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The σ Constants of Substituents Containing Silicon Subgroup Elements

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The general aspects of the correlation equations linking the structure and reactivity of compounds of silicon subgroup elements are examined. Taking into account the specific features of the intramolecular interactions in the organoelemental compounds, the σ constants of substituents containing silicon, germanium, and tin atoms have been analysed.
The bibliography includes 138 references.

CONTENTS

I. Introduction 846
II. Methods for the determination of the σ constants of organoelemental Group IVB substituents 847
III. Analysis of the σ constants 848

I. INTRODUCTION

The search for and investigation of the relations between the chemical structure of molecules and their reactivity is one of the fundamental problems in chemistry. The most significant advances in physical organic chemistry, achieved in this field during the last few decades, are associated with the use of the so called correlation equations based on the principle of the linear relation between the free energy changes (LFE).[1-18] The essential feature of the LFE principle is as follows.[1,4] If the molecule consists of the reacting group A and the non-reacting substituent X, then (a) the change in the logarithm of the rate constant k induced by the influence of X is linearly related to the change in the logarithm of the equilibrium constant K for the same reaction [Eqn.(1)]:

$$\delta_X \lg k_1 = a_1 \delta_X \lg K, \quad (1)$$

and (b) the changes in lg k and lg K induced by the influence of X, for a reaction I with participation of the group A_1 are linearly related to the corresponding changes for another reaction II with participation of the same group A_1 and also for reaction II with participation of another group A_2:

$$\delta_X \lg k_1 = b_{12} \delta_X \lg k_2 = a_2 b_{12} \delta_X \lg K_2, \quad (2)$$

where k_1 and K_1 refer to reaction I and k_2 and K_2 refer to reaction II, a_1, a_2, and b_{12} are independent of X but do depend on the reactions considered, and δ_X is an operator reflecting the influence of the change in the substituent X on k and K.

Experimental data on the basis of which the LFE principle has been formulated have been analysed in a number of studies.[1,5,6,9,18,19] By comparing the ionisation constants of substituted benzoic acids K_a with the constant for the unsubstituted acid K_0 in water at 25 °C, it is possible to obtain from Eqn.(1) the constants σ characterising the substituents

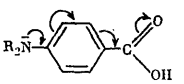
$$\sigma = \lg K_a - \lg K_0 \quad (3)$$

and then the familiar Hammett equation:[1]

$$\lg k - \lg k_0 = \rho\sigma, \quad (4)$$

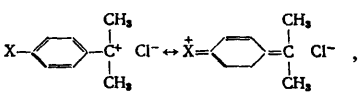
The reaction constant ρ in Eqn.(4) characterises the sensitivity of the reaction to the electronic effects of the substituents compared with the constant 1.00 adopted for the dissociation of benzoic acids.

Thus the first method of determining the Hammett σ_m and σ_p constants for *meta*- and *para*-substituents (including organoelemental substituents) in the benzene ring involves the study of the ionisation constants of benzoic acids or the rate constants k for the reaction involving the side chain of benzene derivatives. However, this procedure cannot be used to calculate the σ constants for *ortho*-substituents, since their influence on the reaction centre is determined not only by electronic effects but also by steric effects. An important characteristic feature of the Hammett σ_p constants (in contrast to the σ_m constants) for π-electron-donating substituents (the $+M$ types of substituents NR_2, OR, and $CH_2.EP_3$, where E is a silicon subgroup element) is their dependence on the direct polar conjugation between these substituents and their reaction centres, which can be described, for example, by the following schemes:



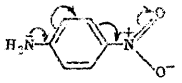
Therefore, in order to estimate the degree of interaction between the substituent and the ring, it is essential to disrupt in such cases the direct polar conjugation system. For example, one can use data for the ionisation constants of the acids $XC_6H_4CH_2COOH$. Similar procedures have been used in a number of investigations.[20-24]

As a result, the constants σ^0 have been obtained for $+M$ type *para*-substituents.[11,13] The σ_p^+ constants have been introduced[15,25] to characterise *para*-substituents of the $+M$ type which are involved in direct polar conjugation with the electron-deficient reaction centre. Thus the stabilisation of the transition state in the reaction involving the solvolysis of cumenyl chlorides by substituents X of this kind (for example, the group CH_3O), i.e.

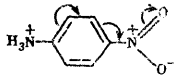


is associated mainly with the enhancement of the electron-donating properties of the group X, i.e. with the increase of the absolute values of the constants σ_p^+ for these substituents compared with the Hammett σ_p constants. The constants σ_m^+ and σ_m for the *meta*-substituents are virtually identical.

In order to characterise the electron-accepting substituents of the $-M$ type (NO_2, CN, CHO, etc.), which are involved in direct polar conjugation with the reaction centre, σ_p^- constants have been introduced.[1,18,19] The enhancement of the electron-accepting properties of the NO_2 group as a substituent ($\sigma_p^- > \sigma_p$), manifested in the ionisation of aniline derivatives, can be accounted for by direct polar conjugation:



which leads to a decrease of the basicity of *p*-nitroaniline. There is no direct polar conjugation in the *p*-nitroanilinium ion:[10]



The constants σ_m^- and σ_m for *meta*-substituents are virtually identical. The σ constants discussed above are represented by the sum of the inductive (σ_I) and resonance (σ_R) contributions: $\sigma = \sigma_I + \sigma_R$. In order to estimate the inductive effect and hence resolve σ into its components, methods based on the LFE principle and the hypothesis that the free energy of activation can be represented by the sum of independent contributions due to the inductive, resonance, and steric effects have been developed.[2] For quantitative estimates of the inductive effects, the following factors were studied: the ionisation of bicyclo[2.2.2]octane-1-carboxylic acids;[11,26,27] the hydrolysis of the aliphatic acid esters XCH_2COOR;[2,3] the ionisation of substituted aliphatic acids;[28] the reactivity of aromatic compounds;[29,30] the chemical shifts of the signals of the ^{19}F nuclei in the NMR spectra of *meta*-substituted fluorobenzenes.[16,31] The constants σ_I, or quantities proportional to them, were obtained in the above studies for a large number of substituents, including those containing silicon subgroup elements.

The problem of the quantitative estimation of the inductive effect has been discussed in greater detail in a number of studies,[9-12,19] in which the possibility of resolving the σ constants into the inductive (σ_I) and resonance (σ_R) components was also analysed:

$$\sigma_R = \sigma_p - \sigma_I , \quad (5)$$

$$\sigma_R^0 = \sigma_p^0 - \sigma_I , \quad (6)$$

$$\sigma_R^+ = \sigma_p^+ - \sigma_I , \quad (7)$$

$$\sigma_R^- = \sigma_p^- - \sigma_I . \quad (8)$$

It has been emphasised[11] that the resonance constants of type σ_R, determined from Eqns.(5)–(8), are least accurate, since they depend on the errors in the determination of the constants σ_p and σ_I. The constants σ_R^0 are calculated from NMR and IR spectroscopic data.[16,31-33] A series of physicochemical and physical methods for the determination of the σ constants of substituents have been described in the review literature[11-13] and certain methods will be considered below.

We may note that, despite the wide variety of methods for the determination of σ constants and the use of different scales for the latter, when account is taken of the electronic effects of substituents, only the constants defined by Eqns.(5)–(8) are usually employed. This group of relations does not include the constants for complex aromatic systems and *ortho*-substituents and also constants characterising the steric effects of substituents. It is clear from the foregoing that the correlation equations relating the chemical structure and reactivity of compounds, based on the LFE principle, are empirical. For this reason, since the publication of the first[1] and subsequent studies[34,35] (see also the relevant reviews[8,12,19,36,37]), attempts have been frequently made to secure a justification of the system of Hammett–Taft constants. As early as the 1950's, it was established[34,35] with the aid of approximate quantum-chemical methods that the σ constants of substituents in the benzene ring are proportional to the change, induced by these substituents, in electron density on the carbon atoms in the *meta*- and *para*-positions in the ring and hence also on the reaction centre linked to these carbon atoms. On the one hand, these studies fundamentally clarified the physical significance of the σ constants, and, on the other hand, they served as the basis for an enormous number of investigations devoted to the analysis of the relations between the σ constants and various physical properties of organic and organoelemental compounds.

The results of some of these studies, which can be treated as sources of useful information about the σ constants of substituents incorporating the silicon subgroup elements and also about the specific features of the intermolecular interactions in organoelemental compounds of Group IVB elements, will be considered below in greater detail. In recent years, additional data, confirming the interpretation of the physical significance of the σ constants formulated in the 1950's, have been obtained with the aid of modern non-empirical quantum-chemical methods. It has been established for benzene derivatives[37,38] and ethylene and acetylene derivatives[39,40] that the π-electronic charge on the substituent is linearly related to the corresponding σ_R^0 constants.

