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INFRARED INTENSITIES AS A MEASURE OF INTRAMOLECULAR INTERACTIONS

XIX.* ELECTRONIC INTERACTIONS IN SUBSTITUTED PHENYL- AND BENZYLTRIMETHYLSILANES

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SUMMARY

An infrared method has been used to establish that the $SiMe_3$ group is a weak resonance acceptor in the ground state when joined to a benzene ring. This acceptance is considerably exalted when resonance donors are attached to the *para* position. The relatively strong resonance donation of a CH_2SiMe_3 group is explicable in terms of hyperconjugation.

INTRODUCTION

Considerable interest continues to be shown[2-15] in the electronic interactions between unsaturated systems and MR_3 or CH_2MR_3 substituents (M = Si, Ge, Sn, Pb). Some controversy exists both as to the relative magnitude of inductive and $p_\pi - d_\pi$ effects for the MR_3 systems[5,7,8,12,15,16] and as to the mechanism leading to the fairly large electron-donating influence of CH_2MR_3 groups[3,7,9,10,17-21]. However, many of the investigating techniques employed, such as reactivity and equilibrium measurements or the determination of ^{19}F NMR shifts, involve the need for another substituent which is added to the unsaturated system to act as a probe. This second substituent can interfere with the conjugation of, say, an MR_3 group with the unsaturated system and thus the conclusion reached is often not independent of the method employed[22]. We therefore used our previously described[4,23] infrared method to investigate such interactions.

DISCUSSION

Monosubstituted benzenes (Table 1)

The intensities have been treated using eqn. (1)[23] to derive substituted σ_R^0 values.

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[*] For Part XVIII see ref. 1.

TABLE 1

SPECTRAL DATA AND CALCULATED σ_R^0 VALUES FOR MONOSUBSTITUTED BENZENES

Compound	*Solvent*	$\pm\sigma_R^0$(*calcd.*[a])	*1600 band*		*1585 band*		A^c	ε^d	*1500 band*	
			ν	$\varepsilon_A{}^b$	ν	ε_A			ν	ε_A
$PhSiMe_3$	CCl_4	0.0	1590	5	1574	2	100[e]	31	1482	7
$PhSiMe_2(SiMe_3)$	CCl_4	0.04	1586	2	1574	2	135	[f]	1485	20
$PhSiMe(SiMe_3)_2$	CCl_4	0.06	1598	2	1583	4	175	[f]	1483	30
$PhCH_2SiMe_3$	CCl_4	0.20	1598	46	1580	8	780	550	1491	93
$PhCH(SiMe_3)_2$	CCl_4	0.24	1597	70	1575	13	1115	700	[g]	[g]
$PhC(SiMe_3)_3$	CCl_4	0.24	1589	52	1572	12	1100	625	[g]	[g]
$PhGeMe_3$	CCl_4	0.05	1574	3	[h]	[h]	140[i]	46	1484	29
$PhSnMe_3$	CCl_4	0.07	1578	4	[h]	[h]	200	37	1479	27
$PhCH_2SnMe_3$	CCl_4	0.26	1598	85	1578	12	1255	1450	1489	178

[a] Calculated using $\sigma_R^0 = [(A-100)/17600]^{1/2}$. [b] Peak extinction coefficient; $\varepsilon_A = a_{max}/cl$ where a_{max} is absorbance at peak maximum, c is concentration in moles per litre and l is cell path length in cm. [c] The integrated intensity of the 1600 and 1585 cm^{-1} band $A = \Sigma a_{max}/cl$. [d] ε is an estimate of the integrated intensity given by $\varepsilon = \varepsilon_A \Delta\nu^{1/2}$. [e] Previous value $A = 95$, see ref. 4. [f] Too complex to be meaningful. [g] Not measured. [h] No observable 2nd band. [i] Previous value $A = 257$, see ref. 4; we believe the previous value to be wrong because it gives a wrong frequency of ν_{16a} according to lit. values[49].

