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GROUP IVB METALLOIDAL SUBSTITUENT EFFECTS STUDIED BY CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Summary

The natural abundance carbon-13 NMR spectra of series of compounds $\text{ArX}(\text{CH}_3)_3$ (Ar = phenyl, 1- and 2-naphthyl, 4-biphenyl and 9-anthryl; X = C, Si, Ge, Sn, Pb), have been recorded and essentially completely assigned by specific deuteration, magnitudes of $^{13}\text{C}-\text{X}$ couplings and other criteria. For these directly bonded metalloidal systems, the substituent chemical shifts at formally conjugated positions have been considered in terms of mesomeric electron withdrawal, associated with orbitals of π -symmetry on X, and opposing electron donation, resulting from the aryl C-X bond polarisation. For silicon the former effect predominates, but for germanium, tin and lead, opposing electron-donating mechanisms assume importance. For 1-naphthyl systems, the effects of molecular distortion on carbon-13 chemical shifts are critical at certain positions. The substituent effects of $\text{M}(\text{CH}_3)_3$ in aromatic systems are very feeble in comparison with the conventional substituents of organic chemistry.

Introduction

The mechanisms by which substituents containing Group IVB elements perturb an adjacent aromatic system are of much current interest [1], and a variety of techniques have been employed in their assessment [2–4]. Regarding ground-state interactions, which are our main present concern, nuclear magnetic resonance spectroscopy [5] and more recently photoelectron spectra [6] seem most capable of providing a meaningful insight into the problem. Infrared intensity

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measurements [7] are also considered to be of much value. Some years ago we commenced a program designed to assess the electronic effects of metal-containing groups, utilising ^{19}F chemical shifts to monitor electron density fluctuations in the aromatic ring [5], and the following conclusion based on an inductive model (which was reasonable at that time) was drawn with respect to Group IVB derived substituents, viz. $\text{M}(\text{CH}_3)_3$ ($\text{M} = \text{Si, Ge, Sn, Pb}$) engage in conjugative electron withdrawal ($-\text{M}$) involving orbitals of π -symmetry on M , the degree of conjugation being a function of M -orbital size, and energy and size of the outer lying orbital of π -symmetry in the aromatic. For $\text{M}(\text{CH}_3)_3$ in certain situations, shielding mechanisms could mask this conjugative electron-withdrawal.

More recently, Adcock and co-workers [8] conducted a Dual Substituent Parameter dissection (DSP) of the overall effect of $(\text{CH}_3)_3\text{M}$ ($\text{M} = \text{Si, Ge, Sn, Pb}$) in fluoronaphthalenes, and this analysis indicated the operation of mesomeric electron withdrawal and donation for Si and Pb , respectively, but no significant net conjugation for Ge and Sn . The following inductive and resonance substituent parameters were derived: $(\text{CH}_3)_3\text{Si}$, $\sigma_{\text{I}} = 0.02$; $\sigma_{\text{R}}^{\text{o}} = 0.05$; $(\text{CH}_3)_3\text{Ge}$, $\sigma_{\text{I}} = 0.06$, $\sigma_{\text{R}}^{\text{o}} = 0.01$; $(\text{CH}_3)_3\text{Sn}$, $\sigma_{\text{I}} = 0.09$; $\sigma_{\text{R}}^{\text{o}} = -0.02$; $(\text{CH}_3)_3\text{Pb}$, $\sigma_{\text{I}} = 0.16$; $\sigma_{\text{R}}^{\text{o}} = -0.10$.

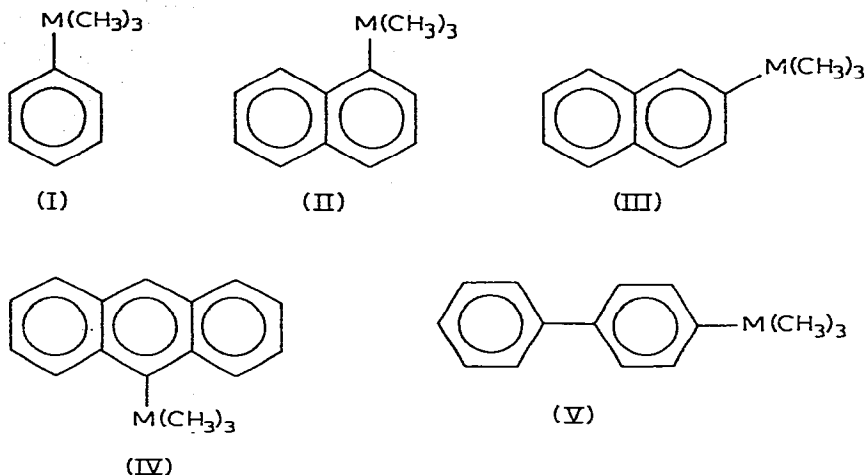
The ^{19}F approach necessarily involves examination of a disubstituted aromatic, and creates the possibility of mutual substituent-probe interactions [7]. The degree of perturbation in a mono-substituted aromatic is therefore more reliably interpreted and perhaps of greater fundamental significance, and some ^{13}C NMR [9], infrared intensity [7] and photoelectron spectroscopy (PES) measurements [6] of $\text{C}_6\text{H}_5\text{M}(\text{CH}_3)_3$ ($\text{M} = \text{Si, Ge, Sn}$) have been conducted in this connection, and generally support the ideas based on the ^{19}F NMR data [5]. It is now recognised that full appreciation of substituent effects on aromatic systems cannot be achieved from examination of benzene derivatives alone, and extensions to naphthalene and anthracene have been eminently fruitful. However, certain techniques readily applied to benzene systems, e.g. infrared intensities [7] seem incapable of routine application to substituted naphthalenes or anthracenes without very complete vibrational analyses. The problems here seem to be colossal. For such derivatives also, of low symmetry, problems could arise for accurate estimation and assignment of the various ionisation energies in the PES*. Based on impressive experimental and computational work [10], the realisation is that ^{13}C chemical shifts in closely related aromatic systems provide important insight into π -electron density patterns, and correlate well with other measures of substituent-substrate interactions. These ^{13}C shifts, while in some respects complementing ^{19}F shifts, provide simultaneous measures of perturbations at all carbons in the system, and provided care is exercised, therefore reveal a more complete picture, than a solitary ^{19}F probe. In anticipation that examination of metalloidal substituted naphthyl and anthryl systems would be illuminating regarding these substituent effects, we have measured and assigned the natural abundance ^{13}C NMR spectra of the compounds I-V and recorded the conclusions that seem to follow.

Results and discussion

Synthesis of compounds

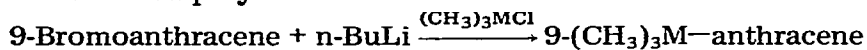
Series I, II, III and V were obtained by treating the appropriate bromoaromat-

* For example, see the spectra in ref. 6.



(I, II, III, V : M = C, Si, Ge, Sn, Pb ; IV : M = C, Si, Sn)

ic sequentially with *n*-butyl-lithium or -magnesium, in ether and $(\text{CH}_3)_3\text{MX}$. The *t*-butyl compounds were obtained by direct *t*-butylation under Friedel-Craft conditions, or other standard routes. Surprising difficulty was encountered with the 9-anthryl series (IV), although what appeared to be a perfectly plausible route was employed:



Generally, substantial quantities of anthracene were formed, (even before the addition of $(\text{CH}_3)_3\text{MX}$) under scrupulously dry conditions. Fortunately, a very low yield of the $9\text{-(CH}_3)_3\text{Sn}$ compound was isolated, nevertheless. Taylor [11] and Eaborn [12] had experienced similar frustration in their attempted 9-functionalisation of anthracene. 9-Anthryllithium appears to have a very surprising capacity for hydrogen abstraction yielding anthracene and some very careful work has been reported recently on this subject [11]. Using an *in situ* technique at low temperatures, Eaborn [12] did succeed in obtaining a low yield of the $9\text{-(CH}_3)_3\text{Si}$ compound, and very kindly provided us with its ^{13}C spectrum. In view of our experiences, we must be somewhat skeptical of reports involving 9-anthryllithium in which high yields of 9-functionalised compounds were obtained. Attempts to synthesise the $9\text{-(CH}_3)_3\text{Pb}$ derivative were not rewarding as only di-9-anthryldimethyllead was obtained in low yield. 9-*t*-Butylanthracene, after some initial difficulties was synthesised essentially as described in the literature [13].

Carbon-13 substituent chemical shifts

In order to calculate ^{13}C substituent chemical shifts (SCS) for Group IV phenyl systems, unequivocal carbon assignments and accurate ^{13}C chemical shifts are required. A reasonably detailed description of our assignment strategies is presented below.

System I

For the symmetric phenylmetal compounds, four main criteria were used.

These were (a) signal intensity, (b) specific deuteration, (c) ^{13}C -M coupling constants and (d) chemical shift data.

