Journal of Organometallic Chemistry, 63 (1973) 67–77
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CARBON MAGNETIC RESONANCE OF ORGANOMETALLIC COMPOUNDS: HYPERCONJUGATIVE EFFECTS IN BENZYLSILANES

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(Received March 15th 1973)

SUMMARY

A number of benzylsilanes have been synthesised and characterised, and the structural features of certain of these compounds are such that the C–Si bond is constrained to varying degrees to the nodal plane of the aromatic system. The proton-decoupled, natural-abundance ^{13}C NMR spectra of these compounds have been obtained and essentially completely assigned on the basis of signal intensities, chemical shifts, selective deuteration and (in some cases) the magnitudes of ^{13}C–^{19}F coupling constants. Comparison of ^{13}C chemical shifts of carbons formally *para* to the silylmethyl group (CH_2Si) in the bicyclic silatetralins and -indanes with the corresponding carbon shifts in the carbon analogues, indicates suppression of the electron-donating effect of the CH_2Si group, when the optimum alignment for interaction of the C–Si σ-bond and the π-system is prevented. Effects related to strain and special influences operating on the chemical shifts of carbon bearing fluorine, render interpretation for some compounds less straight-forward.

INTRODUCTION

The pronounced electron-releasing ability of many metallomethyl groups has stimulated several inquiries into the origin of this effect. A most useful device, employed by Pitt[1] and Traylor[2], involves examination of molecules in which the dihedral angles between the C–M bonds and the π-systems differ, and are known with reasonable precision. See for this approach to C–C and C–H hyperconjugation ref. 27. This approach has more recently been utilised by Adcock and Kitching[3], and all studies demonstrate quite convincingly that the electron releasing effect of $-MCH_2-$ groups is dependent on proper alignment of the C–M σ-bond and the π-system. This is in accord with a σ–π hyperconjugative mechanism for electron release[4]

We recently interpreted ^{19}F chemical shift data for a number of bicyclic silicon compounds in terms of hyperconjugative C–Si electron release on the basis of the strong conformational dependence of the ^{19}F substituent chemical shifts[3] While this

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interpretation seemed to have a sound theoretical basis[5] and was subsequently supported by experimental and computational work[6], we were aware that molecular deformations in the aromatic portion of some molecules could influence the magnitude of the ^{19}F chemical shift[7] Although ^{19}F chemical shifts in *para*-substituted fluorobenzenes correlate rather well with *para*-^{13}C shifts in monosubstituted benzenes[8], the former measurements, nevertheless, are characteristic of disubstituted benzenes Because of the additional structural complexity in tetralin and indan systems (compared with simple benzene systems) it seemed most desirable to pursue the question of ground-state σ–π interactions in benzylsilanes with data from another probe The response of ^{13}C chemical shifts to π-electron perturbations was anticipated to be sensitive enough to monitor variations in the extent of σ–π interactions, as crucial geometrical relationships were altered[8–12]

In this paper we report our ^{13}C NMR measurements on a variety of moncyclic and bicyclic benzylsilanes.

EXPERIMENTAL

Compounds: Toluene, tetralin, indan, *p*-fluorotoluene and *m*-fluorotoluene are commercially available. 3- and 4-Deutero-*o*-xylenes were synthesised by standard transformations of 3-amino- and 4-bromo-*o*-xylenes The ^1H spectra indicated approximately 70% deuterium incorporation

p-Fluorobenzyltrimethylsilane

Was obtained (via a Grignard synthesis) as a colorless oil, b p 83° (16 mm lit [13] 115–120° 60 mm). PMR (CCl_4) δ2 05 (2H, singlet, CH_2) and δ6 9 (4H, "doublet", aromatic protons). (($(CH_3)_3Si$ at δ0.0)

Benzyltrimethylsilane

Was prepared according to the method of Hauser and Hance[14], and distillation afforded a colorless oil, b.p. 76° (20 mm) (lit.[2] 76° (20 mm)). PMR (CCl_4) (from $(CH_3)_3Si$ at δ0.00): δ2.03 (2H, singlet, CH_2) and δ7.0 (5H, complex, aromatic protons)

