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# INFRARED INTENSITIES AS A MEASURE OF INTRAMOLECULAR INTERACTIONS: SUBSTITUTED BENZYLTRIMETHYL-SILANES AND -STANNANES*

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## Summary

Infrared intensities are recorded for the $\nu_8$ ring-stretching band near 1600 $cm^{-1}$ of a series of *meta*- and *para*-substituted $ArCH_2SiMe_3$ and $ArCH_2SnMe_3$ compounds. The substituents $CH_2SiMe_3$ and $CH_2SnMe_3$ are confirmed as resonance donors, with $\sigma^0_R$ of —0.20 and —0.26 respectively.

## Introduction

The $CH_2MR_3$ groups (M = Si, Sn) show strong electron release [2,3] as demonstrated by spectroscopic, reactivity, or equilibrium measurements or by the determination of $^{19}F$ NMR shifts [4]. However, these methods either utilise another substituent as a probe which may disturb [5] the electronic effect of the $CH_2MR_3$ group, or involve excited or transition states. We have therefore applied our infrared spectral [6] method to these above groups.

Our previously observed infrared intensities of the $\nu_8$ bands ($\nu_{16}$ in Herzbergs notation) of the corresponding monosubstituted benzenes and the earlier derived [6] eqn. (1), had given $\sigma^0_R$ values of ± 0.20 and ± 0.26 for $CH_2SiMe_3$ and $CH_2SnMe_3$ respectively [4].

$$A_{mono} = 17600(\sigma^0_R)^2 + 100 \tag{1}$$

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[*] This paper is part XXX in our series: Infrared intensities as a measure of intramolecular interactions. For part XXIX see ref. 1.

## Experimental

Stock samples of previously reported [2,6] $XC_6H_4CH_2MMe_3$ (M = Si, Sn) compounds were redistilled and had the following properties: [X, M, b.p. (°C/mmHg), $n_D^{25}$]: H, Si, 66/10, 1.4910; *p*-Me, Si, 82/8.0, 1.4918; *p*-Cl, Si, 90/6.0, 1.5102; *m*-Cl, Si, 82/4.0, 1.5095; *p*-F, Si, 71/10, 1.4745; *m*-F, Si, 71/10, 1.4770; *p*-I, Si, 94/1.0, 1.5600; H, Sn, 70/3.0, 1.5410; *p*-Me, Sn, 79/2.0, 1.5385; *m*-Me, Sn, 85/3.0, 1.5387; *p*-Cl, Sn, 96/2.0, 1.5565; *m*-Cl, Sn, 85/1.0, 1.5558; *p*-F, Sn, 81/4.0, 1.5260.

The following new $XC_6H_4CH_2MMe_3$ compounds were prepared from the appropriate Grignard reagent, $XC_6H_4CH_2MgBr(Cl)$, and chlorotrimethylsilane or bromotrimethylstannane in ether: [X, M, b.p. (°C/mmHg), $n_D^{25}$]: *m*-Me, Si, 74/6.0, 1.4912 (Found: C, 74.3; H, 10.0. $C_{11}H_{18}Si$ calcd.: C, 74.1; H, 10.2%); *m*-OMe, Si, 83/3.0, 1.5039 (Found: C, 68.0; H, 9.4. $C_{11}H_{18}OSi$ calcd.: C, 67.95; H, 9.35%); *m*-F, Sn, 60/1.0, 1.5272 (Found: C, 43.8; H, 5.6. $C_{10}H_{15}FSn$ calcd.: C, 44.0; 5.55%); *m*-OMe, Sn, 80/0.6, 1.5457 (Found: C, 46.5; H, 6.5. $C_{11}H_{18}OSn$ calcd.: C, 46.4; H, 6.4%).

Benzyltriethylstannanes, $YC_6H_4CH_2SnEt_3$ were prepared analogously from bromotriethylstannane: [Y, b.p. (°C/mmHg), $n_D^{25}$]: H, 85/0.7, 1.5375; *p*-Me(nc), 90/0.8, 1.5352 (Found: C, 53.9; H, 7.8. $C_{14}H_{24}Sn$ calcd.: C, 54.05; H, 7.8%); *p*-Cl(nc), 97/0.5, 1.5544 (Found: C, 47.0; H, 6.3; Cl, 9.9. $C_{13}H_{21}ClSn$ calcd.: C, 47.1; H, 6.4; Cl, 10.1%).