Of the five Group IVB elements, only two have magnetically active isotopes of any significance. These are ^{207}Pb ($I = \frac{1}{2}$) which contributes 21.1% of total isotopic abundance and ^{117}Sn and ^{119}Sn which are present in 7.7 and 8.7% natural abundance respectively. The ^{13}C -M coupling constants to C(2) and C(3) are of similar magnitude and much greater than those to C(4) [9], presumably reflecting the favorable *trans*- C_3 -M array. It has been assumed that this phenomenon generally holds for the 1-naphthyl and 9-anthryl systems. In the 1-naphthyl case, the molecule is unsymmetric and the only convenient deuteration possible is at C(4), making assignments based on ^{13}C -M coupling constants of major importance.

Regarding chemical shifts, resonances from quaternary carbons usually occur some three to five ppm further downfield than protonated carbons [10] and often are of reduced intensity, particularly under pulsed conditions (FT). Signal intensities associated with quaternary carbons often become a major problem when accumulating spectra in the FT mode. Relaxation times (t_1 s) for quaternary carbons in many polynuclear hydrocarbons are extremely long, (greater than 30 seconds in some cases) and the recycle time for each pulse has to be increased from 4-5 seconds for a normal hydrocarbon to greater than 25 seconds for a polynuclear system.

The chemical shifts and assignments for each carbon in the series $\text{PhM}(\text{CH}_3)_3$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) are given in Table 1. The ^{13}C spectrum of *t*-butylbenzene has been assigned by direct deuteration at the *ortho* carbon by Maciel and co-workers [14].

1-Naphthyl system

Carbon-13 assignments. Positive assignment of C(4) in the trimethyl-silicon, -germanium and -tin compounds was achieved by direct deuteration. Quaternary carbons in all compounds were assigned by off-resonance noise decoupling [15] (CW mode) and in the 1-naphthyl-tin and -lead compounds, ^{13}C -M coupling constants provided valuable information concerning accurate assignment of ring carbons (Table 2).

TABLE 1
CARBON-13 CHEMICAL SHIFTS (ppm) OF THE GROUP IVB SUBSTITUTED PHENYL SYSTEM
 ^{119}Sn - ^{13}C AND ^{207}Pb - ^{13}C COUPLING CONSTANTS (Hz) GIVEN IN BRACKETS

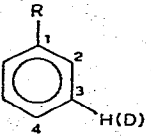
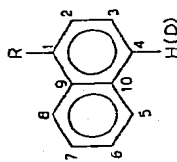
Compound	R	C(1)	C(2)	C(3)	C(4)	* $\text{C}(\text{CH}_3)_3$	CH_3
	H	128.4					
	CH_3	137.6	129.1	128.3	125.4		21.5
	$\text{C}(\text{CH}_3)_3$	151.0	125.3	128.1	125.5	34.6	31.4
	$\text{Si}(\text{CH}_3)_3$	140.2	133.4	127.8	128.8		-1.1
	$\text{Ge}(\text{CH}_3)_3$	142.2	133.0	128.0	128.3		-1.8
	$\text{Sn}(\text{CH}_3)_3$	141.9	135.9	128.3	128.2		-9.9
	$\text{Pb}(\text{CH}_3)_3$	(450.0)	(35.4)	(45.4)	(10.0)		(351.4)
	148.6	136.4	128.4	127.5		-2.5	
	(364.0)	(63.4)	(68.8)	(16.2)		(269.7)	

TABLE 2
 CARBON-13 CHEMICAL SHIFTS (ppm) OF THE GROUP IVB SUBSTITUTED 1-NAPHTHYL SYSTEM, ^{119}Sn - ^{13}C AND ^{207}Pb - ^{13}C COUPLING CONSTANTS
 (Hz) IN BRACKETS

Compound	R	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	a C(CH ₃) ₃	CH ₃
	H	127.9	125.8							133.6	133.6		
	CH ₃	134.2	126.6	125.5	126.6	128.6	125.4	125.7	124.1	132.7	133.6		19.3
	C(CH ₃) ₃ ^a	145.9	123.1	125.0	127.4	129.6	124.5	124.5	126.8	132.0	135.8	35.8	31.7
	Si(CH ₃) ₃	137.8	133.1	125.5	129.7	129.2	125.1	125.2	128.1	137.4	133.8		-1.0
	Ge(CH ₃) ₃	140.4	132.0	125.6	129.1	129.1	125.3	125.1	128.3	137.2	134.2		-0.2
	Sn(CH ₃) ₃	142.0	134.6	125.3	128.8	129.0	125.8	125.4	129.9	133.8	140.1		-8.4
			(31.6)	(37.0)	(12.2)				(32.6)	(34.1)	(35.6)		(349.0)
	Pb(CH ₃) ₃	150.1	134.6	125.8	128.1	129.0	125.8	125.3	130.6	134.3	139.2		-1.2
		(388.0)	(60.0)	(78.0)	(16.0)	(8.0)	—	—	(50.0)	(40.0)	(48.0)		(271.1)

^a Recorded at 22.63 MHz. Chemical shifts slightly different from those recorded at 15.086 MHz and located in Table 3.



1-*t*-Butylnaphthalene. Carbon assignments are given in Table 2. The three quaternary carbons have been assigned by off-resonance noise decoupling, and of these, C(1) would be expected at lowest field (β -effect). 4-Deutero-1-*t*-butylnaphthalene was synthesised and permitted the unambiguous assignments of C(4), C(2), C(3), C(9), C(10) and C(5), on the basis of ^2H -isotope effects on chemical shifts, and vicinal ^2H - ^{13}C coupling [16]. C(6) and C(7) anticipated to have very similar chemical shifts are assigned to resonances at 125.0 and 125.2 ppm, with C(8) at 127.3 ppm. An alternative approach to the assignment of the spectrum of 1-*t*-butylnaphthalene employed *t*-butyl SCS values calculated from 1-fluoronaphthalene and 4-fluoro-1-*t*-butylnaphthalene. A somewhat unsatisfactory correlation between predicted and observed chemical shifts resulted but this was traced to the incorrectness of an assignment for 1-fluoronaphthalene itself [16]. With correct assignments for 1-fluoronaphthalene [17], a correlation in harmony with the assignments listed in Table 2 was obtained (Table 3).

1-Naphthyltrimethylsilane and 1-naphthyltrimethylgermane. The spectra of these compounds are very similar, and the assignments are located in Table 2. The quaternary carbons, C(1), C(9) and C(10) have been assigned by off-resonance noise decoupling. The remaining carbons have been assigned on the basis of chemical shift trends, substituent effects of these groups at various positions in naphthalene as determined by ^{19}F chemical shifts, and our general knowledge of substituent effects on ^{13}C shifts in a wide range of substituted naphthalenes [17]. In addition, the secure assignments in the related tin and lead compounds, based on ^{13}C -M coupling, provide chemical shift trends for the whole series that are very satisfactory. Examination of certain fluoro-substituted derivatives, and assumptions regarding additivity provide consonant assignments.

1-Naphthyltrimethylstannane. In this compound, ^{13}C - ^{119}Sn coupling constants provide valuable information with regard to carbon assignments. The three quaternary carbons and C(4) have been assigned using methods previously mentioned. In this case, C(9) and C(10) can be readily distinguished on the basis of ^{13}C - ^{119}Sn coupling constants. It has been found that in phenyltrimethylstannanes and substituted phenyltrimethylstannanes [5], the ^{13}C - ^{119}Sn coupling constant for the *meta* carbon is generally slightly larger than that for the *ortho* carbon. On this basis, C(2) and C(3) can be assigned with confidence. C(8), *cis* vicinal to Sn-(CH_3)₃ [18] would be anticipated to couple to $^{117,119}\text{Sn}$ with *J* being somewhat smaller than the C(3) coupling. C(5) we know to suffer a slight downfield shift in compounds of this type, while C(6), C(7) have chemical shifts very similar to those of C_β in naphthalene.

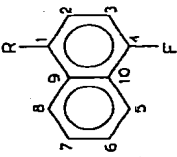
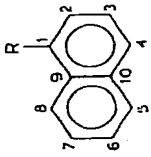
1-Naphthyltrimethylplumbane. A complete carbon assignment for this compound is almost possible owing to significant ^{13}C - ^{207}Pb couplings to eight of the ten ring carbons. The three quaternary carbons are associated with coupling constants of 388.0, 40.0 and 48.0 Hz respectively. C(2), C(3) and C(8) have been assigned as outlined above for the tin compound, while C(4) and C(5), both exhibit coupling to ^{207}Pb , but the coupling constants, and chemical shift trends are consistent only with the indicated (Table 2) assignments.