5-*Fluoroindan and* 6-*fluorotetralin*

Available from another investigation[15]

2,2-*Dimethyl*-1,2,3,4-*tetrahydro*-2-*silanaphthalene*

Prepared from benzyl magnesium chloride and vinyltrichlorosilane in the manner outlined by Nametkin and coworkers[16] Distillation under reduced pressure yielded a colorless oil, b p 60° (0 7 mm) (lit [16] 227–229° (760 mm)). PMR data ($CDCl_3$): δ0.72 (triplet, J 7.5Hz, 2H, $CH_2\underline{CH_2}Si$), δ1 92 (singlet, 2H,$\underline{CH_2}Si$), δ2 72 (triplet, J 7.5Hz, 2H, $\underline{CH_2}CH_2Si$), and δ7.05 ("singlet", 4H, aromatic protons).

2,2-*Dimethyl*-6-*methyl*-1,2,3,4-*tetrahydro*-2-*silanaphthalene*

2,2-Dichloro-6-methyl-1,2,3,4-tetrahydro-2-silanaphthalene was prepared according to the method outlined by Corriu, Henner, and Massé[17] The dichloro compound was converted to the 2,2-dimethyl derivative by treatment with excess methylmagnesium chloride Distillation afforded a colorless oil, b p 72–74° (0.6–0 7 mm), $n_D^{19.5}$ 1.5275. PMR data (CCl_4): (From $(CH_3)_2Si$ group at δ0.0) δ0.69 (triplet, J 7.5Hz, 2H, $CH_2\underline{CH_2}Si$), δ1.85 (singlet, 2H, $\underline{CH_2}Si$), δ2.23 (singlet, 3H, CH_3), δ2.65 (triplet, J 7.5Hz, 2H, $\underline{CH_2}CH_2Si$), and δ6.82 ("singlet", 3H, aromatic protons). Anal Found: C, 76.30; H, 9.60 $C_{12}H_{18}Si$ calcd.: C, 75.72; H, 9.53 %

2,2-Dimethyl-6-fluoro-1,2,3,4-tetrahydro-2-silanaphthalene

Prepared from *p*-fluorobenzyl magnesium chloride in the same manner as described above for the unfluorinated analogue Distillation afforded a colorless oil (4.5 g, 74 %), b.p. 96–98° (13 mm), n_D^{21} 1.5085. PMR data (CCl_4): (From $(CH_3)_2Si$ group at δ0.0) δ0.68 (multiplet, 2H, $CH_2\underline{CH_2}Si$), δ1.87 (singlet, 2H, $\underline{CH_2}Si$), δ2.68 (multiplet, 2H, $\underline{CH_2}CH_2Si$), and δ6.95 (multiplet, 3H, aromatic protons). Anal Found. C, 67.6; H, 7.9 $C_{11}H_{15}FSi$ calcd. C, 68.0; H, 7.8 %

2,2-Dimethyl-7-fluoro-1,2,3,4-tetrahydro-2-silanaphthalene

Prepared from *m*-fluorobenzyl magnesium chloride as described above for the 6-fluoro isomer. Distillation afforded a colorless oil (6.8 g, 82 %), b.p. 142–145° (65 mm), n_D^{23} 1.5117. PMR data (CCl_4) (From $(CH_3)_2Si$ group at δ0.0) δ0.67 (multiplet, 2H, $CH_2\underline{CH_2}Si$), δ1.88 (singlet, 2H, $\underline{CH_2}Si$), δ2.69 (multiplet, 2H, $\underline{CH_2}CH_2Si$), and δ6.77 (multiplet, 3H, aromatic protons). Anal Found: C, 68.6; H, 8.2. $C_{11}H_{15}FSi$ calcd.. C, 68.0; H, 7.8 %

