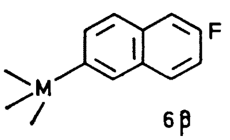
Group IVB Metalloidal Substituent Effects in the Naphthalene System by Fluorine-19 Nuclear Magnetic Resonance

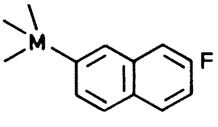
By WILLIAM ADCOCK*
(*School of Physical Sciences, The Flinders University of South Australia, Bedford Park, South Australia*)
and WILLIAM KITCHING
(*Department of Chemistry, University of Queensland, Brisbane, Queensland, Australia*)

Summary ^{19}F Substituent chemical shift (SCS)† data for substituents of the type Me_3M (where M represents Si, Ge, Sn, and Pb) attached to the naphthalene system provide experimental evidence that all the metalloidal substituents engage in d_π–p_π conjugative electron-withdrawal ($-M$) in the ground state: and suggest that certain approaches to the analysis of ^{19}F SCS may be invalid.

IN a recent paper[1] we presented and summarised earlier evidence that all substituents of the type Me_3M, where M is a Group IVB metalloid (Si, Ge, Sn, and Pb), engage in conjugative electron-withdrawal ($-M$ effect) *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. Although this analysis appears conclusive it cannot be regarded as being unequivocal since only the trimethylsilyl substituent causes net electron-withdrawal in 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) *i.e.* d_π–p_π interactions are masked by an opposing inductive mechanism.



6β



7β

We have extended our studies to the naphthalene system since we anticipated that in this aryl substrate the mesomeric effect would be transmitted efficiently across the ring (no interannular problems as in biphenyl)[2] thereby further enhancing $-M$ effects relative to $+I$ effects (*cf.* phenyl and biphenyl) for the metalloidal substituents.[1] We have accordingly prepared the naphthalene compounds listed in the Table and measured their ^{19}F SCS.‡

The negative SCS for Me_3Si, Me_3Ge, and Me_3Sn in the conjugated 6β disposition indicate unambiguously that these substituents engage in conjugative electron-withdrawal ($-M$) *via* d_π–p_π interaction with an adjacent aryl

---

† Defined as the difference between the chemical shift of the unsubstituted fluoroaromatic and the substituted fluoroaromatic (ref. 2).

‡ The proton and fluorine n.m.r. spectra were in accordance with the assigned structures; details of their syntheses will be given in the main paper. The ^{19}F n.m.r. spectra were measured at 56·4 MHz with a Varian DP-60 spectrometer on solutions containing 15% w/w solute with 5% TCTFB (1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane) as internal standard. The spectrometer had been modified to obtain spectra in the HA mode.

system. The negative SCS imply net electron-withdrawal indicating that the mesomeric effect ($-M$) outweighs the inductive effect ($+I$). The value for the Me$_3$Sn substituent is in contrast to the positive SCS observed in both the phenyl and biphenyl systems.[1] The small shielding influence indicated for Me$_3$Pb compared to the methyl substituent strongly suggests that a d_π–p_π interaction is also significant for this group. It is apparent from the relative magnitude of the SCS that the smaller silicon atom conjugates more effectively with the adjacent ring system confirming our previous observations.[1]

Substituent chemical shifts (p.p.m.) of 6β- and 7β-substituted fluoronaphthalenes[a,b] *in dimethylformamide and benzene*

	Benzene		DMF	
Substituent	6β	7β	6β	7β
Me	+1·45	+0·21	+1·48	+0·25
Me$_3$Si	−0·77	−0·19	−0·70	−0·21
Me$_3$Ge	−0·36	−0·26	−0·28	−0·27
Me$_3$Sn	−0·33	−0·34	−0·12	−0·23
Me$_3$Pb	+0·11	—	+0·34	—

[a] For brevity these compounds are designated by the symbol for the substituent, preceded by a numeral giving its position and a Greek letter denoting the position of fluorine [ref. 2(b).]

[b] The 6β and 7β series are ideal dispositions for studies in the naphthalene system because neither the substituent, nor the probe centre suffers steric interference from the *peri*-hydrogens.

Further, contrary to the positive SCS values observed for all the metalloidal substituents in the *meta*-position (unconjugated) of the phenyl system,[1] the SCS in the 7β (unconjugated) disposition of naphthalene do not reflect the electropositive nature of the metalloids. The results in this disposition clearly indicate that the mesomeric effect outweighs any inductive phenomena. This confirms the cogent arguments of Dewar[2] that the SCS value in unconjugated positions will not be a pure inductive parameter and any interpretation of substituent effects based on the assumption that indirect mesomeric effects are absent in these dispositions is invalid *i.e.*, the effect of a substituent in the *meta*-position (phenyl system) is the result of a polar effect (inductive effect) and a mesomeric effect, the latter being a combination of two effects: a mesomeric field effect and a true *meta* mesomeric interaction.[2]

Thus, the ^{19}F SCS data in Table have provided not only important information about metalloidal substituents but have serious implications for certain approaches to the analysis of ^{19}F SCS[4,5] as well as substituent effects in general.[4]

We thank the University of Adelaide for the use of their n.m.r. facilities and the Australian Research Grants Committee for some of the equipment used in the investigation.

(*Received, May 11th*, 1970; *Com.* 704.)

---

[1] A. J. Smith, W. Adcock, and W. Kitching, *J. Amer. Chem. Soc.*, accepted for publication.

[2] (a) M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, 1966, **88**, 3318; (b) W. Adcock and M. J. S. Dewar, *ibid.*, 1967, **89**, 379.

[3] R. W. Taft, E. Price, I. R. Fox, I. E. Lewis, K. K. Anderson, and G. T. David, *J. Amer. Chem. Soc.*, 1963, **85**, 709, 3136, plus references cited therein.

[4] A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **21**, 91.