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SUBSTITUENT EFFECTS ON METHYL PROTON CHEMICAL SHIFTS IN SUBSTITUTED PHENYLTRIMETHYLSILANES AND tert-BUTYLBENZENES

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SUMMARY

The chemical shifts of methyl protons in six mono-substituted phenyltrimethylsilanes and in thirteen tert-butylbenzenes have been determined at infinite dilution in carbon tetrachloride. Electron-releasing groups lead to an increase in shielding of the methyl protons of their trimethylsilyl or tert-butyl groups, whereas electron withdrawing groups decrease this shielding. Good correlations exist between the chemical shifts of the methyl protons and the Hammett σ constants for both series of compounds. The Hammett ρ values were found to be -5.86 and -5.38 (in cps/σ) for phenyltrimethylsilanes and tert-butylbenzenes, respectively.

INTRODUCTION

During the course of an investigation of the structure and reactivity of organosilicon compounds, it became desirable to examine substituent effects on chemical shifts of methyl protons attached to silicon in substituted phenyltrimethylsilanes.

In substituted phenyl derivatives, changes in electron densities at reaction sites connected to a benzene ring carrying substituent(s) in the *meta* and *para* positions can be correlated conveniently with Hammett's equation[1]. Accordingly, there has been a number of studies showing general correlations of chemical shifts of p-^{1}H, ^{19}F, and ^{13}C of benzene ring with the corresponding Hammett σ constants of substituents[2]. Although changes in proton chemical shifts in a side chain of aromatic compounds resulting from effects of ring substituents are relatively small, several examples of good correlations of them with σ of substituents have been reported. Recently, Marcus, Reynolds, and Miller[3] compiled a table of such examples. However, no systematic study has been done on the PMR spectra of substituted phenyltrimethylsilanes, although the chemical shifts of methyl protons attached to a silicon atom in substituted silanes have frequently been discussed in connection with the nature of the bonding in silicon compounds.

In this paper, the data on chemical shifts of methyl protons are reported for a series of *meta-* and *para*-substituted phenyltrimethylsilanes as well as of tert-butylbenzenes for comparison.

EXPERIMENTAL

tert-Butylbenzenes

tert-Butylbenzene and eight derivatives, *p*-hydroxy-, *p*-methyl-, *p*-ethyl-, *m*-hydroxy-, *p*-mercapto-, *p*-bromo-, *m*-carboxyl-, and *p*-carboxyl-tert-butylbenzene, were commercial samples and were used as delivered without further purification. *p*-Nitro-tert-butylbenzene[4] and *p*-tert-butylanisole[5] were prepared according to the reported procedures. By the reaction with diazomethane *p*- and *m*-carbomethoxy-tert-butylbenzenes were prepared from the corresponding acids.

Phenyltrimethylsilanes

(*p*-Methoxyphenyl)-, (*p*-methylphenyl)-, phenyl-, and (*p*-chlorophenyl)trimethylsilane were prepared from trimethylchlorosilane and the corresponding Grignard reagents. (*p*-Nitrophenyl)trimethylsilane was prepared by the procedure of Deans and Eaborn[6]. (*m*-Nitrophenyl)trimethylsilane was isolated from a mixture of nitration of phenyltrimethylsilane by preparative GLC. Physical properties for these compounds agreed closely with those in literatures.

NMR Spectra

All the PMR spectra were taken with a Varian A-60 spectrometer. The calibrations were performed by the usual side-band method by using a Hewlett–Packard HP-200 CD audio-oscillator and an HP-521C electronic counter. The samples were dissolved into carbon tetrachloride containing about 1% tetramethylsilane or cyclohexane as an internal reference to determine the respective chemical shifts of methyl protons at successively diluted concentrations and at ordinary probe temperature. Chemical shifts were determined by extrapolation to infinite dilution.