2,2-Dimethyl-2-silaindan

Prepared from benzyl magnesium chloride and chloromethyltrichlorosilane in the manner outlined by Nametkin and co-workers[18]. Distillation afforded a colorless oil, b.p 50–54° (1 mm) (lit [18] 210–211° (760 mm)). PMR data (CCl_4): (from $(CH_3)_2Si$ group at δ0.0). δ1.80 (singlet, 4H, CH_2Si) and δ6.81 ("doublet", 4H, aromatic protons)

A further sample was prepared from α,α′-dibromo-*o*-xylene using the procedure outlined by Fessenden and Coon[19] for the synthesis of 1,1-dimethylsilacyclopentane

2,2-Dimethyl-5-fluoro-2-silaindan

Prepared from *p*-fluorobenzylmagnesium chloride in the same manner indicated above for the unfluorinated analogue Distillation gave the product as a colorless oil (8.0 g, 75 %), b.p. 86–88° (46 mm), n_D^{21} 1.5051. PMR data (CCl_4): (from $(CH_3)_2Si$ group at δ0.0). δ1.78 (multiplet, 4H, CH_2Si) and δ6.7 (multiplet, 3H, aromatic protons). Anal. Found: C, 66.0; H, 7.2 $C_{10}H_{13}FSi$ calcd.: C, 66.6; H, 7.3 %

^{13}C Spectra

Proton decoupled natural abundance ^{13}C spectra were determined at 15.1 MHz on a modified Varian HA60 IL spectrometer with the field locked to an enriched sample of methyl iodide. The spectrometer is controlled by a Varian 8K 620i computer which was also used for data averaging. Internal cyclohexane was used as a reference.

RESULTS AND DISCUSSION

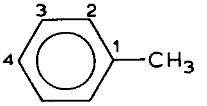
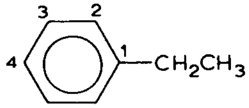
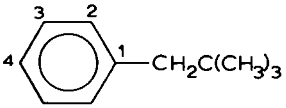
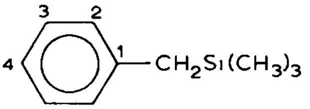
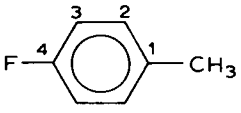
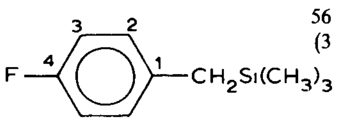
It is convenient to discuss the results for the simple benzylsilanes and model carbon compounds initially, since an appreciation of the range of ^{13}C chemical shifts involved, is obtained.

In Table 1 the assignments for a series of such benzyl compounds are presented.

The resonance pattern for the ring carbons in compounds I–IV consisted of four signals with intensity ratio 1/2/2/1 approximately. (This is slightly modified by Overhauser effects). The less intense signals are assigned to C(1) and C(4) and because carbons not bearing a proton, and alkyl-substituted, resonate at characteristically

TABLE 1

^{13}C CHEMICAL SHIFTS[a]

Compound		*Carbon position*							
		1	2	3	4	α	β	γ	Si–C
I		55.0	63.6[b]	64.5[b]	67.3	171.7	—	—	—
II		48.5	65.1[c]	64.6[c]	67.3	163.8	177.5	—	—
III		53.3	62.5[c]	65.0[c]	67.1	161.3	142.1	163.7	—
IV		52.4	64.5[c]	64.4[c]	68.6	165.4	—	—	194.7
V		59.4 (3.0)	62.4 (8.1)	78.0 (20.3)	31.0 (246.2)	[d]	—	—	—
VI		56.8 (3.26)	63.6 (7.3)	77.9 (21.0)	32.0 (245.3)	166.6	—	—	195.0

[a] In ppm from CS_2 Referenced to internal benzene (+64.4 ppm from CS_2) or cyclohexane (+165.8 ppm from CS_2) Values in parenthese are ^{13}C–^{19}F coupling constants

