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THE SUBSTITUENT EFFECT OF THE TRIMETHYLSTANNYLMETHYL GROUP, STUDIED BY CARBON-13 NUCLEAR MAGNETIC RESONANCE

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Summary

The natural abundance carbon-13 NMR spectra of the compounds $\text{ArCH}_2\text{Sn}(\text{CH}_3)_3$ (Ar = phenyl, 1- and 2-naphthyl and 4-biphenyl) have been recorded and essentially completely assigned by specific deuteration, magnitudes of ^{13}C – $^{117,119}\text{Sn}$ couplings and other criteria. Comparisons have been made with the appropriate neopentyl compounds, and at conjugated positions, substantial shielding is experienced, and $\Delta\delta$ (the substituent chemical shift) correlates well with Δq (the SCF- π MO change in π -charge density for the change $\text{Ar}-\text{CH}_3 \rightarrow \text{ArCH}_2^-$) as expected for a conjugative interaction. The present data indicate essentially no conjugative transmission to the 5-position in the 1-naphthyl system, in line with previous reports showing such mesomerism to be trifling. The conclusions that follow from these ^{13}C studies agree with those previously based on ^{19}F investigations. Some comments on ^{13}C – $^{117,119}\text{Sn}$ coupling in $\text{ArCH}_2\text{Sn}(\text{CH}_3)_3$ are recorded.

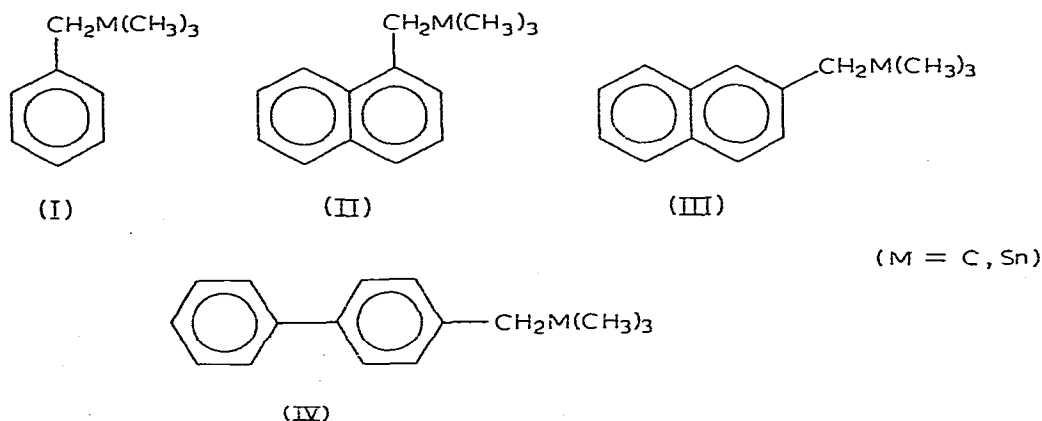
Introduction

The experimental evidence regarding the hyperconjugative (σ – π) nature of electron donation by $\text{CH}_2\text{M}(\text{CH}_3)_3$ (M = Si, Ge, Sn, Pb) in aromatic systems is now quite definitive [1]. Some time ago we reported that, as judged by ^{19}F substituent chemical shifts, charge transfer from CH_2M varied with the nature of Ar in ArCH_2M in the fashion expected for a conjugative interaction [2]. With the

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growing realisation that carbon-13 chemical shifts in aryl systems can be useful monitors of π - (and total) charge density (provided closely related systems are scrutinised) [3] it seemed worthwhile to examine the ^{13}C chemical shifts in $\text{ArCH}_2\text{M}(\text{CH}_3)_3$, as such a study would simultaneously register fluctuations in electron-density patterns at all carbon sites. In this sense, the range of information is clearly superior to that from a solitary ^{19}F probe, but in addition pertains to a monosubstituted aromatic system. Although it would be useful to examine the complete series of $\text{ArCH}_2\text{M}(\text{CH}_3)_3$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) we decided to examine the $\text{M} = \text{C}, \text{Sn}$ series only, for several reasons: (i) assignments of the ^{13}C spectra of the tin compounds were facilitated by ^{13}C — $^{117,119}\text{Sn}$ couplings, (ii) the tin compounds were more directly accessible synthetically and (iii) the $\text{CH}_2\text{Sn}(\text{CH}_3)_3$ group, based on previous data, would exert a sufficiently large perturbation on the aryl ^{13}C shifts to allow unambiguous conclusions and (iv) the general features would emerge and be applicable to $\text{M} = \text{Si}, \text{Ge}$, and Pb as well*.

