α_M being the spectrometer sensitivity to M and (M) is the steady state concentration of M in the reactor. Thus, one obtains γ by measuring the steady-state amounts of **AB**, $\mathbf{A_2}$, $\mathbf{B_2}$, $\mathbf{A_{-H}}$, $\mathbf{A_{+H}}$, $\mathbf{B_{-H}}$, and $\mathbf{B_{+H}}$, and by knowing or estimating the equilibrium constant K_{rd}.

It is important to note that if the correct value of is used, k_d will be independent of flow rate at a given temperature. Therefore, one knows when one has the correct value of γ. One may then use various estimates of

$$K_{rd} = 10^{\Delta S_{rd}/4.58\Delta H_{rd}/\theta}$$

to achieve the correct γ.

This procedure alone may enable a choice to be made as to correct thermochemical parameters when differences which would lead to values of K_{rd}, differing by a factor of 10 or so, are in question.

Group IVb Metalloidal and Mercury Substituent Effects in the Naphthalene System by Fluorine-19 Nuclear Magnetic Resonance[1]

William Adcock,[2a] S. Q. A. Rizvi,[2a] William Kitching,[2b] and Alan J. Smith[2b]

Contribution from the School of Physical Sciences,
The Flinders University of South Australia, Bedford Park, Australia,
and the Department of Chemistry, University of Queensland,
Brisbane, Queensland, Australia. Received March 4, 1971

Abstract: A number of substituted α (1)- and β (2)-fluoronaphthalenes with metallo substituents of the type MR_3 (when M is a group IVb metalloid; R = methyl) and HgX (X = halogen or aryl) in the 4, 6, and 7 positions have been synthesized and their fluorine nmr spectra have been measured. The ^{19}F substituent chemical shift data (the extent to which a substituent electronically perturbs the C–F neighborhood is indicated by the substituent chemical shift (SCS), which is defined as the difference between the chemical shift of the unsubstituted fluoroaromatic and the substituted fluoroaromatic) provide experimental evidence for d_π–p_π and $6p_\pi$–p_π conjugative electron withdrawal ($-$M) in the ground state by the metalloidal and mercuri substituents, respectively. Comparisons with SCS data from metallo-substituted fluorobenzenes and fluorobiphenyls suggest that this conjugating ability depends on the energy and size of the outer lying orbital with π symmetry. This supports previous conclusions concerning the electronic behavior of metalloidal substituents as well as providing additional insight into the nature of aryl-carbon-mercury bonds. Further, the data from the 7β disposition suggest that certain approaches to the analysis of ^{19}F SCS may be invalid. SCS information from two dicyclopentadienyltitanium derivatives indicates that hyperconjugation is probably an unnecessary concept to invoke for ground-state alkyl substituent effects.

The widespread applicability of fluorine-19 substituent chemical shifts (SCS) for investigating ground-state substituent–substrate interactions[3,4] now extends to many organometallic derivatives from which information on the electronic behavior of metallo-type substituents provides valuable insight into the nature of aryl–carbon–metal bonds.[5] As part of a general program on metallo substituent effects, we have recently utilized the technique to investigate the ground-state electronic properties of mercuri substituents (HgX and CH_2HgX where X = aryl or halogen)[5b,c] as well as metalloidal substituents of the MR_3 and CH_2MR_3 type where M is a group IVb metalloid (R = methyl or phenyl).[5e] From these studies we concluded that in mono- and bisphenylmercury systems there is little net movement of π charge either in or out of the phenyl ring (*i.e.*, there is no detectable ground-state resonance interaction), whereas with substituents of the MR_3 type the firm conclusion made was that all the groups engage in conjugative electron withdrawal ($-$M) *via* d_π–p_π interaction with an adjacent aryl system, the degree of conjugative interaction being not only a sensitive function of d-orbital size but also a function of the adjacent aromatic system. However, the conclusion for the mercury systems was based essentially on the small difference between the meta and para SCS without due consideration to the "anomalous" behavior of substituents in unconjugated positions. On the basis of a simple inductive model and the fact that mercuri substituents (HgX) are more electropositive[5b,c] than the methyl substituent, it could be concluded that considerable mesomeric electron withdrawal occurs *via* vacant

---

(1) A preliminary account has been published: W. Adcock and W. Kitching, *Chem. Commun.*, 1163 (1970).

(2) (a) School of Physical Sciences, The Flinders University of South Australia, Bedford Park, Australia. (b) Department of Chemistry, University of Queensland, Brisbane, Queensland, Australia.

(3) (a) H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *J. Amer. Chem. Soc.*, **74**, 4809 (1952); (b) R. W. Taft, *ibid.*, **79**, 1045 (1957); (c) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 709, 3146 (1963), and references cited therein.