However, the theoretical justification of both the correlation equations and of the LFE principle itself is inadequate. Furthermore, there exist a number of experimental limitations. For this reason, the σ constants can be used only with a certain degree of caution. The present review does not discuss the contradictions between the LFE principle and Hammond's postulate[6,9,10] and the influence of the field effects and bond polarisation on the σ_I constants is not dealt with in detail.[41,42] We may note that, in choosing the most reliable values of the σ constants (see below), account was taken of the dependence of the constant σ on temperature,[43] the solvent, the type of conducting system, and the nature of the reaction centre. Furthermore the hyperconjugation effects,[44] which are more important for organoelemental compounds than for organic compounds, and also the specific features of the steric effects in compounds of silicon subgroup elements[45] were taken into account.

It is essential to note that the limited amount of the available literature data and also in many instances the inadequate reliability (see below) of some of the σ constants preclude so far the formulation of reliable (statistical) values[11] for these quantities referring to substituents containing silicon subgroup elements. Therefore, our choice of the most and least reliable σ constants was made taking into account the views of the authors of the original publications and our own. As literature data accumulate and methods for the determination of σ constants develop and improve, a correction of many of their values will become inevitable.

II. METHODS FOR THE DETERMINATION OF THE σ CONSTANTS OF ORGANOELEMENTAL GROUP IVB SUBSTITUENTS

The methods for the determination of the σ constants of organoelemental substituents can be divided into two groups. The first group includes the physical (mainly spectroscopic) methods for the determination of σ constants. Different versions of NMR,[16,31,44-59] the IR spectroscopy of individual

compounds and molecular complexes,[32,33,60–64] the UV spectroscopy of charge-transfer complexes (CTC),[38,65–67] the ionisation potentials[66] and dipole moments[68] of compounds with organoelemental substituents, as well as many other less common physical methods have been employed. The second group includes methods for the determination of the σ constants of organoelemental compounds based on the study of the chemical properties of various compounds containing such substituents.

Overall, the use of physical methods is preferable. The errors of the determination associated with the possibility of the involvement in the reaction of not only the main reaction centre but also of the organoelemental substituents ER_3 (E is a silicon subgroup element), whose E atom may be solvated in consequence of the high reactivity of organoelemental compounds and E–C bonds may be cleaved, are reduced to a minimum in this instance. The values of σ found without a sufficiently correct estimation of such complicating factors cannot therefore be regarded as fully reliable.

The Tables presented below indicate, together with the values of the σ constants, also the methods of their determination and (in the footnotes to the Tables) a brief description of the characteristics of the methods. In the Tables, the most reliable σ constants are included in square brackets and the least reliable ones are in round brackets. If experimental literature data were used to calculate the σ constants, the number of the corresponding literature reference in the Table is followed by an asterisk.

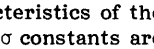
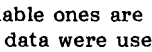
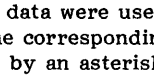
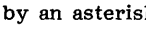
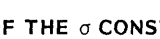
III. ANALYSIS OF THE σ CONSTANTS

The σ constants are a source of quantitative information about the electronic effects of substituents containing the elements E. The tasks dealt with in this Section are a systematic arrangement and analysis of such information and also the selection (in accordance with the principles indicated above) of the most and least reliable values of σ.

Table 1. The constants σ_I of silicon-containing substituents.

Substituent	σ_I	Method of determination	Refs.
SiH_3	−0.05	NMR-C-B	[53]
SiH_3	−0.04	NMR-C-B	[80]
SiH_3	+0.01	NMR-F-B	[81]
$SiH(CH_3)_2$	−0.02	NMR-F-B	[81]
$Si(CH_3)_3$	−0.24	NMR-C-B	[53]
$Si(CH_3)_3$	[−0.15]	IR-SiH	[64]
$Si(CH_3)_3$	−0.15	NMR-C-B	[80]
$Si(CH_3)_3$	−0.15	X-1	[82]
$Si(CH_3)_3$	−0.13	X-2	[28]
$Si(CH_3)_3$	−0.12	X	[2]
$Si(CH_3)_3$	−0.11	IR-M-H	[62]
$Si(CH_3)_3$	−0.10	X	[8]
$Si(CH_3)_3$	−0.10	NMR-C-B	[17]
$Si(CH_3)_3$	−0.09	NMR-C-S, NMR-H-S	[57]
$Si(CH_3)_3$	−0.04	NMR-F-B	[81]
$Si(CH_3)_3$	(−0.03)	NMR-F-B	[46]
$Si(CH_3)_3$	+0.02	NMR-F-N	[46]
$Si(C_2H_5)_3$	−0.18	IR-SiH	[64]
$Si(C_6H_5)_3$	−0.18	IR-M-H	[62]
$Si(C_6H_5)_3$	−0.24	NMR-C-B	[53]
$Si(n\text{-}C_3H_7)_3$	−0.27	NMR-C-B	[53]
$Si(iso\text{-}C_4H_9)_3$	−0.36	NMR-C-B	[53]
$Si(CH_3)_2CH{=}CH_2$	−0.03	NMR-F-B	[81*]
$Si(CH{=}CH_2)_3$	−0.19	NMR-C-B	[53]
$Si(CH_3)_2C_3H_5$	+0 02	NMR-F-B	[81]
$Si(CH_3)(C_6H_5)_2$	+0.07	NMR-F-B	[81]
$Si(C_6H_5)_3$	(−0.17)	NMR-C-B	[53]
$Si(C_6H_5)_3$	−0.15	NMR-C-B	[80]
$Si(C_6H_5)_3$	−0.19	IR-M-H	[62]
$Si(C_6H_5)_3$	(+0.13)	NMR-F-B	[81]
$Si(C{=}CH)_3$	+0.08	NMR-C-B	[53]
$Si[N(CH_3)_2]_3$	(−0.20)	NMR-C-B	[53]
$Si[N(CH_3)_2]_3$	−0.11	NMR-C-B	[80]

Table 1 (continued).