Therefore, we have synthesized the compounds I–IV, and assigned their ^{13}C NMR spectra and correlated the substituent chemical shifts (^{13}C SCS) with π -charge densities.



Results and discussion

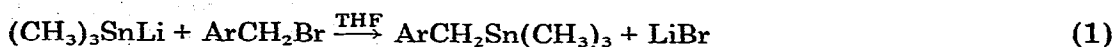
(a) Synthesis of compounds

The following neopentyl compounds were obtained by a new procedure which will be reported fully elsewhere [4]. The analytical and spectroscopic data fully confirm the structures. Neopentylbenzene, 1-neopentyl-1,2,3,4-tetrahydronaphthalene (and its 4-D analogue), 2-neopentyl-1,2,3,4-tetrahydronaphthalene, 6-methyl-2-neopentyl-1,2,3,4-tetrahydronaphthalene and 4-neopentylbiphenyl.

The trimethylstannylmethyl aromatics were obtained from the reaction of trimethyltinlithium with the appropriate bromomethylaromatic in tetrahydro-

* One aspect of our previous study (ref. 3) viz. that as judged by ^{19}F SCS, the C — Pb bond was a less effective electron donor than the C — Sn bond in $\text{F-Aryl-CH}_2\text{M}(\text{C}_6\text{H}_5)_3$ is being investigated by ^{13}C NMR.

furan (eq. 1). In this manner, the following compounds were obtained: 1-naph-



thylmethyltrimethylstannane, 2-naphthylmethyltrimethylstannane, 6-methyl-2-naphthylmethyltrimethylstannane and 4-biphenylmethyltrimethylstannane. Benzyltrimethylstannane was obtained from benzylmagnesium chloride and trimethyltin chloride. All attempts to synthesis 9-anthrylmethyltrimethylstannane failed. Details are given in the Experimental section.

(b) Carbon-13 spectra: assignment strategies

(i) Neopentyl series

Neopentylbenzene. The aromatic ring carbons have been readily assigned on the basis of signal intensity (CW mode). C(1) and C(4), although of equal intensity when recorded using the CW mode, are of vastly different intensities using FT accumulation. Also C(1) being a quaternary carbon is some 13.8 ppm further downfield than C(4). Some ambiguity could arise concerning the assignment of C(3) and C(2). The C(3) chemical shift in neopentylbenzene should closely resemble the chemical shift of C(3) in toluene [3] (127.5 ppm). The resonance at 130.0 ppm has been assigned to C(2).

1-Neopentyl-naphthalene. The ^{13}C spectrum of the aromatic ring in 1-neopentyl-naphthalene consisted of seven well separated resonances, three being of much reduced intensity and well downfield from the remaining carbons. C(4) has been assigned by direct deuteration but owing to the small amount of sample available (<100 mg), no further assignments could be made on the basis of deuterium isotope effects [5] (vide infra). The carbons in the unsubstituted ring should have chemical shifts similar to the corresponding carbons in 1-methylnaphthalene [6] and have been assigned accordingly. C(1), C(2) and C(3) have been assigned, partly on the basis of the effect the neopentyl group has on chemical shifts in benzene, and general trends observed by us in a wide range of 1-substituted naphthalenes [7]. Very acceptable correlations were observed.

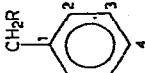
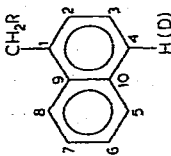
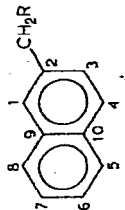
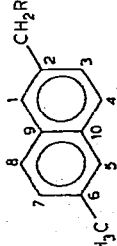
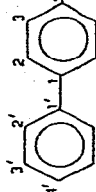
2-Neopentyl-naphthalene and 6-methyl-2-neopentyl-naphthalene. Because of the difficulties encountered in the synthesis of the 6-deutero compound, a methyl substituent located on C(6) was used to provide additional information concerning carbon assignment [6]. An excellent fit (Table 1) has been obtained, by using CH_3 SCS values [6], for the observed and predicted chemical shifts of 6-methyl-2-neopentyl-naphthalene assuming the initial assignment for 2-neopentyl-naphthalene to be correct. There seems little doubt concerning the assignment for C(6) (125.1 ppm). As expected, the chemical shifts of the carbons in the unsubstituted ring of 2-neopentyl-naphthalene resemble those for the corresponding carbons in 2-methylnaphthalene [6].