(4) (a) M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 3318 (1966); (b) W. Adcock and M. J. S. Dewar, *ibid.*, **89**, 379 (1967); (c) M. J. S. Dewar and T. J. Squires, *ibid.*, **90**, 200 (1968); (d) G. L. Anderson and L. M. Stock, *ibid.*, **91**, 6804 (1969); (e) W. Adcock, P. D. Bettess, and S. Q. A. Rizvi, *Aust. J. Chem.*, 23, 1921 (1970).

(5) (a) G. W. Parshall, *J. Amer. Chem. Soc.*, **88**, 704 (1966); (b) W. Adcock, B. F. Hegarty, W. Kitching, and A. J. Smith, *J. Organometal. Chem.*, 12, 21 (1968); (c) W. Kitching, W. Adcock, and B. F. Hegarty, *Aust. J. Chem.*, 21, 2411 (1968); (d) R. P. Stewart and P. M. Treichel, *J. Amer. Chem. Soc.*, **92**, 2710 (1970), and references cited therein; (e) A. J. Smith, W. Adcock, and W. Kitching, *ibid.*, **92**, 6140 (1970); (f) R. G. Adler and M. F. Hawthorne, *ibid.*, **92**, 6174 (1970).

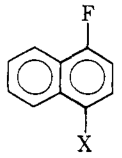
Table I. Analytical Data for Metallo-Substituted Fluoronaphthalenes

Compd	Orientation	Precursor[a]	Mp or bp (mm), °C	$n^{24}D$	Calcd (found) C, %	Calcd (found) H, %
1. $FC_{10}H_6Si(CH_3)_3$	4α[b]	g	91–93 (0.3)		71.49 (75.21)	6.93 (7.70)
2.	6β	8	76–76.5		71.49 (71.40)	6.93 (6.86)
3.	7β	4e	60–80 (1)	1.5525	71.49 (72.09)	6.93 (6.94)
4. $FC_{10}H_6Ge(CH_3)_3$	4α	g		1.5850	59.38 (58.67)	5.75 (5.50)
5.	6β	8	80.5–82		59.38 (58.66)	5.75 (5.99)
6.	7β	4e	60–80 (1)	1.5660	59.38 (60.09)	5.75 (5.70)
7. $FC_{10}H_6Sn(CH_3)_3$	4α	g		1.5968	50.52 (51.03)	4.89 (5.31)
8.	6β	8	83.5–85		50.52 (50.20)	4.89 (4.72)
9.	7β[c]	4e	90–100 (0.3)	1.5870	50.52 (51.63)	4.89 (4.97)
10. $FC_{10}H_6Pb(CH_3)_3$	4α	g		1.6308	39.26 (39.86)	3.80 (4.18)
11.	6β	8	86.5–88		39.26 (39.16)	3.80 (3.87)
12.	7β[d]	4e	80–90 (0.05)			
13. $FC_{10}H_6HgCl$	4α	g	217–219		31.51 (31.52)	1.58 (1.73)
14.	6β	4e[e]	294.5–296		31.51 (31.76)	1.58 (1.56)
15.	7β	4e	289–290		31.51 (32.10)	1.58 (1.61)
16. $FC_{10}H_6HgC_{10}H_6F$	4α[f]	g	245		48.93 (45.17)	2.46 (2.65)
17.	6β	4e[e]	269–270		48.93 (48.92)	2.46 (2.53)
18.	7β	4e	276–277.5		48.93 (49.23)	2.46 (2.70)

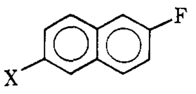
[a] Reference to synthetic method employed for the appropriate bromo- or aminofluoronaphthalene. [b] A further attempt to obtain this product in the pure state was unsuccessful. Although integrating satisfactorily in the pmr spectrum (6 aromatic hydrogens, 9 CH_3Si), the ^{19}F spectrum showed a minor impurity which was not identified. [c] Proton nmr and glpc (SE-30) indicated that the compound was better than 95% pure. Only one resonance region was observed in the fluorine nmr spectrum; no 2-fluoro-7-bromonapthalene was detected. [d] According to proton nmr the crude oil was approximately 50% pure. An attempt to purify the pale yellow viscous oil by distillation led to extensive decomposition. No further attempt was made to obtain this metalloid derivative in the pure state. [e] Prepared from 6-fluoro-2-naphthol according to the procedure outlined for 2-amino-7-fluoronaphthalene. Recrystallized from petroleum ether in light pink plates, mp 110–111° (lit.[8] 110–111°). [f] The compound was contaminated with 1-fluoro-4-chloromercurinaphthalene which could not be removed by recrystallization. It is highly insoluble in most organic solvents and recrystallization was extremely difficult. [g] G. Schiemann, W. Gueffray, and W. Winkelmuller, *Justus Liebigs Ann. Chem.*, **487**, 270 (1931).