Substituent	σ_I	Method of determination	Refs.
$Si[N(CH_3)_2]_3$	−0.04	NMR-F-B	[81]
$Si(CH_3)(C_6H_5)OCH_3$	−0.22	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OC_2H_5$	−0.25	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OC_3H_7$	−0.25	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH(CH_3)_2$	−0.31	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OC_4H_9\text{-}n$	−0.25	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OC_4H_9\text{-}iso$	−0.25	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OC_4H_9\text{-}s$	−0.31	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH_2C_6H_5$	−0.24	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH_2CH_2Cl$	−0.30	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH_2C{\equiv}CH$	−0.30	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH_2CH_2CH_2CN$	−0.18	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH_2CF_3$	−0.06	NMR-C-B	[83]
$Si(OH)_3$	−0.22	NMR-C-B	[53]
$Si(OCH_3)_3$	(−0.07)	NMR-C-B	[53]
$Si(OCH_3)_3$	0.00	NMR-F-B	[81]
$Si(OCH_3)_3$	+0.01	NMR-C-B	[80]
$Si(OCH_3)_3$	+0.01	NMR-C-B	[52]
$Si(OC_2H_5)_3$	(−0.18)	NMR-C-B	[52]
$Si(OC_2H_5)_3$	−0.13	NMR-C-B	[53]
$Si(OC_2H_5)_3$	−0.08	NMR-C-B	[80]
$Si(OC_2H_5)_3$	−0.04	NMR-F-B	[81]
$Si(OC_3H_7\text{-}n)_3$	−0.19	NMR-C-B	[80]
$Si(OC_3H_7\text{-}iso)_3$	−0.24	NMR-C-B	[53]
$Si(OC_3H_7\text{-}iso)_3$	−0.16	NMR-C-B	[52]
$Si[OC(CH_3)_3]_3$	(−0.43)	NMR-C-B	[53]
$Si(OC_6H_5)_3$	(−0.14)	NMR-C-B	[80]
$Si(OC_6H_5)_3$	−0.05	NMR-C-B	[53]
$Si(CH_3)_2OSi(CH_3)_3$	−0.13	X-2	[28]
$Si[OSi(CH_3)_3]_3$	−0.29	NMR-C-B	[53]
	(−0.56)	NMR-C-B	[53]
	−0.40	NMR-C-B	[80]
	−0.40	NMR-C-B	[52]
	−0.2	Ph	[84]
	−0.2	Ph	[85]
	−0.15÷−0.2	Ph	[86]
$Si(OCH_2CH_2NH_2)_3$	−0.10	NMR-C-B	[53]
$Si(OCOCH_3)_3$	+0.07	NMR-C-B	[53]
$Si(OCOCF_3)_3$	+0.76	NMR-C-B	[53]
$Si(SC_2H_5)_3$	+0.06	NMR-C-B	[53]
$Si(CH_3)_2F$	+0.08	NMR-F-B	[81]
SiF_3	+0.42	NMR-F-B	[81]
SiF_3	+0.43	NMR-C-B	[80]
SiF_3	+0.43	NMR-C-B	[53]
SiF_3	(+0.57)	NMR-M-H	[62]
$Si(CH_3)_2Cl$	(+0.05)	IR-M-H	[62]
$Si(CH_3)_2Cl$	+0.11	NMR-F-B	[81]
$Si(CH_3)Cl_2$	+0.21	IR-M-H	[62]
$Si(CH_3)Cl_2$	+0.24	NMR-F-B	[81]
$SiCl_3$	(+0.15)	NMR-C-B	[80]
$SiCl_3$	+0.21	NMR-C-B	[53]
$SiCl_3$	+0.36	IR-M-H	[62]
$SiCl_3$	[+0.39]	NMR-F-B	[81*]
$Si(CH_3)ClBr$	+0.25	NMR-F-B	[81*]
$SiBr_3$	(−0.09)	NMR-C-B	[80]
$SiBr_3$	+0.08	NMR-C-B	[53]
$SiBr_3$	+0.29	IR-M-H	[62]
$SiBr_3$	[+0.39]	NMR-F-B	[81]
$Si(CH_3)_2CH_2CH_2CF_3$	+0.08	NMR-F-B	[81*]
$Si(CH_3)_2CH_2Cl$	+0.06	NMR-F-B	[81*]
$CH_2Si(CH_3)_3$	−0.10	NMR-C-S, NMR-H-S	[57]
$CH_2Si(CH_3)_3$	−0.08	NMR-F-B	[87]
$CH_2Si(CH_3)_3$	−0.07	NMR-F-B	[16]
$CH_2Si(CH_3)_3$	−0.06	NMR-F-B	[88]
$CH_2Si(CH_3)_3$	[−0.05]	IR-SiH, Ph	[89]
$CH_2Si(CH_3)_3$	−0.05	X-2	[28]
$CH_2Si(CH_3)_3$	−0.04	X	[2]
$CH_2Si(CH_3)_3$	(+0.01)	NMR-F-N	[88]
$CH_2Si(C_6H_5)_3$	+0.01	NMR-F-N	[88]
$CH_2Si(OCH_3)_3$	−0.10	NMR-F-B	[90]
	−0.36	NMR-F-B	[90]
$CH_3CH_2Si(CH_3)_3$	−0.04	X-2	[28]
$CH_3CH_2Si(CH_3)_3$	−0.03	IR-SiH, Ph	[89]
$CB_{10}H_{10}CSi(CH_3)_2H$	+0.30÷+0.35	Ph	[91]
$C_6H_5Si(CH_3)_2H$	+0.07÷+0.12	Ph	[91]
	+0.10÷+0.15	Ph	[91]
$COOCH_2Si(OC_2H_5)_3$	+0.10	NMR-C-B	[92]
	−0.05	NMR-C-B	[92]
$COOCH_2SiF_3$	+0.61	NMR-C-B	[92]
$NHSi(CH_3)_3$	+0.09	NMR-C-B	[93]
$OSi(CH_3)_3$	+0.05	NMR-C-B	[93]
$-O[Si(CH_3)_2O]_3-$	~+0.3	Ph	[93]

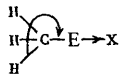
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Table 1 (continued).

Notation: NMR-C-B—analysis of the chemical shifts of the signals of the *meta*- and *para*-carbon atoms in the ^{13}C-derivatives of benzene. The specific form of the relations between the chemical shifts or their differences and the constants σ, σ_R^0, and ρ^* has been indicated in a series of communications;[44-55] NMR-F-B—analysis of the chemical shifts δ in the ^{19}F NMR spectra of the *meta*-substituted (δ_m) and *para*-substituted (δ_p) fluorobenzenes. The most widely used is the method of Taft and co-workers[16,31] using the relations $\delta_m = -7.1\ \sigma_I + 0.60$ and $\delta_p = 7.1\ \sigma_I - 29.5\ \sigma_R^0 + 0.60$. The chemical shifts are measured relative to the shift of fluorobenzene for solutions in chloroform; IR-SiH—analysis of the stretching vibration frequency of the Si–H bond in the IR spectra of silane derivatives;[64] X-1—the study of the p*K* of substituted benzoic acids;[69,70] X-2—the study of the p*K* of substituted acetic acids;[28] X—on the basis of reactivity data but using less common methods; IR-M-H—analysis of the vibrational spectra and force constants of the M–H bonds (M = silicon subgroup element);[62] NMR-C-S—analysis of the chemical shifts of the signals of the carbon atoms in the vinyl group and the benzene ring in the ^{13}C NMR spectra of 4-substituted styrenes $XC_6H_4.CH{=}CH_2$;[56,57] NMR-H-S—analysis of the chemical shifts in the ^1H NMR spectra of 4-substituted styrenes $XC_6H_4.CH{=}CH_2$;[56,57] NMR-F-N—analysis of the chemical shifts in the ^{19}F NMR spectra of β-fluoronaphthalenes;[46] Ph—on the basis of physical research methods but using less common procedures.

1. The Inductive Constants σ_I

The constants σ_I characterise quantitatively the inductive effects of the substituents EX_3, where X are various groups. The changes in the values of σ_I for EX_3 and CX_3 with fixed X and variable E reflect the changes in the electronegativities of the Group IV elements E. However, the electronegativities of the Group IV elements E have not been generally accepted. Thus, according to Marrot and Maire,[75] the electronegativities of the elements E and groups of the type $E(C_2H_5)_nCl_{3-n}$ diminish in the sequence C > Ge > Si > Sn. However, according to other data,[76] the character in the changes in the electronegativities is different: C(2.55) > Pb(2.33) > Ge(2.01) > Sn(1.96) > Si(1.90) (the numerical values are given in brackets). The differences between these two series are caused not only by the different accuracies of the methods for the determination of electronegativity but also by more profound causes.[44,77] One of these is the effect (together with the inductive effect) of the σ,σ conjugation, whose influence increases in the sequence C < Si < Ge < Sn < Pb and depends on the type of substituents linked to E. For this reason, both inductive and hyperconjugation contributions are significant for the constants of certain substituents EX_3.[78] We may note that, in systems of the type



the contribution of σ,σ conjugation increases with the increase of the atomic number of E and with enhancement of the electron-accepting properties of X.[44]

The second cause is the conjugation within the substituent EX_3, which influences its electronegativity. If X is an atom or fragment with unshared electron pairs or an αβ-unsaturated hydrocarbon group, then, as will be shown in greater detail in the analysis of the constants σ_R, resonance effects arise. The role of the latter increases with increase of the σ_R for the groups X and also in the sequence Sn < Ge < Si and with increase of the effective positive charge on E, which depends on the fourth substituent linked to E.[79]

Table 2. The constants σ_I of germanium-, tin-, and lead-containing substituents.