An in situ technique, in which a mixture of *p*-methoxybenzyl chloride and chlorotrimethylsilane or bromotrimethylstannane in ether was added to magnesium turnings in boiling ether, was used to prepare *p*-$MeOC_6H_4CH_2SiMe_3$, b.p. 88°/4.0 mmHg, $n_D^{25}$ 1.5042 and *p*-$MeOC_6H_4CH_2SnMe_3$(nc), b.p. 86°/0.8 mmHg, $n_D^{25}$ 1.5472 (Found: C, 46.6; H, 6.3. $C_{11}H_{18}OSn$ calcd.: C, 46.6; H, 6.4%).

All products were checked for purity by GLC, NMR, and IR spectroscopy.

Spectroscopic grade carbon tetrachloride was stored over molecular sieves (4A). Benzene was dried over sodium wire, redistilled and stored over molecular sieves. The IR spectra of the compounds were measured as solutions in carbon tetrachloride containing 10% benzene as an aid to cell balancing as previously described [8]. The integration of the $\nu_8$ bands was performed as before [6] and reproducibility errors in $A^{1/2}$ are ± 1.

## Results and discussion

### *meta-Disubstituted benzenes*

Equation (2) has been developed [8] to relate the integrated intensities of the $\nu_8$ vibrations of *meta*-disubstituted benzenes to $\sigma_R^0$ terms.

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

The results obtained are shown in Table 1. The $\sigma_R^0$ values for $CH_2MMe_3$ groups obtained from the monosubstituted benzenes could be either positive or negative. Plotting $[(A - 340)/19000]^{1/2}$ against $[(\sigma_R^0 1)^2 + (\sigma_R^0 2)^2 + \sigma_R^0 1 . \sigma_R^0 2]^{1/2}$

TABLE 1

SPECTRAL DATA FOR *meta*-DISUBSTITUTED BENZENES

| Substituent 1 | 2 | $\sigma_R^0 2$ | 1600/1585 band $\nu$ | $\epsilon_A$ [a] | $A$ [b] | $\left[\frac{A - 340}{19000}\right]^{1/2}$ | $f_m$ [c] |
|---|---|---|---|---|---|---|---|
| $CH_2SiMe_3$ | Me | −0.10 | 1606 | 99 | 1690 | 0.27 | 0.26 |
| | | | 1586 | 38 | | | |
| | Cl | −0.22 | 1595 | 180 | 2975 | 0.37 | 0.36 |
| | | | 1568 | 60 | | | |
| | F | −0.34 | 1614 | 124 | 4860 | 0.49 | 0.47 |
| | | | 1587 | 158 | | | |
| | | | 1578 | 80 | | | |
| | OMe | −0.43 | 1608 | 129 | 6425 | 0.57 | 0.54 - 0.57 [d] |
| | | | 1599 | 213 | | | |
| | | | 1592 | 137 | | | |
| | | | 1580 | 137 | | | |
| $CH_2SnMe_3$ | Me | −0.10 | 1603 | 117 | 2170 | 0.31 | 0.32 |
| | | | 1584 | 48 | | | |
| | Cl | −0.22 | 1593 | 288 | 3730 | 0.42 | 0.41 |
| | | | 1569 | 77 | | | |
| | F | −0.34 | 1611 | 201 | 6140 | 0.54 | 0.52 |
| | | | 1585 | 157 | | | |
| | OMe | −0.43 | 1604 | 200 | 7485 | 0.61 | 0.58 - 0.62 [d] |
| | | | 1597 | 250 | | | |
| | | | 1588 | 156 | | | |
| | | | 1578 | 168 | | | |

[a] Peak extinction coefficient $\epsilon_A = a_{max}/c \cdot l$ where $a_{max}$ is absorbance at peak maximum, $c$ is concentration and $l$ is cell path length. [b] $A$ is the integrated intensity of the 1600/1585 $cm^{-1}$ band in $l \cdot mol^{-1} \cdot cm^{-2}$. [c] $f_m = [(\sigma_R^0 1)^2 + (\sigma_R^0 2)^2 + (\sigma_R^0 1 \cdot \sigma_R^0 2)]$, $\sigma_R^0$ for $CH_2MMe_3$ taken as negative. [d] Corrected for asymmetry.