6p mercury orbitals, given that this effect is probably dampened by the strong donor solvent (DMSO) employed to determine the SCS. Furthermore, although the analysis for the metalloidal substituents appears conclusive it cannot be regarded as being unequivocal since only the trimethylsilyl substituent effects net electron withdrawal in both the phenyl and biphenyl systems (negative SCS) while the trimethylgermyl group causes net electron withdrawal in only the biphenyl substrate (negative SCS). The remaining groups all cause net electron donation (positive SCS); thus, possible d_π–p_π interactions are masked by an opposing inductive mechanism.

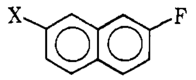
It seemed to us that further light could be thrown on these problems by a study of the ^{19}F nmr spectra of mercuri- and metalloidal-substituted fluoronaphthalenes since we anticipated that in this aryl substrate mesomeric electron withdrawal (−M) might be sufficiently enhanced relative to inductive effects (+I),[6] that all the SCS of the metallo substituents might become negative. Data of this kind would be definitive experimental evidence for invoking d_π–p_π and $6p_\pi$–p_π orbital interactions for the metalloidal and mercury substituents, respectively, without recourse to an argument based on a simple inductive model for those groups which have a small positive SCS. We have accordingly prepared a number of metallo-substituted α- and β-fluoronaphthalenes with the mercuri and metalloidal groups located in the 4α (I), 6β (II), and 7β (III) dispositions. (The Greek letter indicates the position of the fluorine atom, the numeral that of the other substituent.)



I



II



III

Unlike the 4α disposition, the 6β and 7β dispositions are ideal for studies in the naphthalene system because neither the substituent nor the probe suffers steric interference from the peri hydrogen.

Experimental Section

The ^{19}F spectra were obtained at 56.4 MHz using a Varian DP60 spectrometer which had been modified to obtain spectra in the HA mode. The spectra were calibrated using a "Racal" SA535 universal counter timer. All the fluorine nmr spectra were obtained for 15% (w/w) solutions containing 5% (w/w) of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane as internal calibrant. Proton nmr spectra of all compounds were obtained using a Varian A-60 spectrometer; all spectra were integrated for the assigned structures.

The metalloidal compounds and the 4α disposed mercury derivatives (Table I) were synthesized *via* the appropriate lithio derivative which was prepared according to a previously described lithiation procedure[5e] with some modification (anhydrous ether or anhydrous ether–hexane was employed as the solvent rather than hexane). The 6β and 7β disposed mercury compounds were prepared from the corresponding amines according to the method outlined by Nesmajanow[7] for the preparation of 2-naphthylmercuri chloride and bis(2-naphthyl)mercury. Purification problems were encountered for four of the compounds (1, 9, 12, and 16) but since only SCS data was required from the derivatives no persistent attempt was made to obtain reasonable elemental analytical figures for these particular compounds (Table I). SCS information from

---

(6) We previously suggested[5e] that the enhancement of the mesomeric effect over the inductive effect observed in the biphenyl substrate compared to benzene can be attributed to two factors: (a) lower ionization potential; (b) dampening of the inductive effect by distance. The same phenomenon is expected to a greater degree in the naphthalene system since no interannular problems are encountered as in biphenyl, thus allowing conjugative effects to be transmitted more efficiently across the ring (see Discussion).

(7) A. N. Nesmajanow, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943: (a) p 432; (b) p 381.

the 7β disposition clearly demonstrated that analytical purity is not an absolute prerequisite for ^{19}F chemical shift data, the same SCS being obtained for the 7β $(CH_3)_3Si$ and $(CH_3)_3Ge$ substituents on solutions prepared from samples ranging from 50% (by proton and fluorine nmr) to analytical purity.

1-Fluoro-4-methylnaphthalene. 4-Fluoro-1-naphthoic acid was prepared in the manner outlined by Adcock and Dewar[8] and recrystallized from aqueous ethanol in needles, mp 224–225° (lit.[8] 224–225°). The acid was reduced to 1-fluoro-4-methylnaphthalene according to the method outlined by Benkeser, *et al.*[9] Distillation afforded a colorless oil, bp 121° (25 mm) [lit.[10] 107.5–109.5° (12 Torr], $n^{24}D$ 1.5898 (lit.[10] $n^{20}D$ 1.5926).

An attempt to prepare this compound *via* the lithiated 1-fluoro-4-bromonaphthalene by reaction with methyl iodide proved unsuccessful. A mixture of 1-fluoro-4-methylnaphthalene and 1-fluoronaphthalene was obtained which could not be readily separated by fractional distillation.

2-Fluoro-6-methylnaphthalene. 2-Acetyl-6-methylnaphthalene was prepared as described by Wells and Alcorn.[11] The crude material was converted to the oxime by treatment with hydroxylamine hydrochloride in the presence of sodium acetate. The oxime (mp 170–171°) crystallized from benzene in colorless needles, mp 178–179° (lit.[12] 180–181°). A sample of the oxime was hydrolyzed by heating under reflux with 15% hydrochloric acid for 5 hr. The hot solution was cooled and 2-acetyl-6-methylnaphthalene separated as an oil which crystallized from methanol in leaflets, mp 68.5–69.5° (lit.[12] 70–71°).