[b] Assignments confirmed by deuteration

[c] Assignments could be reversed

[d] Not measured

lower fields, C(1) and C(4) are thus distinguished. The C(1) resonance would be expected also to exhibit the greater fluctuation, as the alkyl group is varied. The C(1) resonance is also less intense than that for C(4) due to a reduction in Overhauser enhancement. The C(2) and C(3) resonances are more difficult to assign, and at the commencement of this work the assignments for toluene were unclear*. Our examination of *ortho*-deuterotoluene led to the assignments in Table 1, for now the deuterium-bearing C(2) resonance appears as a 1/1/1 triplet slightly to higher field than the signal for protium-bearing C(2). This difference (~0.3 ppm) represents the deuterium isotope effect on the C(2) resonance[21]. In this fashion the assignments for ethylbenzene and neopentylbenzene were made (II and III), except that the C(2) and C(3) resonances in ethylbenzene could conceivably be reversed. However, there is considerable experimental and theoretical justification[8-12] (see later) for expecting the *meta* (C(3) carbon resonance to show a small range for different alkyl substituents[21]. This is also the reason for assigning the 65.0 ppm signal to C(3) in neopentylbenzene because it is in better agreement with the C(3) values for toluene and ethylbenzene than is 62.5 ppm. These assignments agree in appropriate cases with some recently reported by Ihrig and Marshall[20], Maciel[21], and some time ago by Spiesecke and Schneider[9]. The assignments for the alkyl-carbons were straight-forward because increasing alkyl substitution reduces the nuclear shielding.

In the present context, then, we emphasise for compounds I–IV the essential constancy of the *meta*-C shifts (*i.e.* C(3)), and of the *para*-carbon (C(4)) shifts in I–III, but the very definite increased shielding of C(4) (Δ 1.5 ppm) in benzyltrimethylsilane (IV) when properly compared with C(4) for neopentylbenzene (III). Since the increased shielding is most unlikely to be due to field, σ-inductive or related effects (constancy of *meta*-C-shifts) emanating from silicon or the carbon–silicon bond, a resonance effect, of little consequence at the *meta* position, seems operative. This most likely involves "σ–π" hyperconjugative electron-release from the C–Si bond. The same type of effect is observed in V and VI where an increased shielding (Δ 1.0 ppm) of C(4) in *para*-fluorobenzyltrimethylsilane is observed. (Compared with C(4) in *para*-fluorotoluene). The same explanation also seems appropriate. In V and VI the increased shielding of C(3) of ca. 13.5 ppm when compared with C(3) in I–IV is to be ascribed to the *ortho* fluorine effect on ^{13}C chemical shifts[9]. It should be noted that the increased shielding of 1.5 ppm of C(4) in IV (compared with C(4) in III) is not necessarily the maximum to be associated with C–Si σ–π electron release, since the orientation of the C–Si bond with respect to the π-system is unknown. The result represents a mean effect, derivable in principle from the populations of the conformers and the cosines of the σ–π interaction angles.

Because σ–π conjugation is expected to exhibit a similar stereoelectronic dependence to p–π conjugation, it follows that the chemical shifts of appropriate carbons, in benzylsilanes in which the dihedral angle between the interacting orbital systems is varied, should respond in a predictable way. In particular, the increasing constraint of the C–Si bond to the nodal plane of the π-system, should lead to diminished electron release by the CH$_2$Si group. To test this hypothesis, a number of bicyclic (sila)indans and tetralins have been examined.

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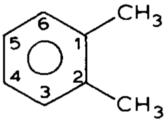
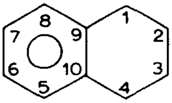
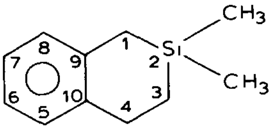
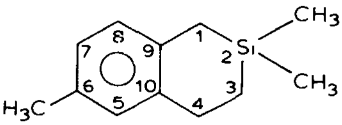
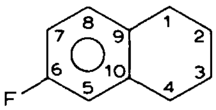
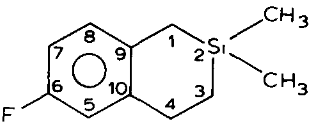
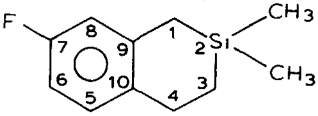
* The assignments for toluene were confirmed also by Ihrig and Marshall, who examined *m*-deuterotoluene[20].

