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# POLAR FIELD-INDUCTIVE PARAMETERS OF SOME GROUP IVB METALLOIDAL SUBSTITUENTS: A $^{13}C$ AND $^{19}F$ NMR STUDY IN THE PHENYLBICYCLO[2.2.2]OCTANE RING SYSTEM

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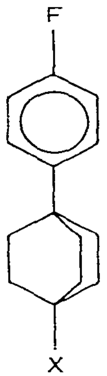
## Summary

A number of bridgehead metalloidal-substituted phenylbicyclo[2.2.2]octyl and (*m*- and *p*-)fluorophenylbicyclo[2.2.2]octyl derivatives have been synthesized and their $^{13}C$ and $^{19}F$ NMR spectra have been recorded. The appropriate $^{13}C$ and $^{19}F$ substituent chemical shifts of these stereochemically well-defined model systems, together with the known polar susceptibility parameters, provide a definitive scale of polar field-inductive parameters ($\sigma_I$ values) for a representative array of metalloidal substituents attached to an $sp^3$ hybridized carbon center. The implication of these results with respect to the physical interpretation of $\sigma_I$ parameters is discussed. In addition, the previously reported results for alkyl groups in these systems have been re-evaluated in terms of possible through-bond effects involving orbitals of $\pi$ symmetry of the bicyclo[2.2.2]octane ring system. Factors determining $\alpha$, $\beta$, $\gamma$ and $\delta$ effects are briefly alluded to.

## Introduction

In recent papers [1,2,3,4] we have proposed new methodology for quantitatively estimating polar field-inductive substituent parameters ($\sigma_I$ values) based on $^{19}F$ substituent chemical shifts (SCS) of model systems 1 and 2 (1-X-4-(*p*- and *m*-)fluorophenyl)bicyclo[2.2.2]octanes respectively), as well as $^{13}C$ SCS of C(4) in system 3 (1-X-4-phenylbicyclo[2.2.2]octanes), and the appropriate



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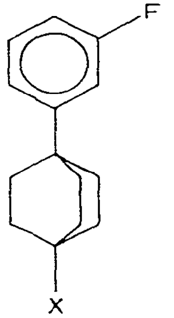

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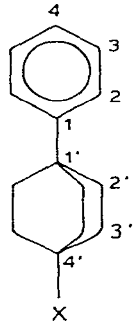

(3)

polar susceptibility parameters ($\rho_I$ values) *. Several attractive features of the method are noteworthy. Firstly, the phenylbicyclo[2.2.2]octyl skeletal framework allows the construction of stereochemically well-defined model systems (1, 2, and 3) in which the polar field effect emanating from substituent polarity can be assessed quantitatively in total isolation of localized interactions (mesomeric ($M$) and inductomesomeric effects ($I_\pi$)) involving the $\pi$-electrons of the aromatic ring. Thus, the need to use multiparameter regression analysis to separate polar and mesomeric (or resonance) effects is avoided. This latter procedure is always necessary when the substituent is directly attached to the aryl ring in a model system and, hence, $\sigma_I$ values derived by such methodology (e.g., $^{19}$F SCS of *m*-substituted fluorobenzenes (4)) [5,6] for very weak polar groups must be viewed as being insecure since statistical dissection of electronic effects may not be complete.

Although two other important model systems for defining $\sigma_I$ effects are known (4-substituted bicyclo[2.2.2]octane-1-carboxylic acids (5) [7] and 4-substituted quinuclidines (6) [8,9]) which possess the aforementioned desirable structural feature inherent in 1, 2, and 3, the latter systems have the advantage in that the appropriate bridgehead-substituted derivatives are very readily accessible by fairly common synthetic procedures. Furthermore, unlike chemical reactivity studies (p$K$'s of 5 and 6), $\sigma_I$ values can be derived from the SCS of 1, 2, and 3 in a wide range of solvents including cyclohexane which, being nonpolar and chemically inert, provides a medium closely approximating the gas phase. Hence, solvation effects, which are a problem associated with chemical reactivity procedures, can be completely excluded. Moreover, intrinsic polar effects of substituents (including kinetically labile groups) may be unambiguously evaluated.

Secondly, the large number of bonds intervening between the probe ($^{19}$F or $^{13}$C) and the bridgehead-substituent ensures that short-range phenomena (steric, polarizability, and $\sigma$-inductive or electronegativity effects), which are impossible to disentangle from polar field effects ($\sigma_I$ effects) in various model systems

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* System 1, $\rho_I$ = 2.49 (c-$C_6H_{12}$) [1] and 2.19 ($CH_2Cl_2$) [1]; System 2, $\rho_I$ = 1.49 (c-$C_6H_{12}$) [1] and 1.14 ($CH_2Cl_2$) [1]; System 3, $\rho_I$ = 1.28 (c-$C_6H_{12}$) [1,3] and 1.20 ($DCCl_3$) [1,3,4].

in which the substituent is only one or two bonds removed from the probe site, are essentially inoperative.

Thirdly, through-bond [10] and substituent-induced structural effects [11] involving the saturated bicyclo[2.2.2]octyl skeletal framework, which may complicate model systems where the probe site is incorporated into the saturated skeleton [2] (e.g., system **6**), may be distinguished from polar field effects in systems **1**, **2**, and **3** (vide infra). This latter point is particularly important for the case of extremely weak polar or nonpolar substituents ($\sigma_I \simeq 0$) and is exemplified by the $\sigma_I$ values for alkyl substituents deduced from the SCS of **1**, **2**, and **3** [2] versus those derived from the p$K$'s of **6** [8].

Finally, it is important to stress that the method is of high experimental precision. This point is particularly applicable to the determination of $^{19}$F SCS parameters for systems **1** and **2** which can be obtained quickly and directly from very dilute solutions with an accuracy much better than 0.01 ppm (see experimental section).