The oxime (20 g, 0.1 mol) was treated with polyphosphoric acid (600 g) at 95° according to the method outlined by Horning and Stromberg.[13] 2-Acetamido-6-methylnaphthalene was obtained, which crystallized from aqueous ethanol in colorless plates (16 g, 80%), mp 156–157° (lit.[14] 155–156°). The acetamido derivative (20 g) was hydrolyzed by heating with 6 *N* HCl (200 ml) and the amine, isolated *via* its hydrochloride salt, crystallized from petroleum ether in colorless plates, mp 130–131° (lit.[14] 129–130°). 2-Amino-6-methylnaphthalene (5 g, 0.032 mol) was diazotized in dilute hydrochloric acid and a solution of sodium tetrafluoroborate (3.6 g, 0.032 mol) in water (100 ml) was added dropwise with manual stirring. The diazonium tetrafluoroborate was collected and washed with water, ethanol, and ethyl acetate. The air-dried salt, mp 94–96° dec, which on decomposition (120°) and steam distillation gave 2-fluoro-6-methylnaphthalene, crystallized from petroleum ether in colorless plates (2.6 g, 51%), mp 78–79°. *Anal.* Calcd for $C_{11}H_9F$: C, 82.47; H, 5.66; mol wt, 160. Found: C, 82.21; H, 5.85; *m/e* 161.

2-Fluoro-7-methylnaphthalene. 7-Fluoro-2-naphthoic acid, prepared according to Adcock, Bettess, and Rizvi,[4e] crystallized from aqueous ethanol in light yellow needles, mp 211–212.5° (lit.[4e] 211–212.5°). A solution of the acid (2.85 g, 0.015 mol) in dry ether (200 ml) was treated cautiously with a benzene solution (70%) of sodium dihydrobis(2-methoxyethoxyaluminate) (10 ml). After the mixture was allowed to stir at room temperature for 1.5 hr, the complex was decomposed by dropwise addition of water and the ether layer separated. The aqueous layer was extracted with more ether and the combined ether extract was dried. Evaporation of the ether under reduced pressure gave 2-fluoro-7-hydroxymethylnaphthalene, which crystallized from *n*-hexane in shining plates (2.4 g, 91%), mp 97.5–98.5°. *Anal.* Calcd for $C_{11}H_9OF$: C, 74.96; H, 5.15; mol wt, 176. Found: C, 75.13; H, 5.51; *m/e* 177.

2-Fluoro-7-hydroxymethylnaphthalene (2.11 g, 0.012 mol) in dry ether (100 ml) was treated with phosphorus tribromide (3.25 g, 0.012 mol) according to the procedure outlined by Gay and Hauser.[15] The crude 2-fluoro-7-bromomethylnaphthalene crystallized from *n*-pentane in colorless needles (2.3 g, 80%), mp 66–66.5°. *Anal.* Calcd for $C_{11}H_8FBr$: C, 55.25; H, 3.37; mol wt, 239. Found: C, 56.02; H, 3.37; *m/e* 240.

2-Fluoro-7-bromomethylnaphthalene (2.39 g, 0.01 mol) was treated with lithium aluminum hydride according to the procedure described by Dewar and Grisdale[16] for the reduction of 5-bromo-1 bromomethylnaphthalene. The crude 2-fluoro-7-methylnaphthalene crystallized from *n*-pentane in colorless needles (1.2 g, 75%), mp 79.5–80°. *Anal.* Calcd for $C_{11}H_9F$: C, 82.47; H, 5.66; F, 11.86; mol wt, 160. Found: C, 82.33; H, 5.66; F, 11.40; *m/e* 161.

Results and Discussion

Although the potentiality of ^{19}F SCS for evaluating substituent–substrate interactions remains unquestioned, the interpretation of these ground-state parameters has developed into a controversial issue.[4d,e] However, as in previous papers,[5b,c,e] we shall adopt in this discussion a purely qualitative theoretical approach to the ^{19}F SCS data on the basis of Dewar's proposals,[4a,b] the long-range electronic interactions determining the magnitude of the SCS being conveyed by an inductive field effect[17] and polarization of the π-electron system (mesomeric and π-inductive effect). Further, the main conclusions from a previous study[4b] of substituent effects in the 1- and 2-fluoronaphthalene systems will be kept in mind and no attempt will be made here to analyze the data in terms of Taft's approach[3b,c] since its claimed success is based solely on data for substituted fluorobenzenes. Moreover, it has recently been claimed that meta SCS in benzene are unique.[18] In fact, recent attempts to interpret ^{19}F SCS of metallotype substituents in the phenyl ring system in terms of Taft's σ_I/σ_R analysis have failed.[19,20]

The ^{19}F substituent chemical shifts for the metalloidal-substituted 4α-, 6β-, and 7β-substituted fluoronaphthalenes (I, II, and III) in benzene and dimethylformamide are listed in Table II together with the appropriate values for the methyl substituent. Previously published results[5e] for the phenyl and biphenyl systems are listed in Tables III and IV for comparison.

