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ELECTRONIC EFFECTS OF MONO-, BIS-, AND TRIS-(TRIMETHYLSILYL)-METHYL GROUPS. THE ^{19}F NUCLEAR MAGNETIC RESONANCE SPECTRA OF *m*- AND *p*-$[(Me_3Si)_xCH_{(3-x)}]C_6H_4F$ COMPOUNDS ($x=0$–3)

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SUMMARY

The ^{19}F NMR spectra of *m*- and *p*-$[(Me_3Si)_xCH_{(3-x)}]C_6H_4F$ ($x=0$–3) compounds have been recorded. The σ_I and σ_R^0 constants for the $(Me_3Si)_xCH_{(3-x)}$ groups which can be derived from the ^{19}F chemical shifts are of doubtful validity, and the results suggest this method of obtaining σ_I and σ_R^0 constants may not be applicable to substituents of this type.

From studies of the ease of cleavage of the aryl–$SiMe_3$ bonds in *m*- and *p*-$[(Me_3Si)_xCH_{(3-x)}]C_6H_4SiMe_3$ compounds and of ^{19}F NMR spectra of *p*-$[(Me_3Si)_x$-$CH_{(3-x)}]C_6H_4F$ compounds ($x=0$–3 in both cases) we recently concluded that the strong electron release of the $(Me_3Si)_xCH_{(3-x)}$ groups arises mainly from hyperconjugative electron release from the Me_3Si–C bonds (σ–π conjugation)[1], rather than from inductive effects[2]. In this paper we describe an inconclusive attempt to assess the relative importance of the inductive and hyperconjugative effects by deriving inductive and resonance substituent constants, σ_I and σ_R^0, respectively from the ^{19}F NMR spectra of *m*- and *p*-$[(Me_3Si)_xCH_{(3-x)}]C_6H_4F$ compounds[3].

Taft and his coworkers have demonstrated for a wide range of substituents, that σ_I and σ_R^0 constants for each X group can be derived by use of eqns. (1) and (2) from the shielding parameters δ_m^F and δ_p^F, which represent the ^{19}F chemical shifts (in ppm) of *m*- and *p*-XC_6H_4F compounds, respectively, relative to that of fluorobenzene. Although Taft's theoretical interpretation of the shielding effects has been criticised[4], eqn. (1) does apply to a large number of *m*-substituents, and, furthermore, the values

$$\delta_m^F = -7.10\,\sigma_I + 0.60 \tag{1}$$

$$\delta_p^F = -29.5\,\sigma_R^0 + \delta_m^F = -29.5\,\sigma_R^0 - 7.10\,\sigma_I + 0.60 \tag{2}$$

of σ_I and σ_R^0 derived by use of eqns. (1) and (2) are in good agreement with those derived in other ways[3].

The chemical shifts for the *m*- and *p*-$[(Me_3Si)_xCH_{(3-x)}]C_6H_4F$ compounds are shown in Table 1, along with the values of σ_I and σ_R^0 derived by use of eqns. (1) and (2). The most striking feature is that the values of δ_m^F or σ_I indicate that the inductive release of electrons decreases in the order Me > Me_3SiCH_2 > $(Me_3Si)_2CH$ > $(Me_3Si)_3C$. The values of δ_m^F and σ_I for the $(Me_3Si)_3C$ group even indicate that the overall inductive effect of this group relative to hydrogen is one of electron withdrawal.

TABLE 1

^{19}F CHEMICAL SHIFTS (IN PPM) OF *m*- AND *p*-$[(Me_3Si)_xCH_{(3-x)}]C_6H_4F$ COMPOUNDS (IN CCl_4), AND DERIVED σ_I AND σ_R^0 CONSTANTS FOR THE $[(Me_3Si)_xCH_{(3-x)}]$ GROUPS

x	δ_m^F	δ_p^F	σ_I	σ_R^0
0	1.23	5.34	−0.089[a]	−0.140[a]
1	1.14	7.06	−0.076[a]	−0.200[a]
2	0.84	7.47	−0.034	−0.224
3	−0.30	6.93	+0.127	−0.245

[a] Previously reported values of σ_I and σ_R^0 derived from ^{19}F shielding parameters are (*a*) 0.08 and −0.146 for Me, and (*b*) −0.07 and −0.20 for Me_3SiCH_2.