Herein we report on the application of this new methodology to the quantitative assessment of polar substituent parameters ($\sigma_I$ values) for a representative number of Group IVB-metalloidal substituents ($MR_3$; M = Si, Ge, Sn and Pb). A comparison of the previously reported [12,13,14] $\sigma_I$ values for many of these groups indicates several serious discrepancies, hence, there is a need to establish a reliable and valid scale of $\sigma_I$ parameters for this interesting class of substituents.

## Experimental

*Synthesis of compounds.* The alkyl derivatives of **1** and **3** (X = Me, Et, i-Pr, t-Bu) were available from a previous investigation [2]. Except for system **2** (X = I), the syntheses of the appropriate precursors (X = I or Br) of the metalloidal-substituted derivatives of **1**, **2**, and **3** have been previously reported [1]. The former compound (m.p. 116—118°C) was similarly prepared from **2** (X = OMe) [1] in excellent yield. An improvement in the final step of the synthesis of the precursor (X = OMe) for the iodo and bromo derivatives of **1** was achieved by utilizing a reduction procedure reported by Grundon, Henbest, and Scott [15] rather than the standard Wolff—Kishner procedure [1]. This modification led to a significantly higher yield (70%) than that previously reported (31%) [1].

The standard synthetic methods employed for preparing the metalloidal-substituted derivatives of system **3**, together with yields and physical properties, are listed in Table 1. All the compounds sublimed as white solids except the $M(OEt)_3$ derivatives (M = Si and Ge), which distilled as colourless oils. It should be noted that GLPC/mass spectral analysis of the compounds indicated that the Si and Ge derivatives were contaminated with varying amounts (~3—15%) of phenylbicyclo[2.2.2]octane which proved difficult to eliminate by gradient sublimation. The formation of this by-product is apparently the result of hydrogen scavenging from the ethereal solvent by the highly reactive phenylbicyclo[2.2.2]octyllithium reagent. The problem was noticeably worse for the Ge derivatives due to the apparent slow exchange between the lithium reagent and $Ge(OEt)_4$ below —50°C. An attempt to prepare the $GeCl_3$ and $SnCl_3$ derivatives

TABLE 1

SYNTHETIC METHODS, YIELDS, AND MELTING (OR BOILING) POINTS OF 1-X-4-PHENYLBICYCLO[2.2.2]OCTANES (3)

| System, X | Precursor | Synthetic method | Yield (%) | M.p. (°C) |
|---|---|---|---|---|
| 3, $SiCl_3$ | I | 1, t-BuLi/$Et_2O$/—80°C.<br>2, $SiCl_4$, —80 to 25°C | 90 | 66— 69.5 |
| 3, $SiH_3$ | $SiCl_3$ | $LiAlH_4$/$Et_2O$/Reflux | 85 | 105—108 |
| 3, $SiMe_3$ | $SiCl_3$ | MeMgCl/THF/Reflux | 75 | 90— 93 |
| 3, $Si(OEt)_3$ | $SiCl_3$ | EtOH/$CH_2Cl_2$/$Et_3N$ | 46 | b.p. 140—150°C (0.01 mm/Hg)<br>$n_D^{23}$ 1.5071 |
| 3, $Ge(OEt)_3$ | I | 1, t-BuLi/$Et_2O$/—80°C.<br>2, $Ge(OEt)_4$, —80 to 25°C | 81 | b.p. 250°C (0.01 mm/Hg) |
| 3, $GeH_3$ | $Ge(OEt)_3$ | $LiAlH_4$/$Et_2O$/Reflux | 53 | 77— 81 |
| 3, $GeMe_3$ | $Ge(OEt)_3$ | MeMgCl/THF/Reflux | 52 | 77— 81 |
| 3, $GeCl_3$ | $Ge(OEt)_3$ | HClgas/$CH_2Cl_2$/$CaCl_2$ | 49 | 64— 70 |
| 3, $SnMe_3$ | Br | $Me_3SnLi$/THF | 65 | 71— 72 (lit. [1] 71.5—72) |
| 3, $SnCl_2Me$ | $SnMe_3$ | $SnCl_4$/200°C/2 h | 53 | 128—130 |
| 3, $SnH_2Me$ | $SnCl_2Me$ | $LiAlH_4$/$Et_2O$/Ambient temp. | 52 | Decomp. |
| 3, $PbMe_3$ | I | 1, t-BuLi/$Et_2O$/—80°C.<br>2, $Me_3PbCl$, —80 to 25°C | 50 | 58— 60 |

of 3 by metal—halogen exchange between phenylbicyclo[2.2.2]octyllithium and the appropriate metal halide ($MCl_4$; M = Ge or Sn) proved unsuccessful. It is of interest to note that previous similar attempts to prepare the corresponding t-Bu derivatives also failed [16,17]. A redistribution reaction between 3 (X = $SnMe_3$) and $SnCl_4$ (see Table 1) also failed to yield the $SnCl_3$ derivatives.

Except for the $GeMe_3$ derivatives, the metalloidal derivatives of systems 1 and 2 were prepared and purified in similar yield to those for 3 by the methods outlined in Table 1. After sublimation, the Si derivatives of 1 and 2 were shown (GLPC/mass spectral analysis) to be consistently more contaminated (~20%) with the appropriate hydrocarbon (1 and 2, X = H) than the corresponding derivatives of 3. However, we made no attempt to remove the contaminant since the measurement of $^{19}F$ SCS (vide infra) involves having the parent hydrocarbon present. The exchange reaction between $Ge(OEt)_4$ and the lithiated species of 1 and 2 (X = Li) proved to be unsuccessful due to the apparent slow exchange below —50°C (hydrocarbon is the predominant product) and the loss of fluorine (benzyne formation) above this temperature. The $GeMe_3$ derivatives of 1 and 2 were prepared by treating the appropriate precursor (X = Br) with $Me_3GeLi$ in HMPA as solvent [18]. The isolated sublimed products were shown (GLPC/mass spectral analysis) to be contaminated with unreacted bromide (X = Br) and the hydrocarbon (X = H). These impurities were also readily distinguished during the course of $^{19}F$ SCS measurements.

