Substituent Effects of the Groups $CH_2M(CH_3)_3$ (M = C to Pb) and $M(CH_3)_3$ (M = Si to Pb) from Proton and Carbon-13 Chemical Shift Measurements on 4-Substituted Styrenes

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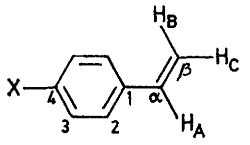
Proton and carbon-13 chemical shifts for 4-substituted styrenes are used to estimate σ_I and $\sigma_R{}^\circ$ for $M(CH_3)_3$ and $CH_2M(CH_3)_3$ derivatives (M = Si, Ge, Sn, or Pb). The derived constants are consistent with previous conclusions concerning electronic effects of these groups and indicate that σ–π hyperconjugation is an important mechanism for their transmission.

THE nature of the interaction of C–M bonds (M = Si, Ge, Sn, or Pb) with aromatic π-electron systems is of continuing interest.[1-3] In compounds of the type $ArMR_3$ (R = H or alkyl), there is net electron withdrawal from the aromatic π-electron system.[4-7] By contrast, in compounds of the type $ArCH_2MR_3$, there is significant electron donation to the π-system.[1,2,8-10] The former effect is most commonly attributed to d_π–p_π interactions with the *d* orbitals on M acting as π-acceptors;[4-7,11] the latter has been attributed to σ–π hyperconjugation (vertical stabilization) in which the polar $\overset{\delta-}{C}-\overset{\delta+}{M}$ σ-bond acts as a π-electron source.[1,2,10] However, it has recently been pointed out that σ–π hyperconjugation could also be important in $ArMR_3$ derivatives, with the $\overset{\delta+}{M}-\overset{\delta-}{R}$ σ-bond acting as an electron acceptor in this case.[1]

We have shown that ^1H and ^{13}C chemical shifts in 4-substituted styrenes can be used as a probe for electronic substituent effects in aromatic derivatives.[12] Owing to the geometric arrangement of the vinyl group, the vinyl β-protons H_B and H_C [see formula (i)] have different sensitivities to electric field effects but similar sensitivities to resonance effects. Similarly, C-1 and C_β also have significantly different relative sensitivities to field and resonance effects.[12] The major advantage of this approach is that, from a single compound, one obtains four parameters [$\delta(H_B)$, $\delta(H_C)$, δ(C-1), and $\delta(C_\beta)$] which can be used to estimate dual substituent parameters (DSP) which measure field/inductive and resonance effects. Previous approaches have generally used only two parameters (^{19}F chemical shifts[13] or p*K* values for carboxylic acids[14]) estimated from two compounds.



(1)

We have already utilized $\delta(H_B)$ and $\delta(H_C)$ for 4-substituted styrenes to estimate field (F) and resonance (R) substituent parameters[14] for the groups $M(CH_3)_3$.[12] In view of the interest in the electronic effects of the groups $M(CH_3)_3$ and $CH_2M(CH_3)_3$, it was decided to use the styrene system to estimate σ_I and $\sigma_R{}^\circ$ for these substituents, since a complete set of DSP constants for these derivatives was not available.

RESULTS AND DISCUSSION

Vinylic region ^1H spectra for 4-substituted styrenes were analysed by using an exact ABC analysis.[15] For $CH_2M(CH_3)_3$ derivatives, the chemical shift changes between concentrations of 1 and 4 mole % were <0.15 Hz (0.001 5 p.p.m.). Consequently, chemical shifts for 1 mole % solutions were taken as infinite dilution values. The CH_2Cl derivative gave significant (linear) dilution shifts and infinite dilution values were estimated by extrapolation of values for three solutions of concentrations between 1 and 4 mole %. Infinite dilution chemical shifts are listed in Table 1. Estimated errors in ^1H and ^{13}C shifts are, respectively, ± 0.002 and ± 0.04 p.p.m.[12]