TABLE 2

CARBON-13 CHEMICAL SHIFTS[a] FOR TETRALIN-TYPE COMPOUNDS

Compound	*Carbon position*	*Chemical shift(ppm)*	*Carbon position*	*Chemical shift(ppm)*
o-xylene (VII) 	1,2	54 5	4 5	66 8
	3,6	63 0	CH_3	173 4
tetralin (VIII) 	1,4	163 1	6,7	67 2
	2,3	169 2	9,10	55 8
	5,8	63 6		
2-silatetralin (IX) 	1	171 9	6	67 6
	2-CH_3	195 0	7	66 1
	3	181 0	8	64 7
	4	162 9	9	54 9
	5	63 1	10	51 3
6-methyl-2-silatetralin (X) 	1	172 8	6	58 7
	2-CH_3	195 2	7	66 0
	3	181 1	8	64 2
	4	163 2	9	59 4
	5	63 5	10	52 0
			C-CH_3	172 1
6-fluorotetralin (XI) 	1	164 7	6	32 0 (247 8)
	2	170 1[b]	7	81 0 (21 3)
	3	170 4[b]	8	63 0 (8 1)
	4	163 9 (1 4)	9	60 8 (2 7)
	5	78 3 (20 2)	10	54 3 (7 4)
6-fluoro-2-silatetralin (XII) 	1	173 6	6	31 6 (244 8)
	2-CH_3	194 9	7	81 0 (21 3)
	3	181 6	8	62 6 (7 5)
	4	163 6 (1 2)	9	59 6 (2 3)
	5	78 3 (20 2)	10	49.5 (6 9)
7-fluoro-2-silatetralin (XIII) 	1	171 9	6	81 9 (20 6)
	2	195 0	7	31 0 (245 8)
	3	181 4	8	77 1 (20 6)
	4	164 0	9	52 5 (7 6)
	5	64 1 (8 40)	10	55 9

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[a] Chemical shifts in ppm from CS_2

[b] Indicates assignments could be reversed Values in parentheses refer to $^{13}C-^{19}F$ coupling constants in Hz

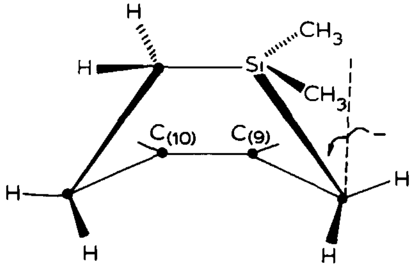
Tetralin-type systems

The formulae and ^{13}C data of the compounds studied are shown in Table 2.

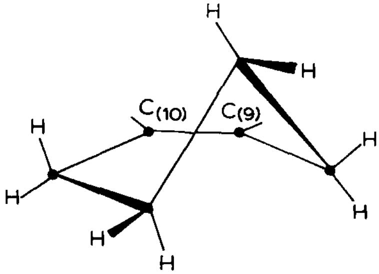
To provide a basis for comparison with the silatetralins, the compounds *o*-xylene (VII) and tetralin (VIII) were examined, and in the former case the only ambiguity concerns C(3,6) and C(4,5) since the alkylated carbonsC(1,2) are characteristically to lower field. Some time ago, Lauterbur[22] assigned these positions on the basis of results for partially 4-deuterated *o*-xylene, such assignments being consistent with the shielding effect of a methyl group on a carbon *para* to it However, Lauterbur employed the rapid-passage dispersion mode method, and it was desirable to provide unambiguous assignments from high-quality spectra. Examination of *o*-xylenes, specifically deuterated at the 3- and 4-positions (See Experimental) establish the assignments in Table 2. Utilising this information, the assignments for tetralin (II) follow logically, with the chemical shifts of C(5,8) (63.6 ppm) and C(6,7) (67.2 ppm) closely resembling those for C(3,6) (63 0 ppm) and C(4 5) (66.8 ppm) in *o*-xylene. These assignments are completely consistent with the data for 6-fluorotetralin (XI) where the assignment for C(8) is based on the magnitude of $^{13}C-^{19}F$ coupling[23,24] as well as the chemical shift. 4-Fluorosubstitution in toluene and benzene results in a deshielding effect of ca. 1.2 ppm on carbons *meta* to fluorine and the assignments for C(8) in (VIII) and (XI) differ by 0.6 ppm in good agreement. Such consistency is not obtained for any other combination of shifts in (VIII) and (XI), given the restraints imposed by established trends in $^{19}F-^{13}C$ coupling and fluoring shielding effects.,