2-Naphthyl system

2-*t*-Butylnaphthalene. The assignments given for each carbon are listed in Table 5. The three quaternary carbons have been assigned by off-resonance noise

TABLE 3

CARBON-13 CHEMICAL SHIFTS (ppm) FOR 1-FLUORONAPHTHALENE, 4-FLUORO-1-t-BUTYLNAPHTHALENE AND 1-t-BUTYLNAPHTHALENE [17].
¹⁹F-¹³C COUPLING CONSTANTS (Hz) GIVEN IN BRACKETS

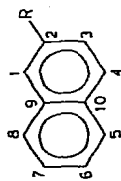
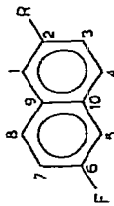
Compound	R	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	*C(CH ₃) ₃ CH ₃	
	H	124.2 (4.6)	126.0 (8.0)	109.8 (19.8)	159.5 (253.6)	120.9 (5.0)	126.6 (2.0)	127.3 —	128.1 (3.0)	135.7 (5.0)	124.3 (17.2)		
	t-Bu	142.0 (5.1)	122.9 (8.7)	108.0 (19.4)	158.2 (254.3)	121.8 (6.6)	125.0 —	125.6 —	127.0 (2.0)	133.3 (4.1)	125.5 (17.3)	35.6	31.6
	t-Bu	145.8	122.8	124.7	127.3	129.5	124.1	124.1	126.6	131.8	135.6	35.7	31.6
		Chem. shifts from t-Bu SCS +17.8	122.7	124.0	126.6	128.8	124.2	124.1	126.8	131.2	134.8		

t-Bu SCSs calc. from fluoro compound
 +17.8 -3.1 -1.8 -1.3 +0.9 -1.6 -1.7 -1.1 -2.4 +1.2

TABLE 4

CARBON-13 CHEMICAL SHIFTS (ppm) FOR 6-FLUORONAPHTHALENE, 6-FLUORO-2-t-BUTYLNAPHTHALENE AND 2-t-BUTYLNAPHTHALENE [17].
¹⁹F-¹³C COUPLING CONSTANTS (Hz) GIVEN IN BRACKETS

Compound	R	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	* C(CH ₃) ₃ CH ₃
	H	128.1 (0)	125.2 (2.8)	127.0 (1.2)	127.5 (5.1)	130.9 (21.0)	161.0 (248.8)	116.2 (25.9)	130.5 (10.1)	130.8 (~0)	134.7 (9.9)	
	t-Bu	123.1 (0)	147.9 (2.5)	126.1 (~0)	127.3 (5.1)	110.4 (20.4)	160.0 (249.7)	116.1 (25.5)	130.6 (10.2)	130.9 (~0)	132.8 (10.2)	34.7 (31.2)
	<i>t</i> -Bu SCS values	-5.0	+22.7	-0.9	-0.2	-0.5	-1.0	-0.1	+0.1	+0.1	-1.9	
	t-Bu	122.9	148.4	124.7	127.6	128.0	125.2	125.7	127.4	134.0	132.3	34.8 31.3



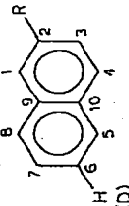
Chem. shifts from *t*-Bu SCS

122.9 148.5 124.8 127.7 127.4 124.8 125.4 128.0 133.7 131.7

TABLE 5

CARBON-13 CHEMICAL SHIFTS (ppm) OF THE GROUP IVB SUBSTITUTED 2-NAPHTHYL SYSTEMS. ¹¹⁹Sn-¹³C AND ²⁰⁷Pb-¹³C COUPLING CONSTANTS (Hz) IN BRACKETS

Compound	R	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	* C(CH ₃) ₃ CH ₃
	H	127.9	125.8					125.8		133.6	133.6	
	CH ₃	126.9	135.4	128.0	127.3	127.8	125.0	125.9	127.6	133.6	131.8	21.6
	C(CH ₃) ₃	124.7	148.4	122.9	127.4	128.0	125.2	125.7	127.6	134.0	132.3	34.8 31.3
	Si(CH ₃) ₃	133.1	137.8	129.8	127.0	128.1	126.2	125.7	128.1	133.8	133.8	-1.1
	Ge(CH ₃) ₃	133.0	139.6	129.7	127.2	127.7	125.7	125.7	127.8	133.2	133.5	-1.7
	Sn(CH ₃) ₃	136.1 (34.9)	139.4 (37.9)	132.3 (~46)	127.1	127.6	125.7	125.7	127.6	133.5 (50.8)	133.5 (9.1)	-9.5 (351.0)
	Pb(CH ₃) ₃	135.2 (60.4)	146.8 (332.2)	133.4 (64.9)	127.4	127.8	125.6	125.5	127.5	133.9 (69.5)	133.1 (12.1)	-2.1 (271.6)



decoupling. *t*-Butyl SCS values were calculated from 2-fluoronaphthalene and 2-*t*-butyl-6-fluoronaphthalene, and a disappointing correlation resulted for some positions. It was then established that several assignments listed [19] for 2-fluoronaphthylene itself were incorrect. Utilising unambiguously determined [17] chemical shifts, an excellent fit between calculated and observed data for 2-*t*-butylnaphthalene was obtained (Table 4). The most serious discrepancies (~ 1.00 ppm) occurred for C(1) and C(3), i.e. *ortho* to the *t*-butyl group, but the high-field positions (relative to C_α and C_β in naphthalene) of these signals (γ -effect of methyls) makes assignment quite straight forward. A fully proton-coupled spectrum of 2-*t*-butylnaphthalene supports the indicated assignments.

2-Naphthyltrimethylsilane and 2-naphthyltrimethylgermane (Table 5). The carbon assignments for these compounds were greatly facilitated by deuterium incorporation at C(6) which identifies C(6) and C(8) (^2H — ^{13}C coupling). The three quaternary carbons have been assigned by off-resonance noise decoupling, while C(1) and C(3) experience substantial downfield (~ 4 – 5 ppm) shifts, associated with the $(\text{CH}_3)_3\text{M}$ group, (cf. the phenyl system). C(4), C(5), C(7), in unconjugated positions have chemical shifts very similar to those of C_α and C_β in naphthalene, and also harmonise with the shifts for the tin and lead compounds (vide infra). Analysis of the spectra of certain fluoro derivatives, and additivity consideration, provide acceptable agreement.

2-Naphthyltrimethylstannane (Table 5). An essentially complete assignment for this compound is possible on the basis of ^{13}C — ^{119}Sn coupling constants, off-resonance noise decoupling and deuterium substitution at C(6) together with deuterium isotope effects [16] and the large downfield "*ortho* effects" of $(\text{CH}_3)_3\text{M}$. The two quaternary carbon resonances at 133.5 ppm (two carbon intensity) having coupling constants of 50.8 and 9.1 Hz have been assigned to C(9) and C(10) and the signals at 136.1 and 132.3 ppm having J values of 34.9 and 37.9 Hz have been assigned to C(1) and C(3). The signal at 127.1 ppm (with $J \sim 46$ Hz based on observation of one satellite) is appropriate for C(4), *trans* vicinal to tin.

The C(8) signal in the deuterated compound is again very broad owing to substantial ^{13}C —D coupling [16] and has been assigned the resonance at 127.6 ppm. C(5) and C(7), the remaining carbons, cannot be definitely assigned, but the chemical shifts of 127.6 and 125.7 ppm respectively, are completely consistent with the chemical shift trends, and with C_α and C_β in naphthalene.

2-Naphthyltrimethylplumbane (Table 5). Positive assignments for the substituted ring have been made on the basis of ^{13}C — ^{207}Pb coupling constants. The three quaternary carbons have been readily identified and C(9) and C(10) distinguished on the basis of a small coupling (12.1 Hz) to C(10) and a larger coupling (69.5 Hz) to C(9) (Table 5). C(6) would be expected to be similar to C(6) in the germanium and tin compounds and has been assigned a chemical shift of 125.6 ppm, although it is difficult to distinguish from C(7) (125.5 ppm) as expected. C(5) and C(8) have been assigned on the basis of chemical shift trends in the series.

4-Biphenyl system (Table 6)

Carbon assignments in the biphenyl system are facilitated by the presence of a plane of symmetry through the two aromatic rings, and C(4) exhibits the only single intensity carbon resonance not associated with a quaternary carbon. Carbon as-

signments for biphenyl have been made by Alger and co-workers [20] and those for 4-methylbiphenyl by Schulman and Walling [21]. Quaternary carbons were identified by their low field position and low intensity signal where PFT accumulation was used. Our main concern was with C(4).

4-t-Butylbiphenyl. Carbon assignments for several of the compounds were calculated by considering the effect of a phenyl substituent (calculated from biphenyl) at the *para* position in the substituted ring. The five carbon resonance at δ 126.9 ppm has been assigned to C(2), C(2') and C(4'). The low field resonance at 149.8 ppm compares quite nicely with C(1) in *t*-butylbenzene and has been assigned to C(4) in biphenyl. Since it is known that the methyl group has a similar effect to the *t*-butyl group at sterically remote positions [4], the unsubstituted ring carbons have been assigned chemical shifts similar to those in 4-methylbiphenyl [21].

4-Biphenyltrimethylsilane and 4-biphenyltrimethylgermane. A similar argument to that for 4-butylbiphenyl has been used for the carbon assignments in these two compounds. The assignments of the unsubstituted ring carbons are very similar to those given for the CH_3 , $(\text{CH}_3)_3\text{C}$, and $(\text{CH}_3)_3\text{Sn}$ compounds. C(4') appears as a one carbon intensity signal at 127.1 ppm.