The basic assumption in utilizing substituent-induced changes in ^1H and ^{13}C chemical shifts to monitor electronic effects is that these parameters reflect changes

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in ground-state electronic density. There is ample evidence for a linear relationship between ground-state carbon electron densities and ^{13}C chemical shifts in aromatic derivatives, provided that the substituent is remote from the carbon atom of interest.[16] Similarly, we have shown that ^{1}H chemical shifts in 4-substituted styrenes [12] and phenylacetylenes,[17] measured under inert conditions (at infinite dilution in C_6H_{12}), are dominated by intramolecular electronic effects. Further evidence is obtained by plotting $\delta(C_\beta)$ *versus* $\delta(H_C)$ for 29 styrene derivatives.* Since $\delta(C_\beta)$ and $\delta(H_C)$ show nearly identical relative sensitivities to field and resonance effects (see Table 2), this plot should be linear, with a slope of 16—20,† provided that both parameters reflect ground-state electron density.[17] In fact, the plot is linear with the expected slope [$\delta(C_\beta) = 18.2\ \delta(H_C)$ (r 0.996)], supporting our belief that ^{1}H and ^{13}C chemical shifts can be used to monitor electronic substituent effects.

TABLE 1

Proton and ^{13}C chemical shifts [a] and ^{1}H,^{1}H-coupling constants for 4-X-styrenes [b]

X	δ(C-4)	δ(C-3,-5)	δ(C-2,-6)	δ(C-1)	$\delta(C_\alpha)$	$\delta(C_\beta)$	$\delta(H_A)$	$\delta(H_B)$	$\delta(H_C)$	J_{AB} [c]	J_{AC}	J_{BC}	Ref.
H	127.46	128.15	126.00	137.40	136.96	113.20	6.628 9	5.630 2	5.113 5	17.56	10.90	1.09	12
$CH_2C(CH_3)_3$	138.81	130.26	125.39	135.09	136.78	112.43	6.613 8	5.607 6	5.076 8	17.56	10.85	1.15	This work
$CH_2Si(CH_3)_3$	139.50	127.77	125.97	133.44	136.79	111.62	6.583 7	5.561 9	5 031 4	17.56	10.89	1.15	
$CH_2Ge(CH_3)_3$	140.40	127.35	126.00	133.39	136.79	111.54	6.580 2	5.556 5	5.025 4	17.55	10.86	1.15	
$CH_2Sn(CH_3)_3$	142.17	126.47 [d]	126.18 [d]	132.73	136.76	111.22	6.562 9	5.535 5	5.004 6	17.55	10.88	1.17	
$CH_2Pb(CH_3)_3$	142.45	126.01 [d]	126.36 [d]	132.79	136.66	111.21	6.569 4	5.525 4	4.990 8	17.58	10.87	1.18	
$Si(CH_3)_3$	139.27	133.15	125.37	137.78	136.98	113.45	6.612 7	5.644 5	5.108 3	17.58	10.87	1.15	12
$Ge(CH_3)_3$	141.41	132.73	125.56	137.29	136.98	113.22	6.628 5	5.652 5	5.115 1	17.57	10.89	1.17	
$Sn(CH_3)_3$	141.05	135.58	125.67	137.32	137.07	113.22	6.597 1	5.629 3	5.087 5	17.54	10.90	1.14	
$Pb(CH_3)_3$	148.04	136.29,	126.13	136.72	137.06	113.00	6.613 1	5.632 7	5.086 4	17.55	10.89	1.16	
CH_2Cl	136.75	128.50	126.22	137.44	136.21	113.99	6.632 8	5.660 7	5.160 5	17.57	10.89	0.97	This work

[a] In p.p.m. to low field of tetramethylsilane. [b] For labelling, see formula (1). [c] Coupling constants in Hz. [d] Assignment uncertain.