Substituent	σ_I	Method of determination	Refs.
$Ge(CH_3)_3$	−0.12	IR-M-H	[62]
$Ge(CH_3)_3$	[−0.11]	IR-SiH, Ph	[89]
$Ge(CH_3)_3$	−0.10	NMR-C-S, NMR-H-S	[57]
$Ge(CH_3)_3$	−0.01	X	[46]
$Ge(CH_3)_3$	+0.06	NMR-F-N	[46]
$Ge(C_6H_5)_3$	−0.19	IR-M-H	[62]
$Ge(C_2H_5)_3$	−0.13	IR-SiH	[64]
$Ge(OCH_3)_3$	+0.37	NMR-C-B	[51]
$Ge(OC_2H_5)_3$	+0 29	NMR-C-B	[51]
$Ge(OC_3H_{7\text{-iso}})_3$	+0.19	NMR-C-B	[51]
$Ge(OC_4H_{9\text{-t}})_3$	−0.01	NMR-C-B	[51]
$Ge(OCH_2CH_2)_3N$	−0.23	NMR-C-B	[51]
GeF_3	+0.74	NMR-F-B	[94]
$GeCl_3$	+0.63	NMR-F-B	[94]
$GeBr_3$	+0.59	NMR-F-B	[94]
$CH_3Ge(CH_3)_3$	−0.10	NMR-C-S, NMR-H-S	[57]
$CH_3Ge(CH_3)_3$	[−0.04]	IR-SiH, Ph	[89]
$CH_3Ge(CH_3)_3$	−0.04	NMR-F-B	[88]
$CH_3Ge(CH_3)_3$	(+0.02)	NMR-F-B	[88]
$CH_3Ge(C_2H_5)_3$	−0.05	IR-SiH, Ph	[89]
$CH_3Ge(C_6H_5)_3$	+0.02	NMR-F-N	[88]
$Sn(CH_3)_3$	−0.15	IR-M-H	[62]
$Sn(CH_3)_3$	[−0.13]	IR-SiH, Ph	[89]
$Sn(CH_3)_3$	−0.11	NMR-C-S, NMR-H-S	[57]
$Sn(CH_3)_3$	0 0	X	[46]
$Sn(CH_3)_3$	+0.01	NMR-F-B	[95]
$Sn(CH_3)_3$	(+0.09)	NMR-F-N	[46]
$Sn(C_2H_5)_3$	+0.02	NMR-F-B	[95]
$Sn(n\text{-}C_4H_9)_3$	+0.02	NMR-F-B	[95]
$Sn(C_6H_5)_3$	+0.18	NMR-F-B	[96, 97]
$Sn(C_6H_5)_3$	+0.15 ($CDCl_3$)	NMR-F-B	[95]
$Sn(C_6H_5)_3$	+0.20 (CCl_4, $(CD_3)_2CO$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}4)_3$	+0.25 ($(CD_3)_2CO$, $CDCl_3$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}4)_3$	+0.28 (CCl_4)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	+0.28 ($CDCl_3$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	+0.26 ($(CD_3)_2CO$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	+0.33 (CCl_4)	NMR-F-B	[95]
$SnCl_3$	+0.82 ($CDCl_3$)	NMR-F-B	[95]
$SnCl_3$	+0.42 ($(CD_3)_2CO$)	NMR-F-B	[95]
$SnCl_3$	+0.80 (CCl_4)	NMR-F-B	[95]
$CH_3Sn(CH_3)_3$	−0.11	NMR-C-S, NMR-H-S	[57]
$CH_3Sn(CH_3)_3$	[−0.05]	IR-SiH, Ph	[89]
$CH_3Sn(CH_3)_3$	−0.04	NMR-F-B	[88]
$CH_3Sn(CH_3)_3$	(+0.05)	NMR-F-N	[88]
$CH_3Sn(C_6H_5)_3$	0.0	NMR-F-B	[96, 97]
$CH_3Sn(C_6H_5)_3$	+0.07	NMR-F-N	[88]
$CH_2CH_2Sn(CH_3)_3$	−0.02	IR-SiH, Ph	[89]
$OSn(C_2H_5)_3$	+0.08	NMR- F-B	[98, 99]
$OSn(C_6H_5)_3$	+0.10	NMR-F-B	[99]
$SSn(C_2H_5)_3$	+0.23	NMR-F-B	[100]
$SSn(C_6H_5)_3$	+0.11	NMR-F-B	[97, 99]
$Pb(CH_3)_3$	−0.12	NMR-C-S, NMR-H-S	[57]
$Pb(CH_3)_3$	+0.03	X	[46]
$Pb(CH_3)_3$	+0.12	NMR-F-N	[46]
$Pb(C_6H_5)_3$	+0.22	NMR-F-B	[96, 97]
$CH_3Pb(CH_3)_3$	−0.12	NMR-C-S, NMR-H-S	[57]
$CH_3Pb(CH_3)_3$	[−0.04]	NMR-F-B	[88]
$CH_3Pb(CH_3)_3$	+0.06	NMR-F-N	[88]
$CH_3Pb(C_6H_5)_3$	0.0	NMR-F-B	[96, 97]
$CH_3Pb(C_6H_5)_3$	+0.07	NMR-F-N	[88]
$OPb(C_6H_5)_3$	+0.06	NMR-F-B	[99]
$SPb(C_6H_5)_3$	0.00	NMR-F-B	[99]

Notation: The solvents are indicated in brackets; for the significance of the designation of the methods, see the footnote to Table 1.

Ultimately the effective charge on the atom E changes in a complex manner and the electronegativity of the group EX_3 depends not only on the atom E but also on the type of substituent X and the organoelemental molecule as a whole. For this reason, the constants σ_I for organoelemental substituents (Tables 1 and 2) can be regarded as constants only by convention. As experimental data accumulate, a subsystem of σ_I constants will apparently be created for each comparatively narrow type of compounds.

On the basis of the data in Tables 1 and 2, one may reach several conclusions of a general character. For a fixed atom E, the constants σ_I of substituents of the type EX_3 vary in parallel with the enhancement of the electron-accepting properties of the group X: Alk < C_6H_5 < OAlk < Br < Cl < F. A higher value of σ_I corresponds to the substituent CH_2EX_3 than to the substituent EX_3. This is associated primarily with the electronegativity of the carbon atom, which exceeds the electronegativity of other Group IVB elements, which also agrees with the higher values of σ_I for $CAlk_3$ compared with $EAlk_3$. For example, the values of σ_I for $E(CH_3)_3$ are −0.07 (E = C[11]), −0.15 (E = Si), −0.11 (E = Ge), and −0.13 (E = Sn). However, constants σ_I which in many cases appreciably exceed the analogous values for carbon compounds correspond to the substituents $EHal_3$; 0.41–0.45 (CF_3); 0.30–0.41 (CCl_3); 0.26 (CBr_3).[11] We may note that, among the constants σ_I for halogenoalkyl groups, appreciable anomalies are also observed which cannot be accounted for solely from the standpoint of electronegativity. It is believed[101] that these anomalies are caused by the field effect, which has also been confirmed by data[42] indicating the predominance of the field effect over electronegativity for substituents of this type.

Smaller σ_I constants correspond to the silantranyl and germantranyl groups than to the corresponding trialkoxy-derivatives, which may be associated with the decrease of the electronegativity of the central atom owing to the partial electron transfer to this atom from nitrogen. The constants σ_I for the substituents $OEAlk_3$ and $SSnAlk_3$ are lower than the corresponding values for the analogous carbon derivatives apparently mainly owing to the more pronounced electron-donating properties of the groups $EAlk_3$ (compared with alkyl groups) (the constants σ_I for OAlk and SAlk are 0.3–0.2).[11]

2. The Resonance Constants σ_R^0

The constants σ_R^0 characterise the ability of substituents to be conjugated with n-donor groups or π-systems. Being involved in conjugation, the substituents EX_3 are electron donors (negative σ_R^0) (Tables 3 and 4). In this respect, the substituents EX_3 differ sharply from their carbon analogues CX_3. On the other hand, weakly electron-donating properties, arising in consequence of hyperconjugation, are typical for the substituents CX_3. Electronegative groups X can exhibit weak electron accepting properties.

The traditional interpretation of the resonance electron-accepting properties of EX_3 is based on the idea that the unoccupied *nd* orbitals of the atoms E participate in conjugation with *n*- or π-donor fragments D in compounds of the type $D-EX_3$ [(*p*–*d*)π interaction]. This problem has been discussed in greater detail by Egorochkin and Khorshev.[79] Clearly the resonance interactions between the fragments D and EX_3 are determined both by the electron-donating properties of D and the electron-accepting properties of EX_3. Therefore, by fixing the fragment EX_3 and varying the fragment D, it is possible to vary the degrees of resonance interactions between EX_3 and D. It follows from the general theory[111] and experimental studies on organosilicon and organogermanium compounds[77,79] that the character of the variation of the degree of the (p–*d*)π interaction between the fixed fragment EX_3 and the variable fragment D is determined by the σ_R constants of D. On the other hand, if both fragments EX_3 and D, vary, then the effective positive charge on the atom E becomes decisive. The constants σ_R^0 can therefore be regarded as characteristics of substituents of type EX_3 only for a fixed fragment D; an analogous situation obtains also for the constants σ_I.

Table 3. The constants σ_R^0 of silicon-containing substituents.