If the results are accepted at their face value, they imply, contrary to all expectations, that the Me_3Si group *withdraws* electrons by the inductive effect when attached to a saturated (sp^3-hybridized) carbon atom, but it seems to us more likely that the validity of eqn. (1) breaks down for the kind of substituent under investigation*. It is true that there is not a great deal of evidence in favour of the commonly held view that the Me_3Si group releases electrons inductively to an sp^3-hybridized carbon atom, but the strengths of amines such as $Me_3SiCH_2NH_2$ and $(Me_3SiCH_2)_2NH$ and acids such as Me_3SiCH_2COOH are consistent with such electron release[5]. There is little doubt that the Me_3Si group releases electrons inductively when attached to the more electronegative sp^2-hybridized carbon atom of the aromatic ring, since there is clear evidence that the group can slightly release electrons overall to the ring in spite of the operation of conjugative electron withdrawal, which is normally attributed to p_π–d_π bonding[5,6,7,8]. For the Me_3Si group the value[9] of δ_m^F (in CCl_4) is +0.90, which corresponds to a value of −0.042 for σ_I.

Detailed analysis of the variations in δ_m^F as x is increased from 0 to 3 in the compounds *m*-$[(Me_3Si)_xCH_{(3-x)}]C_6H_4F$ confirms that inductive (and/or field) effects of the Me_3Si–C bonds are not the only influences operating. If only these inductive effects were involved we would expect the extra Me_3Si groups to have at most simple additive effects, and more probably to have a decreasing influence with increasing x, whereas the increase in x is, in fact, accompanied by increasing change in δ_m^F and σ_I, as follows:

Change in x	0→1	1→2	2→3
Change in δ_m^F	0.09	0.30	1.14
Change in σ_I	0.013	−0.042	−0.161

A steep rise in additional effects on adding additional large groups is most commonly associated with serious steric compressions, and models indicate that there is, indeed, marked interference between the $(Me_3Si)_3C$ group and the aromatic ring, so that there might, for example, be some distortion of the ring and/or significant lengthening of the aryl–$C(SiMe_3)_3$ bond, but no indication of unusual structural effects has emerged from spectroscopic studies of aryl$C(SiMe_3)_3$ compounds[7]. A more likely reason for the anomalies is that in the case of the *m*-compounds the environment of the fluorine atom can be influenced more by through-space effects from Me–Si and

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* There are similar trends with *m*-$Me_xCH_{(3-x)}$ groups, for which the δ_m^F shifts in carbon tetrachloride are as follows[9]: CH_3, +1.20; $MeCH_2$, +0.75; Me_3C, +0.45.

C–H bonds than by the dipoles of the Me_3Si–C bonds, and models show that the C–H bonds of the Me_3Si groups can lie relatively close to the *m*-F atom.

Since the validity of the σ_I constants deduced from the δ^F_m parameters is suspect, so also is the validity of the σ^0_R constants derived by use of eqn. (2). We merely note that the variations in the σ^0_R values are consistent with our view that the predominant electron release from $(Me_3Si)_xCH_{(3-x)}$ groups attached to aromatic rings is hyperconjugative rather than inductive[1], and that the hyperconjugation would be expected[2] to increase substantially with the change from $x=0 \rightarrow 1$, markedly less for $x=1 \rightarrow 2$, and little further, if at all, for $x=2 \rightarrow 3$. The apparent increase in σ^0_R on going from $x=2$ to $x=3$ is not in keeping with our previous analysis of ground state effects[2], but this increase is a consequence of assigning a positive value of σ_I to the $(Me_3Si)_3C$ group, which, as we have seen, is probably in error.