TABLE 2

Correlations of ^{1}H and ^{13}C chemical shifts for twelve 4-X-styrenes [a] *versus* σ_I and σ_R° [b]

δ	ρ_I [c]	ρ_R [c]	δ_o	r [d]	R.m.s.[e]	f [f]	λ [g]
$\delta(H_B)$	+0.177 1	+0.461 2	5.624 0	0.997	0.011	0.085	2.60
$\delta(H_C)$	+0.286 8	+0.471 7	5.100 4	0.997	0.012	0.083	1.64
δ(C-1)	+4.303	+19.515	137.08	0.997	0.41	0.073	4.54
$\delta(C_\beta)$	+4.801	+8.774	113.32	0.998	0.20	0.069	1.82

[a] X = H, $N(CH_3)_2$, NH_2, OCH_3, SCH_3, CH_3, C_6H_5, $COCH_3$, CO_2CH_3, CF_3, C≡N, or NO_2; experimental data from ref. 12, with ^{1}H chemical shifts for the C_6H_5 and CN derivatives corrected for magnetic anisotropy effects.[12] [b] Values of σ_I and σ_R° from ref. 13. [c] Coefficients for equation $\delta = \delta_o + \rho_I\sigma_I + \rho_R\sigma_R$. [d] Correlation coefficient. [e] Root means square error between experimental and calculated shifts. [f] R.m.s. difference between experimental and calculated shifts divided by r.m.s. difference of individual shifts from that for the unsubstituted derivative.[13] Taft *et al.* suggest that correlations with $f < 0.1$ are sufficiently precise to use for evaluation of σ_I and σ_R. [g] $\lambda = \rho_R^\circ/\rho_I$.

Chemical shifts for 12 styrenes were used in determining the correlation equations given in Table 2 (halogens were omitted for reasons previously discussed [12]). Agreement between calculated and experimental shifts was uniformly excellent, with correlation coefficients $\geqslant 0.997$. Values of σ_I and σ_R° for individual substituents were then estimated by using the experimental data to solve pairs of correlation equations [*e.g.* $\delta(H_B)$ plus $\delta(H_C)$ and δ(C-1) plus $\delta(C_\beta)$]. Average values of σ_I and σ_R° are listed in Table 3. Average standard deviations were respectively 0.04 and 0.02 σ units for σ_I and σ_R°.

Previously reported σ_I and σ_R° values for $M(CH_3)_3$ and $CH_2M(CH_3)_3$ derivatives are summarized in Table 3. Agreement with our values is generally very good. The major disagreement is with a recent report on $M(CH_3)_3$ derivatives that the groups with M = Si to Pb all had an electron-withdrawing field/inductive effects; this is inconsistent with our results, the results of Taft for $Si(CH_3)_3$,[13] and the usual ideas concerning the electronegativities of these elements.[20] Similarly, the negative σ_R° values for $Sn(CH_3)_3$ and $Pb(CH_3)_3$ are inconsistent with both our results and the generally accepted idea that these groups are π-acceptors.[4-7] Present values of σ_I and σ_R° for $CH_2Si(CH_3)_3$ and σ_R° for $CH_2Sn(CH_3)_3$ are smaller than those previously reported. However, the earlier values were obtained from correlations based on constants for the CH_3 group (σ_I −0.07;[21] σ_R° −0.15 [4]) which were larger than the values currently recom-

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* Data from ref. 12 and this work.

† Proton and ^{13}C chemical shifts in aromatic derivatives, respectively, vary by *ca.* 10 p.p.m. per π-electron [18] and 160—200 p.p.m. per π-electron.[19]

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mended by Taft (σ_I −0.4; σ_R° −0.11).[13] The latter values were used in our correlations. If one compares changes from CH_3 to $CH_2M(CH_3)_3$, our values are in very good agreement with those previously reported. Since the CH_2Cl derivative was available (as an intermediate in syntheses), σ_I and σ_R° values were also estimated for this group; again the results are in good agreement with previous values,[22] providing further evidence for the reliability of our methods.