In the silatetralin (IX), the assignments for C(1), C(3) and C(4) were straight forward after due regard to the electropositive nature of silicon compared with carbon C(9) and C(10) were distinguished on the basis that the effect of the Si should be more pronounced at C(9) than C(10), but these assignments are tentative. Separate signals were detected for C(5), C(6), C(7), C(8) and C(5,8) and C(6,7) could be so grouped on the basis of the data for tetralin. There is a danger here in that Dreiding models indicate a conformational difference between tetralin and the silatetralins (see later). The 64.7 ppm resonance was assigned to C(8) and the 63.1 ppm resonance to C(5), since C(8) is quite definitely closer to the Si atom in the half-boat conformation preferred by this molecule. We expected that the silyl-methyl group would exert some shielding effect at C(6) (formally *para* to it), even given the conformational constraint to $\sigma-\pi$ electron release imposed on it. Hence preliminary assignments for C(6) (67.6 ppm) and C(7) (66.1) were arrived at. Since our main concern was to identify the C(6) resonance with certainty, we attempted to synthesise the 6-deutero analogue of (IX). Unfortunately, with the use of Lewis acids under Friedel–Crafts conditions, the deuterium was scrambled and this approach abandoned. However, methyl-substitution is distinctly useful in clarifying assignments, and the 6-methyl compound (X) was synthesised. Remembering that methyl-substitution scarcely affects the resonance positions of *meta*-carbons (in this situation C(10), C(8), has a pronounced shielding effect on *para*-carbons ($\sim$3 ppm) (here C(9)) and a very marginal effect on *ortho* carbons (C(5), C(7)) (*e.g.* a deshielding effect on ca. 0.7 ppm is experienced at C(2) in toluene compared with benzene In Table 1 the assignments for (IX) and (X) are derived and appear to be the only mutually consistent sets of data, when the methyl group is considered.

It is to be noted, therefore, that the substitution of silicon in (IX) for carbon in (VIII) leads to an increased shielding of only 0.4 ppm for C(6). This is to be compared with the increase of 1 5 ppm in the C(4) shielding when benzyltrimethylsilane is compared with neopentylbenzene or toluene (Table 1). Examination of molecular models shows that whereas tetralin prefers the half-chair arrangement, the sila-tetralins *e.g.* (IX) and (X) prefer the half-boat form[3]. In the latter, the benzylic hydrogens are eclipsed with H_5 and H_8, but staggered in tetralin. These conformations are partially drawn below



Half-boat



Half-chair

By considering a simple cosine dependence of the σ–π interaction, and assuming no strain in either the half-boat or half-chair forms of (IX) or (VIII), and that Δ 1.5 ppm represents the maximum effect of the $CH_2Si(CH_3)_3$ group (in the simple benzyl systems), a computed difference, Δ, for C(6) in (IX) and (VIII) of ca. 1.00 ppm is obtained. (The appropriate dihedral angle is $\sim 40°$). The experimental quantity of 0.4 ppm is somewhat below this, but a number of subtle influences on the carbon shifts in these molecules could account for this. The fact that Δ is reduced substantially on imposition of the conformational constraint is strong evidence that a resonance phenomenon is involved.