4-Biphenyltrimethylstannane. In this compound, the two resonances at 126.9 and 136.3 ppm with ^{119}Sn - ^{13}C coupling constants of 42.6 and 37.5 Hz have been assigned to C(2) and C(3), respectively. The three quaternary carbons were identified by their low intensity signals but because no ^{119}Sn satellites were visible about C(4), these assignments are not unambiguous. C(4') has been assigned to the one carbon intensity signal at 127.2 ppm.

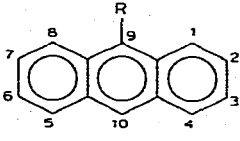
9-Anthryl system (Table 7)

9-t-Butylanthracene. The three quaternary carbons in this compound can readily be distinguished from C(10) on the basis of signal intensity and their low field position. The assignment has been greatly facilitated by the complete ^{13}C assignment for 9-methylanthracene made by Marshall and co-workers [22]. Carbons which are well separated from the *t*-butyl moiety, are assumed to have similar chemical shifts to the corresponding carbons in the 9-methyl compound although some disagreement may result from ring distortions caused by the bulky *t*-butyl group. Differences between 1-methyl- and 1-*t*-butyl-naphthalene are useful in this regard. C(10) has been assigned on the basis of signal intensity and a comparison of C(10) in 9-methylanthracene and anthracene itself. C(1) and C(8) should be at lower field than in the 9-methyl compound since a δ - rather than a γ -methyl effect is operative, (cf. naphthyl system). The outer ring carbons, C(2), C(7) and C(3), C(6) being well separated from the *t*-butyl group should have chemical shifts similar to the corresponding carbons in 9-methylanthracene but slightly to higher field. C(9) has been assigned at 143.1 ppm on the basis of signal intensity.

9-Anthryltrimethylsilane. The ^{13}C spectrum of this compound is in many ways similar to that of 9-*t*-butylanthracene. Relief of steric congestion in the C(1) and C(8) vicinity, owing to the increase in the C(9)-Si bond length, is quite noticeable with the chemical shift of C(1) and C(8) (128.6 ppm). (Similar low field shift occurred at C(8) in 1-naphthyltrimethylsilane.) C(10) has been readily assigned on the basis of chemical shift and signal intensity. The outer ring carbons

TABLE 7

CARBON-13 CHEMICAL SHIFTS (ppm) FOR GROUP IVB DERIVATIVES OF ANTHRACENE. ^{119}Sn - ^{13}C COUPLING CONSTANTS (Hz) ARE IN BRACKETS

Compound	R	C(1)	C(2)	C(3)	C(4)	C(5)
	H	128.2	125.3	125.3	128.2	128.2
	CH_3	124.5	125.0	124.5	128.8	128.8
	$\text{C}(\text{CH}_3)_3$	127.0	123.8	122.7	129.0	127.0
	$\text{Si}(\text{CH}_3)_3$	128.6	124.4	124.7	129.5	129.5
	$\text{Sn}(\text{CH}_3)_3$	130.0	125.1	124.5	129.4	129.4
		(~30)				

(excluding C(1) and C(8)) should have chemical shifts similar to those in the 9-methyl compound. However, some doubt must arise concerning the assignments for the remaining quaternary carbons, C(11/14) and C(12/13), but those indicated are consistent with "ortho deshielding" effect of $(\text{CH}_3)_3\text{M}$.

9-Anthryltrimethylstannane. In this compound, ^{13}C - ^{119}Sn coupling constants associated with the two quaternary ring junction carbons (C(11)/C(14) and C(12)/C(13)) C(10) and C(1,8) are quite evident (Table 7). Again, it has been assumed that coupling to C(11)/C(14) (39.0 Hz) is greater than that to C(12)/C(13) (30.0 Hz), on the basis of a *trans* array being favored. The one carbon intensity signal associated with ^{13}C - ^{119}Sn coupling of 18.0 Hz at 128.5 ppm has been assigned to C(10). ^{119}Sn - ^{13}C coupling to C(1)/C(8) was tentatively identified and its magnitude is appropriate for a *cis* vicinal coupling [18]. The C(1,8) assignment, along with the others, is in agreement with chemical shift trends in the series, and with the movements of the C(8) resonance of 1-naphthyl systems.

Model

Before analysing these ^{13}C substituent chemical shifts (Tables 8, 9) it is important to consider the mechanisms by which metalloidal substituents can perturb electron density patterns at remote conjugated positions. Until very recently, two distinct models had been proposed to account for the electronic behaviour of spherically symmetrical MR_3 groups, viz. the inductive and hyperconjugative models. The latter description is now generally accepted [23]. For the *t*-butyl group, the carbon analogue of the $\text{M}(\text{CH}_3)_3$ groups, the well-known apparent electron donation in the neutral ground state involves polarisation without charge transfer, if extrapolation from the methyl group is accepted. The hyperconjugative electron donation of MR_3 responds to demand, e.g. σ_p for $(\text{CH}_3)_3\text{C}$ is -0.197 but in situations of electron deficiency, a mix with more resonance character ($\sigma_p^+ = -0.256$) is required. Of particular significance are two observations which suggest C-Si (electron donating) hyperconjugation in $\text{Si}(\text{CH}_3)_3$ is very feeble. Brown [24] has determined $\sigma_p = -0.07$ and $\sigma_p^+ = 0.021$ for $\text{Si}(\text{CH}_3)_3$ compared with -0.256 (σ_p^+) for $\text{C}(\text{CH}_3)_3$, from solvolysis of the appropriate *t*-cumyl chlorides. Solvolytic data for chloromethyltrimethylsilane [25] suggests no accelera-

C(6)	C(7)	C(8)	C(9)	C(10)	C(11)/ C(14)	C(12)/ C(13)	*C(CH ₃)	CH ₃
125.3	125.3	128.2	126.2	126.2	131.8	131.8		
124.5	125.0	124.5	129.7	125.2	131.2	129.9		13.5
122.7	123.8	127.0	143.1	127.0	132.3	130.5	39.2	35.4
124.7	124.4	128.6	137.0	129.9	131.3	135.6		-4.6
124.5	125.1	130.0	143.1	128.5	131.7	138.5		-4.6
		(~30)		(18.0)	(39.0)	(30.0)		

tion by this hyperconjugative mechanism. We are forced to conclude, contrary to theoretical predictions [1], that Si-C electron donation in situations of demand is not measurably significant. This result implies that *p*-electron density at the atom directly bonded to the aryl system is crucial [1], with other factors, e.g. overlap or perturbation integral being almost inconsequential.

On progressing from C(CH₃)₃ to Si(CH₃)₃ the following modes of interaction are conceivable: (1) Si-C hyperconjugative *e*-donation, but this has been suggested above to be feeble, (2) the π -inductive effect (increased electron density at conjugated positions if Si is more electropositive than *sp*²C) associated with the polarity of the aryl C-Si bond. We know of no data permitting a reliable estimate of this effect, but we believe it would be small. Similar considerations apply to the field effect, (3) electron withdrawal by a conjugative interaction. The attachment of M(CH₃)₃ directly to an aryl system can be treated in terms of an extension of conjugation if M contributes a vacant orbital of π -symmetry. Such an orbital (e.g. for Si(CH₃)₃) could be 3*d* or even C-Si σ^* in character. This conjugation will depend on the energy match of the 3*d* Si orbitals and HOMO of the aromatic, but accurate data for 3*d* orbital energies is lacking. Indications are that for Si, Ge, and Sn the *d* levels are above the LUMO's of naphthalene and benzene [26-28]. This $d_{\pi}-p_{\pi}$ or $\sigma^*-\pi$ interaction will be energy lowering and affect the LUMO more than the HOMO of the aromatic. It should be noted that

TABLE 8

CARBON-13 SUBSTITUENT CHEMICAL SHIFTS (ppm) FOR THE 4 α , 5 α AND 7 α DISPOSITIONS IN NAPHTHALENE AND THE *meta* AND *para* POSITIONS IN BENZENE

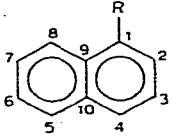
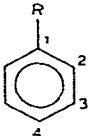
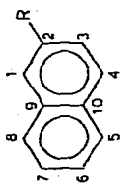
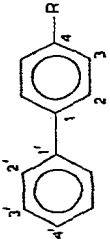
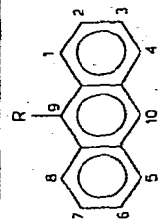
Compound	R	4 α	5 α	7 α	Compound	R	C(3)- <i>meta</i>	C(4)- <i>para</i>
	CH ₃	-1.3	+0.7	-0.1		CH ₃	-0.1	-3.0
	C(CH ₃) ₃	-0.5	+1.7	-1.3		C(CH ₃) ₃	-0.3	-2.9
	Si(CH ₃) ₃	+1.8	+1.3	-0.6		Si(CH ₃) ₃	-0.6	+0.4
	Ge(CH ₃) ₃	+1.2	+1.2	-0.7		Ge(CH ₃) ₃	-0.4	-0.1
	Sn(CH ₃) ₃	+0.9	+1.1	-0.4		Sn(CH ₃) ₃	-0.1	-0.2
	Pb(CH ₃) ₃	+0.2	+1.1	-0.5		Pb(CH ₃) ₃	0.0	-0.9