TABLE 3

Estimated σ_I and σ_R° values for $CH_2M(CH_3)_3$, $M(CH_3)_3$, and CH_2Cl

	This work [a]		Previous values (^{19}F measurements) [b]		Previous values (i.r. measurements)
X	σ_I	σ_R°	σ_I	σ_R°	σ_R°
$CH_2C(CH_3)_3$	−0.07	−0.06			
$CH_2Si(CH_3)_3$	−0.10	−0.15	−0.07,[c] −0.08	−0.20 [d,e]	±0.20 [f]
$CH_2Ge(CH_3)_3$	−0.10	−0.15			
$CH_2Sn(CH_3)_3$	−0.11	−0.19			
$CH_2Pb(CH_3)_3$	−0.12	−0.19		−0.23[f]	±0.26 [f]
$Si(CH_3)_3$	−0.09	+0.07	−0.10,[g] +0.02 [i]	+0.06,[g] +0.04,[f] +0.05 [i]	±0.02 [f]
$Ge(CH_3)_3$	−0.10	+0.07	+0.06 [i]	+0.01,[f] +0.01 [i]	±0.05[f]
$Sn(CH_3)_3$	−0.11	+0.05	+0.09 [i]	+0.01,[f] −0.02 [i]	±0.07 [f]
$Pb(CH_3)_3$	−0.12	+0.05	+0.12 [i]	−0.10 [i]	
CH_2Cl	+0.19	−0.01	+0.14,[d] +0.15 [h]	+0.03,[e] −0.03 [h]	

[a] Based on a correlation using $\sigma_I = -0.04$ and $\sigma_R^\circ = -0.11$ for CH_3 (ref. 13). [b] Most σ_I and σ_R° values obtained from correlations of ^{19}F chemical shifts which gave $\sigma_I = -0.07$ and $\sigma_R^\circ = -0.15$ for CH_3 (refs. 4 and 21). [c] Ref. 21. [d] Ref. 9. [e] Ref. 4. [f] Ref. 7. [g] Ref. 13. [h] Ref. 22. [i] Ref. 3.

The σ_I and σ_R° values for $M(CH_3)_3$ and $CH_2M(CH_3)_3$ show regular trends which can be related to the electronic effects of these groups. The derived substituent constants indicate that the groups $CH_2M(CH_3)_3$ are electron-donating by both field/inductive and resonance effects. While the increase in magnitude in σ_I from C to Pb parallels the expected electron-donating ability of M,[11] the actual variation is small. There is a larger variation of σ_R° for $CH_2M(CH_3)_3$, with the largest change between C and Si. The σ_R° values for $CH_2Si(CH_3)_3$ to $CH_2Pb(CH_3)_3$ are consistent with previous conclusions that the polar C–M bond releases electrons to the phenyl π-electron system by σ–π hyperconjugation.[1,2,10] Since the $\overset{\delta-}{C}$–$\overset{\delta+}{M}$ bond can be regarded as a partially formed lone pair of electrons,[10] it seems reasonable that σ_R° for $CH_2M(CH_3)_3$ should be between zero and σ_R° for groups with formal non-bonding pairs of electrons [*e.g.* $\sigma_R^\circ(NH_2)$ −0.48; $\sigma_R^\circ(OCH_3)$ −0.45].[13]

CNDO/2 molecular orbital calculations for $CH_2Si(CH_3)_3$ derivatives reproduce the electron-donating properties of this group (Table 4) and are consistent with σ–π hyperconjugation.* Brownlee and Taft pointed out that there should be a linear relation between σ_R° and Σq_π, the total change in π-charge density for the aromatic group.[23] The relation obtained by using π-charge densities for 4-substituted styrenes[12] is: $\sigma_R^\circ = 5.85\ \Sigma q_\pi$(styrene) ($r$ 0.983). For the $CH_2Si(CH_3)_3$ derivative, $\Sigma q_\pi = -4.05 \times 10^2$, corresponding to $\sigma_R^\circ = -0.24$, in reasonable agreement with the derived value.