A similar conclusion is possible when the data for the fluoro-substituted compounds are considered (XI, XII, XIII). The assignments in these cases were greatly facilitated by the known magnitudes of ^{13}C–^{19}F couplings in aryl ring systems[23,24]. There may be some ambiguity for C(5) and C(7) in (XI) and (XII) and C(6) and C(8) in (XIII), but the assignments given are consistent with the established higher-field resonance for β-carbons in tetralin systems (*e.g.* C(6) and C(7) in (VIII) compared with C(5), C(8) On comparing C(6) in (XI) with C(6) in (XII) the chemical shifts are almost within experimental error, indicating again extensive reduction in shielding. It should be noted that σ–π electron release in (XII) would enhance π-charge density in the region of C(6), to which the fluorine is attached. This would be unfavorable as regards the repulsive energy term for the C–F bond, and probably accounts for the elimination of electron release in this system. (A similar analysis is probably appropriate for *p*-fluorobenzyltrimethylsilane) It is meaningful to compare C(7) in (XI) with C(6) in (XIII) if the shielding effect of fluorine on *ortho*-carbons is constant in these cases. A shielding effect of 0.9 ppm, in the range estimated, operates at C(6) in (XIII) compared with C(7) in (XI).

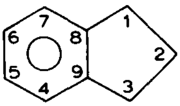
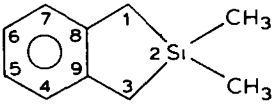
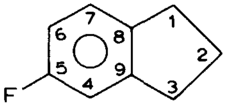
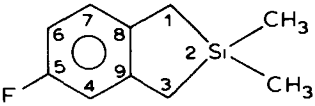
Indan-type systems

The 2-silaindan systems have the attraction that the benzylic carbon–silicon bond is almost perfectly constrained to the nodal plane of the π-system, and no σ–π electron release mechanism can operate. Given that any other influences *e.g.* related to ring strain, on carbon shifts are negligible, or can be estimated fairly well, these systems offer a further test of the hyperconjugative explanation of the silyl-methyl substituent effect

The results for the compounds examined are located in Table 3.

TABLE 3

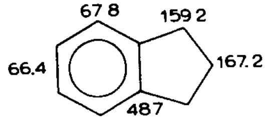
CARBON-13 CHEMICAL SHIFTS[a] FOR INDAN-TYPE COMPOUNDS

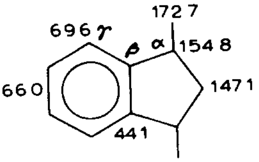
Compound	*Carbon position*	*Chemical shift(ppm)*	*Carbon position*	*Chemical shift(ppm)*
indan (XIV)				
	1,3	159.8	5,6	66.6
	2	167.4	8,9	48.8
	4,7	68.4		
2-silaindan (XV)				
	1,3	171.8	5,6	67.3
	2-CH_3	195.9	8,9	51.3
	4,7	64.5		
5-fluoroindan (XVI)				
	1	161.3	6	80.3 (22.5)
	2	167.5	7	68.0 (8.7)
	3	160.4 (2.2)	8	53.9 (2.0)
	4	81.8 (22.7)	9	46.9 (8.0)
	5	30.0 (245.6)		
5-fluoro-2-silaindan (XVII)				
	1	173.4	6	80.3 (21.7)
	2-CH_3	196.5	7	62.9 (8.1)
	3	171.9	8	55.5 (2.6)
	4	77.5 (20.2)	9	48.6 (8.3)
	5	31.8 (245.6)		

[a] In ppm from CS_2. Values in parentheses refer to ^{13}C–^{19}F coupling constants in Hz.

The assignments for C(1,3), C(2) and C(8,9) in indan (XIV) were straightforward, but distinction between C(4,7) and C(5,6) was achieved by examining 5-fluoroindane (XVI), which was assigned mutually with indane, by considering the magnitudes of ^{13}C–^{19}F couplings, and the substituent effect of the fluoro group. Since C(7) in (XVI) is positively assigned by its chemical shift and ^{13}C–^{19}F coupling constant, and knowing the fluoro group has a deshielding effect of ca. 1.00 ppm on carbons *meta* to it, it follows that in indan (XIV), the 68.4 ppm resonance must be C(4,7).

This conclusion is supported strongly by recently published data[25], which is condensed below. (The published figures have been converted to the CS_2 reference scale by subtracting from 192.8 ppm, the difference in chemical shift between CS_2 and TMS.)