4-Neopentylbiphenyl. The three quaternary carbons have been readily distinguished by their low intensity signals and low field position. The signal at 127.0 ppm was considered to be of three carbon intensity, one carbon being C(4). The remaining substituted ring carbons have been assigned by considering the effect a phenyl group has at the *para*-position in neopentylbenzene. The unsubstituted ring carbons have been assigned by considering the chemical shift of similar carbons in 4-methylbiphenyl [8].

TABLE 1

CARBON-13 CHEMICAL SHIFTS (ppm) OF SOME NEOPENTYL SUBSTITUTED PHENYL, NAPHTHYL AND BIPHENYL SYSTEMS

CH₃ chemical shift in 6-methyl-2-neopentyl-naphthalene 21.6 ppm.

Compound	R	C(1)	C(2)	C(3)	C(4)	C(1')	C(2')	C(3')	C(4')	C(9)	C(10)	C(11)/C(14)	C(12)/C(13)	CH ₂ C(CH ₃) ₃	C(CH ₃) ₃	
	C(CH ₃) ₃	139.1	130.0	127.5	125.4									50.3	29.5	28.9
	C(CH ₃) ₃	135.9	128.9	125.2	126.6	128.5	125.2	125.2	125.2	133.3	133.9			44.9	32.9	30.2
	C(CH ₃) ₃	128.6	137.5	129.5	126.9	127.5	125.1	125.7	127.5	133.4	132.1			50.4	32.1	29.5
	C(CH ₃) ₃	128.4	136.5	129.5	126.2	128.5	134.6	128.0	127.4	131.6	132.3			50.4	32.1	29.5
Calc. chem. shifts using CH ₃ SCS values																
		128.3	136.7	129.6	126.6	126.5	134.7	128.0	127.4	131.6	132.3					
	C(CH ₃) ₃	138.9	126.4	130.9	138.7	141.2	127.0	128.7	127.0					50.0	31.9	29.5

(ii) *Arylmethyltrimethylstannyl system*

Benzyltrimethylstannane. Deuterium substitution at carbon three together with ^{13}C — ^{119}Sn satellite information has provided an unambiguous assignment for this compound. It is interesting to note that in this compound ^{13}C — ^{119}Sn coupling to C(4) (14.8 Hz) is greater than the coupling to C(3) (12.0 Hz). This phenomenon has been discussed in detail elsewhere [9].

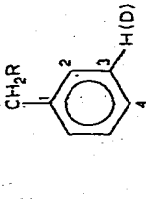
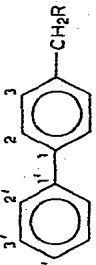
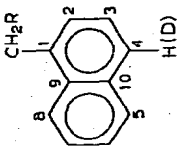
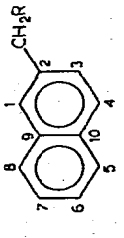
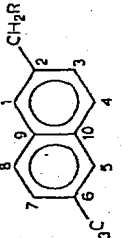
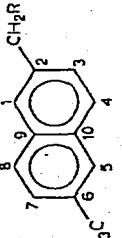
1-Naphthylmethyltrimethylstannane. Deuterium substitution at C(4) together with detectable ^{13}C — ^{119}Sn coupling to eight of the ten ring carbons allow almost a complete and unambiguous carbon assignment for the molecule [5]. C(1) and C(5) in the deuterated compound are considerably broadened by a three bond (vicinal) ^{13}C —D coupling of approximately 1.0 Hz, and C(3) suffers a substantial isotope shift. Thus the resonances at 123.5, 125.6 and 123.9 ppm with coupling constants of 28.7, 15.1 and 6.0 Hz have been assigned to C(2), C(3) and C(4) respectively. In this system, however, coupling to the formally *para* carbon (C(4)) is substantially smaller than coupling to C(3), opposite to what it is in the benzyl compound. On the basis of this information, the quaternary carbons at δ 130.8 and 133.9 ppm with ^{13}C — ^{119}Sn coupling constants of 18.1 and 11.3 Hz have been assigned to C(9) and C(10) respectively. The signal at 124.8 ppm with a coupling constant of 4.5 Hz has been assigned to C(8). Resonances at 125.2 and 123.9 ppm have been assigned to C(6) and C(7) in agreement with the expected shielding at the conjugated 7-position. The carbon chemical shifts together with relevant ^{13}C — ^{119}Sn coupling constants for the 1-naphthylmethyltri-*n*-butyltin compound are also included in Table 2. The agreement is excellent.