All the solutions showed no significant dilution shift in the concentration range below 5% (w/v). Solvents effects, if any, were thus minimized by selecting an inert, non-polar solvent, carbon tetrachloride. The data of *m*-tert-butylbenzoic acid is not reliable because of incomplete infinite dilution due to its low solubility, hence this compound is excluded from the consideration

RESULTS AND DISCUSSION

The data on chemical shifts of methyl protons for tert-butylbenzenes and for phenyltrimethylsilanes are presented in Tables 1 and 2, respectively. It is obvious from the data that changes in the chemical shifts are dependent upon the nature of the substituent group although the changes are rather small.

Figs. 1 and 2 show the plot of the chemical shifts of methyl protons for the substituted tert-butylbenzenes *versus* the Hammett σ and σ^0 constants of the corresponding substituents, respectively. Figs. 3 and 4 show the same correlations for phenyltrimethylsilanes. The correlations are tolerably good.

The fact that the Hammett correlation exists indicates that the dependence of the chemical shift of protons of trimethylsilyl group on the nature of substituent is substantially due to the electronic effect of the substituent through silicon, as pointed out for analogous systems involving carbon, oxygen, nitrogen, or sulfur.

TABLE 1

CHEMICAL SHIFTS OF METHYL PROTONS OF tert-BUTYLBENZENES IN CARBON TETRACHLORIDE SOLUTION

Substituent	Chemical shift[a] (cps)	σ^b	σ^0
p-OH	76.6	−0 37	-0.16^c
p-OCH$_3$	76.9	−0.268	-0.100^c
p-CH$_3$	77.2	−0 170	-0.124^c
p-CH$_2$CH$_3$	77.7	−0 151	-0.131^c
H	79.1	0	0
m-OH	77 5	0.121	$0\ 04^d$
p-SH	77.2	0 15	
p-Br	78.1	0 232	$0\ 30^c$
m-COOCH$_3$	81.7	0.37	0.36^d
m-COOH	(82.9)	0 37	
p-COOCH$_3$	80.4	0 385	0.46^d
p-COOH	81 8	0.45	
p-NO$_2$	82 1	0.778	$0\ 82^d$

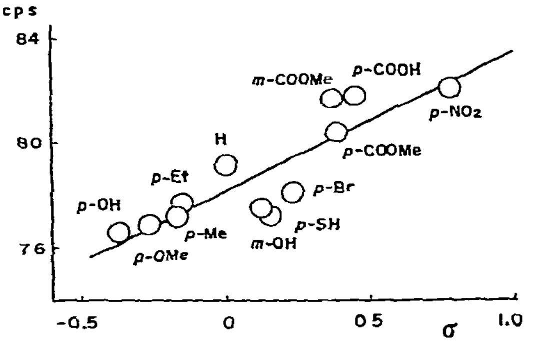
[a] Chemical shifts are given in cps downfield from internal tetramethylsilane at 60 Mc. [b] Hammett substituent constants, σ, based on the ionization of substituted benzoic acids are taken from ref. 15. [c] Taken from ref. 16. [d] Taken from ref. 17.

TABLE 2

CHEMICAL SHIFTS OF METHYL PROTONS OF PHENYLTRIMETHYLSILANES IN CARBON TETRACHLORIDE SOLUTION

Substituent	Chemical shift[a] (cps)	σ^b	σ^0
p-OCH$_3$	−72.5	−0 268	$-0\ 100^c$
p-CH$_3$	−72.1	−0 170	$-0\ 124^c$
H	−70 2	0	0
p-Cl	−71.2	0.227	$0\ 281^c$
m-NO$_2$	−65.6	0.710	$0\ 70^d$
p-NO$_2$	−67.2	0.778	0.82^d

[a] Chemical shifts are given in cps downfield from internal cyclohexane at 60 Mc [b] See ref. 15. [c] See ref. 16 [d] See ref. 17.