Table II. Substituent Chemical Shifts (SCS) in Parts per Million of 4α-, 6β-, and 7β-Substituted Fluoronaphthalenes

	Benzene			DMF		
Substituent	4α	6β	7β	4α	6β	7β
CH_3	+2.96	+1.45	+0.21	+2.94	+1.48	+0.25
$(CH_3)_3Si$	−1.69	−0.77	−0.19	−1.75	−0.70	−0.21
$(CH_3)_3Ge$	−0.55	−0.36	−0.26	−0.62	−0.28	−0.27
$(CH_3)_3Sn$	−0.23	−0.33	−0.34	−0.12	−0.12	−0.23
$(CH_3)_3Pb$	+0.73	+0.11	−0.50	+0.85	+0.34	−0.35

Table III. Substituent Chemical Shifts (SCS) in Parts per Million of Meta- and Para-Substituted Fluorobenzenes

	Cyclohexane		DMF	
Substituent	Meta	Para	Meta	Para
CH_3	+1.27	+5.48	+1.13	+5.45
$(CH_3)_3C$	+0.55	+5.60	+0.65	+5.51
$(CH_3)_3Si$	+0.85	−0.50	+0.45	−0.60
$(CH_3)_3Ge$	+0.70	+0.55	+0.60	+0.50
$(CH_3)_3Sn$	+0.60	+0.20	+0.60	+0.30
$(CH_3)_3Pb$	+0.40	+0.20		

---

[8] W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 386 (1967).

[9] R. A. Benkeser, K. M. Foley, J. M. Gaul, and G. S. Li, *ibid.*, **92**, 3232 (1970).

[10] J. Saver, R. Huisgen, and A. Hauser, *Chem. Ber.*, **91**, 1461 (1958).

[11] P. R. Wells and P. G. E. Alcorn, *Aust. J. Chem.*, **16**, 1108 (1963).,

[12] K. Dziewonski and M. Brand, *Chem. Abstr.*, **27**, 4533 (1933).

[13] E. C. Horning and V. L. Stromberg, *J. Amer. Chem. Soc.*, **74**, 2630 (1952).

[14] K. Dziewonski, J. Sehdenowna, and E. Waldmann, *Ber.*, **58**, 1211 (1925).

[15] R. L. Gay and C. R. Hauser, *J. Amer. Chem. Soc.*, **89**, 2297 (1967).

[16] M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3541 (1962).

[17] A recent study strongly supports Dewar's proposals that the field effect makes a considerable contribution to the overall SCS (see ref 4e).

[18] R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, **92**, 7007 (1970).

[19] A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Organometal. Chem.*, **21**, 91 (1970).

[20] L. G. Vaughan and A. Sheppard, *ibid.*, **22**, 739 (1970).

Table IV. Substituent Chemical Shifts (SCS) in Parts per Million of 4′-Substituted Fluorobiphenyls

Substituent	DMF	HMPA[a]
$(CH_3)_3Si$	−0.18	−0.20
$(CH_3)_3Ge$	−0.11	−0.14
$(CH_3)_3Sn$	+0.10	

[a] Hexamethylphosphoramide.

Several important conclusions follow from the ^{19}F SCS data of the metalloidal substituents from the naphthalene ring system. Firstly, it can be seen from the data in Table II that the SCS for the $(CH_3)_3Si$, $(CH_3)_3Ge$, and $(CH_3)_3Sn$ groups in the conjugated 4α and 6β dispositions are negative (implying net electron withdrawal) indicating unambiguously that these substituents engage in conjugative electron withdrawal (−M) *via* d_π–p_π interactions with the adjacent naphthyl system. The observed deshielding, which is opposite to what is expected from simple inductive effects emanating from the electropositivity of the metalloids, is the resultant of the shielding effect (inductive field and π inductive) and the deshielding effect (−M). The very small shielding influence indicated for the $(CH_3)_3Pb$ substituent compared to the methyl substituent strongly suggests that a d_π–p_π interaction is also significant for this group.[5e] Ideally, the *tert*-butyl substituent should have been examined in order to make a proper comparative analysis with the metalloidal groups, but the synthesis of the appropriate *tert*-butyl-substituted fluoronaphthalenes posed a considerable operational problem. However, since the replacement of the hydrogen atoms in methyl by methyl affects only a small perturbation of the overall SCS (see Table III), we consider comparisons with the SCS value of the methyl groups to be valid within the framework of the limiting localized bond model.