The NMR ($^1H$ and $^{13}C$) and mass spectra of all compounds were clearly in accord with the assigned structures. Full details of the $^1H$ NMR spectra and synthetic procedures may be found elsewhere [19].

*Spectra.* The broad-band proton-decoupled $^{13}C$ NMR spectra of system 3 were recorded in the pulse Fourier transform mode on Bruker spectrometers operating at 67.89 MHz (spectral width 7500 Hz, 64K/32K data points, resolution of 0.003 ppm) or 25.0 MHz (spectral width 4000 Hz, 16K/8K data points, resolution of 0.02 ppm or 2000 Hz, 16K/8K data points, resolution of 0.01 ppm) using cyclohexane (0.1 *M*; containing $CCl_4$ or $C_6H_6$ (1%) as an internal reference) and $DCCl_3$ solutions (0.1—0.3 *M*; $Me_4Si$ or central resonance of $DCCl_3$ as an internal reference). Assignments for all compounds followed normally from methods previously indicated [1].

The $^{19}F$ NMR spectra of solutions (cyclo-$C_6H_{12}$ or $CH_2Cl_2$ as solvent) of systems 1 and 2 were obtained under proton-decoupled conditions in the pulse Fourier transform mode with a Bruker spectrometer operating at 84.66 MHz. A spectral width of 1202 Hz was used and the data collected into 16K/8K data points giving a resolution of better than 0.01 ppm. Each sample consisted of a mixture of the unsubstituted compound (4—5 mg) and substituted compound (5—10 mg) dissolved in 0.5 ml of the appropriate solvent.

$^1H$ NMR spectra were measured with a Varian A60 spectrometer.

## Results and discussion

Before examining the $^{19}F$ and $^{13}C$ SCS of 1, 2, and 3 assembled in Tables 2 and 3, respectively, for the metalloidal substituents, it is instructive to briefly recapitulate on the corresponding data [2] for the congeneric alkyl substituents. Although a study [1] of the infrared spectra (intensity of the $\upsilon_{8}$ vibrations) of several derivatives of 3 indicated that the mesomeric parameter ($\sigma_R^0$ = —0.17) of the bicyclo[2.2.2]octyl group remains constant (within the limits of experimental error (±0.01) with respect to bridgehead-substitution, an analysis of the $^{19}F$ SCS for alkyl groups (Me, Et, i-Pr, t-Bu) in systems 1 and 2 indicated unequivocally a small but significant change in the hyperconjugative interaction between the phenyl and bicyclo[2.2.2]octyl moieties (change in $\sigma_R^0$ of less than 0.005) [1]. The phenomenon is characterised by positive (downfield shifts) $^{19}F$ SCS (Table 4) for the alkyl groups in system 1 (conjugated orientation) with corresponding zero values in system 2 (unconjugated orientation) [2]. Furthermore, in accord with expectations for an electronic perturbation transmitted by mesomerism (or resonance) [20,21], the former parameters remain essentially constant with respect to solvent changes [2].

It is important to note that the previously published $^{13}C$ SCS (C(4)) of system 3 for the alkyl groups [1,2] did not reveal this phenomenon which, at the time, we attributed to the limits of experimental error for measuring these parameters (±0.14 ppm ($DCCl_3$) and ±0.06 ppm (c-$C_6H_{12}$)). Hence, because the unequivocal establishment of this effect has an important bearing on the interpretation of the SCS for several of the weak polar metalloidal substituents under investigation in this study, we have remeasured the aryl $^{13}C$ SCS for the alkyl groups in system 3 with an accuracy of ±0.01 ppm (listed in Table 2, $DCCl_3$ as solvent) in order to ensure that the $^{19}F$ SCS for system 1 (Table 4) do not simply reflect an effect peculiar to the fluorine probe. Note that the $^{13}C$ SCS (C(4)) for these groups in system 3 (Table 2, $DCCl_3$) are clearly positive

TABLE 2

$^{13}$C SUBSTITUENT CHEMICAL SHIFTS (SCS) [a] OF ALKYL AND METALLOIDAL SUBSTITUENTS FOR 1-X-4-PHENYLBICYCLO[2.2.2]OCTANES (3)