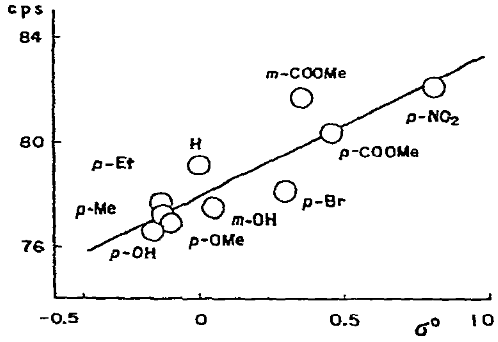
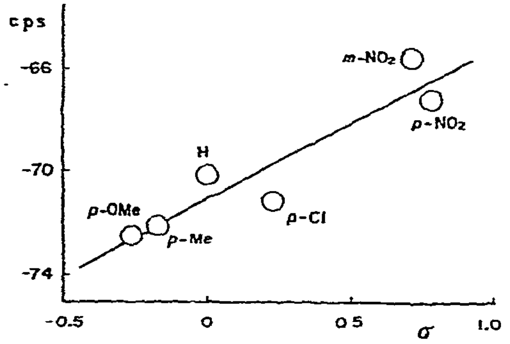


Fig. 1. Correlation of chemical shift (relative to internal TMS) of methyl protons in tert-butylbenzenes with σ.

Fig. 2. Correlation of chemical shift (relative to internal TMS) of methyl protons in tert-butylbenzenes with σ^0.



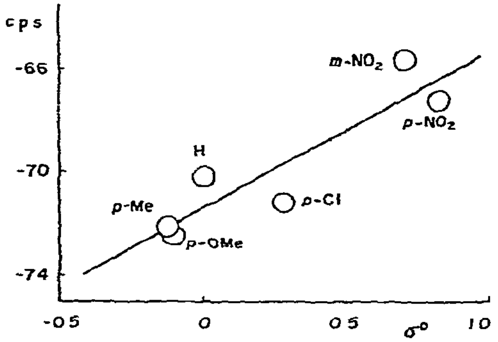


Fig. 3. Correlation of chemical shift (relative to internal cyclohexane) of methyl protons in phenyltrimethylsilanes with σ.

Fig. 4. Correlation of chemical shift (relative to internal cyclohexane) of methyl protons in phenyltrimethylsilanes with σ°.

From Tables 1 and 2, slopes (ρ values) are calculated against σ values by the method of least squares to be −5.38 cps/σ for tert-butylbenzenes and −5.86 cps/σ for phenyltrimethylsilanes. The ρ values were also calculated against σ° values and tabulated in Table 3 together with the standard deviations. For protons not directly bound to benzene ring, an application of σ° constants, which provide a measure of pure inductive effect, seems preferable to correlate the chemical shift changes. However, distinction between σ and σ° is not clear in this case because of limited experi-

TABLE 3

THE ρ VALUES (in cps) AND STANDARD DEVIATIONS (s), FOR PMR CHEMICAL SHIFTS OF PHENYLTRIMETHYLSILANES AND tert-BUTYLBENZENES

Compounds	With σ		With σ°	
	ρ	s	ρ	s
$R{-}C_6H_4Si(CH_3)_3$	−5.86	0.936	−6.14	1.08
$R{-}C_6H_4C(CH_3)_3$	−5.38	0.990	−5.44	0.913

TABLE 4

THE ρ VALUES FOR $R{-}C_6H_4M{-}CH_2{-}H$ OBSERVED FOR PMR CHEMICAL SHIFTS

$R{-}C_6H_4M{-}CH_2{-}H$	Solvent	−ρ (cps/σ)	s^a	n^b	Ref.
$R{-}C_6H_4CH_2{-}CH_2{-}H$	CCl_4	6.76	0.789	9	18
$R{-}C_6H_4O{-}CH_2{-}H$	CCl_4	16.2	0.0442	15	19
$R{-}C_6H_4N{-}(CH_3)CH_2{-}H$	$CDCl_3$	10.10	1.07	15	20
$R{-}C_6H_4S{-}CH_2{-}H$	CCl_4	6.88	1.10	14	3
$R{-}C_6H_4CO{-}CH_2{-}H$	CCl_4	8.34	0.895	8	3
$R{-}C_6H_4C(CH_3)_2{-}CH_2{-}H$	CCl_4	5.38	0.990	12	[c]
$R{-}C_6H_4Si(CH_3)_2{-}CH_2{-}H$	CCl_4	5.86	0.936	6	[c]

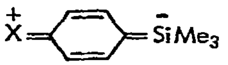
[a] Standard deviation. [b] Number of compounds. c This study.

mental accuracies. As predicted from the similar location of the relevant protons, that is, interposition of two atoms between the protons and a benzene ring, the ρ values for tert-butylbenzenes and phenyltrimethylsilanes are quite similar to each other. In Table 4 are listed the ρ values for the terminal protons of the R–C_6H_4–M–CH_2–H, where R = substituent and M = transmitting atom. These values are within a normal range of magnitude except one for anisoles[3].