TABLE 9
 CARBON-13 SUBSTITUENT CHEMICAL SHIFTS (ppm) FOR THE 6 β AND 8 β DISPOSITIONS IN NAPHTHALENE, C(4') IN BIPHENYL AND C(10) IN ANTHRACENE

Compound	R	C(6)	C(7)	C(8)	Compound	R	C(4')	Compound	R	C(10)
	CH ₃	-0.8	+0.1	-0.3		CH ₃	-0.2		CH ₃	-1.0
	C(CH ₃) ₃	-0.6	-0.1	-0.3		C(CH ₃) ₃	-0.3		C(CH ₃) ₃	+0.8
	Si(CH ₃) ₃	+0.4	-0.1	+0.2		Si(CH ₃) ₃	-0.1		Si(CH ₃) ₃	+3.7
	Ge(CH ₃) ₃	-0.1	-0.1	-0.1		Ge(CH ₃) ₃	-0.2		Sn(CH ₃) ₃	+2.5
	Sn(CH ₃) ₃	-0.1	-0.1	-0.3		Sn(CH ₃) ₃	0.0			
	Pb(CH ₃) ₃	-0.2	-0.3	-0.4						

the π -inductive effect would act in opposition to mechanism 3.

Regarding the lower members of Group IVB, i.e. Ge, Sn, Pb, mechanism 1 would almost certainly decline in importance for two reasons. Firstly, as C—M bond length increases, the perturbation integral should progressively decrease [1]. Secondly, if electropositivity increases down the series, the p -electron density on M must decrease. Mechanism 2 could become more important as the electropositivity increases, but mechanism 3 should be less important as energy and radial matching of interacting orbitals worsen. These considerations mean that the parent hydrocarbon is an acceptable basis for comparison in providing an experimental measure of net π -electron movement. (Comparisons with $C(CH_3)_3$, while of interest, are clouded by the σ — π effect, which we reason is almost entirely absent in $M(CH_3)_3$.)

Carbon-13 substituent chemical shifts for Group IVB derivatives (Tables 8, 9)

It was pointed out in the Introduction that ^{13}C substituent chemical shifts appear to be reliable experimental monitors of π -electron density fluctuations in a closely related series of aromatic molecules. On this premise, SCS for the series of compounds described were obtained from careful comparisons with the parent aromatic. In most cases, spectra were obtained with the parent as internal standard. (See Experimental). The SCS values are assembled in Tables 8 and 9. We wish to direct attention primarily to the formally conjugated positions in these aryl systems, namely C(4) in phenyl, C(4), C(5) and C(7) in 1-substituted naphthalenes, C(6) and C(8) in 2-substituted naphthalenes, C(4') in the 4-substituted biphenyls and C(10) in 9-substituted anthracenes.

Phenyl series. Compared with the C(4) SCS of methyl and *t*-butyl (ca. 3.00 ppm shielding) indicating substantial electron donation, the values for the metalloid systems are very much reduced, and for $Si(CH_3)_3$ of opposite sign (+0.4 ppm). A somewhat complex blend of possibilities is associated with the $C(CH_3)_3$ to $Si(CH_3)_3$ change but the definite positive value for $Si(CH_3)_3$ indicates quite strongly, that the resultant substituent effect is one of electron withdrawal, and that +0.4 ppm is a minimum measure of the conjugative interaction (mechanism 3) involving vacant orbitals of π -symmetry on silicon. This is because residual field and π -inductive effects would partially counter the complete π -type electron withdrawal. The small negative values for $Ge(CH_3)_3$ and $Sn(CH_3)_3$ do not indicate the operation of mechanism 3. However, this could be in action but cancelled by shielding contributions (mechanism 2). There is a somewhat surprising but clear demarcation between $Sn(CH_3)_3$ and $Pb(CH_3)_3$, and the appreciably negative (−0.9 ppm) SCS value for the latter implies the operation of a relatively forceful shielding mechanism (mechanism 2). Alternatively, we raise the idea of enhanced Pb—C hyperconjugation, noticing the requirement that Pb be more electronegative than the other Group IVB metalloids, as well as carbon [29].

More pronounced electron withdrawal, as judged by the C(4) SCS (+1.4 ppm) is achieved by the SiH_3 group compared with $Si(CH_3)_3$ (+0.4 ppm). The more electronegative hydrides could conceivably affect the radial component of $3d$ orbitals, resulting in contraction, lower energy and improved interaction with the π -system. Alternatively, it could be suggested that variation in the σ -ligands on Si, should not appreciably affect the $3d$ levels, but replacement of CH_3 by H could lower the energy of a σ^* orbital (on Si) of pseudo- π symmetry. Again, interaction would be promoted, since the value of the perturbation integral is a

function (inverse) of the energy separation. There is evidence that mixing of d and σ levels in methylsilanes is not significant [30].

However, there is another factor to be borne in mind when comparing the C(4) SCS in $C_6H_5Si(CH_3)_3$ and $C_6H_5SiH_3$. This is associated with the much larger steric requirement of $Si(CH_3)_3$, and the ensuing structural alterations resulting from ortho H- CH_3 interactions. A comparison of the C(4) chemical shifts [31] for C_6H_5R ($R = CH_3, CH_3CH_2, (CH_3)_2CH, (CH_3)_3C$) of 125.66, 125.92, 126.06 and 125.65 ppm, respectively illustrates the point. Note that the movement to low field as CH_3 replaces H is reversed in the *t*-butyl case *. Therefore this structural factor produces a shielding effect of at least 0.5 ppm. It is reasonable that a comparable effect operates for $Si(CH_3)_3$, so that the C(4) SCS observed (+0.4 ppm) is lower than it would be if a purely electronic phenomenon was being registered. This could mean that the C(4) SCS, in the absence of structural distortion, for $Si(CH_3)_3$ would be in the region of ~ 0.80 – 1.00 ppm. This could make interpretation of the difference between SiH_3 and $Si(CH_3)_3$ difficult.

Treatment of the phenyl SCS by the Dual Substituent Parameter technique (DSP analysis) [33] yields (for seven data points). $SCS = 4.23 \sigma_I + 19.27 \sigma_R^0$ and $SD = 0.57$; $f = 0.138$ $\lambda = 4.555$. Utilising the σ_I and σ_R^0 values alluded to earlier, it is possible to compute the expected ^{13}C SCS as follows: C(4) SCS in $C_6H_5M-(CH_3)_3$: $M = Si$, found 0.4, calcd. 1.05; $M = Ge$, found -0.1 , calcd. 0.45; $M = Sn$, found -0.2 , calcd. -0.00 ; $M = Pb$, found -0.9 , calcd. -1.25 . The agreement is quite good given that structural factors are perturbing the SCS for Si and probably (to a lesser extent) Ge.

1-Naphthyl system. If the SCS in Tables 8 and 9 are accepted as reliable monitors of electron density fluctuations, along with the theoretical predictions that conjugative effects at C(4) in 1-substituted naphthalenes are greater than at *p*-C in monosubstituted benzenes [34] (while electrostatic effects should be comparable) the conclusion that mesomeric electron withdrawal operates for Si, Ge, Sn (and perhaps Pb) seems inescapable. A similar conclusion, based on ^{19}F SCS was reported by us previously. It is important, however, to consider the origin and magnitude of the C(5) SCS, in conjunction with C(4) SCS. The evidence is from ^{19}F [7] and ^{13}C studies [35,36] that mesomeric effects at C(5) are insignificant. This is formalised in the results of the DSP correlative analysis of ^{19}F shifts for this position, which indicates an essentially zero value for the resonance sensitivity parameter [7]. It is of related interest that in 1-aminonaphthalene [3], the C(5) SCS is close to zero [36]. Chemical reactivity studies, e.g. solvolysis of 5-methoxy-1-chloromethylnaphthalene show clearly the trifling nature of 1,5-mesomerism in this system as well. All theoretical treatments, in contrast, predict 1,5-mesomerism to be substantial [34,35]. The SCS of CH_3 and $(CH_3)_3C$ at C(5) are positive, not in accord with the expected donor action by these groups in conjugated positions. In view of their feeble electronic effects, and the above comments on 1,5-mesomerism, we anticipated insignificant SCS at C(5). Clearly, other factors are involved, and the most likely possibility is a substituent induced structural distortion, originating in 1,8-*peri*-interactions. A similar suggestion has been made with respect to apparently anomalous ^{19}F data for this disposition [7]. Now it is inconceivable that this distortion should be manifested only at C(5),

* These trends are reproduced in the corresponding fluorophenyl series [32].

as X-ray studies show that in *peri*-substituted naphthalenes, the crowding strain leads to an increase in the adjacent *peri*-angle, and a decrease in the remote *peri*-angle, relative to the angles in naphthalene [38]. This implicates C(4) as well as C(5), and suggests a more satisfactory measure of mesomerism at C(4) would be the difference between the C(4) and C(5) SCS, which effectively eliminates the structural distortion factor. This procedure provides data (for C(4) SCS) for the metalloids, almost identical with those for C(4) in the corresponding benzenes. Thus, on this basis, only $\text{Si}(\text{CH}_3)_3$ would be unequivocally engaging in mesomeric electron withdrawal.

