-Cl	6.8	13.5	56.0, 59.3		112.1
m-Cl				51.4	
p-Br			55.4, 58.7		110.6
m-Br					
H	12.35	19.7	63.1, 66.4	59.2	119.7
p-CH$_3$	13.8		64.9, 68.3	61.0	123.1
m-CH$_3$				61.4	122.3
p-C$_2$H$_5$		20.6			
p-t-C$_4$H$_9$	15.3				124.9
p-OCH$_3$	14.2		64.7, 68.1	61.2	125.2
m-OCH$_3$	13.1	19.5			
p-OC$_2$H$_5$	14.6		65.2, 68.6		
p-N(CH$_3$)$_2$	18.3	24.0	71.6, 84.6		131.3

Table IV. Coupling Constant Regression Analysis Parameters

 Y	ρ, cps/σ [a]	C, cps [a]	r [b]	S [c]	n [d]
C [e]	1.03	125.6	0.928	0.186	8
Si	0.130	119.2	0.150	0.248	9
Ge	0.903	125.6	0.815	0.176	8
N [e]	1.74	134.5	0.945	0.229	9
N(σ*) [e]	1.49	134.5	0.974	0.158	9
P(C$_6$H$_6$)	1.24	128.4	0.943	0.142	7
As	0.502	132.1	0.613	0.161	7
O [e]	1.83	143.1	0.915	0.308	12
O(σ*) [e]	1.38	143.0	0.970	0.184	17
S	1.29	139.4	0.934	0.205	9

[a] Parameters of the equation $J = \rho\sigma + C$. [b] Correlation coefficient. [c] Standard deviation of residuals. [d] Number of compounds. [e] Ref. 1.

Table V. Chemical Shift Regression Analysis Parameters

 Y	ρ, cps/σ [a]	C, cps [a]	r	S	n
C CCl$_4$ [b]	4.56	78.3	0.946	0.752	7
Si CCl$_4$	3.83	14.4	0.923	0.464	9
CHCl$_3$	2.83	15.3	0.881	0.439	9
DMSO	4.65	13.8	0.963	0.395	7
C$_6$H$_6$	−11.3	12.0	0.893	1.58	8
Ge CCl$_4$	4.48	21.5	0.975	0.279	8
CHCl$_3$	3.02	22.2	0.925	0.338	8
DMSO	4.85	20.8	0.977	0.119	7
C$_6$H$_6$	−10.2	18.6	0.874	2.12	5
N CCl$_4$ [b]	9.59	173.9	0.964	1.50	9
P CHCl$_3$	1.51	77.7	0.382	0.933	6
C$_6$H$_6$	−23.0	62.6	0.974	1.76	7
As CCl$_4$	6.39	69.5	0.984	0.289	7
CHCl$_3$	3.56	71.5	0.910	0.460	5
C$_6$H$_6$	−16.4	58.4	0.947	1.58	5
O CCl$_4$ [b]	10.1	6.36	0.916	0.0392	14
S CCl$_4$	7.91	145.0	0.961	0.950	9
CHCl$_3$	5.27	147.6	0.893	1.11	9
C$_6$H$_6$	−22.7	118.9	0.983	1.743	9

[a] Parameters of the equation $\delta = \rho\sigma + C$. [b] Ref. 1.

obviously rather insensitive to substituent effects.

The differences in chemical shifts within a given series are considerably larger, and the δ–σ correlations are generally good. The CCl_4 and DMSO relations all have correlation coefficients greater than 0.92, while correlations in $CHCl_3$ are somewhat poorer. Our chemical shift slope for the silicon series (3.83, CCl_4) is considerably lower than the value of 5.86

Table VI. Methyl ^{13}C–H Coupling Constants (±0.2Hz)