2-Naphthylmethyltrimethylstannane and 6-methyl-2-naphthylmethyltrimethylstannane. Owing to the difficulties encountered in the synthesis of the 6-deutero compound, the 6-methyl analogue was synthesised and CH_3 SCS values [6] used to assign ring carbons. This procedure appears to be quite satisfactory for non-*peri* substituted naphthalenes [6,7]. It can be seen from Table 2 that an excellent fit was obtained for observed and calculated ^{13}C chemical shifts for the 2-naphthylmethyl compound. Resonances at 140.8 (*J* 40.8 Hz), 134.0 (*J* 13.6 Hz), 130.6 (*J* 9.1 Hz), 127.8 (*J* 12.6 Hz), and 126.9 ppm (*J* 19.0 Hz) have been assigned to C(2), C(9), C(10), C(4) and C(1), respectively. The high field absorption at 123.3 ppm with a coupling constant of ~ 25 Hz has been assigned to C(3) and the chemical shift of the remaining carbons determined by the CH_3 SCS method [6].

4-Biphenylmethyltrimethylstannane. The three quaternary carbons were identified by their low intensity signals. However, ^{119}Sn — ^{13}C coupling to the two quaternary carbons in the substituted ring were not visible and an unambiguous assignment cannot be made. The signals at 142.3, 141.2 and 136.0 ppm have been assigned to C(4), C(1') and C(1) on the basis that C(1) will experience significant shielding by the CH_2Sn group, and other substituent effects. The two resonances at 128.6 and 127.2 ppm of two carbon intensity with ^{119}Sn — ^{13}C coupling of 39.0 and 12.0 Hz have been assigned to C(3) and C(2) respectively. The three carbon intensity signal at 126.6 ppm has been assigned to C(4') and C(3'), although it is difficult to distinguish between C(3') and C(2') on the basis of chemical shift.

TABLE 2

CARBON-13 CHEMICAL SHIFTS (ppm) OF SOME TRIMETHYLSNANYLMETHYL SUBSTITUTED PHENYL, NAPHTHYL AND BIPHENYL SYSTEMS
¹³C-119 Sn COUPLING CONSTANTS (Hz) ARE GIVEN IN BRACKETS

Compound	R	C(1)	C(2)	C(3)	C(4)	C(1')	C(2')	C(3')	C(4')	C(8)	C(9)	C(10)	CH ₂	CH ₃	Sn-CH ₃
	Sn(CH ₃) ₃	143.0 (36.6)	126.6 (22.6)	128.1 (12.0)	123.0 (14.8)								20.3 (285.4)		-10.0 (322.0)
	Sn(CH ₃) ₃	136.0 (12.0)	127.2 (39.0)	128.6 (12.0)	142.3	141.2	126.9	126.6	126.6				19.9		-10.0
	Sn(CH ₃) ₃	139.4 (40.8)	123.5 (28.7)	125.6 (15.1)	123.9 (6.0)	128.7 (4.2)	125.2	123.9	124.8	130.8 (4.5)	130.8 (18.1)	133.9 (11.3)	17.7 (234.6)		-9.3 (327.0)
	Sn-n-Bu ₃	139.9 (39.3)	123.8 (~32.0)	125.5 (13.7)	123.8	128.7 (~5)	125.0	123.6	124.7	131.2 (~5)	131.2 (15.2)	134.2 (8.6)	α-CH ₂ β-CH ₂ γ-CH ₂ δ-CH ₂	9.9 28.9 27.2 13.2	
	Sn(CH ₃) ₃	126.9 (~19.0)	140.8 (40.8)	123.3 (25.0)	127.8 (12.6)	127.6	123.9	125.7	126.7	134.0 (13.6)	134.0 (9.1)	130.6 (9.1) ^a	20.6 (287.0)		-10.0 (342.7)
	Sn(CH ₃) ₃	126.7 (27.2)	139.7 (40.8)	123.2 (28.7)	127.2 (12.0) ^a	126.7	133.3	128.0	127.0	132.4 (15.1)		130.9	20.5	21.5	-10.0
Calc. chem. shift using CH ₃ SCS values															
		126.7	140.0	123.4	127.5	126.6	133.5	128.0	127.3	132.2		130.8			

^a Tentative

(c) Carbon-13 Substituent chemical shifts

The ^{13}C chemical shifts of the arylmethyltrimethylstannanes and neopentylaromatics are located in Tables 1 and 2, and the derived chemical shift changes (relative to the methyl or neopentyl aromatic on a site for site comparison) are assembled in Table 3. The HMO and SCF- π MO changes in π -charge density at each unencumbered, formally conjugated carbon position, for the change $\text{ArCH}_3 \rightarrow \text{ArCH}_2^-$ are also included *. (For purposes of analysis data pertaining to *ortho*-type positions are rejected since steric and compressional effects at these sites may mask any bona fide electronic effect.) It is immediately apparent that the chemical shift changes ($\Delta\delta$, Table 3) are substantial and negative at conjugated positions (other than C(5) in the 1-naphthyl case) and consistent with electron-release from the C—Sn bond. The variation of $\Delta\delta$ with disposition is also noteworthy, superficially in line with the dependence expected for a conjugative interaction [3e].