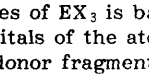
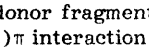
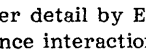
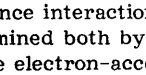
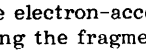
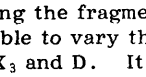
Substituent	σ_R^0	Method of determination	Refs.
SiH_3	+0.08	NMR-C-B	[53, 80]
SiH_3	+0.09	NMR-F-B	[81]
$SiH(CH_3)_2$	+0.06	NMR-F-B	[81]
$Si(CH_3)_3$	+0.02	IR-B	[102]
$Si(CH_3)_3$	+0.03	NMR-C-S1	[50]
$Si(CH_3)_3$	+0.04	NMR-F-B	[46]
$Si(CH_3)_3$	+0.04	X	[103]
$Si(CH_3)_3$	+0.04	NMR-C-B	[17]
$Si(CH_3)_3$	+0.04	Ph	[104]
$Si(CH_3)_3$	+0.04	IR-HB-A	[63]
$Si(CH_3)_3$	+0.05	NMR-C-B	[50, 53]
$Si(CH_3)_3$	[+0.05]	NMR-F-B	[81]
$Si(CH_3)_3$	+0.06	Ph	[8]
$Si(CH_3)_3$	+0.07	NMR-C-S, NMR-H-S	[57]
$Si(CH_3)_3$	+0.09	IR-B	[105]
$Si(CH_3)_3$	+0.10	NMR-C-B	[80]
$Si(CH_3)_3$	+0.04	IR-HB-A	[63]
$Si(C_2H_5)_3$	+0.05	NMR-C-B	[50, 53]
$Si(n\text{-}C_3H_7)_3$	+0.05	NMR-C-B	[53]
$Si(iso\text{-}C_4H_9)_3$	+0.05	NMR-C-B	[53]
$Si(t\text{-}C_4H_9)_3$	+0.05	NMR-C-B	[50]
$Si(CH_3)_2CH{=}CH_2$	+0.05	NMR-F-B	[81]
$Si(CH{=}CH_2)_3$	+0.08	NMR-C-B	[53]
$Si(C{\equiv}CH)_3$	+0.14	NMR-C-B	[50, 53]
$Si(CH_3)_2C_6H_5$	+0.05	NMR-F-B	[81]
$Si(CH_3)(C_6H_5)_2$	+0.06	NMR-F-B	[81]
$Si(C_6H_5)_3$	(0.66)	Ph	[106]
$Si(C_6H_5)_3$	0.0	IR-B	[107]
$Si(C_6H_5)_3$	[+0.06]	NMR-F-B	[81]
$Si(C_6H_5)_3$	+0.08	NMR-C-B	[80]
$Si(C_6H_5)_3$	+0.09	NMR-C-B	[50, 53]
$Si[N(CH_3)_2]_3$	0.0	NMR-F-B	[81]
$Si[N(CH_3)_2]_3$	+0.11	NMR-C-B	[50, 53, 80]
$Si(OH)_3$	+0.14	NMR-C-B	[53]
$Si(CH_3)(C_6H_5)(OCH_3)$	+0.10	NMR-C-B	[83]
$Si(OCH_3)_3$	[+0.08]	NMR-C-B	[52]
$Si(OCH_3)_3$	+0.11	NMR-C-B	[80]
$Si(OCH_3)_3$	+0.12	NMR-C-S1	[50]
$Si(OCH_3)_3$	+0.13	NMR-F-B	[81]
$Si(OCH_3)_3$	+0.13	NMR-C-B	[50, 53]
$Si(CH_3)(C_6H_5)(OC_6H_5)$	+0.10	NMR-C-B	[83]
$Si(OC_2H_5)_3$	[+0.08]	NMR-C-B	[52]
$Si(OC_2H_5)_3$	+0.08	IR-B	[84, 105]
$Si(OC_2H_5)_3$	+0.08	IR-E	[84]
$Si(OC_2H_5)_3$	+0.10	NMR-C-S1	[50]
$Si(OC_2H_5)_3$	+0.12	NMR-C-B	[50, 53, 80]
$Si(OC_2H_5)_3$	+0.26	IR-A	[84]
$Si(CH_3)(C_6H_5)(OC_3H_7\text{-}n)$	+0.10	NMR-C-B	[83]
$Si(OC_3H_7\text{-}n)_3$	+0.13	NMR-C-B	[80]
$Si(CH_3)C_6H_5)(OC_3H_7\text{-}iso)$	+0.09	NMR-C-B	[83]
$Si(OC_3H_7\text{-}iso)_3$	+0.08	NMR-C-B	[52]
$Si(OC_3H_7\text{-}iso)_3$	+0.11	NMR-C-B	[50, 53]
$Si(OC_4H_9\text{-}t)_3$	+0.08	NMR-C-B	[50, 53]
$Si(OC_6H_5)_3$	+0.11	NMR-C-B	[80]
$Si(OC_6H_5)_3$	+0.16	NMR-C-B	[53]
$Si(CH_3)(C_6H_5)(OC_4H_9\text{-}n)$	+0.10	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OC_4H_9\text{-}iso)$	+0.10	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OC_4H_9\text{-}s)$	+0.09	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OCH_2C_6H_5)$	+0.10	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OCH_2CH_2Cl)$	+0.10	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OCH_2C{\equiv}CH)$	+0.10	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OCH_2CH_2CN)$	+0.11	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OCH_2CF_3)$	+0.11	NMR-C-B	[83]
$Si(OCOCH_3)_3$	+0.20	NMR-C-B	[50, 53]
$Si(OCOCF_3)_3$	+0.28	NMR-C-B	[50, 53]
$Si(CH_3)_2OSi(CH_3)_3$	+0.12	NMR-F-B	[81]
$Si[OSi(CH_3)_3]_3$	+0.10	NMR-C-B	[50, 53]
	0.0	NMR-C-S1	[50]
	[+0.02]	NMR-C-B	[50, 52, 53]
	+0.02	IR-B	[84]
	+0.05	IR-E	[84]
	+0.06	NMR-C-B	[80]
	+0.10	IR-A	[84]
$Si(OCH_2CH_2NH_2)_3$	+0.13	NMR-C-B	[50, 53]
$Si(SC_2H_5)_3$	+0.16	NMR-C-B	[53]
$Si(CH_3)_2F$	+0.11	NMR-F-B	[81]
SiF_3	(+0.17)	NMR-C-B	[80]
SiF_3	+0.23	NMR-C-B	[50, 53]
SiF_3	+0.24	NMR-F-B	[81]
SiF_3	+0.24	NMR-C-S1	[50]
$Si(CH_3)_2CH_2CH_2CF_3$	+0.06	NMR-F-B	[81*]
$Si(CH_3)_2Cl$	+0.10	NMR-F-B	[81]
$Si(CH_3)Cl_2$	+0.15	NMR- F-B	[81]
$SiCl_3$	+0.09	IR-B	[105]
$SiCl_3$	[+0.17]	NMR-C-B	[80]
$SiCl_3$	+0.19	NMR-F-B	[81*]
$SiCl_3$	+0.21	NMR-C-S1	[50]
$SiCl_3$	+0.21	NMR-C-B	[50, 53]
$Si(CH_3)_2CH_2Cl$	+0.08	NMR-F-B	[81*]
$Si(CH_3)ClBr$	+0.15	NMR-F-B	[81*]
$SiBr_3$	+0.18	NMR-F-B	[81*]
$SiBr_3$	+0.20	NMR-C-B	[80]
$SiBr_3$	+0.21	NMR-C-B	[50, 53]

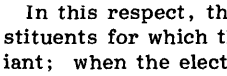
Table 3 (continued).