However, it is still noteworthy that the ρ value of phenyltrimethylsilanes is comparable in the magnitude with that of tert-butylbenzenes in spite of different natures of both transmitting atoms. In several studies of the PMR spectra of substituted methylsilanes, it has been concluded that the results can be interpreted in terms of p_π–d_π bonding between silicon and electronegative atoms or groups. Thus, Brown and Webster[7] reported that chemical shifts of protons of the series of compounds $(CH_3)_nMCl_{4-n}$ (M = C, Si, Sn; $n = 1$–4) are shifted downfield in a fairly regular manner to lower field as additional chlorine atoms were introduced. This is the expected result, if the electron-withdrawing inductive effect of chlorine atoms were predominant. The shift is, however, less for silicon and tin than for carbon. This result has been explained in terms of p_π–d_π conjugation[8]. Schmidbaur[9] showed the decrease in shielding in $(CH_3)_3SiX$, and the increase in $J(^{13}CH_3)$ of $(^{13}CH_3)SiX(^{12}CH_3)_2$ and in $J(^{29}SiH)$ of $(CH_3)^{29}SiX$ in the following order of X; $CH_3 < F < Cl < Br < I$. The results were also explained by the assumption of a systematic decrease of p_π–d_π interactions between silicon and X.

Dipole-moment studies also suggest the importance of participation of d-orbitals of silicon in variously substituted silanes[10]. Soffer and DeVries[11] summarized the dipole moment data of substituted phenyltrimethylsilanes and concluded that the moment of trimethylsilyl group varies depending upon the nature of the substituents. Thus, electron-supplying groups produce a marked decrease in the algebraic values of the moment of trimethylsilyl group.

We have incidentally found that the data of Soffer and DeVries can be fitted satisfactorily with σ^+ values[12]. Fig. 5 shows the correlation. The applicability of σ^+ constants strongly supports the contribution of p_π–d_π bonding between the electrons of the ring and the d-orbitals of silicon.



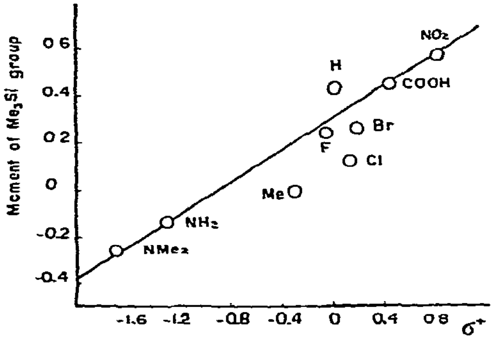


Fig. 5. Correlation of moment of trimethylsilyl group in phenyltrimethylsilanes with σ^+.

One of us has also reported an application of σ^+ constants to the reaction of substituted phenylpentamethyldisilanes with perbenzoic acid[13]. Effects of substituents on desilylation of $XC_6H_4SiMe_3$ compounds are known to correlate reasonably well with σ^+, and the recent suggestion[14] that the effects of the substituents on the stabilization of the initial state by p_π–d_π bonding would be expected to correlate with σ^+ is in accord with our observations.

The application of the σ^+ constants[12] for the present data of phenyltrimethylsilanes does not improve the correlation ($s = 1.07$), but affords a smaller ρ in absolute value, -4.30 cps. This fact itself is consistent with the observations cited above[7,8], suggesting some contribution of p_π–d_π conjugation in phenyltrimethylsilanes.

In this connection, we are interested in PMR spectra of substituted phenylpentamethyldisilanes and 1,2-diphenyltetramethyldisilanes to check the efficiency of the transmission of polar effect through a silicon–silicon bond. The results will be presented in a forthcoming paper.

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