Although it has been suggested that steric inhibition of mesomerism can occur by permanent bending of the group out of the plane of the aromatic ring (called "steric" distortion),[21] the magnitude and sign of the SCS of the metalloids in the 4α disposition give no indication of this since they parallel the results observed in the unhindered 6β disposition. As was expected, the results in the 4α disposition exemplify that there is no angular deformation of d orbitals.[22]

It is apparent from the relative magnitude of the SCS in each disposition (4α and 6β) that the smaller silicon atom conjugates more effectively with the adjacent ring system than the other metalloids, an observation which is in agreement with our earlier results.[5e]

Secondly, contrary to the positive SCS values observed for all the metalloidal substituents in the meta position (unconjugated) of the phenyl system (Table III), the SCS in the 7β (unconjugated) disposition of naphthalene (Table II) do not reflect the electropositive nature of the metalloids. The results in this disposition clearly indicate that the mesomeric effect outweighs any inductive phenomena (M > I). Not only do these results support our conclusions from the conjugated 4α and 6β dispositions, they also confirm the argument that SCS values from unconjugated positions will not be pure inductive parameters and any interpretation of substituent effects based on the assumption that indirect mesomeric effects are absent in these dispositions is invalid. Certainly the quantity para-SCS–meta-SCS should not be considered a resonance parameter only.[3b,c] The situation may be further clarified by examining MO calculations that have been performed on compounds of the type $ArCOCH_3$ where the substituent is the conjugatively electron-withdrawing acetyl group (p_π–p_π).[23] Unfortunately, no calculations of electron density changes effected by metalloidal substituents in aryl ring systems are available since there are no reliable methods for including d atomic orbitals in MO calculations. The charge at the 7 position in β-naphthaldehyde is *positive* which is the same sign as the charges in the adjacent 6 and 8 positions. Therefore, in the 7β disposition the mesomeric field effect and the true mesomeric effect operate to *reinforce* one another. The observed *negative* SCS for the metalloidal substituents indicates that this combined mesomeric effect outweighs the inductive mechanism which has been "damped" considerably by distance compared to the meta position. In the positions meta to carbonyl, quite large *negative* charges are predicted which are much larger than those determined by HMO theory.[24] Here the mesomeric field effect and the *true* mesomeric effect *oppose* one another and the SCS values listed in Table III indicate that this combined effect is not sufficient to overcome the inductive influence of the metalloid.

The results in this unconjugated dispostion (7β) of naphthalene make it unreasonable that negative SCS be attributed simply to mutual conjugation between fluorine and the substituent (electromeric effect), a conclusion which had already been reached from results in the biphenyl system.[5e]

Thirdly, an important feature of the SCS values in the naphthalene system is that the SCS for the $(CH_3)_3Sn$ substituent is *negative* (Table II) indicating net electron withdrawal (−M > +I). This is in contrast to the *positive* SCS (implying net electron donation) observed in both the phenyl and biphenyl systems (Tables III and IV). We previously suggested[5e] for the $(CH_3)_3Ge$ substituent (phenyl and biphenyl) that this phenomenon may be atrributed to essentially two factors: (a) Conjugative electron withdrawal (−M) by a substituent would be expected to increase on lowering the ionization potential of the aromatic substrate. (b) The inductive effect is more effectively "dampened" by distance than is the mesomeric effect.

Both these factors operate to enhance the mesomeric effect relative to the inductive effect. However, the magnitude of the SCS for the methyl substituent in the 4α disposition of naphthalene (Table II), which is formally analogous to the para position in benzene, suggests an additional factor may be contributing to the observed trends. It can be seen from Table III that the SCS for the methyl group (or *tert*-butyl) in the para position of benzene is considerably more positive than the value in the 4α disposition of naphthalene (Table II).[25] This experimental observation indicates that the

---

(21) G. M. Hoop and J. M. Tedder, *J. Chem. Soc.*, 4853 (1962).

(22) (a) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *ibid.*, 2423 (1960); (b) L. Goodman and R. W. Taft, *J. Amer. Chem. Soc.*, **87**, 4386 (1965), and references cited therein.

(23) M. J. S. Dewar and T. Morita, unpublished data (see ref 4b).

(24) MO calculations on other benzene derivatives also indicate this: (a) N. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **91**, 352 (1969); (b) W. J. Hehre and J. A. Pople, *ibid.*, **92**, 2191 (1970), and references cited therein.

mechanisms by which the methyl group conveys its electronic effect to the "probe" are considerably dampened on going from phenyl to the naphthalene system. On the basis of a simple inductive model,[27] the magnitude of the SCS of an alkyl substituent will be determined largely by the inductive field effect and the π-inductive or inductomesomeric effect.[28] It is not unreasonable then to expect that since the effects of these two mechanisms will extend over the whole of an adjacent aromatic system,[4c] the electronic effect of an alkyl group will be considerably "damped" when attached to a larger π system, given that the polarity of the bond between the substituent and the aryl ring will remain the same. We believe that this factor contributes to the phenomenon observed for the metalloidal substituents since it would lead to an enhancement of the mesomeric effect relative to the inductive effect on going from benzene to the larger aryl ring systems. The situation in the conjugated positions may be summarized as follows in Table V. It is clear from the results outlined in Table V that the mesomeric effect or conjugating ability of the metalloidal substituents depends on the energy and size of the outer lying orbitals with π symmetry, the order being Si > Ge > Sn > Pb.