| Substituent, X | Carbon number | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 1′ | 2′ | 3′ | 4′ | Other [d] |
| *In DCCl$_3$* [b,c] | | | | | | | | | |
| Me [e] | −0.39 | −0.14 | −0.07 | 0.07 | 0.46 | 0.65 | 7.22 | 3.44 | 28.02($CH_3$) |
| Me [f] | −0.39 | 0.04 | 0.02 | 0.05 | | | | | |
| Et [f] | −0.29 | 0.03 | 0.01 | 0.03 | | | | | |
| i-Pr [f] | −0.19 | 0.01 | 0.02 | 0.03 | | | | | |
| t-Bu [e] | −0.22 | −0.13 | −0.04 | 0.00 | 0.07 | 0.43 | −0.58 | 11.05 | 25.36($CH_3$) 34.2(C) |
| t-Bu [f] | −0.14 | −0.02 | 0.03 | 0.02 | | | | | |
| $SiH_3$ [g] | −0.45 | −0.03 | 0.07 | 0.17 | −0.19 | −0.03 | 2.83 | −9.39 | |
| $SiH_3$ [h] | −0.46 | 0.00 | 0.10 | 0.18 | | | | | |
| $GeH_3$ [g] | −0.56 | −0.02 | 0.10 | 0.18 | −0.50 | 0.69 | 4.59 | −2.53 | |
| $GeH_3$ [h] | −0.55 | −0.02 | 0.09 | 0.16 | | | | | |
| $SiMe_3$ [g] | 0.17 | 0.05 | 0.02 | 0.03 | 0.29 | 0.00 | 0.24 | −8.00 | −4.71($CH_3$) |
| $GeMe_3$ [g] | 0.02 | 0.02 | 0.02 | 0.03 | 0.12 | 0.46 | 1.41 | −3.86 | −5.66($CH_3$) |
| $SnMe_3$ [g] | 0.05 | 0.02 | 0.03 | 0.03 | −0.41 | 1.05 [i] | 4.22 [j] | −2.46 [j] | −12.55($CH_3$) [k] |
| $PbMe_3$ [g] | −0.39 | 0.03 | 0.04 | 0.09 | 2.49 | 2.63 [l] | 6.92 [m] | 1.97 [n] | −5.12($CH_3$) [o] |
| $PbMe_3$ [h] | −0.35 | 0.05 | 0.06 | 0.09 | | | | | |
| $Si(OEt)_3$ [g] | 0.12 | 0.00 | −0.01 | 0.00 | −0.02 | −0.44 | 0.02 | −6.83 | 58.72($CH_2$) 18.42($CH_3$) |
| $Ge(OEt)_3$ [g] | −1.00 | −0.22 | 0.07 | 0.27 | −0.61 | −0.32 | 0.80 | −5.56 | 60.19($CH_2$) 18.57($CH_3$) |
| $Ge(OEt)_3$ [h] | −1.01 | −0.15 | 0.12 | 0.29 | | | | | |
| $SiCl_3$ [g] | −1.56 | −0.17 | 0.22 | 0.52 | −0.04 | −1.01 | −1.53 | 2.41 | |
| $SiCl_3$ [h] | −1.52 | −0.13 | 0.27 | 0.54 | | | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $GeCl_3$ [g] | −2.54 | −0.26 | 0.33 | 0.76 | −0.34 | 0.00 | −0.20 | 3.38 | |
| $GeCl_3$ [h] | −2.50 | −0.24 | 0.35 | 0.76 | | | | | |
| $SnCl_2Me$ [g] | −1.97 | −0.24 | 0.24 | 0.57 | −0.82 | 0.93 [p] | 3.05 [h] | 19.93 [j] | 2.70($CH_3$) [j] |
| $SnCl_2Me$ [h] | −1.93 | −0.22 | 0.26 | 0.56 | | | | | |
| *In cyclo-$C_6H_{12}$* [q,r] | | | | | | | | | |
| Me [f] | −0.40 | 0.04 | 0.01 | 0.04 | | | | | |
| $SiH_3$ [h] | −0.43 | −0.01 | 0.08 | 0.18 | | | | | |
| $GeH_3$ [h] | −0.54 | −0.03 | 0.07 | 0.18 | | | | | |
| $SnH_2Me$ [h] | −0.27 | −0.03 | 0.05 | 0.11 | | | | | |
| t-Bu [f] | −0.18 | −0.02 | 0.03 | −0.02 | | | | | |
| $SiMe_3$ [f] | 0.18 | 0.08 | 0.04 | −0.01 | | | | | |
| $GeMe_3$ [f] | 0.02 | −0.01 | 0.01 | −0.01 | | | | | |
| $SnMe_3$ [f] | 0.05 | 0.00 | 0.02 | 0.00 | | | | | |
| $PbMe_3$ [f] | −0.39 | 0.08 | 0.05 | 0.08 | | | | | |
| $Ge(OEt)_3$ [h] | −0.59 | −0.09 | 0.11 | 0.23 | | | | | |
| $GeCl_3$ [h] | −2.27 | −0.26 | 0.37 | 0.77 | | | | | |

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[a] Defined as the difference (ppm) between the $^{13}C$ chemical shift of the substituted compound and that of the appropriate carbon in the parent hydrocarbon (X = H). Positive values indicate decreased shielding. The carbon numbering system is as shown on the structural formula (1) in the Introduction. [b] X = H ($DCCl_3$ (77.0 ppm), relative to $Me_4Si$): 150.57(C(1)); 125.52(C(2)); 127.96(C(3)); 125.32(C(4)); 34.11(C(1')); 32.09(C(2')); 26.51(C(3')); 24.49(C(4')). [c] Benzene ($DCCl_3$(77.0 ppm), relative to $Me_4Si$) 128.32. [d] Relative to $Me_4Si$. [e] Taken from ref. 1. Accurate to ±0.14 ppm. [f] Accurate to ±0.01 ppm. Measured at 67.89 MHz using 0.1 *M* solutions. [g] Accurate to ±0.04 ppm. Measured at 25.0 MHz using 0.3 *M* solutions. [h] Accurate to ±0.02 ppm. Measured at 25.0 MHz using 0.3 *M* solutions. [i] *J*(C—Sn), 55.34 Hz. [j] *J*(C—Sn), not observed. [k] *J*(C—Sn), 300.30 Hz, 285.92 Hz. [l] *J*(C—Pb), 101.31 Hz. [m] *J*(C—Pb), 6.45 Hz. [n] *J*(C—Pb), not observed. [o] *J*(C—Pb), 136.7 Hz. [p] *J*(C—Sn), 98.88, 94.61 Hz. [q] X = H (c-$C_6H_{12}$/c-$C_6D_{12}$, relative to $Me_4Si$): 150.66(C(1)); 125.73(C(2)); 128.34(C(3)); 125.73(C(4)); 34.65(C(1')); 32.86(C(2')); 27.33(C(3')); 25.53(C(4')). [r] X = H (c-$C_6H_{12}$, relative to internal benzene set at 128.32 ppm): 150.32(C(1)); 125.49(C(2)); 128.07 (C(3)); 125.44(C(4)).