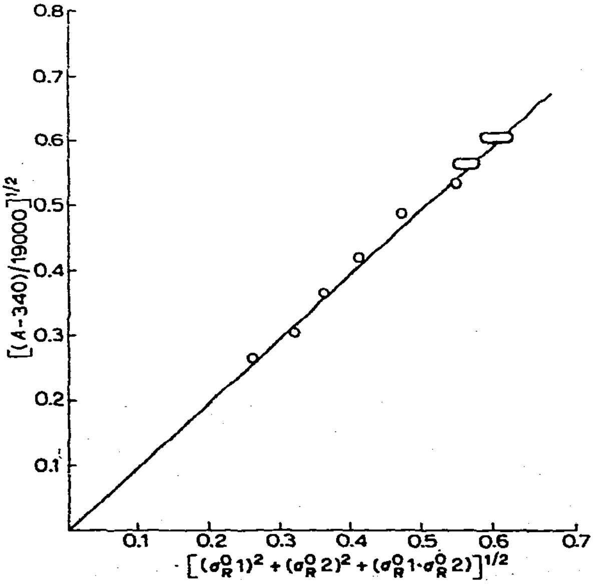

Fig. 1. Plot of $[(A - 340)/19000]^{1/2}$ against $[(\sigma_R^0 1)^2 + (\sigma_R^0 2)^2 + (\sigma_R^0 1 \cdot \sigma_R^0 2)]^{1/2}$ for *meta*-substituted benzyltrimethylsilanes and *meta*-substituted benzyltrimethylstannanes. The line shown has unit slope.

TABLE 2

SPECTRAL DATA FOR *para*-DISUBSTITUTED BENZYL COMPOUNDS

| Substituent | | $\sigma_R^0 2$ | 1600/1585 band | | $A$ [b] | $\left[\frac{A-170}{15000}\right]^{1/2}$ | $(\sigma_R^0 1 - \sigma_R 2)$ | $K_X \cdot \sigma_R^0 D$ | $f_p$ [c] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | | $\nu$ | $\epsilon_A$ [a] | | | | | |
| $CH_2SiMe_3$ | Me | −0.10 | 1614 | 11 | 240 | 0.07 | −0.10 | | 0.10 |
| | Cl | −0.22 | 1595 | 7.5 | 200 | 0.04 | +0.02 | −0.05 | 0.03 |
| | I | −0.22 | 1584 | 25 | 180 | 0.03 | +0.02 | −0.09 | 0.07 |
| | F | −0.34 | 1610 | 7.6 | 640 | 0.18 | +0.14 | | 0.14 |
| | | | 1581 | 53 | | | | | |
| | OMe | −0.43 | 1610 | 56.5 | 1230 | 0.27 | +0.23 | | 0.23 |
| | | | 1580 | 27.5 | | | | | |
| $CH_2SnMe_3$ | Me | −0.10 | 1608 | 26.5 | 300 | 0.09 | −0.16 | | 0.06 |
| | Cl | −0.22 | 1592 | 25.5 | 290 | 0.09 | −0.04 | −0.06 | 0.10 |
| | F | −0.34 | 1603 | 25 | 725 | 0.20 | +0.08 | | 0.08 |
| | | | 1593 | 27 | | | | | |
| | OMe | −0.43 | 1609 | 46.0 | 1085 | 0.25 | +0.17 | | 0.17 |
| | | | 1578 | 24.0 | | | | | |
| $CH_2SnEt_3$ | Me | −0.10 | 1604 | 0 | <150 | 0 | −0.18 | | 0.18 |
| | Cl | −0.22 | 1596 | 0 | <150 | 0 | −0.04 | −0.07 | 0.11 |

[a] Peak extinction coefficient; $\epsilon_A = a_{max}/c \cdot l$ where $a_{max}$ is absorbance at peak maximum, $c$ is concentration and $l$ is cell path length. [b] The integrated intensity in $l \cdot mol^{-1} \cdot cm^{-2}$. [c] $f_p = [(\sigma_R^0 1 - \sigma_R^0 2 + K_X \cdot \sigma_R^0 D)]$.