This conclusion is in accord with the σ_R for these groups as determined from ^{19}F data in the 6β and 7β fluoronaphthyl DSP correlative equations [7]. Our previous conclusion [4], however, that enhanced mesomerism operated in the 1-naphthyl system, failed to recognise the deshielding effects (at C(4)—F) due to structural factors. The question naturally arises why mesomerism is not appreciably greater at C(4) in naphthalene compared with C(4) in benzene. A possible compensating factor could be the π -inductive effect, but there is no evidence available.

The C(7) SCS are uninformative regarding the operation of conjugative effects but it is possible the small negative SCS are a further manifestation of molecular distortions. In particular, note the identical C(6) and C(7) chemical shifts for 1-*t*-butylnaphthalene, implying some factor other than conjugation is at work. The effect at C(7) (equal to that at C(5) in simple HMO theory [34]) would be small, and easily clouded by other effects.

β -Naphthyl system

The 6 and 7 positions in 2-substituted naphthalenes are free of the *peri*-effects that we have seen cloud interpretation in other situations. Although theory predicts [34] and experiment supports the view that 6β conjugation is substantially less than 4α conjugation, the evidence is that data from 6β (compared with the unconjugated 7β) can be confidently interpreted in terms of substituent parameters [7]. The data in Table 9 confirm the trends outlined above and only $\text{Si}(\text{CH}_3)_3$ exhibits net mesomeric electron withdrawal. Simple HMO theory equates 6β and 8β regarding conjugative interactions, and here too, a positive SCS for $\text{Si}(\text{CH}_3)_3$ is recorded.

9-Anthryl system

The substituent behaviour of 9-substituted anthracenes can be decisively regulated by the severe *peri*-interactions with the 1,8-hydrogens, and this is particularly so for groups lacking cylindrical or tetrahedral symmetry [39,40]. For the $(\text{CH}_3)_3\text{M}$ groups, the major effect would seem to be a distortion placing such groups out of the "aromatic plane" with accompanying disturbances at C(9) and C(10). While such structural changes would affect the (formally *para*) C(10) chemical shift, we felt such effects could not be more severe for $\text{M}(\text{CH}_3)_3$ than for $\text{C}(\text{CH}_3)_3$, given the increasing C—M bond lengths. The 9-anthryl system was attractive also because theory predicts conjugation to be considerably enhanced in the 9, 10 disposition, compared with 4α -naphthyl [34,39].

The C(10) SCS in the 9-*t*-butyl compound is +0.8 ppm, compared with -1.00 ppm for C(10) in the CH_3 case, contrary to the close agreement for these groups

in phenyl, C(4) α (C(4)) and β naphthyl (C(6)), with however, C(CH₃)₃ consistently having a slightly less negative SCS. The difference here must be ascribed to molecular deformations in response to severe *peri*-effects experienced by C(CH₃)₃. These positive SCS are reminiscent of the C(5)-1-naphthyl data. The SCS value (−1.00 ppm) for CH₃ is also worrying, as it is smaller than at C(4) in benzene and C(4) in 1-naphthyl. However, the origin of the apparent electron donation of the methyl group in the neutral ground state has been traced (theoretically) [23] to a second-order mixing term of the π^* orbitals into the π -orbitals, via the interaction of both with the hyperconjugating CH₃ σ -orbital. This may mean that enhanced electron donation in the sequence benzene, 1-naphthyl and 9-anthryl is confined to substituents which operate by charge transfer. However, with appreciable charge development, external (α) to the aryl system, the methyl group may now operate by actual charge transfer. Experimental distinction of these modes is not available. The SCS for Si(CH₃)₃ and Sn(CH₃)₃ are very impressive (+3.7 and +2.5 ppm, respectively) and even allowing for structural effects on the chemical shift (a maximum value indicated by C(CH₃)₃ SCS) strongly indicate substantial conjugation. We emphasise however, that the actual geometries of these 9-anthryl systems are unknown.

4-Biphenyl system

Substituent chemical shifts for C(4') are located in Table 6 and the effects are very small as expected. Variation of the interannular angle as a function of substituent is a complication in this system, but overall a very feeble donor interaction is observed.

Recent data based on other techniques suggest the operation of the effects discussed above. Photoelectron spectra of PhM(CH₃)₃ (M = C, Si, Ge, Sn) which provide insight into individual orbital energies (Koopman's Theorem) were regarded as consistent with the operation of a large p_π - d_π -conjugative effect, in the order Si > Ge > Sn, for the π_1 -ionisation energies [6]. Significant inductive and hyperconjugative (donor) effects, (but less than p_π - d_π) were also indicated. A careful study of a series of Si(CH₃)₃- and C(CH₃)₃-substituted naphthalenes, by polarography and charge-transfer and UV spectroscopy has been reported [41]. The polarographic $E_{1/2}$ values, which relate to the energy of the LUMO, were consistent with lowering of this level by 1- and 2-Si(CH₃)₃ groups, but raising by C(CH₃)₃. For the LUMO, then, this energy-lowering overcomes the presumed +I effect of Si(CH₃)₃, and was associated with π -electron withdrawal. Estimates of the π -bond order to Si and Ge have been derived for a series of aromatic radical anions from ESR measurements [42].

Experimental

Compounds

t-Butylbenzene was purchased from the Aldrich Chemical Co. and used without further purification. *meta*-Deuterobromobenzene was obtained from the D₂O quench of the Grignard reagent from *m*-dibromobenzene. The mass-spectrum indicated 85% deuterium incorporation.

Method A: General Grignard procedure for metalloidal substituted benzenes

To magnesium turnings (2.4 g; 0.1 mol) in dry ether (50 ml) in a 250 ml three-

necked flask equipped with condenser, pressure-equalising dropping funnel and nitrogen inlet was added slowly bromobenzene (or *m*-deuterobromobenzene) (15.6 g; 0.1 mol) in dry ether (20 ml). After reaction had ceased (~1 h) the appropriate quantity of $(\text{CH}_3)_3\text{MX}$ (0.08 mol) was added. After several hours, the mixture was worked up with saturated ammonium chloride, extracted with ether which was dried (Na_2SO_4). Removal of ether and distillation (reduced pressure) provided the required products. Each was examined by VPC and PMR to ensure >95% purity and by mass spectrometry to ensure >85% deuterium incorporation.

Phenyltrimethylsilane. Method A in 76% yield. B.p. 66–69°C/20 mmHg (Lit. [43] 170–173°C/760 mmHg.) PMR: $(\text{CH}_3)_3\text{Si}$ δ 0.26 ppm; aromatics δ 7.2–7.6 ppm.

Phenyltrimethylgermane. Method A in 80% yield. B.p. 69–71°C/20 mmHg. (Lit. [43] 182–183°C/760 mmHg.) PMR: $(\text{CH}_3)_3\text{Ge}$ δ 0.38 ppm; Aromatics δ 7.2–7.4 ppm.

Phenyltrimethylstannane. Method A in 75% yield. B.p. 65–67°C/10 mmHg. (Lit. [44] 203–205°C/760 mmHg.) PMR: $(\text{CH}_3)_3\text{Sn}$ δ 0.28 ppm ($J(^{119}\text{Sn}-\text{CH}_3)$ 56.0 Hz) Aromatics δ 7.2–7.4.

Phenyltrimethylplumbane. Method A with the following modification. $(\text{CH}_3)_3\text{PbCl}$ dissolved in a minimum of dry THF was added dropwise until the solution developed a black coloration. The addition was discontinued immediately, and the solution worked up with saturated NH_4Cl . The ether/THF mixture was dried for several hours over anhydrous Na_2SO_4 and the solvent removed under vacuum. The yellow oil remaining was distilled under vacuum. B.p. 76–79°C/3 mmHg. (Lit. [45] 77–78°C/3 mmHg.) PMR: $(\text{CH}_3)_3\text{Pb}$, δ 0.89 ppm ($J(^{207}\text{Pb}-\text{CH}_3)$ 64.0 Hz); Aromatics δ 7.0–7.4 ppm.

1-t-Butylnaphthalene. This compound was donated by Dr B.M. Wepster from the Laboratory of Organic Chemistry, Technische Hogeschool, Delft, Netherlands. 4-deutero-1-t-butylnaphthalene was synthesised from 4-deutero-1-naphthyllithium, involving condensation with acetone to yield the tertiary alcohol, the chloride of which was treated with methylmagnesium iodide [46]. Deuterium content ~80%.