TABLE 3

$^{19}$F SUBSTITUENT CHEMICAL SHIFTS (SCS) [a,b] OF METALLOIDAL SUBSTITUENTS

| Substituent, X | Cyclohexane | $CH_2Cl_2$ |
|---|---|---|
| *1-X-4-p-Fluorophenylbicyclo[2.2.2]octanes (1)* | | |
| $SiH_3$ | 0.38 | 0.28 |
| $SiMe_3$ | 0.00 | 0.01 |
| $GeMe_3$ | 0.03 | 0.03 |
| $SnMe_3$ | 0.02 | 0.00 |
| $PbMe_3$ | 0.14 | 0.09 |
| $SiCl_3$ | 1.06 | 0.86 |
| $Si(OEt)_3$ | —0.20 | 0.04 |
| *1-X-4-m-Fluorophenylbicyclo[2.2.2]octanes (2)* | | |
| $SiH_3$ | 0.21 | 0.17 |
| $SiMe_3$ | 0.03 | 0.00 |
| $GeMe_3$ | 0.05 | 0.03 |
| $SnMe_3$ | 0.06 | 0.04 |
| $PbMe_3$ | 0.12 | 0.08 |
| $SiCl_3$ | 0.71 | 0.48 |
| $Si(OEt)_3$ | —0.10 | 0.02 |

[a] Defined as the difference (ppm) between the $^{19}$F chemical shift of the substituted compound and that of the parent compound (X = H). A positive sign implies deshielding. [b] Accurate to better than ±0.01 ppm.

and, moreover, display the same trend (Me > Et > i-Pr > t-Bu) as the corresponding $^{19}$F SCS (system 1, Table 4). Furthermore, the relative magnitude of the corresponding $^{13}$C SCS (system 3, C(4)) are in accord with expectations based on sensitivity considerations ($^{13}$C SCS are ca. one-half the magnitude of $^{19}$F SCS for a given electronic perturbation) [1]. In addition, the $^{13}$C SCS of C(2) (conjugative disposition) in system 3 (Table 2, $DCCl_3$) for the Me and Et groups also appear to reflect this phenomenon. However, it must be borne in mind that the $^{13}$C SCS of C(2) in system 3 are not nearly as well behaved for deducing pure electronic effects as carbon center C(4) [1]. Hence, it is not surprising that the smaller change in hyperconjugation of the bicyclo[2.2.2]octyl group induced by the larger alkyl groups (i-Pr and t-Bu) is apparently obscured at C(2) by some other small unidentified perturbation. We believe that the aforementioned $^{13}$C NMR data, together with the previously reported $^{19}$F SCS [2], leaves no doubt that substitution at the bridgehead of the phenylbicyclo-

TABLE 4

$^{19}$F SUBSTITUENT CHEMICAL SHIFTS (SCS) [a,b] OF ALKYL SUBSTITUENTS FOR SYSTEM 1

| Substituent, X | Cyclohexane [2] | DMF [2] | $DCCl_3$ [This study] |
|---|---|---|---|
| Me | 0.09 | 0.07 | 0.08 |
| Et | 0.07 | 0.07 | 0.07 |
| i-Pr | 0.05 | 0.05 | 0.06 |
| t-Bu | 0.03 | 0.02 | 0.05 |

[a] See footnote a to Table 3. [b] Accurate to better than ±0.01 ppm.

TABLE 5

NMR DERIVED POLAR SUBSTITUENT PARAMETERS OF METALLOIDAL SUBSTITUENTS

| Substituent | $\sigma_I$ Values | | | | | |
|---|---|---|---|---|---|---|
| | $^{19}F$ NMR | | | | $^{13}C$ NMR system **3**(C(4)) | |
| | system **1** | | system **2** | | | |
| | c-$C_6H_{12}$ [a] | $CH_2Cl_2$ [a] | c-$C_6H_{12}$ [a] | $CH_2Cl_2$ [a] | c-$C_6H_{12}$ | $DCCl_3$ |
| $SiH_3$ | 0.15 | 0.13 | 0.14 | 0.15 | 0.14 [b] | 0.15 [b] |
| $GeH_3$ | | | | | 0.14 [b] | 0.13 [b] |
| $SnH_2Me$ | | | | | 0.09 [b] | |
| $SiMe_3$ | 0.00 | 0.00 | 0.02 | 0.00 | −0.01 [a] | 0.03 [c] |
| $GeMe_3$ | 0.01 | 0.01 | 0.03 | 0.03 | −0.01 [a] | 0.03 [c] |
| $SnMe_3$ | 0.01 | 0.00 | 0.04 | 0.04 | 0.00 [a] | 0.03 [c] |
| $PbMe_3$ | 0.06 | 0.04 | 0.08 | 0.07 | 0.06 [a] | 0.08 [b] |
| $Si(OEt)_3$ | −0.08 | 0.02 | −0.07 | 0.02 | | 0.00 [b] |
| $Ge(OEt)_3$ | | | | | 0.18 [b] | 0.24 [b] |
| $SiCl_3$ | 0.43 | 0.39 | 0.48 | 0.42 | | 0.45 [b] |
| $GeCl_3$ | | | | | 0.60 [b] | 0.63 [b] |
| $SnCl_2Me$ | | | | | | 0.47 [b] |

[a] Accurate to ±0.01. [b] Accurate to ±0.02. [c] Accurate to ±0.04.

[2.2.2]octyl ring system by alkyl groups effects a small change in the $\sigma_R^0$ value of the bicyclo[2.2.2]octyl group. Previously [2], we attributed this phenomenon to a possible perturbation of the angular relationship of the C—C bonds with respect to the $\pi$ electron system at the point of attachment of the bicyclo-[2.2.2]octyl moiety. However, a recent X-ray crystallographic study [22] of some bridgehead-substituted derivatives of system 3 offers no support for this proposal based on the likelihood of substituent-induced structural changes of the saturated skeletal framework [11]. We are forced to conclude, therefore, that through-bond effects [10] are responsible since it can be readily envisaged that the pseudo $\pi$ orbitals of the bridgehead-alkyl substituents and the $\pi$ system of the phenyl group maybe coupled by an appropriate molecular orbital of the bicyclo[2.2.2]octane system (a component of the $E''$ HOMO set is of appropriate $\pi$ symmetry). The fact that the $^{19}F$ and $^{13}C$ SCS for the alkyl substituents in systems 1 and 3 (C(4)) are positive suggests that the aforementioned coupling leads to a decrease in the hyperconjugative interaction [23] between the bicyclo[2.2.2]octyl group and the phenyl ring system.