The model. The above dependence of $\Delta\delta$ on the aryl system in $\text{ArCH}_2\text{Sn}(\text{CH}_3)_3$ and previous information [1] establishing a strong hyperconjugative (σ — π) mode of interaction between the C—Sn bond and adjacent aryl system, encouraged examination of a simplified model, in which ArCH_2^- was approximated to the polar C—Sn bond in $\text{ArCH}_2\text{Sn}(\text{CH}_3)_3$. It is recognised that *p*-electron density on the benzylic carbon is crucial in this type of interaction [10]. For the alternant HC systems under study both HMO and SCF- π MO measures of the transmission of mesomerism between CH_2 and ring carbons have been obtained [3e]. With the ^{13}C $\Delta\delta$ values taken as a reflection of the π -charge levels in the immediate vicinity of the carbon atom, a satisfactory correlation with Δq , the change in π -charge density (for the change ArCH_3 or $\text{ArCH}_2\text{C}(\text{CH}_3)_3 \rightarrow \text{ArCH}_2^-$) should emerge [2].

To place this on a more quantitative basis, $\Delta\delta$ has been plotted against Δq calculated by the simple HMO and SCF- π MO techniques. For the HMO parameters, for C(4), C(5) and C(7) in the 1-naphthyl system, C(6) and C(8) in the 2-

TABLE 3

CARBON-13 SUBSTITUENT CHEMICAL SHIFTS (ppm) FOR THE TRIMETHYLSTANNYLMETHYL GROUP AT VARIOUS DISPOSITIONS IN BENZENE, NAPHTHALENE AND BIPHENYL, TOGETHER WITH RELEVANT π -CHARGE DENSITIES

Compound	Benzene	Naphthalene					Biphenyl
	C(4)	4 α	5 α	7 α	6 β	8 β	C(4')
ArCH_2R , R = H	125.4	126.6	128.6	125.7	125.0	127.6	127.0
ArCH_2R , R = $\text{Sn}(\text{CH}_3)_3$	123.0	123.9	128.7	123.9	123.9	126.7	126.6
$\Delta\delta$	-2.4	-2.7	+0.1	-1.8	-1.1	-0.9	-0.4
Δq HMO	0.14	0.20	0.05	0.05	0.06	0.06	0.03
Δq SCFMO	0.22	0.26	0.09	0.13	0.13	0.06	0.09
ArCH_2R , R = $\text{C}(\text{CH}_3)_3$	125.4	126.6	128.5	125.2	125.1	127.5	127.0
ArCH_2R , R = $\text{Sn}(\text{CH}_3)_3$	123.0	123.9	128.7	123.9	123.9	126.7	126.6
$\Delta\delta$	-2.4	-2.7	+0.2	-1.3	-1.2	-0.9	-0.4

* A complete listing of these HMO and SCF- π MO charges is contained in ref. 3e.

naphthyl, 4-benzyl and 4'-biphenyl, a linear dependence (with $r = 0.90$ at the 95% confidence level) is observed. The most serious discrepancy occurs for C(5) in 1-naphthyl. The HMO method applied to a planar biphenyl molecule would surely overestimate interannular conjugation, since the solution geometry is non-planar [2]. Omission of the data for C(5) in 1-naphthyl and C(4') in biphenyl, provides a very satisfactory linear dependence. ($r = 0.96$ at 99% confidence level).

The correlation based on the SCF π treatment is shown in Fig. 1, and the hatched area for 4'-biphenyl corresponds to a calculation of Δq corrected for non-planarity of the biphenyl system ($\theta = 45^\circ$) [3e]. Neglecting the very poorly correlated C(5)-1-naphthyl datum, a linear dependence between Δq and $\Delta \delta$ with $r = 0.98$ at the 99% confidence level, is obtained. The best correlation line passes very close to the origin, implying any contribution to the substituent chemical shifts, other than the hyperconjugative one, must be rather small. The apparently ill-disciplined behaviour of C(5)-1-naphthyl is in fact quite consoling, since the evidence is that any conjugation here is extremely small [3e,11]. Analysis of substituent behaviour by the Dual Substituent Parameter (DSP) approach for 1-substituted naphthalenes indicates ρR to be small, but positive, in line with the present result [11] *. Therefore, at this position, $\text{CH}_2\text{Sn}(\text{CH}_3)_3$ is reproducing the behaviour of authentic conjugating substituents. It is gratifying to note this analysis of the ^{13}C data completely harmonises with our previous deductions based on ^{19}F chemical shifts of fluoroarylmethylmetalloidal systems [2].