Substituent	σ_R^0	Method of determination	Refs.
$Si(CH_3)_2Si(CH_3)_3$	+0.04	IR-B	[102]
$Si(CH_3)[Si(CH_3)_3]_2$	+0.06	IR-B	[102]
CH_2SiH_3	+0.16	NMR-C-B	[49]
$CH_2Si(CH_3)_3$	+0.21	NMR-C-B	[88]
$CH_2Si(CH_3)_3$	+0.20	NMR-C-B	[49]
$CH_2Si(CH_3)_3$	+0.20	NMR-F-B	[16, 87, 108]
$CH_2Si(CH_3)_3$	+0.20	IR-B	[102]
$CH_2Si(CH_3)_3$	+0.19	NMR-F-N	[88]
$CH_2Si(CH_3)_3$	+0.18	NMR-C-B	[17*, 49]
$CH_2Si(CH_3)_3$	+0.17	IR-B	[109]
$CH_2Si(CH_3)_3$	(−0.15)	NMR-C-S, NMR-H-S	[57]
$CH_2SiH(C_2H_5)_2$	−0.23	IR-B	[109]
$CH_2Si(C_2H_5)_3$	−0.21	NMR-C-B	[49]
$CH_2Si(C_2H_5)_3$	−0.19	NMR-C-B	[17*, 49]
$CH_2Si(n\text{-}C_3H_7)_3$	−0.21	NMR-C-B	[49]
$CH_2Si(n\text{-}C_3H_7)_3$	−0.19	NMR-C-B	[17*, 49]
$CH_2SiH(t\text{-}C_4H_9)_2$	−0.22	IR-B	[109]
$CH_2Si(CH_3)_2C_6H_5$	−0.20	NMR-C-B	[49]
$CH_2Si(CH)_3(C_6H_5)_2$	−0.19	NMR-C-B	[49]
$CH_2Si(C_6H_5)_3$	−0.18	NMR-C-B	[49]
$CH_2Si(C_6H_5)_3$	−0.16	NMR-F-N	[88]
$CH_2Si(CH_3)_2OCH_3$	−0.19	NMR-C-B	[49]
$CH_2Si(CH_3)_2OCH_3$	−0.17	NMR-C-B	[17*, 49]
$CH_2Si(CH_3)(OCH_3)_2$	−0.18	NMR-C-B	[49]
$CH_2Si(CH_3)(OCH_3)_2$	−0.17	NMR-C-B	[17*, 49]
$CH_2Si(OCH_3)_3$	−0.18	NMR-F-B	[90]
$CH_2Si(OCH_3)_3$	−0.17	NMR-C-B	[49]
$CH_2Si(OCH_3)_3$	−0.16	NMR-C-B	[17*, 49]
$CH_2Si(OCH_2CH_2)_3N$	−0.21	NMR-F-B	[90]
$CH_2SiH(CH_3)(CH_2C_6H_5)$	−0.21	IR-B	[109]
$CH_2SiH(C_6H_5)(CH_2C_6H_5)$	−0.22	IR-B	[109]
$CH_2Si(CH_3)(CH_2C_6H_5)_2$	−0.24	IR-B	[109]
$CH[Si(CH_3)_3]_3$	−0.24	IR-B	[102]
$CH[Si(CH_3)_3]_2$	−0.22	NMR-C-B	[49]
$C[Si(CH_3)_3]_3$	−0.22	NMR-C-B	[49]
$COOCH_2Si(OC_2H_5)_3$	+0.22	NMR-C-B	[92]
$COOCH_2Si(OCH_2CH_2)_3N$	+0.20	NMR-C-B	[92]
$COOCH_2SiF_3$	+0.22	NMR-C-B	[92]
$NHSi(CH_3)_3$	−0.78	NMR-C-B	[93]
$OSi(CH_3)_3$	−0.53	NMR-C-B	[93]
$OSi(CH_3)_3$	−0.48	IR-B	[110]

Notation: IR-B—analysis of the intensities of the A absorption band in the region of 1600 cm^{-1} in the IR spectra of monosubstituted benzenes using the relation $\sigma_R^0 = 0.0075\ (A-100)^{1/2}$; [32,33,60] NMR-C-S1—analysis of the chemical shifts in the ^{13}C NMR spectra of the β-substituted styrenes $C_6H_5CH{=}CHX$; [50] IR-HB-A—IR spectroscopic study of the hydrogen bond formed by acetylene derivatives with phenol; [63] IR-E—analysis of the intensity of the A stretching vibration band of the double bond in the IR spectra of monosubstituted ethylenes using the relation $\sigma_R^0 = 0.0060\ (A-80)^{1/2}$; [60] IR-A—analysis of the intensity of the A stretching vibration band of the triple bond in the IR spectra of monosubstituted acetylenes using the relation $\sigma_R^0 = 0.0046\ A^{1/2} - 0.05$; [60] for the significance of the remaining designations of the methods, see the footnote to Table 1.

In this respect, the groups EX_3 resemble organic substituents for which the values of σ_R are likewise not invariant; when the electronic characteristics of the reaction centre are changed significantly, the sign of the constants may also change. [112] The condition that the fragment D is invariant holds for the majority of studies in which the σ_R^0 constants have been obtained for the substituents EX_3. These constants have been determined mainly for benzene derivatives. Almost all the values of σ_R^0 presented in Tables 3 and 4 characterise the resonance properties of the substituents EX_3 in relation to the benzene ring (D = C_6H_5). (See below, for the acetylene derivatives).

Another feature of the constants σ_R^0 (Tables 3 and 4) is that their values reflect not only the effects due to the $(p-d)\pi$ interaction but also the σ,π conjugation



[113].

These two resonance effects act in opposite directions.

Table 4. The constants σ_R^0 of germanium-, tin-, and lead-containing substituents.

Substituent	σ_R^0	Method of determination	Refs.
$Ge(CH_3)_3$	(−0.1)	Ph	[106]
$Ge(CH_3)_3$	−0.06	IR-HB-A	[63*]
$Ge(CH_3)_3$	+0.01	NMR-F-N	[46]
$Ge(CH_3)_3$	+0.01	NMR-F-B	[46, 104, 108]
$Ge(CH_3)_3$	+0.05	IR-B	[102]
$Ge(CH_3)_3$	(+0.07)	NMR-C-S, NMR-H-S	[57]
$Ge(C_6H_5)_3$	−0.07	IR-HB-A	[63*]
$Ge(C_6H_5)_3$	0.0	IR-B	[107]
$Ge(C_6H_5)_3$	0.0	Ph	[106]
$Ge(OCH_3)_3$	~+0.14	NMR-C-B	[51]
$Ge(OC_2H_5)_3$	~+0.14	NMR-C-B	[51]
$Ge(OC_3H_7\text{-iso})_3$	~+0.13	NMR-C-B	[51]
$Ge(OC_4H_9\text{-}t)_3$	~+0.10	NMR-C-B	[51]
$Ge(OCH_2CH_2)_3N$	~+0.05	NMR-C-B	[51]
GeF_3	+0.23	NMR-F-B	[94]
$GeCl_3$	+0.16	NMR-F-B	[94]
$GeBr_3$	+0.14	NMR-F-B	[94]
$CH_3Ge(CH_3)_3$	−0.23	IR-B	[109]
$CH_2Ge(CH_3)_3$	−0.21	NMR-C-B	[88]
$CH_2Ge(CH_3)_3$	−0.20	NMR-F-N	[88]
$CH_2Ge(CH_3)_3$	(−0.15)	NMR-C-S, NMR-H-S	[57]
$CH_2GeH_2C_2H_5$	−0.24	IR-B	[109]
$CH_2Ge(C_2H_5)_3$	−0.21	NMR-C-B	[49]
$CH_2Ge(C_6H_5)_3$	−0.17	NMR-F-N	[88]
$CH_2Ge(OC_2H_5)_3$	−0.24	IR-B	[109]
$CH_2GeH_2(CH_2C_6H_5)$	−0.23	IR-B	[109]
$CH_2GeH(C_2H_5)(CH_2C_6H_5)$	−0.24	IR-B	[109]
$CH_2GeH(CH_2C_6H_5)_2$	−0.24	IR-B	[109]
$Sn(CH_3)_3$	−0.13	IR-HB-A	[63*]
$Sn(CH_3)_3$	−0.02	NMR-F-N	[46]
$Sn(CH_3)_3$	0.0	IR-E	[105]
$Sn(CH_3)_3$	[+0.01]	NMR-F-B	[46, 95, 104, 105, 108]
$Sn(CH_3)_3$	+0.05	NMR-C-S, NMR-H-S	[57]
$Sn(CH_3)_3$	+0.07	IR-B	[102]
$Sn(C_6H_5)_3$	+0.01	NMR-F-B	[95]
$Sn(n\text{-}C_4H_9)_3$	0.00	NMR-F-B	[95]
$Sn(CH{=}CH_2)_3$	0.00	IR-E	[105]
$Sn(C_6H_5)_3$	0.0	Ph	[106]
$Sn(C_6H_5)_3$	0.0	IR-B	[107]
$Sn(C_6H_5)_3$	+0.03	NMR-F-B	[95, 97, 99]
$Sn(C_6H_4F\text{-}4)_3$	+0.03	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	+0.04	NMR-F-B	[95]
$SnCl_3$	+0.15 ($CDCl_3$)	NMR-F-B	[95]
$SnCl_3$	+0.07 ($(CD_3)_2CO$)	NMR-F-B	[95]
$SnCl_3$	+0.14 (CCl_4)	NMR-F-B	[95]
$CH_3Sn(CH_3)_3$	−0.26	IR-B	[102]
$CH_2Sn(CH_3)_3$	−0.25	NMR-F-N	[88]
$CH_2Sn(CH_3)_3$	−0.25	NMR-C-B	[88]
$CH_2Sn(CH_3)_3$	−0.24	NMR-C-N	[88]
$CH_2Sn(CH_3)_3$	−0.23	NMR-F-B	[108]
$CH_2Sn(CH_3)_3$	(−0.19)	NMR-C-S, NMR-H-S	[57]
$CH_2Sn(C_6H_5)_3$	−0.22	NMR-F-N	[88]
$CH_2Sn(C_6H_5)_3$	−0.21	NMR-F-B	[96, 97, 99]
$OSn(C_6H_5)_3$	−0.48	NMR-F-B	[98]
$OSn(C_6H_5)_3$	−0.45	NMR-F-B	[98]
$SSn(C_6H_5)_3$	−0.17	NMR-F-B	[101]
$SSn(C_6H_5)_3$	−0.14	NMR-F-B	[97, 99]
$Pb(CH_3)_3$	−0.08	NMR-F-N	[46]
$Pb(CH_3)_3$	[−0.02]	NMR-F-B	[46]
$Pb(CH_3)_3$	+0.05	NMR-C-S, NMR-H-S	[57]
$Pb(C_6H_5)_3$	−0.01	NMR-F-B	[99]
$Pb(C_6H_5)_3$	0.0	Ph	[106]
$Pb(C_6H_5)_3$	(0.0)	IR-B	[107]
$CH_2Pb(CH_3)_3$	−0.25	NMR-C-B	[88]
$CH_2Pb(CH_3)_3$	−0.25	NMR-F-N	[88]
$CH_2Pb(CH_3)_3$	−0.24	NMR-C-N	[88]
$CH_2Pb(CH_3)_3$	(−0.19)	NMR-C-S, NMR-H-S	[57]
$CH_2Pb(C_6H_5)_3$	−0.21	NMR-F-N	[88]
$CH_2Pb(C_6H_5)_3$	−0.19	NMR-F-B	[96, 99]
$OPb(C_6H_5)_3$	−0.46	NMR-F-B	[97, 99]
$SPb(C_6H_5)_3$	−0.11	NMR-F-B	[97, 99]