An important operational consequence of the recognition of through-bond effects being manifested by the $^{19}F$ and $^{13}C$ SCS of systems 1 and 3 (C(4)), respectively, is that $\sigma_I$ values determined from these parameters for a new class of substituents may be in error and, therefore, require cautious evaluation. Hence, it is important to test for the presence of the phenomenon by also determining $\sigma_I$ values for the corresponding $^{19}F$ SCS of system 2 in which through-bond effects appear relatively unimportant.

If we accept the $^{19}F$ and $^{13}C$ SCS for the metalloidal substituents of systems 1, 2, and 3 (C(4)) (Tables 2 and 3 respectively) at their face value as being exclusive manifestations of electric field perturbations, $\sigma_I$ values may be calculated (listed in Table 5) by employing the appropriate polar susceptibility parameters *. Several significant conclusions follow from these results. Firstly, it can be seen (Table 5) that for the silyl substituent ($SiH_3$), the $\sigma_I$ values determined from systems 1 and 3 (C(4)) are similar to those derived from system 2. This result clearly demonstrates that a through-bond transmission effect of the kind noted above for the congeneric methyl group is not significant for $SiH_3$. This is perhaps not unexpected since the interaction between appropriate orbitals of $\pi$ symmetry on Si [25] and adjacent $\pi$ systems is not large in the neutral ground state [26] and, therefore, it is difficult to envisage significant interactions with CC $\sigma$ bonding levels of the bicyclo[2.2.2]octane ring system. Since $\pi$ bonding involving Si is more efficient than the other Group IVB elements [26], it may be safely concluded that through-bond effects involving the bicyclo[2.2.2]octyl skeletal framework should not be a problem obscuring $\sigma_I$ effects for all other metalloidal substituents described in this paper.

Secondly, it can be seen (Table 5) that although all systems (except possibly 2 (c-$C_6H_{12}$)) yield $\sigma_I$ values of zero (within experimental error) for the $SiMe_3$ group, a mixed array of results prevails for the $GeMe_3$ and $SnMe_3$ substituents. Note that whereas the values for these groups from systems 1 and 3 (C(4)) are all effectively zero (within experimental error), the values from system 2 imply small but significant electron-withdrawing influences (downfield shifts). However, because the substituent dipole is aligned along the major axis of the ring system in the former model systems (1 and 3 (C(4)) but not in the latter (2), we are inclined to dismiss these results from system 2 as being aberrations of either solvent influences or possibly intramolecular Van der Waals shifts [27] by these very polarizable groups. On the latter point, it is of interest to note that the distance dependency ($1/r^6$) of this effect suggests a greater influence (factor of 2) in system 2 than 1.

Thirdly, except for $PbMe_3$ (see below) the values listed in Table 5 for these electropositive substituents clearly exemplify that $\sigma_I$ parameters provide a measure, by definition, of the field effect ($F$) of a substituent [25,28,29]. This is an important point since many workers have misconstrued this polar parameter as a measure of the electronegativity effect ($\sigma$-inductive effect ($I_\sigma$) of a substituent [29]. It should always be borne in mind that whereas the field effect ($\sigma_I$ effect) is proportional to the group dipole moment of the substituent as a whole, which in turn is the net result of the vectorial summation of all relevant bond moments comprising a polyatomic substituent, the electronegativity or $\sigma$-inductive effect (short range influence) refers essentially to the bond moment between the substrate and the substituent **. On this point, the noteworthy observations from Table 5 are as follows: (1) the $\sigma_I$ values for the $MH_3$ groups are positive (implies electron-withdrawal) since the respective group moments are dominated by the relatively large $\overset{\delta+}{M}-\overset{\delta-}{H}$ bond moments [25,30]. Based on additivity considerations, a $\sigma_I$ value of +0.14 is predicted for $SnH_3$ from the result for $SnH_2Me$. The similar $\sigma_I$ values for the hydride substituents ($MH_3$; M = Si,

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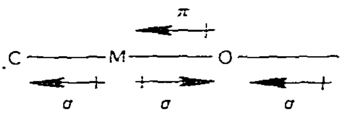
* See footnote page 386. It should be noted that Ewing and Toyne [24] report a similar $\rho_I$ value (1.16, $DCCl_3$) for C(4) of system 3.

** There is undoubtedly a parallel between electronegativity and $\sigma_I$ parameters for monoatomic substituents (e.g., halogens) since the bond moment determining the latter parameter pertains to the bond directly between the substituent and substrate.



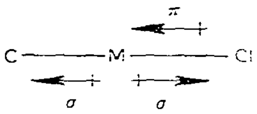


Fig. 1. Diagram illustrating bond moment contributions to group moment of $M(OEt)_3$ groups.

Fig. 2. Diagram illustrating bond moment contributions to group moment of $MCl_3$ groups.

Ge and Sn) is reasonable since changes in electronegativity of the metalloids [31,32,33] leads to differential changes in $\overset{-\delta}{C}—\overset{+\delta}{M}$ and $\overset{+\delta}{M}—\overset{-\delta}{H}$ bond moments, which cancel on vectorial summation; (2) the $\sigma_I$ values for the $MMe_3$ groups (except M = Pb, see below) are zero because vectorial summation of the $\overset{+\delta}{M}—\overset{-\delta}{C}$ bond moments essentially cancel out (based on $T_d$ symmetry about M) and, therefore, the net group moment must approximate the small $\overset{-\delta}{C}—\overset{+\delta}{H}$ bond moment [30]; (3) the $\sigma_I$ values for $Si(OEt)_3$ and $SiCl_3$ are substantially smaller than those for $Ge(OEt)_3$ and $GeCl_3$, respectively, because of the considerably larger π bond moment contributions (see Fig. 1 and 2) to the group moments of the former substituents [16,34]. Note that the group moment for $Si(OEt)_3$ ($c\text{-}C_6H_{12}$) is in the opposite direction to that for $Ge(OEt)_3$ *.
The apparent solvent dependence of the $\sigma_I$ parameters for the $M(OEt)_3$ groups (Table 5; $c\text{-}C_6H_{12}$ versus $DCCl_3$) is understandable in terms of a decreased π bond moment contribution in hydrogen-bond donor solvents presumably due to the electrons on oxygen being partially "tied up" by hydrogen-bonding to the solvent.