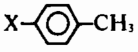
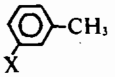
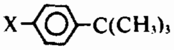
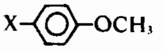
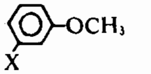
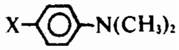
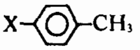
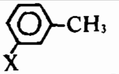
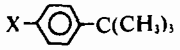
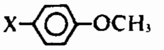
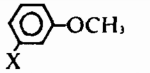
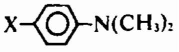
X						
H	125.8	125.8	125.5	143.0	143.0	134.5
$C(CH_3)_3$	125.8		125.45	142.7		134.1
$Si(CH_3)_3$	126.0		125.4	143.3	143.1	135.2
$Ge(CH_3)_3$	125.5	126.0		143.0	143.15	135.0
$N(CH_3)_2$	125.2		125.0	142.3		
$P(CH_3)_2$	126.0			143.7		135.4
$As(CH_3)_2$	126.1	126.0		143.4	143.2	
OCH_3	125.7		125.3	142.6		134.4
SCH_3	126.3	126.7	125.8	143.4		134.9

Table VII. Methyl Chemical Shifts (±0.3Hz)

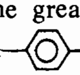
												
X	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$
H	140.0	141.1			78.8		225.5	228.0			175.3	
$C(CH_3)_3$	136.9	138.6			77.7	78.8	223.5	226.6			172.2	174.3
$Si(CH_3)_3$	139.0	140.3			78.3	79.6	225.3	227.9	225.7	228.3	176.1	176.5
$Ge(CH_3)_3$	138.5	140.0	139.6	140.9			224.6	227.7	225.4	228.5	174.7	175.8
$N(CH_3)_2$	132.9	134.8			75.85	77.4	221.1	225.0				
$P(CH_3)_2$		140.6						228.2				180.6
$As(CH_3)_2$	138.7	140.3	139.9	140.8			225.3	227.7	226.3			
OCH_3	135.4	136.8			76.9	77.9	222.2	225.7			169.0	170.3
SCH_3	137.4	138.1	138.2	139.1	77.7	78.1	224.6	226.6			174.6	175.5

reported by Sakurai and Ohtsuru.[39] The difference in slopes may be attributed to the absence, in our work, of the *m* and *p*-nitro derivatives, which have values that fall above the least-squares line. Not only is ρ dependent upon which derivatives are included, but also, as is obvious from Table V, upon the solvent used for the measurements. The chemical shift slopes determined in benzene are negative in accord with the observations of Bowie, Ronayne, and Williams.[40]
The chemical shifts of several compounds in each series were measured at a number of different concentrations and the shifts were found to be independent of concentration (at least below 3%) to within experimental error.

Asuming that the magnitudes of the δ–σ slopes are indicative of the relative transmitting ability of the Y atom, we offer the following remarks about these transmittivities: a) The transmitting abilities of the group IV elements (Y=C, Si, Ge) appear to be roughly the same, with silicon perhaps somewhat lower than carbon and germanium. b) In group VI the transmitting ability of the third row element S is less than that of the second row element O. c) The transmitting abilities within a row may increase slightly from left to right. Conclusions regarding transmittivities of the group V elements we believe to be unwarranted because of a lack of common solvent and poor correlation coefficients for some series.

Tables VI and VII list the methyl coupling constants and chemical shifts of tonuenes, *t*-butylbenzenes, anisoles, and dimethylanilines *meta-* or *para*-substituted with $Y(CH_3)_n$ groups. These data show the relative substituent effects of the $C(CH_3)_3$, $Si(CH_3)_3$, $Ge(CH_3)_3$, $N(CH_3)_2$, $P(CH_3)_2$, $As(CH_3)_2$, OCH_3, and SCH_3 groups. Both coupling constant and chemical shift data for the anisoles and dimethylanilines agree on the following orders for the *para*-$Y(CH_3)_n$ groups: Si>Ge>C; P>As>N; S>O. The toluene chemical shift data also support this order.