Because of variation in the overtone contribution to the band, σ_R^0 values in the range +0.1 to −0.1 are subject to significant errors, which are at their largest for values near zero[23]. For such substituents, more reliable σ_R^0 values are obtainable from *meta*-disubstituted benzenes[24], or from substituted ethylenes[25]. The magnitude of the σ_R^0 value can be deduced from the monosubstituted benzene or ethylene, but to obtain the sign, *meta*-disubstituted compounds must be used.

$$A_{mono} = 17600(\sigma_R^0)^2 + 100 \qquad (1)$$

The substituents MMe_3 (M = Si, Ge, Sn) disclose small σ_R^0 values which are compared in Table 2 with values derived from available ^{19}F NMR results[2,3]. Although these NMR values indicate that Me_3Ge and Me_3Sn are weak electron acceptors, our earlier results indicated[4] that the apparent electron-acceptor character arises from the presence of substituent–substituent interaction in the *p*-fluorophenyl compounds and that, in the absence of such interactions, whereas Me_3Si is a π-electron acceptor, Me_3Ge and Me_3Sn are weak π-electron donors in the parent C_6H_5-

TABLE 2

COMPARISON OF IR AND ^{19}F NMR DERIVED σ_R^0 VALUES

	σ_R^0(*IR*)	σ_R^0(*NMR*)[a]	σ_R^0(*NMR*)[b]
$SiMe_3$	+0.02[c]	+0.04	+0.046
$GeMe_3$	±0.05[d], −0.08[e]	+0.01	+0.006
$SnMe_3$	±0.07[d], −0.10[e]	+0.01	+0.014

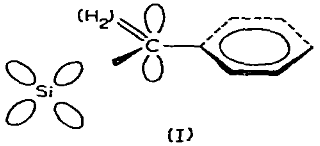
[a] See ref. 2. [b] See ref. 3. [c] From *meta* compounds (see text). [d] From mono-substituted compounds. [e] From *meta*-fluoro derivatives (ref. 4).

MMe_3 derivatives. Previous evidence from dipole moments[26], UV[18], and ESR[27], indicates that the order of π-acceptance is $Si > Ge > Sn$. Evidently hyperconjugation, involving M–Me electron release, nearly balances this acceptance, so that the resulting numerically small value of σ_R^0 may be positive or negative. ^{19}F NMR work by Adcock[15] on MMe_3–fluoronaphthalenes where direct conjugation is impeded indicates that $SiMe_3$ is a nett weak acceptor and $GeMe_3$ and $SnMe_3$ are weak electron donors. Each MMe_3 substituent is usually thought to engage in $d_\pi - p_\pi$ electron withdrawal, though Pitt[8,9] has suggested that such effects are small in the ground states of the monosubstituted benzenes.

For the substituents $CH_2MMe_3(M=Si, Sn)$, the intensities of the benzyl compounds indicate large σ_R^0 values which agree well with the results obtained by NMR[3]:

	$\sigma_R^0(IR)$	$\sigma_R^0(NMR)$
$PhCH_2SiMe_3$	± 0.20	-0.20
$PhCH_2SnMe_3$	± 0.26	-0.23

Powerful electron release by Me_3MCH_2 and related groups has previously been revealed by spectroscopic studies of appropriately substituted ethylenes and benzenes[5,17,20,28–35]. For Me_3SiCH_2, the $(\sigma^+ - \sigma)$ value of -0.25 lies between those of p-OMe -0.51 and p-Me -0.14[6]. Kitching and Adcock[3] favour an enhanced π-inductive effect explanation based on the observed order of the polarity of the $Me_3\overset{\delta+}{M}-\overset{\delta-}{CH_2}$ bond. The present results indicate significant hyperconjugation from the metal–CH_2 bond even in the ground state, as already suggested by Eaborn[17], although Traylor and his colleagues have recently concluded that such hyperconjugation is fairly unimportant for neutral molecules[48]. Nagy[18] has proposed an "extended" hyperconjugation picture with the d-orbital of the metal overlapping with a pseudo $C{=}(H_2)$ π orbital as in (I). (This has been criticized by Ramsey[19].)