Table V

Substituent	Aromatic system		
	Benzene	Biphenyl	Naphthalene
$(CH_3)_3Si$	M > I	M > I	M > I
$(CH_3)_3Ge$	I > M	M > I	M > I
$(CH_3)_3Sn$	I > M	I > M	M > I
$(CH_3)_3Pb$	I > M		I > M

From the data in Table II it can be seen that changing the solvent from benzene to DMF causes only a modest change in the SCS of the metalloids. The increased shielding of the ^{19}F nucleus by $(CH_3)_3Sn$ and $(CH_3)_3Pb$ in DMF could be atrributed to strong coordination reducing the requirements for $\pi \rightarrow d$ bonding and promoting polarization of the $M–C_{aryl}$ bond by stabilization of the positive charge.

The effect of *mercuri* substituents in the naphthalene systems has been investigated and the results are shown in Table VI together with the appropriate values from the phenyl ring system[5b,c] for comparison.

Table VI. Substituent Chemical Shifts (SCS) in Parts per Million of Mercuri Substituents in the Naphthalene and Phenyl Ring Systems

Substituent	Naphthalene			Phenyl	
	4α[a]	6β[b]	7β[b]	Meta	Para[c]
HgCl	−0.08	−0.06	+0.01	+0.70	+0.70
HgR[d]	+0.03	+1.05	+0.80	+1.10	+1.20

[a] THF. These derivatives appear to decompose in HMPA and DMSO (Hg precipitate) and it was impossible to obtain spectra. [b] HMPA (hexamethylphosphoramide). These derivatives were insoluble in THF. [c] DMSO. Taken from ref 5b. [d] R = 1- or 2-fluoronaphthyl and -fluorophenyl.

It can be seen that the SCS for the mercuri substituents (Table VI) are quite small implying that there is little net movement of π charge either in or out of both ring systems. However, whereas the data from the phenyl ring system offer no unequivocal evidence for conjugative electron withdrawal ($6p_\pi–p_\pi$) since the effect is masked by an opposing inductive mechanism, the *negative* SCS values for the chloromercuri group in the 4α and 6β disposition suggests that the aryl–mercury bond has a π component of unknown magnitude. This becomes apparent in the naphthalene system for the same reasons expounded for the metalloidal substituents earlier in the discussion. Further, solubility problems necessitated the use of strong donor solvents which are capable of satisfying some of the electron demand of the mercuri substituent. The negative SCS might be more pronounced if the determinations could have been performed in less donor solvents (benzene or cyclohexane). The more positive SCS observed for the RHg substituent compared to the chloromercuri group is in accord with the expected electronegativity differences.

Another interesting conclusion follows from a study of the ^{19}F spectra of two titanium compounds with the general formula Cp_2TiR_2 where R = *p*-fluorophenyl and *m*-fluorophenyl,[29] respectively. X-Ray studies[30] have shown that the configuration of titanium in compounds of this type is a distorted tetrahedron. In the localized-bond picture,[31] tetrahedral molecules of this type are derived from the first excited state of titanium, sd^3, which would lead to tetrahedral bond distribution by sd^3 hybridized orbitals. However, it has been suggested that a substantial improvement in bonding power is attained by a small admixture of sp^3. From this model one can envisage that mesomeric electron withdrawal *via* outer-lying vacant p or d orbitals (or hybrids thereof) might be expected to oppose the electron "donating" inductive effects (inductive field effect and π-inductive effect) of the metallo substituent ($TiCp_2R$). On the other hand, according to a detailed MO description[32] of the electronic structure of compounds of the type Cp_2TiR_2, the titanium atom has a low vacant orbital whose symmetry requirements would prevent it from interacting with the π system of the attached aryl groups.

It is clear then that both models suggest no conjugative electron-donating mechanism. Any polarization

---

(25) According to the classical and standard procedure for evaluating the polar effects of substituents, measuring the dissociation of substituted aryl carboxylic acids, the effect of the methyl group in both systems (4α and para) is virtually the same.[17,26] This is not surprising since it is now well known that equilibrium constants are often controlled by factors other than the internal energy difference between the two states, whereas the SCS parameter is a direct manifestation of the electronic perturbation of the substituent on the substrate in the ground state.

(26) J. D. Roberts and C. M. Reagan, *J. Amer. Chem. Soc.*, 75, 4102 (1953).