4-Deutero-1-bromonaphthalene. To 1,4-dibromonaphthalene (28.6 g; 0.1 mol) in anhydrous ether (50 ml) was added under N_2 , n-butyllithium (32 ml of a 0.2 M solution in hexane). This solution, after 45 min, was quenched with excess D_2O , and then extracted with ether. Standard work-up and distillation provided 10.6 g of the title compound. B.p. 97–101°C/2 mmHg. (Lit. [47] 139°C/16 mmHg.) Deuterium level was 75% on the basis of PMR and mass spectra.

Method B: General procedure for metalloidal 1-substituted naphthalenes

To 1-bromonaphthalene (or 4-deutero-1-bromonaphthalene) (20.7 g; 0.1 mol) in anhydrous ether (50 ml) under N_2 , was added n-butyllithium (6.4 g of a 0.2 M solution in hexane). This was stirred for 45 min and the appropriate quantity of trimethylmetal halide added. After a further 12 h stirring, the mixture was worked up with saturated NH_4Cl in the standard way. The products were fractionally distilled and each fraction examined (VPC) to establish purity. In each case samples >95% pure were obtained in yields ranging from 30–60%. Mass spectral examination of the major impurity revealed a molecular ion m/e 184 and a base peak of m/e 127. This, together with PMR data indicates the major impu-

rity to be 1-n-butyl-naphthalene. This could result from displacement of bromide ion from n-butylbromide (by 1-naphthyllithium) once metal-halogen exchange has occurred.

1-Naphthyltrimethylsilane. Method B in 46% yield. B.p. 95–98°C/1.5 mmHg. (Lit. [48] 162–163°C/30 mmHg.) PMR: $(\text{CH}_3)_3\text{Si}$ δ 0.46 ppm; aromatics δ 7.2–7.7 ppm. Gas chromatography (Se-30 at 175°C) revealed >95% purity.

1-Naphthyltrimethylstannane. Method B in 32% yield. In order to obtain a sample of 98% purity for accurate measurement of $^{117,119}\text{Sn}$ – ^{13}C coupling in the ^{13}C spectrum, the compound was distilled (reduced pressure) on a spinning band apparatus with approximately fifteen theoretical plates. B.p. 82–82.5° at 0.05 mmHg. (Lit. [49] 120–121°C/1.0 mmHg.) PMR: $(\text{CH}_3)_3\text{Sn}$, δ 0.44 ppm ($J(^{119}\text{Sn}$ – $\text{CH}_3)$ 54.0 Hz); aromatics δ 7.2–7.8 ppm.

1-Naphthyltrimethylgermane. Method B in 56% yield. B.p. 88–90°C/1.5 mmHg. Gas chromatography (SE-30 at 150°C) showed ca. 95% purity. Dry column chromatography of 400 mg of the above on alumina (hexane eluent) produced six fractions of >99% purity. Removal of solvent and distillation provided 60 mg of analytically pure 1-naphthyltrimethylgermane. Found: C, 66.91; H, 5.96. $\text{C}_{15}\text{H}_{16}\text{Ge}$ calcd.: C, 67.01; H, 5.96%. PMR: $(\text{CH}_3)_3\text{Ge}$ δ 0.40 ppm, aromatics δ 7.6 (br) ppm.

1-Naphthyltrimethylplumbane. Method B was attempted several times, without success.

To Mg turnings (2.4 g; 0.1 mol) in anhydrous ether (75 ml) under N_2 was added slowly 1-bromonaphthalene (20.5 g) in ether (25 ml). After some time, the mixture began to reflux gently, but ceased well before the addition of 1-bromonaphthalene was complete. The solution was refluxed for a further 3 h, leading to consumption of ca. 75% of the magnesium. Trimethyllead chloride (25 g) in a minimum of dry THF was added to the brown solution which was stirred for a further 3 h. The solution was worked up with saturated NH_4Cl , extracted with ether and dried. Distillation produced one fraction, homogeneous on TLC (silica gel/hexane). PMR integration indicated >95% purity. The yield was 17%. B.p. 114–116°C/0.1 mmHg. PMR: $(\text{CH}_3)_3\text{Pb}$ δ 1.08 ppm ($J(^{207}\text{Pb}$ – $\text{CH}_3)$ 62.0 Hz); aromatics δ 7.6 (br) ppm.

An analytical pure sample was obtained by redistillation of the 95% pure product. Found: C, 41.31; H, 4.17. $\text{C}_{15}\text{H}_{16}\text{Pb}$ calcd.: C, 41.14; H, 4.22%.

2-t-Butyl-naphthalene. This compound was synthesised as reported in overall 32% yield from naphthalene. B.p. 115–118°C/6 mmHg. (Lit. [50] 115°C/6 mmHg.) PMR: $(\text{CH}_3)_3\text{C}$ δ 1.41 ppm (9H); Aromatics δ 7.2–7.8 (7H) ppm.

Method C: General procedure for metalloidal 2-substituted naphthalenes

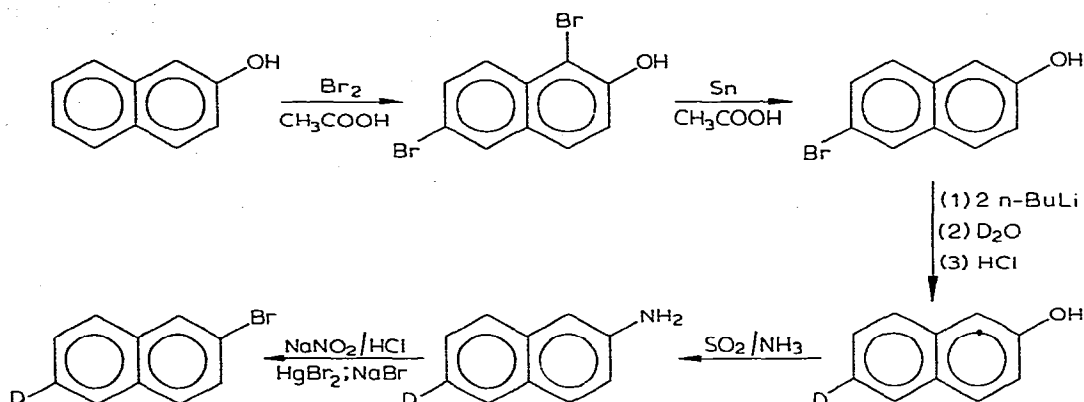
The procedure used is identical to that of method B, except 2-bromonaphthalene and 6-deutero-2-bromonaphthalene are employed instead of the 1-naphthyl analogues.

6-Deutero-2-bromonaphthalene. This compound was prepared according to Scheme 1.

6-Bromo-2-naphthol. This compound was prepared in 83% yield in the reported manner. M.p. 126–127°C (Lit. [51] 127–128°C).

6-Deutero-2-naphthol. To 6-bromo-2-naphthol (111 g; 0.5 mol) in anhydrous ether (500 ml) under N_2 was added slowly ca. 80 g (520 ml of a 15% wt/vol solu-

SCHEME 1



tion) of *n*-butyllithium in hexane. A gentle reflux was maintained during this addition and stirring was continued for an additional 2 h. D_2O (30 ml) was added and stirring continued overnight. 5 M HCl (500 ml) was added and the ether layer separated, worked with NaHCO_3 and dried (Na_2SO_4). Solvent was removed and the product crystallised from hexane/chloroform. The yield was 38 g (52%). Mass spectral examination indicated 85% deuterium incorporation later confirmed by the ^{13}C spectrum. M.p. 122–123°C (Lit. [52] 123–124°C).

6-Deutero-2-aminonaphthalene. 6-Deutero-2-naphthol (23.5 g; 0.11 mol) was placed in a pressure vessel together with a solution of ammonium sulfite prepared by passing sulfur dioxide into cooled concentrated ammonia (S.G. 0.880; 63.5 g) until 16.3 g of gas was absorbed. The vessel was heated (150°C) with continual shaking for 8 h and allowed to cool. The mixture was washed from the vessel with ether, washed with H_2O and 6 M NaOH and dried (Na_2SO_4). Recrystallisation of a small sample from hexane/chloroform yielded tan-colored crystals melting at 111–112°C (Lit. [53] M.p. 111–112°). The remainder (12.0 g) was used without purification. The mass spectrum indicated ca. 85% deuterium incorporation, and the deuterium decoupled PMR together with the ^{13}C spectrum indicated no deuterium scrambling.

6-Deutero-2-bromonaphthalene. To a cold diazonium solution from 6-deutero-2-naphthylamine (10 g; 0.07 mol; 135 ml of H_2O ; 28 ml of conc. HCl and a 20% NaNO_2 solution) was added with stirring a cold suspension of HgBr_2 (12.9 g) in H_2O (50 ml). The yellow insoluble complex which separated was collected, washed (H_2O) and dried under vacuum. For decomposition the complex was mixed with finely ground NaBr and added in several portions to a flask fitted with a reflux condenser and heated to 90°C. After addition was complete, the product was extracted with boiling acetone. The black oily material so obtained was extracted with boiling hexane and chromatographed on a small amount of alumina using distilled hexane as eluent. The overall yield of pure material was 6.0 g (42%). M.p. 58–59°C (Lit. [54] 59°C). Mass spectral analysis indicated 85% deuterium incorporation.