(I)

The large diffuse d orbitals of the metal may extend far enough through space to effectively overlap the π-orbitals of the ring (and such an explanation was used by Jaffé[36] to explain the UV spectra of alkyl sulphides and vinyl and allyl derivatives of Group IV[29,30]) but this type of interaction should manifest itself in electron *withdrawal* from the ring. Powerful support for the hyperconjugative electron release mechanism has recently been adduced[8,10,11] from ionisation potential and charge transfer measurements on $Me_3M–CH_2$ systems.

For the substituents $CH_{3-x}(SiMe_3)_x$ $(x=1,2,3)$ the effect on the σ_R^0 of replacing hydrogen in the CH_3 group of toluene by Me_3Si groups is in complete agreement with the trend predicted by Eaborn[37] based upon minimising steric interactions and then considering the effective overlap of the $Me_3Si–C$ bonds with the p_π-orbitals of the ring.

The σ_R^0 magnitudes are in good agreement with the values obtained by Eaborn *et al.*, from a ^{19}F NMR study[21]:

	$x=1$	$x=2$	$x=3$
σ_R^0(IR)	± 0.20	± 0.24	± 0.24
σ^0(NMR)	-0.200	-0.224	-0.245

The strong conjugative electron release from the groups $(Me_3Si)_xCH_{3-x}$ $(x=1,2,3)$ is also shown by their $(\sigma^+ - \sigma)$ values of -0.25, -0.29, -0.25 respectively[6].

The intensities of the compounds $PhSiMe_{(3-x)}(SiMe_3)_x$ $(x=1$ or $2)$ are low and hence the derived σ_R^0 values (*cf.* ± 0.04, ± 0.06) are subject to error. Their sign is uncertain, negative signs could be explained as arising from electron release[38] by hyperconjugation from the $Me_3Si{-}Si$ bonds and positive signs from enhanced $(d_\pi{-}p_\pi)^5$ bonding between the aromatic ring and the attached silicon atom. However, the $(\sigma^- {-} \sigma)$ values indicate that the electron withdrawal by the group $Me_3SiSiMe_2$ is greater than that by Me_3Si[39].

meta-Disubstituted benzenes

$$A_{meta} = 19000[(\sigma_{R^1}^0)^2 + (\sigma_{R^2}^0)^2 + (\sigma_{R^1}^0 \cdot \sigma_{R^2}^0] + 340 \qquad (2)$$

Spectral data for the compounds $XC_6H_4SiMe_3$ in Table 3 were treated by eqn. (2)[24] which was solved for the experimental intensities treating $\sigma_R^0(SiMe_3)$ as an unknown. This shows clearly the positive sign for $\sigma_R^0(SiMe_3)$ and hence confirms the resonance acceptor properties of this group: the numerical value of $\sigma_R^0(SiMe_3)=$

TABLE 3

SPECTRAL DATA FOR *meta*-SUBSTITUTED PHENYLTRIMETHYLSILANES

Substituent	σ_R^0 [a]	*1600 band*		*1500 band*		A [c]	$\bar{R}_m$ [d]	$f_m(\sigma_R^0)$ [e]
		ν	ε_A [b]	ν	ε_A			
OMe[f]	-0.43	1568	168	1480	125	3650	0.42	0.43
F[f]	-0.34	1572	339	1477	245	2410[g]	0.33	0.33
Cl[f]	-0.22	1556	87	1486	73	1160	0.21	0.21
t-Bu[f]	-0.13	1588	18	1473	49	570	0.11	0.12
		1576	17					
Me[f]	-0.10	1592	12	1487	4	440	0.07	0.09
		1574	13					
NO_2[f]	$+0.17$	1604	71	1478	29	1360	0.23	0.18
NMe_3^+[h]	-0.15	1571	32			990	0.13	0.14
PMe_3^+[h]	$+0.08$	1578	31			480	0.09	0.10
$AsMe_3^+$[h]		1579	33			510	0.09	
$CH_2NMe_3^+$[h]	0.0	1556	8			270	0.0	0.03