(27) (a) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962; (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(28) Recent *ab initio* studies of charge distribution by Pople[24b] show show that the π-charge transfer from methyl is small and that the main effect is alternating polarization within the ring. Even if hyperconjugation was significant, it would be unreasonable to attribute the smaller SCS in the 4α disposition to steric inhibition of the $\sigma–\pi$ conjugation by the adjacent peri hydrogen since the methyl group is perfectly symmetrical.

(29) The dicyclopentadienyltitanium derivatives were prepared according to the procedure of H. C. Beachell and S. A. Butter, *Inorg. Chem.*, 4, 1133 (1965). The bis(*p*-fluorophenyl) compound's proton spectrum was in accord with the published data while the unknown bis(*m*-fluorophenyl) derivative gave a proton spectrum in accordance with the expected structure.

(30) N. V. Abkseev and I. A. Ronova, *Zh. Strukt. Khim.*, 7, 105 (1966).

(31) G. E. Coates and F. Glockling, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, p 429, and references cited therein.

(32) (a) J. C. W. Chien, *J. Phys. Chem.*, 67, 2477 (1963); (b) C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, 15, 1333 (1961).

of the π system by the titanium substituent will be entirely due to the difference in electropositivity between the titanium center and the aryl carbon to which it is attached with the possibility of a superimposed $-M$ effect. The SCS values for the two titanium derivatives are assembled in Table VII.

Table VII. Substituent Chemical Shifts (SCS) in Parts per Million of Dicyclopentadienyltitanium Derivatives

Compd	Benzene	DMF
$Cp_2Ti(p\text{-}FC_6H_4)_2$	+7.14	+7.63
$Cp_2Ti(m\text{-}FC_6H_4)_2$	+2.30	+2.42

It can be seen from the data in Table VII that the titanium substituent ($TiCp_2R$) is a more effective electron "donor" than the methyl substituent (Table III). In terms of a simple inductive model, this is probably what one would expect on the basis that the titanium substituent is more electropositive than a methyl group. Since there is no obvious way in which the titanium substituent can conjugatively donate electrons, the SCS in Table VII appear to be good evidence for believing that hyperconjugation is an unnecessary concept to invoke in order to explain the electronic influence of alkyl groups on aryl substrates in the ground state.

Conclusion

Although there are obvious problems of interpretation and of reconciliation of discordant observations (*e.g.*, the considerable *negative* SCS of the $(CH_3)_3Pb$ substituent in the 7β disposition) that remain to be resolved, several conclusions follow from this work, together with the results published in earlier papers. First, it is clear that ^{19}F SCS do not necessarily parallel parameters determined by chemical reactivity methods. A number of serious discrepancies suggest that an interpretation of the ^{19}F SCS data in terms of a Taft σ_I/σ_R analysis would be fruitless. Secondly, the conclusions from our qualitative theoretical approach are based on the premise that SCS parameters are exclusively a manifestation of the electronic influence of a substituent on the aryl substrate in the ground state. Recently, this premise has been questioned and it has been suggested that geometrical distortion of the π system may be a contributing factor in many dispositions.[33] However, it seems that this effect is minimal in the 6β and 7β dispositions of naphthalene as well as the $4'$ disposition in biphenyl. The observation that the behavior of the metallo substituents parallel one another in the 4α and 6β dispositions suggests that the electronic influence of the groups is predominating, even in the hindered 4α disposition. Thirdly, the results clearly demonstrate the inadequacy of present day electronic theory based on studies in the phenyl ring system and that progress in our understanding of substituent–substrate interactions will not be attained by restricting investigations of this kind to this particular system.[34]

Acknowledgments. The authors are indebted to the Department of Organic Chemistry, University of Adelaide, for the use of their nmr facilities and to the Australian Research Grants Committee for their support of this work.

---

(33) Part X: M. J. S. Dewar, R. Golden, and J. M. Harris, *J. Amer. Chem. Soc.*, 93, 4187 (1971). We thank Professor M. J. S. Dewar for a preprint.

(34) NOTE ADDED IN PROOF. Since the acceptance of this paper, new data from our laboratory have shed further light on the interpretation of fluorine SCS (presented for publication in communication form). It is now quite clear that SCS of substituted aryl fluorides do not necessarily reflect the electronic behavior of a substituent; substituent-induced structural distortions can occur which perturb the ^{19}F chemical shift. Thus, certain aspects of the interpretation in this paper require revision. Firstly, the difference between the SCS for the methyl group in the para position of benzene and the 4α disposition of naphthalene is probably a structural effect. Secondly, the anomalous order of electron withdrawal in the 7β disposition [$(CH_3)_3Pb > (CH_3)_3Sn > (CH_3)_3Ge > (CH_3)_3Si$] is now reasonably interpreted as a manifestation of geometrical distortion rather than simple electrical phenomena. However, the small *negative* SCS for the $(CH_3)_3Si$ substituent (7β) indicates that the inductive field effect of the C–Si bond is extremely small. Thirdly, we do not wish to be too dogmatic about the interpretation of the data for the titanium substituent. The conclusion drawn is extremely tenuous.