Notation: NMR-C-N—analysis of the chemical shifts in the ^{13}C NMR spectra of naphthalene derivatives; [58] for the significance of the remaining designations of the methods, see the footnotes to Tables 1 and 3.
Note: The solvents are indicated in brackets.

Although a series of quantum-chemical [113–115] and experimental [44,88,116] studies have been devoted to the characteristics of σ,π conjugation, there are many unsolved problems as regards the estimation of the relative contributions of the $(p-d)\pi$ interaction and the σ,π conjugation to the overall resonance effect of EX_3 relative to the benzene ring. Some of these will be considered below in the analysis of the σ_p

and σ_p^+ constants of EX_3. Here we may note that the $(p-d)\pi$ interaction is weakened as the atomic number of E increases, while the σ,π conjugation actually becomes more intense. Therefore, for isostructural compounds, the contribution of the $(p-d)\pi$ interaction to the overall resonance effect of EX_3 relative to the aromatic ring is most significant when E = Si and the contribution of the σ,π conjugation is greatest when E = Pb. The stronger σ,π conjugation in acetylene derivatives[44,63] leads to negative values of σ_R^0 for E = Ge, Sn and to low values of σ_p (see below) for EX_3 linked by a triple bond.

As noted above, the constants σ_R^0 of the substituents EX_3 in CH_2EX_3 have different signs. The negative signs of the constants σ_R^0 for the groups CH_2EX_3 are due to the σ,π conjugation in benzyl derivatives:

There is no effect of the $(p-d)\pi$ interaction in these compounds.

We may note certain features in the way the constants σ_R^0 of the substituents EX_3 vary as a function of the nature of E and X. For the substituents $E(CH_3)_3$, the constants σ_R^0 decrease with increase of the atomic number of E, which corresponds to the maximum degree of the $(p-d)\pi$ interaction in silicon compounds. The low values of σ_R^0 for the substituents $PbAlk_3$ are caused by the maximum degree of the σ,π conjugation and the minimum degree of the $(p-d)\pi$ interaction for lead compounds. For constant E, the enhancement of the electron-accepting properties of X and EX_3 increases the effective positive charge on E and intensifies the resonance electron-accepting properties of the substituents EX_3 (i.e. increases their σ_R^0 constants) for the following sequence of X: Alk < AlkO < Hal. For the same reason, the constants σ_R^0 increase with increase of n in the groups $E(CH_3)_{3-n}Hal$. The constants σ_R^0 of the substituents CH_2EX_3 show a tendency to decrease following the enhancement of the electron-accepting properties of X and to increase with increase of the atomic number of E, i.e. with increase of the polarisability of the E–C bonds.

Table 5. The constants σ_m and σ_p of silicon-containing substituents.

Substituent	σ_m	σ_p	Method of determination	Refs.
SiH_3	—	+0.07	DM	[68]
SiH_3	+0.05	+0.10	NMR-F-B	[81]
SiH_3	—	+0.10	Ph	[68]
$SiH(CH_3)_2$	+0.01	+0.04	Ph	[81]
$SiH(CH_3)_2$	—	−0.05	DM	[68]
$SiH(CH_3)_2$	—	+0.06	Ph	[68]
$Si(CH_3)_3$	—	−0.11	IR-HB-A	[63]
$Si(CH_3)_3$	—	[−0.10]	Ph	[116]
$Si(CH_3)_3$	−0.09	−0.07	Ph, X	[103]
$Si(CH_3)_3$	−0.04	−0.07	X-1	[69]
$Si(CH_3)_3$	−0.21	−0.06	X-1	[71]
$Si(CH_3)_3$	—	−0.05	DM	[68]
$Si(CH_3)_3$	0.00	−0.05	X-5	[74]
$Si(CH_3)_3$	0.00	−0.03	Ph, X-1, X-4	[70]
$Si(CH_3)_3$	+0.02	0.00	X-4	[72]
$Si(CH_3)_3$	+0.11	0.00	X-1	[117]
$Si(CH_3)_3$	−0.04	+0.03	X	[72]
$Si(CH_3)_3$	—	+0.06	Ph	[68]
$Si(CH_3)_3$	−0.08	+0.07	X	[69]
$Si(CH_3)_3$	−0.03	+0.08	X-3	[69]
$Si(CH_3)_3$	−0.02	(+0.11)	X-3	[69]
$Si(C_6H_5)_3$	—	−0.14	IR-HB-A	[63]
$Si(C_6H_5)_3$	—	0.0÷0.1	X-1	[14]
$Si(CH_3)_2C_6H_5$	+0.04	+0.07	NMR-F-B	[81]
$Si(CH_3)(C_6H_5)_2$	+0.10	+0.13	NMR-F-B	[81]
$Si(C_6H_5)_3$	—	[−0.08]	NMR-C-B	[53]
$Si(C_6H_5)_3$	−0.03	+0.09	X	[73]
$Si(C_6H_5)_3$	−0.03	+0.10	X-4	[73]
$Si(C_6H_5)_3$	+0.16	+0.19	NMR-F-B	[81]
$Si(C_6H_5)_3$	+0.12	+0.27	X	[73]
$Si(C_6H_5)_3$	+0.08	(+0.31)	X	[73]
$Si[N(CH_3)_2]_3$	−0.04	−0.04	NMR-F-B	[81]
$Si[N(CH_3)_2]_3$	—	+0.05	DM	[68]
$Si(CH_3)_2OCH_3$	+0.04	(−0.02)	X-5	[74]
$Si(CH_3)_2OCH_3$	—	+0.10	Ph	[68]
$Si(CH_3)_2OCH_3$	—	+0.12	DM	[68]
$Si(CH_3)(OCH_3)_2$	+0.04	(+0.01)	X-5	[74]
$Si(CH_3)(OCH_3)_2$	—	+0.15	Ph	[68]
$Si(CH_3)(OCH_3)_2$	—	+0.18	DM	[68]
$Si(OCH_3)_3$	—	+0.10	Ph	[68]
$Si(OCH_3)_3$	+0.06	+0.13	NMR-F-B	[81]
$Si(OCH_3)_3$	+0.09	+0.13	X-5	[74]
$Si(OCH_3)_3$	—	+0.19	DM	[68]
$Si(OC_6H_5)_3$	—	−0.01	Ph	[53]
$Si(OC_6H_5)_3$	+0.02	+0.08	NMR-F-B	[81]
$Si(CH_3)_2OSi(CH_3)_3$	−0.01	0.00	Ph, X-1, X-4	[70]
$Si(CH_3)[OSi(CH_3)_3]_2$	−0.03	+0.01	Ph, X-1, X-4	[70]
$Si[OSi(CH_3)_3]_3$	−0.06	+0.02	Ph, X-1, X-4	[70]
$Si(CH_3)_2F$	—	+0.15	Ph	[68]
$Si(CH_3)_2F$	+0.12	+0.16	Ph, X-1, X-4	[70]
$Si(CH_3)_2F$	—	+0.17	X-5	[74]
$Si(CH_3)_2F$	+0.13	+0.19	NMR-F-B	[81]
$Si(CH_3)_2F$	—	+0.23	DM	[68]
$Si(CH_3)F_2$	—	+0.22	X-5	[74]
$Si(CH_3)F_2$	—	+0.28	Ph	[68]
$Si(CH_3)F_2$	—	+0.46	DM	[68]
$Si(CH_3)F_2$	—	[+0.42]	X, Ph	[116]
$Si(CH_3)F_2$	+0.29	—	Ph, X-1, X-4	[70]
SiF_3	—	(+0.01)	X-5	[74]
SiF_3	—	+0.51	DM, Ph	[68]
SiF_3	+0.54	[+0.66]	Ph	[95]
SiH_2Cl	—	+0.26	X, Ph	[116]
$Si(CH_3)_2Cl$	+0.07	+0.02	X-5	[74]
$Si(CH_3)_2Cl$	—	+0.15	Ph	[68]
$Si(CH_3)_2Cl$	+0.16	[+0.21]	NMR-F-B	[81]
$Si(CH_3)_2Cl$	—	+0.30	DM	[68]
$Si(CH_3)Cl_2$	+0.09	[+0.08]	X-5	[74]
$Si(CH_3)Cl_2$	+0.31	[+0.39]	NMR-F-B	[81]
$Si(CH_3)Cl_2$	—	+0.41	DM	[68]
$Si(CH_3)Cl_2$	—	+0.42	Ph	[68]
$SiCl_3$	+0.19	(+0.20)	X-5	[74]
$SiCl_3$	—	+0.37	Ph	[68]
$SiCl_3$	—	+0.43	DM	[68]
$SiCl_3$	+0.48	[+0.56]	Ph	[94]
$Si(CH_3)_2Br$	—	+0.10	X-5	[74]
$Si(CH_3)Br_2$	—	+0.30	X-5	[74]
$SiBr_3$	—	(+0.27)	DM	[68]
$SiBr_3$	—	+0.41	X-5	[74]
$SiBr_3$	+0.48	[+0.57]	Ph	[94]
$CH_2Si(CH_3)_3$	−0.16	−0.21	X-1	[14]
$CH_2Si(CH_3)_3$	−0.20	−0.26	X-1, X-3	[118]
$CH_2Si(CH_3)_3$	−0.17	−0.27	X	[16, 31]
$CH_2Si(C_2H_5)_3$	—	−0.24	X-1, X-3	[118]
$CH_2CH_2Si(CH_3)_3$	—	−0.17	X-1, X-3	[118]
$CH_2CH_2Si(C_2H_5)_3$	—	−0.14	X-1, X-3	[118]
$CH_2OSi(CH_3)_3$	—	−0.05	Ph, X-1, X-5	[70]