Conclusions

According to Bent's isovalent hybridization model,[41] the greater the electronegativity of Y in the system X——$Y(CH_3)_n$, the greater the amount of *s*-character in the C–H bonds of the methyl group(s). Since the magnitude of the ^{13}C–H coupling constants has been shown to increase with the amount of *s*-character in the C–H bond and the effective nuclear charge on carbon,[42] one would expect a more electronegative Y to produce a greater J(^{13}C–H). That such is generally the case was demonstrated by our earlier observation of a linear J–σ relationship for aromatic compounds of types I and II.

The slopes of σ-relationships are generally believed to be indicative of the systems' ability to transmit the electrical effects of the substituent, although such interpretation with chemical shift data have been cautioned against by Yokoyama, Wiley, and Miller.[43] To acocunt for the relative magnitudes of the observed

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(39) H. Sakurai and M. Ohtsuru, *J. Organometal. Chem.*, *13*, 81 (1968)

(40) J.H. Bowie, J. Ronayne, and D.H. Williams, *J. Chem. Soc.* (*B*), 785 (1966); *ibid.*, 535 (1967); J. Ronayne and D.H. Williams, *J. Chem. Soc.* (*B*), 540 (1967).

(41) H.A. Bent, *Chem. Rev.*, *61*, 275 (1961).

(42) D.M. Grant and W.M. Litchman, *J. Amer. Chem. Soc.*, *87*, 3994 (1965).

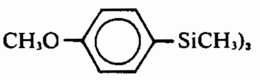
(43) T. Yokoyama, G.R. Wiley, and S.I. Miller, *J. Org. Chem.*, *34*, 1859 (1969).

δ–σ slopes we offer the following rationalizations.

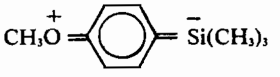
The larger size of silicon and germanium as compared to carbon should result in a decrease in transmittivity because of attenuation of field and inductive effects. The similar slopers for the C, Si, and Ge series (Si perhaps slightly power) can be ascribed, then, to either the greater polarizability of Si and Ge or (p–d) π-interactions in the aromatic-Si an -Ge bond (*vide infra*).

Regarding the group six derivatives, the second row element O was found to have a greater δ–σ slope than the third row element S. Thus, the rather strong (p–p) π-interactions between oxygen and the aromatic ring in addition to the size factor apparently outweigh the greater polarizability of sulfur plus any (p–d)π- or (p–p)π-interactions between it and the aromatic ring.

The trends observed with the $Y(CH_3)_n$ groups as substituents (Tables VI and VII) are amenable to more decisive interpretation. The chemical shift and coupling constant data derived from the group IV anisoles argue for the existence of (p–d)π–bonding in the trimethylsilyl aromatics. These spectral parameters indicate the following order of effective electronegativity of the $Y(CH_3)_3$ groups: Si > Ge > C. (This, of course, assumes that the chemical shifts are not controlled by anisotropy effects, an assumption we believe to be reasonable because of analogous trends in the coupling constants.) The effective electronegativity of Y is a function of the σ-electronegativity of Y, which can be estimated from electronegativity tables, and any π-interaction between Y and the aromatic ring. Since the electronegativities of the third and fourth row elements are almost certainly less than those of the second row elements, the relative effective electronegativities can be rationalized on the basis of π-interactions. Hence, a structure such as IIIb probably contributes significantly to the ground state of *p*-trimethylsilylanisole.



IIIa



IIIb

Furthermore in the *m*-trimethylsilyl- and *m*-trimethylgermylanisoles, the $J(^{13}C–H)$ and the chemical shift of the $O–CH_3$ are very similar, indicating that these groups are of nearly equivalent electronegativity in this position where direct resonance interactions are impossible. A similar conclusion can be reached by comparison of the analogous dimethylanilines and toluenes.

In the group V series the order P > As > N is presumably due to the opposing contributions of the electron-donating effect of N due to (p–p)π-overlap and the electron attracting effect of (p–d)π-overlap of P and As, with the overlap being greater for P. An analogous argument holds for the group VI elements S and O.

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