The photoelectron spectra (PES) of a series $\text{C}_6\text{H}_5\text{CH}_2\text{Sn}(\text{CH}_3)_3$ ($M = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$) have been reported recently and assigned to the various ionisations [12]. The key conclusions were (i) that the hyperconjugative contribution increases in the sequence C, Si, Ge, Sn (in line with the intuitive feeling of p -electron density on the benzylic carbon) and (ii) that the inductive and hyperconjugative effects were of comparable magnitude. This latter conclusion is at variance with data on conformationally constrained systems which indicate "inductive" effects to be rather minor [1,13]. The assumption in the above work of a C-M geometry (in $\text{C}_6\text{H}_5\text{CH}_2\text{M}(\text{CH}_3)_3$) orthogonal to the modal plane is almost certainly incorrect (vide infra), and hence some correction term would need to be applied to adjust the measured conjugative effect. On the other hand, "the inductive effect" would not be dependent on the orientation of the C-M bond with respect to the plane.

^{13}C - ^{119}Sn coupling in arylmethylstannyl systems

We have reported [1f,g] that in benzyltrimethylstannane, $^5J(\text{C}-\text{Sn})$ (i.e. to C(4)) was significantly larger than $^4J(\text{C}-\text{Sn})$ (to C(3)), while the reverse applied for phenyltrimethylstannane [14]. More recently, we outlined in detail the conformational dependence of $^5J(\text{Sn}-\text{C})$ in benzyltin systems, which accorded with a substantial hyperconjugative or π -mode of transmission of coupling [9]. From model rigid indanyl systems [1f] the mobile benzyltin system was suggested to have an "average" dihedral angle with respect to the ring of ca. 60° .

Regarding the naphthylmethyltin systems, we anticipated a more complex situation for ^{13}C - ^{119}Sn coupling, which would be difficult to compare directly with the benzyltin data for several reasons: (i) the fluctuations in bond-lengths

* ^{13}C data for a range of 1-substituted naphthalenes indicate essentially no 1,5-mesomerism.

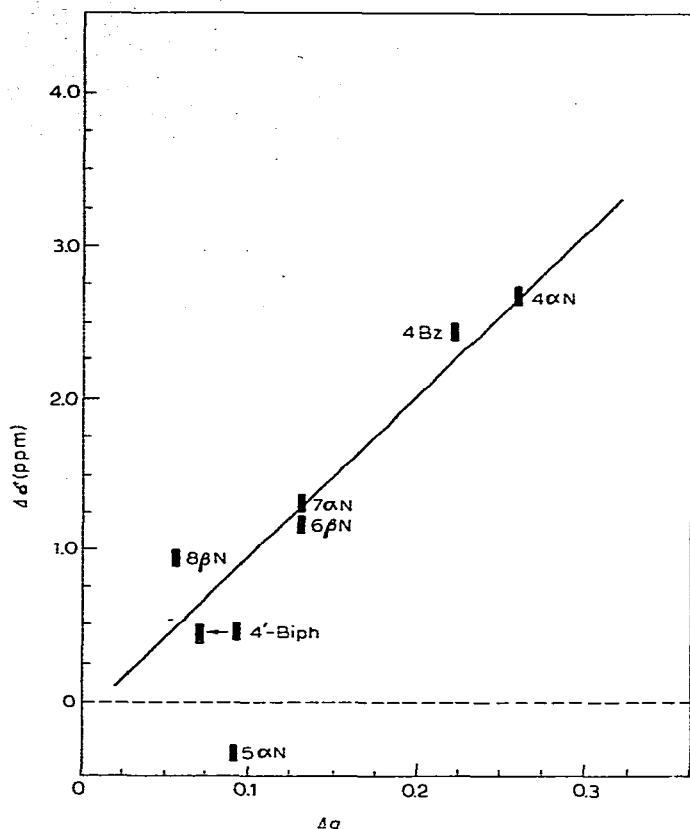


Fig. 1. Plot of Δq (SCFMO) versus $\Delta\delta$ [$(\text{CH}_3)_3\text{CCH}_2 \rightarrow (\text{CH}_3)_3\text{SnCH}_2$] for various dispositions in benzene, naphthalene and biphenyl. The 4-biphenyl value has been corrected for non-coplanarity of the rings. Correlation coefficient $r = 0.98$ at 99% confidence level.

and particularly π -bond orders could be serious for a π -transmission mechanism of coupling, (ii) the possible regulating effect the 8-(*peri*)-H could have on the "averaged" conformation in the 1-naphthylmethyl system and (iii) the possibility of increased importance of coupling mechanisms dependent on the C-Sn σ - and π -energy level separations, which will differ in benzyl and naphthyl.