gave unit slope only if negative values were used as shown in Fig. 1. The negative values of $\sigma_R^0$ for $CH_2MMe_3$ groups indicative of electron donation, are in agreement with the literature results [4]. The $\sigma_R^0$ values derived from the *meta*-series support a hyperconjugative mechanism of electron donation [2,3,4] since the intensities of $\nu_8$ bands in phenyl derivatives are not affected by the $\pi$-inductive effects [5]. This latter effect was originally advocated by Kitching and Adcock [9] on the basis of $^{19}F$ NMR measurements although on the basis of further experiments they are now reconsidering their position [10]. Additional [4] recent evidence for the hyperconjugation mechanism has come from the photoelectron spectra and SCF-MO calculations on allylsilanes [11], from reaction rates and charge transfer complexes [12], from the large rotational barriers (< 5 kcal/mol) and hyperfine coupling constants in free radicals $\beta$ to metal groups [13], from UV spectra of nitrophenyl derivatives [14], and from the observation of the additional stability of carbonium ions [12,15] and free radicals [13] $\beta$ to metal groups. Although Kochi et al. [13] believe that two mechanisms, hyperconjugation and *p—d* homoconjugation contribute to the magnitude of the hyperfine couplings, Symons [16] believes the latter is unnecessary. The present results are incompatible with *p—d* overlap because this interaction would be observed as electron donation to the metal.

*para-Disubstituted benzenes*

Table 2 lists the results for these compounds. Equation (3) relates [17] the intensities of *para*-disubstituted benzenes to the $\sigma_R^0$ value of the substituents,

$$A = 15000[\sigma_R^0 1 - \sigma_R^0 2 + \lambda]^2 + 170 \qquad (3)$$

where interaction between the substituents is measured by $\lambda$.

Interaction is expected between the donor substituents $CH_2MR_3$ and the heavy halogens acting as *d*-orbital acceptors; increments of $K_X.\sigma_R^0 D$ ( = $\lambda$) given in Table 2 where $K_X$ is a measure [11,18] of the tendency to accept electrons into *d*-orbitals. However, the corrected values ($f_p$ in Table 2) obtained still show considerable discrepancies compared to the experimental $[(A - 170)/15000]^{1/2}$ values.

For compounds with substituents other than the heavy halogens, the second substituent is always a resonance electron donor and the discrepancy ($\Delta$) is always positive. Magnitudes of $\Delta$ are small for $CH_2SiMe_3$, (+ 0.03 to + 0.04), increase for $CH_2SnMe_3$ (+ 0.07 to + 0.12) and are large for $CH_2SnEt_3$ (+ 0.18). We believe that this pattern reflects the polarisability of these groups which are evidently less effective electron donors in electron-rich systems. The effects shown are consistent with hyperconjugative electron interaction [19,20] and are analogous to the effects observed for alkyl groups *para* to strong donors [19,20].

For the heavy halogen compounds, the interpretation of the results is less easy because of the ambiguity in the sign of small values of $[A - 170)/15000]^{1/2}$. It appears that *d*-electron acceptance by the halogen at least partially cancels the polarisability effects mentioned in the previous paragraph.

*mono-Substituted benzenes*

The $\sigma_R^0$ values obtained by $^{19}F$ NMR spectroscopy [10] are compared in

TABLE 3

SUBSTITUENT CONSTANTS FOR BENZYL GROUPS

| | $\sigma_R^0$(IR) | $\sigma_R^0$($^{19}$F NMR) |
|---|---|---|
| $PhCH_2SiMe_3$ | −0.20 | −0.20 |
| $PhCH_2SnMe_3$ | −0.26 | −0.23 |
| $PhCH_2SnEt_3$ | −0.285[a] | |

[a] New value, $A$ = 1525, frequencies observed were 1598 and 1577 $cm^{-1}$.

Table 3 with the IR values. The low values for $CH_2SnMe_3$ obtained by the $^{19}F$ method is consistent with the polarisability concept discussed above.

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