[a] Of substituents. [b] Peak extinction coefficient $\varepsilon_A = a_{max}/cl$ where a_{max} is absorbance at peak maximum, c is concentration in moles per litre and l is cell path length in cm. [c] A is the integrated intensity of the 1600 and 1585 bands. $A = \Sigma a_{max}/cl$. [d] $\bar{R}_m = [(A-340)/19000]^{\frac{1}{2}}$. [e] $f_m(\sigma_R^0) = [(\sigma_R^0 Y)^2 + \sigma_R^0(SiMe_3)^2 + \sigma_R^0 Y \cdot \sigma_R^0(SiMe_3)]^{\frac{1}{2}}$. [f] Run in CCl_4–10% C_6H_6 solution. [g] Previous value $A=2858$, see ref. 4. We believe this sample to be impure. [h] Run in Me_2SO (satd. NaCl)–10% C_6H_6 solution.

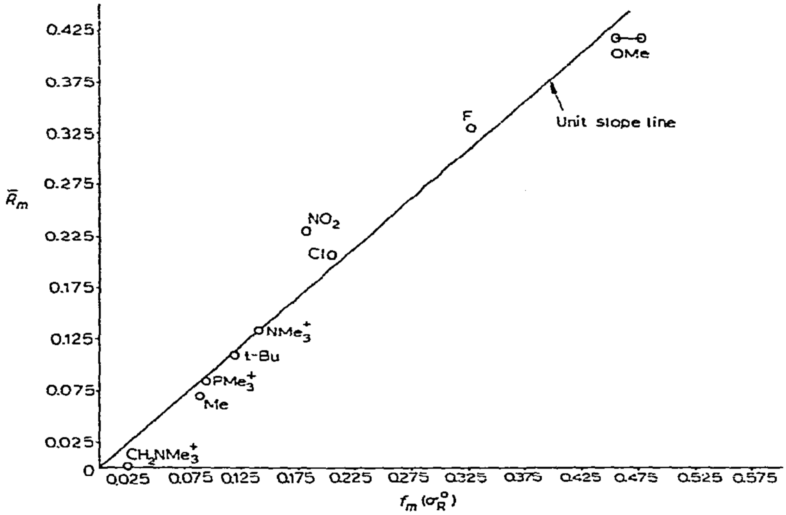


Fig. 1. Plot of observed intensity {in terms of $\bar{R}_m = [(A-340)/19000]^{\frac{1}{2}}$} against expected intensity {in terms of $f_m(\sigma_R^0) = [(\sigma_R^0 Y)^2 + \sigma_R^0(\text{SiMe}_3)^2 + \sigma_R^0 Y \cdot \sigma_R^0(\text{SiMe}_3)]^{\frac{1}{2}}$} for *meta*-substituted phenyltrimethylsilanes.

+0.025 thus obtained was used to calculate the expected intensity which is in good agreement with the observed values (Fig. 1).*

para-Disubstituted benzenes

Spectral data for the *para* derivatives $XC_6H_4SiMe_3$ in Table 4 were treated by

TABLE 4

SPECTRAL DATA FOR *para*-SUBSTITUTED PHENYLTRIMETHYLSILANES

Substituent	σ_R^0 [a]	*1600 band*		*1500 band*		A [c]	R_p [d]	$f_p(\sigma_R^0)$ [e]
		ν	ε_A [b]	ν	ε_A [b]			
NMe_2 [f]	−0.53	1598	568	1512	283	10100	0.92	0.89
OMe [f]	−0.43	1595	299	1502	363	6000	0.70	0.72
F [f]	−0.34	1590	266	1498	273	3360 [g]	0.52	0.58
Cl [f]	−0.22	1576	164	1483	168	1440	0.33	0.38
NMe_3^+ [h]	−0.15	1590	47			990	0.26	0.27
t-Bu [f]	−0.13	1599	80	1492	12	860	0.24	0.24
Me [f]	−0.10	1604	44	1502	23	720	0.22	0.19
$CH_2NMe_3^+$ [h]	0.0	1593	603			180	0.03	0.03
NO_2 [f]	+0.17	1595	109			2000	0.15	