Fourthly, it can be seen (Table 5) that the $PbMe_3$ groups is indicated to be a weak electron-withdrawing substituent by a field-inductive mechanism! Although this was expected from the results of system 2, which also provided anomalous results for the other $MMe_3$ groups (vide supra), the significant $\sigma_I$ values determined from systems 1 and 3 (C(4)) is surprising. However, because the $\sigma_I$ values ($c\text{-}C_6H_{12}$) determined from the latter systems are identical, we believe the result is real and not simply an aberration which can be summarily dismissed as being due to such extraneous factors as magnetic anisotropic influences [35] ** Van der Waals interactions [27], solvent effects, etc. Further supportive evidence for this conclusion is that the trends for the aryl $^{13}C$ SCS (Table 2; cyclohexane) of $PbMe_3$ in system 3 ((C(4)/C(3) ≈ 2 and the significantly negative value for C(1)) are characteristic of electron-withdrawing groups.

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* Based on the Allred—Rochow electronegativity [32] scale, as well as a recent non-empirical scale [33], Ge is more electronegative than Si. Hence, on this basis, ignoring π bond moment contributions leads to the prediction that $\sigma_I$ values for $Si(OEt)_3$ and $SiCl_3$ should be more positive than those for $Ge(OEt)_3$ and $GeCl_3$, respectively.

** Magnetic anisotropic contributions should be the same for all nuclear species (e.g., $^{13}C$ and $^{19}F$) in positions remote from the substituent (ref. 27 and 35). Note that the ratio (1.75) of the $^{19}F$ and $^{13}C$ SCS for $PbMe_3$ in 1 and 3 C(4) (Tables 2 and 3, respectively, $c\text{-}C_6H_{12}$ as solvent) is almost exactly the same as the proportionality constant (1.83) obtained from a least-squares correlation between $^{19}F$ and $^{13}C$ SCS in these systems for conventional polar groups [1].

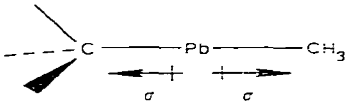

Fig. 3. Diagram illustrating bond moment contributions to group moment of $PbMe_3$.

Given then that the $\sigma_I$ value for $PbMe_3$ is definitely positive, the obvious corollary is that the group moment of this substituent (see Fig. 3) is dominated by the $\overset{\delta+}{\mathrm{Pb}}-\overset{\delta-}{\mathrm{C}}\mathrm{H}_3$ bond moment. Why this should be so is beyond our comprehension, given that there is no reason to believe that $T_d$ symmetry is not achieved by the groups attached to Pb in the model systems (**1** and **3**). It is of interest to note that the possibility of electron-withdrawal by $PbMe_3$ (relative to H) has been considered previously [36].

Finally, a comparison of the unequivocal $\sigma_I$ values determined from systems **1** and **3** (C(4)) listed in Table 5 (cyclohexane) with those previously reported (assembled in Table 6) indicates that, in the main, those determined utilizing the fluorophenyl ($^{19}F$ SCS of *m*-substituted fluorobenzenes) and 2-naphthyl ($^{13}C$ SCS of C(6) and C(7) in 2-substituted naphthalenes) tags are in remarkably good accord. Hence, it appears that these methodologies yield valid estimates (within ±0.05) of polar parameters ($\sigma_I$ values) for metalloidal substituents despite their reliance on multiparameter regression analysis to separate out mesomeric or resonance effects. However, the results from the 2-fluoronaphthyl (except $SiH_3$ and $SiMe_3$) and styrene tags must be rejected as being simply artifacts of the statistical dissection underlying the two methods. Interestingly, based on additivity considerations a $\sigma_I$ value of 0.71 is predicted for $SnCl_3$ from the result for $SnCl_2Me$ (Table 5). It can be seen (Table 6) that this value is significantly less than that derived from the fluorophenyl tag (0.80).

TABLE 6

POLAR SUBSTITUENT PARAMETERS ($\sigma_I$ Values) DERIVED BY OTHER METHODOLOGY FOR SOME METALLOIDAL SUBSTITUENTS

| Substituent | Fluorophenyl tag | 2-Fluoronaphthyl tag | 2-Naphthyl tag | Styrene system |
|---|---|---|---|---|
| $SiH_3$ | 0.09 [a] (0.09)[14] | 0.16 [b] [25] | 0.14 [b] [25] | |
| $SiMe_3$ [c,d] | −0.03[12] (−0.04)[14] | 0.02[12] | 0.01 [b] [25] | −0.09[13] |
| $GeMe_3$ | −0.01[12] | 0.06[12] | 0.03 [a] | −0.10[13] |
| $SnMe_3$ [e] | 0.00[12] (0.01)[45] | 0.09[12] | 0.02 [a] | −0.11[13] |
| $PbMe_3$ | 0.03[12] | 0.12[12] | −0.02 [a] | −0.12[13] |
| $Si(OEt)_3$ | −0.04[14] | | 0.03 [a] | |
| $SiCl_3$ | 0.39[14] | | 0.39 [a] | |
| $GeCl_3$ | 0.63[14] | | | |
| $SnCl_3$ | 0.80[45] | | | |

[a] Unpublished results ($DCCl_3$, solvent). [b] Taken from ref. 25 ($DCCl_3$, solvent). [c] A statistically refined value (−0.10) has been reported [21]. [d] A value of −0.13 has been determined from the p*K*'s of substituted acetic acids in $H_2O$ [14]. [e] $pK_H - pK (\equiv \sigma_I^q$, quinuclidine data) = −0.26 [9]. Correlative analysis of the quinuclidine data, $pK_H - pK$ versus $\sigma_I$, yields $\rho_I = 4.601$ [46]. Therefore, $\sigma_I(SnMe_3) = -0.056$. However, it should be noted that the H datum point is deviant in the correlation.