2-Naphthyltrimethylsilane. Method C in 58% yield. Dry column chromatography using hexane/alumina provided a sample >95% pure. B.p. 110–114°C/5.0

mmHg. (Lit. [55] 95–96°C/0.5 mmHg.) PMR: $(\text{CH}_3)_3\text{Si}$ δ 0.34 ppm, aromatics δ 7.5 (br) ppm.

2-Naphthyltrimethylgermane. Method C in 52% yield. Distillation on a spinning band column of fifteen theoretical plates provided an analytically pure sample. B.p. 72–72.5°C/0.4 mmHg. Found: C, 63.52; H, 6.41. $\text{C}_{13}\text{H}_{16}\text{Ge}$ calcd.: C, 63.78; H, 6.54%. PMR: $(\text{CH}_3)_3\text{Ge}$ δ 0.46 ppm, aromatics δ 7.2–7.6 ppm.

2-Naphthyltrimethylstannane. Method C in 41% yield. Chromatography on neutral alumina (activity II) using hexane as eluent, followed by spinning band distillation yielded the title compound >98% pure. B.p. 81–82°C/0.3 mmHg. (Lit. [49] 115°C/1 mmHg.) PMR: $(\text{CH}_3)_3\text{Sn}$ δ 0.34 ppm ($J(^{119}\text{Sn}-\text{CH}_3)$ 53.0 Hz); aromatics δ 7.6 (br) ppm.

2-Naphthyltrimethylplumbane. To magnesium turnings (1.3 g; 0.05 mol) in dry ether (25 ml) was added 2-bromonaphthalene (10.4 g; 0.05 mol) in dry ether (20 ml). The mixture was refluxed for 3 h resulting in ca. 80% consumption of the Mg and production of a dark brown solution. To this was added trimethyllead chloride (12.0 g; 0.04 mol) in the minimum amount of dry THF. Stirring was continued for a further 2 h, and the mixture worked up with saturated NH_4Cl in the standard way. The ether solution was dried (Na_2SO_4), and the ether removed. Distillation of the product yielded three fractions. Examination of the fraction 127–130°C/0.05 mmHg by TLC (hexane/silica gel) and PMR revealed ca. 95% purity. An analytically pure sample was obtained by redistillation of this sample. Found: C, 41.41; H, 4.28. $\text{C}_{13}\text{H}_{16}\text{Pb}$ calcd.: C, 41.14; H, 4.22%. PMR: $(\text{CH}_3)_3\text{Pb}$, δ 1.0 ppm ($J(^{207}\text{Pb}-\text{CH}_3)$ 64.1 Hz); aromatics δ 7.60 (br) ppm.

4-t-Butylbiphenyl. This compound was obtained as clear plate-like crystals after careful chromatography and recrystallisation of the product of t-butylation of biphenyl. M.p. 51°C (Lit. [42] 51°C). The IR spectrum showed absorptions at 835, 762, 735 and 695 cm^{-1} . PMR: $(\text{CH}_3)_3\text{C}$ δ 1.36 ppm, aromatics δ 7.46 (br) ppm.

General procedure for metalloidal 4-substituted biphenyls

The method used is identical to that of Method B except 4-bromobiphenyl (Eastman Organic Chemicals, Rochester) was used.

4-Biphenyltrimethylsilane. Method B in 37% yield. Distillation of the product at 122–124°C/3.5 mmHg yield a sample of ca. 90% purity. Further purification was accomplished by chromatography on neutral alumina (30 : 1) using hexane as eluent. Pure title compound eluted with the solvent front. M.p. 53–54°C (Lit. [56] m.p. 54°C). PMR: $(\text{CH}_3)_3\text{Si}$ δ 0.28 ppm, aromatics δ 7.3 (br) ppm.

4-Biphenyltrimethylgermane. Method B in 62% yield. Recrystallisation from absolute ethanol provided an analytically pure sample. M.p. 57–58°C. PMR: $(\text{CH}_3)_3\text{Ge}$ δ 0.42 ppm, aromatics δ 7.50 (br) ppm. Found: C, 66.81; H, 6.71. $\text{C}_{15}\text{H}_{18}\text{Ge}$ calcd.: C, 66.52; H, 6.65%.

4-Biphenyltrimethylstannane. Method B in 32% yield. The crude product was crystallised from chloroform/methanol and di-4-biphenyldimethylstannane (m.p. 171–172°C) separated. Removal of solvent and distillation yielded the title compound (ca. 90% pure). Dry column chromatography on silica gel, followed by distillation yielded a compound of ca. 98% purity. M.p. 52–53°C, b.p. 108–110°C/0.3 mmHg. (Lit. [42] m.p. 53°C). PMR: $(\text{CH}_3)_3\text{Sn}$ δ 0.34 ppm ($J(^{119}\text{Sn}-\text{CH}_3)$ 54.0 Hz); aromatics δ 7.4 (br) ppm.

4-Biphenyltrimethylplumbane. Method B was applied but only di-4-biphenyl-dimethylplumbane (m.p. 178–179°C) was obtained. This agrees with a literature report [42].

9-t-Butylanthracene. This compound was obtained by very careful attention to the reported procedure [13], which involved dehydration (P_2O_5 in anhydrous CCl_4) of 9-hydroxy-9-t-butyl-9,10-dihydroanthracene. We found it advantageous to periodically examine the reaction mixture by PMR and VPC (SE-30 at 200°C) to monitor the disappearance of the alcohol. The yellow-brown powdery solid obtained was crystallised from ethanol. M.p. 104–105°C which agrees with the reported value. PMR: $(CH_3)_3C$ δ 1.90 (9H)ppm, $H_{2,3,6,7}$ δ 7.25 (4H) ppm, $H_{4,5}$ δ 7.90 (2H) ppm, H_{10} δ 8.20 (1H) ppm, $H_{1,8}$ δ 8.50 (2H) ppm. Steric deshielding is indicated for $H_{1,8}$.

9-Anthryltrimethylsilane. A number of attempts utilising different procedures failed to provide any of this compound, and other workers had similar experiences. By employing the 9-bromoanthracene-n-butyllithium procedure at low temperatures, Eaborn did obtain the title compound, and very kindly provided a copy of its ^{13}C spectrum [12].

9-Anthryltrimethylstannane. The following procedure, which failed to produce any of the silicon compound, fortunately provided a very small but adequate sample of the tin derivative. To 9-bromoanthracene (12.85 g; 0.05 mol) in dry ether (60 ml) under N_2 was added 3.2 g (15.0 ml of a 21.4% w/v) of n-butyllithium in hexane. After stirring for 20 min, $(CH_3)_3SnCl$ (10 g) in dry ether (20 ml) was added (15 min) and the solution stirred for 2 h. Saturated NH_4Cl was added dropwise and a yellow solid, poorly soluble in ether and water was filtered off. This was later found to be anthracene. The ether solution was dried and removed under vacuum. The orange residue was dissolved in hot ethanol and cooled to room temperature. The light yellow solid (anthracene) was filtered and the volume of solvent reduced. This process was repeated four times until most of the anthracene had been removed. The ethanol solution was filtered and cooled to 0°C for five days, and long needle like crystals and an amorphous yellow solid separated. The solids were filtered and the needle-like crystals manually removed (forceps). Two further crystallisations from absolute ethanol produced pure title compound (~400 mg). Confirmation that the $(CH_3)_3Sn$ moiety was 9-situated followed from the 1H and ^{13}C NMR spectra. M.p. 65–66°C. PMR ($CDCl_3$): $(CH_3)_3Sn$ δ 0.60 ppm ($J(^{119}Sn-CH_3)$ 54.0 Hz); $H_{2,3,6,7}$ δ 7.32 (4H) ppm; $H_{4,5}$ δ 7.86 (2H) ppm; $H_{1,8}$ δ 8.06 (2H) ppm; H_{10} δ 8.26 (1H) ppm. Found: C, 59.80; H, 5.41. $C_{17}H_{18}Sn$ calcd.: C, 59.88; H, 5.28%.

9-Anthryltrimethylplumbane. The synthetic method used was identical to that described above for the tin compound. A light yellow crystalline material was obtained which was crystallised from ethanol and examined by PMR. The spectrum was similar to that of the 9-tin compound, except the aromatic/ CH_3 proton ratio indicated a dianthryldimethyllead compound. M.p. 183–184°C. PMR ($CDCl_3$): $(CH_3)_2Pb$, δ 1.75 (6H) ppm ($J(^{207}Pb-CH_3)$ 62.5 Hz); $H_{2,3,6,7}$ δ 7.37 (8H) ppm; $H_{4,5}$ δ 8.06 (4H) ppm; $H_{1,8}$ δ 8.30 (4H) ppm; H_{10} δ 8.48 (2H) ppm. Found: C, 60.82; H, 4.14. $C_{30}H_{24}Pb$ calcd.: C, 60.89; H, 4.06%.

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