There are also certain experimental problems in unambiguously extracting the coupling constants from the spectra of the naphthyltin compounds. In some spectra the signals are closely spaced and almost overlapping (e.g. in 2-naphthylmethyltrimethylstannane) and often only one satellite is observable creating a degree of uncertainty. The tin compounds are less attractive than the mercury or lead compounds for probing variations in coupling as the magnetically active isotopes (^{119}Hg , ^{207}Pb) of the latter metals are more abundant (~ 17 and 21% , respectively) and produce sharper satellite patterns. (^{117}Sn , ^{119}Sn are each $\sim 8\%$ abundant with a slightly different gyromagnetic ratio). In addition the coupling constants are larger in magnitude [1f].

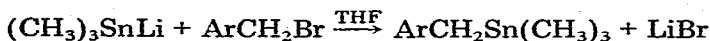
The coupling constants we have been able to measure with confidence are incorporated in Table 2. Compared with the benzyl system, the pattern of coupling is different in that the formally *para* coupling (5J) to C(4) in the 1-naphthyl case

is less than (4J) coupling to C(3). This reversal is presumably associated with the factors outlined above, but the exact nature of the coupling patterns in naphthylmetal systems will have to await data on the mercury and lead compounds currently being examined as part of another study.

Experimental

Method A: General procedure for trimethylstannylmethyl substituted naphthalenes and biphenyl

The following represents the route employed:



The appropriate bromomethylaromatics were obtained usually by treating the methyl aromatic with *N*-bromosuccinimide in the usual way. The new bromomethylaromatics employed here have been fully characterised, and reported as part of another investigation [3e]. Trimethylstannyl lithium was prepared as reported [15].

Method A. The appropriate bromomethylnaphthalene (0.01 mol) was dissolved in dry THF (25 ml) in a 100 ml round bottomed flask fitted with serum cap, dry N_2 inlet and magnetic stirrer. The flask was cooled to 5°C and the CH_3SnLi (0.012 mol) added with an air tight syringe at such a rate as to maintain the temperature $>10^\circ\text{C}$. Periodically a small sample was removed and analysed by VPC (SE-30 (6 ft.) at 110°C). After stirring for 12 h at room temperature, the solution was worked up with saturated NH_4Cl , extracted with ether and dried (Na_2SO_4). The solvent was removed and the product either distilled (vacuum) or recrystallised (absolute ethanol).

1-Naphthylmethyltrimethylstannane. Method A, 64% yield. B.p. $88\text{--}90^\circ\text{C}/0.1\text{ mmHg}$. VPC (SE-30 (6') at 120°C) indicated $>98\%$ purity. A sample for analysis was obtained by redistillation. PMR: $(\text{CH}_3)_3\text{Sn}$ δ 0.04 ppm ($J(\text{Sn}\text{--}\text{CH}_3)$ 53.5 Hz); CH_2 δ 2.74 ppm ($J(\text{Sn}\text{--}\text{CH}_2)$ 62.0 Hz); Aromatics δ 7.4 (br) ppm. Found: C, 55.00; H, 5.82. $\text{C}_{14}\text{H}_{18}\text{Sn}$ calcd.: C, 55.15; H, 5.91%.

The 4-deutero analogue was obtained similarly. The 1-naphthylmethyltributylstannane was kindly donated by Dr. V. Sandel of the Michigan Technological University, Houghton, Michigan.

2-Naphthylmethyltrimethylstannane. Method A, 46% yield. The crude product (yellow oil) crystallised from absolute ethanol as a white solid. M.p. $59\text{--}60^\circ\text{C}$. PMR: $(\text{CH}_3)_3\text{Sn}$ δ 0.05 ppm ($J(\text{Sn}\text{--}\text{CH}_3)$ 54.0 Hz); CH_2 δ 2.45 ppm ($J(\text{Sn}\text{--}\text{CH}_2)$ 63.0 Hz); Aromatics δ 7.4 (br) ppm. Found: C, 54.91; H, 5.90. $\text{C}_{14}\text{H}_{18}\text{Sn}$ calcd.: C, 55.15; H, 5.91%.