The assignments for indan were arrived at by considering the γ-effect (shielding) (normally 2.0–2.5 ppm) of the 1-, or 3-methyl substituents Since δ and ε-effects (deshielding) are quite small in comparison (~0.3 ppm) the essentially unaffected resonances of the aromatic carbons (66.4 and 66.0 ppm) must be assigned to the more remote positions. Any other combinations of aryl carbon chemical shifts lead to γ, δ and ε effects that are of unacceptable sign or magnitude

In the case of the 2-silaindan (XV), it was unclear what effect incorporation of the silicon atom into the ring might have, and hence the 5-D analogue was synthesised, and examination of it led to the assignments for (XV) given in Table 3. It is worthy of note that the order of shielding for C(4,7) and C(5,6) in indan is reversed in the 2-silaindan This, we shall see, is related to ring strain effects on ^{13}C shifts. The assignments for (XVII) are essentially straight-forward, and the only possible ambiguity concerns C(4) and C(6). However, because C(4,7) and C(5,6) in (XV) have been positively assigned by deuteration (with C(5,6) at higher field) the assignments for C(4) and C(6) in (XVII) given in the Table, follow if the contribution to the carbon screening constant from the (*ortho*) fluorine is the same at both C(4) and C(6) in (XVII). This seems likely, because both resonances are now more shielded by 13 ppm compared with C(4), C(6) in (XV).

Because σ–π electron release from the C–Si bond in (XV) is essentially completely suppressed, we would anticipate the resonance positions of C(5,6) in (XV) and (XIV) to be very similar, because C(5,6) are too remote to be influenced by other "inductive" or field effects emanating from the C–Si region. We note however, C(5,6) in (XV) to be more shielded by 0.7 ppm, but consideration of ring strain effects on ^{13}C chemical shifts accounts for the divergence[25]. For example on progressing from tetralin to indan, the resonance position of the β-aryl carbon (C(6,7) in tetralin, C(5,6) in indan) moves downfield by 0.6 ppm, and a further reduction (0.4 ppm) occurs in benzocyclobutene[25]. Because the C–Si bonds in (XV) are longer, ring strain is not expected to be as severe, and molecular models support this view. Hence a substantial part of the divergence for C(5,6) in (XIV) and (XV) is accounted for and the silylmethyl substituent effect is essentially absent when properly constrained. In (XVI) and (XVII) the agreement for the C(5) chemical shifts (30.0 and 31.8 ppm) is not impressive While strain effects in (XVI) account for some of the difference, we did consider that more severe electronic distortions were concentrated closer to the C–F region, (thus perhaps further lowering the chemical shift of C(5) but the agreement in coupling constant (^{13}C–^{19}F) for C(5) (245.6 Hz) with that in other fluoro-substituted strained systems (*e.g.* 4-fluorobenzocyclobutene) does not support this. Another complication relevant to the above has been recognised by Maciel[8], who found from extensive correlative work, that the chemical shifts of aryl-carbons bearing fluorine are less precise monitors of π-electron density, than the *para*-^{13}C shifts in monosubstituted benzenes or the *para*-^{19}F shifts in disubstituted benzenes. This renders interpretation of the fluoroindan and possibly the fluorotetralin results more difficult

While the study of the bicyclic silicon compounds is attractive from a synthetic point of view, the range of chemical shifts involved is only moderate on the ^{13}C scale. From other work[2,3], greater shifts would be expected for bicyclic tin compounds, which also have the advantage of exhibiting identifiable ^{119,117}Sn–^{13}C coupling in their spectra, which greatly facilitates assignments[26], and may remove the necessity for synthesis of fluoro or deutero analogues. Unfortunately synthesis of the required tin compounds in acceptable yields is more difficult, but we hope to report on their spectra in the future

ACKNOWLEDGEMENTS

We are indebted to the Australian Research Grants Committee for generous support of this work at the collaborating institutions. The Dow Corning Corp and Dr W Atwell kindly supplied quantities of the organosilicon precursors.

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