It is noteworthy that the order of electron release, as indicated by the δ^F_p shifts, *viz.* $(Me_3Si)_2CH > Me_3SiCH_2 > (Me_3Si)_3C > CH_3$, is the same as that indicated by the ease of acid cleavage of the aryl–$SiMe_3$ bonds of *p*-$[(Me_3Si)_xCH_{(3-x)}]$-$C_6H_4SiMe_3$ compounds, whereas, for the *m*-compounds the two orders are different. The relative rates of cleavage indicate the same order for *m*- as for *p*-groups[2]; assuming linear free energy relationships and using a value of −0.069 for the σ-constant of the m-Me group, the following approximate σ_m-constants can be derived from the relative rates: Me_3SiCH_2, −0.145; $(Me_3Si)_2CH$, −0.166; $(Me_3Si)_3C$, −0.097.

EXPERIMENTAL

Preparation of materials

(m-Fluorobenzyl)trimethylsilane. *m*-Fluorobenzyl chloride (3.5 g, 0.023 mole) in ether (30 ml) was added to a mixture of magnesium turnings (0.75 g) and trimethylchlorosilane (3.5 g, 0.31 mole) in ether (50 ml). The mixture was subsequently boiled under reflux for a further 3 h, then worked up in the usual way to give (*m*-fluorobenzyl)-trimethylsilane (2.52 g, 70%), b.p. 56°/4.5 mm, n^{29}_D 1.4749. (Found: C, 65.6; H, 8.1. $C_{10}H_{15}FSi$ calcd.: C, 65.9; H, 8.3%.)

(m-Fluorophenyl)bis(trimethylsilyl)methane. *m*-Fluoro-α,α-dichlorotoluene (2.5 g, 0.0143 mole) was added to refluxing tetrahydrofuran (40 ml) containing magnesium turnings (0.9 g) and trimethylchlorosilane (3.5 g, 0.031 mole), the reaction being initiated with 2 drops of 1,2-dibromoethane. A white precipitate appeared and turned black after about 1 h. Reflux was continued for 6 h after the addition, and then the reaction mixture was worked up in the usual way to give (*m*-fluorophenyl)bis(trimethylsilyl)methane (2.25 g, 65%), b.p. 160°/100 mm, n^{23}_D 1.4907. (Found: C, 61.4; H, 9.1. $C_{13}H_{23}FSi$ calcd.: C, 61.35; H, 9.1%.)

m-Fluoro-α,α,α-trichlorotoluene. Chlorine was passed through *m*-fluorotoluene, maintained at 130° and illuminated with ultra-violet light, until the solution acquired a persistent green tinge. Distillation gave *m*-fluoro-α,α,α-trichlorotoluene (95%), b.p. 62°/1.5 mm. (Found: C, 39.4; H, 1.93. $C_7H_4Cl_3F$ calcd.: C, 39.4; H, 1.89%.)

(m-Fluorophenyl)tris(trimethylsilyl)methane. *m*-Fluoro-α,α,α-trichlorotoluene (26 g, 0.12 mole) in an equal volume of tetrahydrofuran, was added to magnesium (10 g) and Me_3SiCl (44 g, 0.40 mole) in refluxing tetrahydrofuran (200 ml). Reflux was continued for 8 h after the addition, and the mixture was then worked up in the usual manner, culminating in fractional distillation. The fraction of b.p. 290–320° was

mixed with an equal volume of methanol, and the mixture was cooled to −78° in a slush bath. After 12 h a white precipitate appeared, and this was recrystallised from methanol to give (*m*-fluorophenyl)tris(trimethylsilyl)methane (4 g, 10%), as a waxy solid, m.p. 115–120°. (Found: C, 58.8; H, 9.6. $C_{16}H_{31}FSi_3$ calcd.: C, 58.8; H, 9.6%.)

NMR spectra

The ^{19}F NMR spectra were recorded in carbon tetrachloride solution as previously described[2].

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