[a] Of substituents. [b] Peak extinction coefficient. $\varepsilon_A = a_{max}/cl$ where a_{max} is absorbance at peak maximum, c is concentration in moles per litre and l is cell path length in cm. [c] A is the integrated intensity of the 1600 and 1585 cm^{-1} bands. $A = \Sigma a_{max}/cl$. [d] $\bar{R}_p = [(A-170)/11800]^{\frac{1}{2}}$. [e] $f_p(\sigma_R^0) = [\sigma_R^0\ Y - \sigma_R^0(\text{SiMe}_3) + K_{\text{SiMe}_3} \cdot \sigma_R^0 D]$. [f] Run in CCl_4–10% C_6H_6 solution. [g] Previous value $A = 2697$, see ref. 4. Previous integration did not include the overtone band at 1640 cm^{-1}. [h] Run in Me_2SO (satd. NaCl)–10% C_6H_6 solution.

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* We consider $\sigma_R^0 = +0.02$ for $SiMe_3$ to be more reliable than the previous value of −0.04 obtained[4] from limited data.

$$A_{para} = 11800[\sigma^0_{R1} - \sigma^0_{R2}]^2 + 170 \tag{3}$$

$$A_{para} = 11800[\sigma^0_{R1} - \sigma^0_{R2} + K_x \sigma^0_{R1}]^2 + 170 \tag{4}$$

eqn. (3)[40] which applies for *para* disubstituted benzenes in which the two substituents do not mutually interact. The calculated values of the intensities for donor substituents from eqn. (3) differ considerably from the observed intensities. This indicates that eqn. (4)[40] must be applied where the term $K_x \cdot \sigma^0_R D$ allows for the resonance interaction between the donor substituent and $SiMe_3$ acting as an acceptor. The best value of $K_x = 0.62$* gave satisfactory agreement with the unit slope line (Fig. 2).

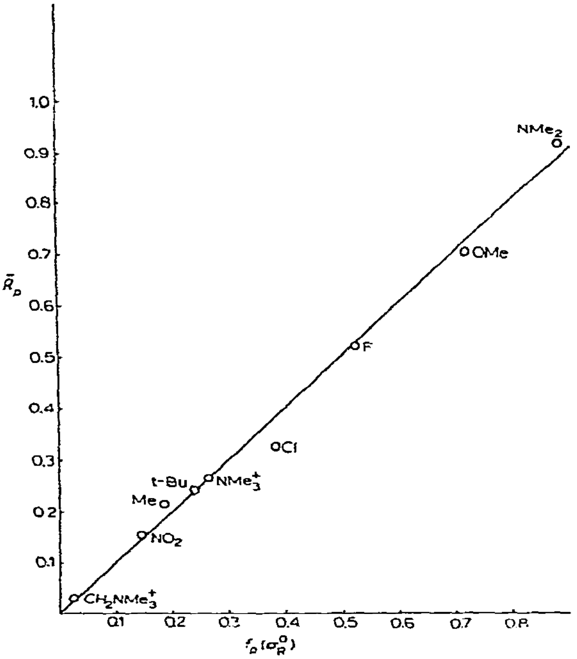

Fig. 2. Plot of observed intensity {in terms of $\bar{R}_p = (A - 170)/11800$} for *para*-substituted phenyltrimethylsilanes against expected intensity including interaction {in terms of $f_p = \sigma^0_R Y - \sigma^0_R(SiMe_3) + K_{SiMe_3} \cdot \sigma^0_R Y$}.

There is considerable evidence of *d*-orbital participation in arylsilicon compounds in which conjugation can occur with a strong donor substituted in the *para* position. The UV intensity criterion of Goodman[41] has been applied by Musker[42]. There is further evidence from UV frequency shifts[32], ionisation energies[31], charge transfer spectra[5], reduction potentials[43] for substituted quinones, ESR spectra[27,44] acidity measurements[45], NMR[3,7,13] and dipole moments[26,46,47]

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* This compares with the previous value of $K_x = 0.48$ based on *meta* and *para* $FC_6H_4SiMe_3$ only[4].

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