The derived σ_I and σ_R° values for $M(CH_3)_3$ (M = Si to Pb) indicate electron-donating field/inductive effects and electron-withdrawing resonance effects. Values of σ_I become more negative from Si to Pb, consistent with the decreasing electronegativity of M,[20] although the actual variation in σ_I is very small. While the positive σ_R° values could reflect d_π–p_π conjugation, CNDO/2 calculations for silylbenzenes indicate that σ–π hyperconjugation could also be a contributing factor,[1] with the polar $\overset{\delta+}{M}$–$\overset{\delta-}{C}$ bond acting as an electron acceptor (similar effects have been noted for $\overset{\delta+}{C}$–$\overset{\delta-}{Cl}$ and $\overset{\delta+}{C}$–$\overset{\delta-}{F}$ in $C_{3-n}XH_n$ substituents[22] where no d_π–p_π interaction is possible). Similarly Cradock *et al.* have pointed out that there are orbitals derived from silicon 3*p* orbitals which are of appropriate symmetry and energy to interact with π-orbitals.[24] Finally, CNDO/2 calculations for 4-substituted styrenes have shown that the $Si(CH_3)_3$ group is a π-electron acceptor even when 3*d* orbitals are excluded

TABLE 4

Excess σ- and π-carbon charge densities for 4-$CH_2Si(CH_3)_3$-styrene, relative to styrene

Carbon	Excess charge density (×10⁴) [a]	Carbon	Excess charge density (×10⁴) [a]
C-4_σ	−12 [d]	C-1_π	−332
C-4_π	+533	$(C\alpha)_\sigma$	−14
C-3, -5_σ [b]	+148	$(C\alpha)_\pi$	+54
C-3, -5_π [b]	−476	$(C\beta)_\sigma$	+54
C-2, -6_σ [b]	−93	$(C\beta)_\pi$	−129
C-2, -6_π [b]	+211	Σq_π [c]	−405
C-1_σ	+122		

[a] Silicon 3*d* orbitals excluded from calculation. [b] Average of two planar conformations of vinyl group. [c] Sum of carbon π charge densities, relative to styrene. [d] Negative sign corresponds to increased electron density.

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* Pitt has provided a more comprehensive discussion of σ–π conjugation in $C_6H_5CH_2M(CH_3)_3$ derivatives, utilizing CNDO/2 calculations.[1]

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from the calculation.[12] Thus σ–π hyperconjugation could, at least in part, account for the σ_R° values for $M(CH_3)_3$. However, this does not rule out the possibility that d_π–p_π conjugation is also present.

The near zero value for σ_R° for CH_2Cl is consistent with opposing hyperconjugative interactions involving C–H and C–Cl bonds;[22] the σ_I value seems reasonable since it is approximately half the value[13] for directly bonded chlorine (+0.44).

EXPERIMENTAL

Diethyl ether was distilled from sodium metal immediately prior to use. I.r. spectra were recorded with a Perkin-Elmer 237B instrument.

Vinylic ^1H spectra were obtained with a Varian HA-100 spectrometer operating in frequency sweep mode at a probe temperature of 30 °C. Spectra were recorded for three samples of each compound (1—4 mole % solutions in C_6H_{12}). ^{13}C Spectra were obtained with a Varian XL-100-15 instrument operating in pulsed Fourier transform mode at a probe temperature of 32 °C. Spectra were recorded for 0.5M-solutions in CCl_4 with 8 vol. % C_6D_{12} added as lock. More complete experimental details are given elsewhere.[12]

CNDO/2 molecular orbital calculations were performed with an IBM 370 computer, by using a standard CN INDO program[25] and standard parameters for most bond angles and bond lengths.[26] The Si–C bonds were taken as 1.87 Å in length and calculations were performed for the situation with the CH_2–Si bond at right angles to the plane of the benzene ring.