6-Methyl-2-naphthylmethyltrimethylstannane. Method A, 62% yield. M.p. $67\text{--}68^\circ\text{C}$ (from absolute ethanol). PMR: $(\text{CH}_3)_3\text{Sn}$ δ 0.05 ppm ($J(\text{Sn}\text{--}\text{CH}_3)$ 54.1 Hz); CH_3 δ 2.44 ppm; CH_2 δ 2.44 ppm ($J(\text{Sn}\text{--}\text{CH}_2)$ 64.0 Hz); Aromatics δ 7.4 (br) ppm. Found: C, 56.44; H, 6.40. $\text{C}_{15}\text{H}_{20}\text{Sn}$ calcd.: C, 56.47; H, 6.27%.

4-Biphenylmethyltrimethylstannane. Method A. VPC examination of the crude product (SE-30 at 130°C) indicated ca. 98% purity. The product was further purified by distillation; B.p. $120\text{--}121^\circ\text{C}/0.05\text{ mmHg}$. PMR: $(\text{CH}_3)_3\text{Sn}$ δ 0.08 ppm ($J(\text{Sn}\text{--}\text{CH}_3)$ 51.0 Hz); CH_2 δ 2.34 ppm ($J(\text{Sn}\text{--}\text{CH}_2)$ 64.0 Hz);

Aromatics δ 7.4 (br) ppm. Found; C, 57.93; H, 6.01. $C_{16}H_{20}Sn$ calcd.: C, 58.06; H, 6.05%.

Benzyltrimethylstannane. This compound was prepared from benzylmagnesium chloride and $(CH_3)_3SnCl$ [9]. B.p. 89–90°C/9 mmHg. (Lit. [16] 90°C/9 mmHg). PMR: $(CH_3)_3Sn$ 0.0 ppm ($J(^{119}Sn-CH_3)$ 54.0 Hz); CH_2 δ 2.2 ppm ($J(^{119}Sn-CH_2)$ 62.5 Hz) Aromatics δ 7.08 (br) ppm.

9-Anthrylmethyltrimethylstannane. All attempts to synthesise this compound met with failure. The reaction of 9-anthrylmethyl bromide with $(CH_3)_3SnLi$ provided at least six products, all lacking the characteristic $(CH_3)_3Sn$ signal in the PMR spectrum. The use of 9-anthrylmethyltosylate (in situ low temperature preparation) in this reaction provided, on the basis of analysis, high resolution mass spectrometry and PMR spectra, a high yield (84%) of 1,2-di-9-anthryl-ethane, m.p. 307–308°C [17].

Neopentyl substituted aromatics. The following neopentyl compounds (along with others) were obtained by a new procedure (utilising *t*-butylmagnesium chloride) which will be reported fully elsewhere [4]. The analytical and spectroscopic data fully confirm the structures. Neopentylbenzene; 1-neopentyl-naphthalene (and its 4-D analogue); 2-neopentyl-naphthalene; 6-methyl-2-neopentyl-naphthalene; 4-neopentylbiphenyl.

Solvents

All solvents were of analytical grade and anhydrous ether (0.01% H_2O) was from the Mallinkrodt Chemical Co. Tetrahydrofuran was dried by refluxing with calcium hydride for two days and distilled from $LiAlH_4$ before use. Alternatively specially dried THF (<0.01% H_2O) from the Merck Chemical Co., Darmstadt (Germany) was used. *n*-Butyllithium was Alfa material and standardised according to Appley and Dixon.

Spectra

Mass spectra were recorded on an AEI MS902-S mass spectrometer and VPC analyses prepared on either a Varian 1200 series or Hewlett Packard 5720 A instruments with FID detectors.

1H NMR spectra were recorded with a JEOL MH-100 spectrometer (100 MHz) (CCl_4 or $CDCl_3$ solutions) at a probe temperature of ca. 30°C. Infrared spectra were obtained on a Perkin–Elmer 247 grating spectrometer. All melting points are uncorrected.

In the ^{13}C NMR spectra all carbon-13 chemical shifts were obtained on 10–15% wt/vol solutions in $CDCl_3$ (with internal TMS) on a Bruker HX90 instrument operating at 22.63 MHz, and are regarded as accurate to at least ± 0.1 ppm. Dilution effects on the spectra were insignificant. For observation of metal–carbon coupling constants, more concentrated solutions were sometimes employed.

Spectra in the CW-mode were obtained at 15.1 MHz on a modified Varian HA60 11 spectrometer with the field locked to an enriched sample of methyl iodide. The spectrometer was controlled by a Varian 8K 620 i computer, also used for data averaging.

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