However, this was expected since a dipole moment study [16] suggests that additivity will fail here due to $\overset{\delta+}{\mathrm{Sn}}—\overset{\delta-}{\mathrm{Cl}}$ bond polarity increasing with progressive chlorine substitution. An interesting corollary of the good correspondence between the $\sigma_I$ values determined from systems 1 and 3 (C(4)) and those determined from the aromatic substrates (fluorophenyl and 2-naphthyl) for strong polar groups is that field parameters for these groups evaluated from aliphatic systems can be validly used in aromatic systems. This is in agreement with other deductions [1,37] but contrary to another claim [36].

One particular aspect of the aryl $^{13}$C SCS data for system 3 (Table 2) we would like the draw attention to are the results of C(1). Although a DSP analysis of the $^{13}$C SCS for conventional polar substituents [1] indicated a marked sensitivity to polar field effects ($\rho_I$ = —5.30 ($DCCl_3$) and —4.49 (c-$C_6H_{12}$)), the analysis also yielded statistically significant resonance susceptibility terms ($\rho_R$ = 1.23 ($DCCl_3$) and 0.62 (c-$C_6H_{12}$)). Hence, we have consistently erred on the cautious side in our work [1—4] and have refrained from using this carbon site as a monitor for quantitatively evaluating $\sigma_I$ values. Interestingly, in the light of the discussion above concerning coupling of the orbitals of the phenyl ring system and the substituent via an appropriate orbital of the bicyclo[2.2.2]-octane ring skeleton, the $\rho_R$ term for C(1) may be an additional manifestation of this phenomenon. Additional insight into the factors underlying the electronic effect of bridgehead-substituents on the $^{13}$C chemical shifts of C(1) may be gained by examining the $^{13}$C SCS for $SiMe_3$ and t-Bu at this carbon site (Table 2; $DCCl_3$ and c-$C_6H_{12}$). It can be seen that the perturbations by these two groups are significant and, moreover, are of equal and opposite sign. Since these isoelectronic substituents have zero $\sigma_I$ values (vide supra) and, in addition, since both have orbitals of $\pi$ symmetry which are not significantly coupled to the $\pi$ systems of the phenyl ring (vide supra), it is tempting to speculate that this may be evidence for through-bond effects involving the 1,4 disposed $\sigma$ bonds (C(1)—C(1′) and C(4′)—$C(CH_3)$; C(1)—C(1′) and C(4′)—$SiMe_3$) via an appropriate $\sigma$ orbital of the bicyclo[2.2.2]octane skeleton [10]. The magnitude and sign of this effect, as manifested by the $^{13}$C SCS, will depend on the energy matching of the appropriate orbitals and the $\sigma$-inductive effect (electronegativity effect) of the substituent *. It is impossible to predict a priori which term ($\rho_I$ or $\rho_R$) will embody this interaction since $\sigma_I$ does not necessarily reflect electronegativity effects (only for monoatomic substituents).

In conclusion, we should mention that the $\alpha$, $\beta$, $\gamma$, and $\delta$ effects of the metalloidal substituents in the bicyclo[2.2.2]octane ring system have been listed in Table 2 essentially for the sake of completeness. These results from a stereochemically well-defined model system should contribute significantly to the accumulating body of data on these effects. Although a detailed analysis is rather pointless in view of the lack of understanding of the origins of these

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[*] Although the common preconception is that $SiMe_3$ and $C(CH_3)_3$ have electronegativity effects of similar sign (i.e., $\overset{\delta-}{\mathrm{C}}—\overset{\delta+}{\mathrm{SiMe_3}}$ and $\overset{\delta-}{\mathrm{C}}—\overset{\delta+}{\mathrm{C(CH_3)_3}}$), it should be noted that a recent theoretical analysis [39] suggests that a methyl substituent attached to an $sp^3$ hybridized carbon center is electron-withdrawing relative to H, i.e., the formal polarity of the bond between the bridgehead C and t-Bu relative to $\overset{\delta-}{\mathrm{C}}—\overset{\delta+}{\mathrm{H}}$ may be $\overset{\delta+}{\mathrm{C}}—\overset{\delta-}{\mathrm{C(CH_3)_3}}$.

effects [40,41,42], several features are worthy of note. Firstly, the α-effects (C(4′) SCS), as expected, are the largest. On the basis that α-effects are dominated by σ-induction (electronegativity effect), as suggested by a recent statistical analysis of α-$^{13}$C SCS in $XCH_3$ and $XCH_2CH_3$ derivatives [43], it is of interest to note that whereas the α-$^{13}$C SCS for Me and t-Bu are positive (steric crowding contributes significantly to the value for the latter group), the corresponding values for $MH_3$ (M = Si and Ge) and $M(CH_3)_3$ (M = Si, Ge, and Sn) are negative. Note, however, the substantial positive value for $PbMe_3$. Although it is tempting to suggest that this result implies a group effect for $PbMe_3$ of opposite character to the other $MMe_3$ groups, the likelihood of large magnetic anisotropic contributions [41] to α-shifts clearly cloud the issue. A further interesting feature is that whereas replacement of H with Me groups on carbon effects a shift of +7.61 ppm (Table 2; Me versus t-Bu), a corresponding structural change on Si and Ge leads to shifts of +1.39 ppm and —1.33 ppm, respectively. Presumably steric crowding by Me groups (deshielding effect) is rapidly attenuated by increasing distance from the α carbon center and is finally obscured by σ-induction or magnetic anisotropic contributions for $GeMe_3$. Secondly, the trends for the β-effects (C(3′) SCS) suggest the dominance of steric and magnetic anisotropic contributions in this disposition [41]. Finally, in line with recent conclusions [41] and the results for the powerfully polar $C(CN)_3$ substituent [3], the γ (C(2′) SCS) and δ (C(1′) SCS) effects for the metalloidal substituents indicate no apparent significant contributions from electric field influences ($\sigma_I$ effect). Magnetic anisotropic contributions [41] as well as possible back-lobe interactions [44] appear to be the dominant factors for these latter orientations. Through-bond effects of the kind mentioned above (of σ-symmetry) may also be a contributing factor.

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