4-Vinylbenzyl chloride was synthesized in 50—60% yield by the treatment of 4-(β-bromoethyl)benzyl chloride with potassium t-butoxide in diethyl ether at 25 °C, in a manner similar to that of Tanimoto *et al.*[27] 1-Neopentyl-4-vinylbenzene was prepared by acid-catalysed dehydration of 1-(α-hydroxyethyl)-4-neopentylbenzene.

Trimethyl-4-*vinylbenzylsilane*.—4-Vinylbenzyl chloride (2 g, 13 mmol) was added over 1/2 h to magnesium (1 g) (in excess), in diethyl ether (50 ml), previously activated by treatment with ethylene dibromide (*ca.* 0.5 ml). The mixture was then refluxed for a further 1/2 h, chloro(trimethyl)silane (2.8 g; 100% excess) was added, and the mixture was refluxed overnight. After work-up with saturated ammonium chloride solution, distillation afforded the *silane* as a liquid (2.0 g, 81%), b.p. 48° at 0.15 mmHg; $\nu_{C=C}$ 6.12 and 6.22 μm (Found: C, 75.85; H, 9.6. $C_{12}H_{18}Si$ requires C, 75.7; H, 9.55%).

Trimethyl-4-*vinylbenzylgermane*.—Similarly bromo(trimethyl)germane (2.86 g; 10% excess) and 4-vinylbenzylmagnesium chloride (13 mmol) in diethyl ether gave the *germane* as a liquid (2.0 g, 66%), b.p. 46—48° at 0.10 mmHg; $\nu_{C=C}$ 6.12 and 6.22 μm (Found: C, 61.6; H, 7.8. $C_{12}H_{18}Ge$ requires C, 61.35; H, 7.7%).

Trimethyl-4-*vinylbenzylstannane*.— Chlorotrimethylstannane (2.83 g; 10% excess) was coupled with 4-vinylbenzylmagnesium chloride (13 mmol) by refluxing in diethyl ether for 2 h. The usual work-up gave the *stannane* as a liquid (2.9 g, 79%), b.p. 70° at 0.07 mmHg; $\nu_{C=C}$ 6.12 and 6.22 μm (Found: C, 51.7; H, 6.55. $C_{12}H_{18}Sn$ requires C, 51.3; H, 6.45%).

Trimethyl-4-*vinylbenzylplumbane*.— Chlorotrimethylplumbane (9.6 g, 33 mmol) was added, as a solid, to 4-vinylbenzylmagnesium chloride (33 mmol). The mixture was left at ambient temperature overnight, then worked up as before. The oily residue obtained on removal of solvents was used immediately for the n.m.r. study. Attempts at distillation led to decomposition. The spectral properties were fully consistent with the residue being reasonably pure plumbane; $\nu_{C=C}$ 6.12 and 6.22 μm; δ_H 6.8—7.4 (4 H, aromatic AA′BB′ pattern) [vinyl protons (3 H) see Table 1], 2.8 (2 H, s, CH_2Pb, $J_{Pb \cdot CH_3}$ 64 Hz), and 0.7 (9 H, s, Me_3Pb, $J_{Pb \cdot CH_3}$ 56 Hz).

4-*Neopentylstyrene*.—1-Bromo-4-neopentylbenzene (prepared in 30% yield by a literature method[28]) (2.8 g, 12.3 mmol) in ether (5 ml) was added over 1/4 h to magnesium (0.5 g; large excess) and the mixture was refluxed for a further 1 h. Acetaldehyde (5 ml; large excess) was added dropwise after cooling, and the mixture was then hydrolysed with saturated ammonium chloride and extracted with ether. The organic layers were separated, dried, and evaporated *in vacuo* and the residue distilled from potassium hydrogen sulphate (100 mg) to afford the crude product (1 g), b.p. 62° at 1 mmHg. A pure *sample* was obtained by preparative g.l.c. (8 ft SK30; 150 °C); $\nu_{C=C}$ 6.12 and 6.22 μm (Found: C, 89.3; H, 10.3. $C_{13}H_{18}$ requires C, 89.6; H, 10.4%).

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