Notation: DM—on the basis of the linear relation between the dipole moments of *para*-substituted toluenes and the σ_p constants of the substituents;[68] X-3—the study of the p*K* of substituted anilines;[69] X-4—the study of the rate constants for the reactions of substituted benzoic acids with diphenyldiazomethane:[70–73] X-5—the study of the rate constants for the bromination of substituted dimethylphenylsilanes;[74] for the significance of the remaining designations of the methods, see the footnotes to Tables 1 and 3.

3. The Hammett Constants σ_p and σ_m

These constants characterise quantitatively the overall electronic effect (inductive and resonance) of the substituents EX_3. Approximate values of σ_p can be obtained, using the relation $\sigma_p = \sigma_I + \sigma_R$, from the approximate estimate $\sigma_m \cong \sigma_I$; the difficulties arising in this procedure have been described.[11] In interpreting the constants σ_p, one should bear in mind the problems discussed in the analysis of the constants σ_I and σ_R^0. Furthermore, a considerable proportion of the constants σ_m and σ_p have been

determined by chemical methods (Tables 5 and 6), which might have led to the appearance of appreciable non-controllable errors. Therefore, a non-critical application of these constants entails inevitably large errors and it is difficult to avoid subjectivity in estimating the most and least reliable values of the constants.

Table 6. The constants σ_m and σ_p of germanium, tin-, and lead-containing substituents.

Substituent	σ_m	σ_p	Method of determination	Refs.
GeH_3	—	+0.01	DM	[68]
$Ge(CH_3)_3$	—	−0.18	IR-HB-A	[63]
$Ge(CH_3)_3$	—	[−0.06]	X, Ph	[116]
$Ge(CH_3)_3$	—	−0.06	DM	[68]
$Ge(CH_3)_3$	0.00	0.00	X-1	[14]
$Ge(CH_3)_3$	—	+0.01	Ph	[68]
$Ge(C_6H_5)_3$	—	−0.20	IR-HB-A	[63]
$Ge(C_6H_5)_3$	0.00	0.00	X-1	[14]
$Ge(C_6H_5)_3$	—	0.0±0.1	X-1	[14]
$Ge(C_6H_5)_3$	+0.05	+0.08	X-4	[73]
$Ge(C_6H_5)_3$	—	[+0.16]	X, Ph	[116]
$Ge(C_6H_5)_3$	+0.15	+0.24	X	[69]
$GeH(C_6H_5)_3$	—	+0.16	X, Ph	[116]
GeF_3	+0.85	+0.97	Ph	[94]
$GeCl_3$	—	+0.60	DM, Ph	[68]
$GeCl_3$	+0.71	[+0.79]	Ph	[94]
$Ge(C_6H_5)_2Br$	—	+0.35	X, Ph	[116]
$Ge(C_6H_5)Br_2$	—	+0.60	X, Ph	[116]
$GeBr_3$	+0.66	+0.73	Ph	[94]
$Sn(CH_3)_3$	—	−0.26	IR-HB-A	[63]
$Sn(CH_3)_3$	—	[−0.12]	X, Ph	[116]
$Sn(CH_3)_3$	—	0.0±0.1	X-1	[14]
$Sn(CH_3)_3$	—	+0.02	NMR-F-B	[95]
$Sn(C_2H_5)_3$	—	0.0±0.1	X-1	[14]
$Sn(C_2H_5)_3$	—	+0.03	NMR-F-B	[95]
$Sn(n\text{-}C_4H_9)_3$	—	+0.02	NMR-F-B	[95]
$Sn(C_6H_5)_3$	—	+0.18 ($CDCl_3$)	NMR-F-B	[95, 99]
$Sn(C_6H_5)_3$	—	+0.23 ($(CD_3)_2CO$	NMR-F-B	[95]
$Sn(C_6H_5)_3$	—	+0.21 (CCl_4)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}4)_3$	—	+0.29 ($CDCl_3$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}4)_3$	—	+0.28 ($(CD_3)_2CO$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}4)_3$	—	+0.32 (CCl_4)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	—	+0.32 ($CDCl_3$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	—	+0.30 ($(CD_3)_2CO$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	—	+0.36 (CCl_4)	NMR-F-B	[95]
$SnH(C_6H_5)_3$	—	+0.20	Ph	[116]
$Sn(C_6H_5)_2Cl$	—	+0.40	Ph	[116]
$SnCl_3$	—	+0.97 ($CDCl_3$)	NMR-F-B	[95]
$SnCl_3$	—	+0.49 ($(CD_3)_2CO$)	NMR-F-B	[95]
$SnCl_3$	—	+0.94 (CCl_4)	NMR-F-B	[95]
$Pb(C_6H_5)_3$	—	+0.21	NMR-F-B	[99]

Note: The solvents are indicated in brackets; for the significance of the designations of the methods, see the footnotes to Tables 1, 3, and 5.

However, one should note that the constants σ_p and σ_m carry nevertheless important qualitative information about the electronic effects of EX_3. Thus the constants σ_p for $E(CH_3)_3$ are larger (−0.06– −0.13) than for the group $C(CH_3)_3$ (−0.20[11]). These estimates show that the resonance electron-accepting properties of organoelemental substituents must be more significant. The above conclusion has also been confirmed by the fact that the constants σ_p are larger than σ_m. The higher values of the constants σ_p for the substituents EX_3 than the corresponding values of σ_m are due to the presence in the former of a considerable resonance component, which is always positive. When this resonance component is negative, then $\sigma_p < \sigma_m$, which has in fact been observed for the substituent $CH_2Si(CH_3)_3$. It was noted above that, following the enhancement of the electron-accepting properties of X and EX_3, the constants σ_I and σ_R^0 increase; naturally, this also entails an increase of the constants σ_p.

Table 7. The constants σ_p^+ of silicon-containing substituents.

Substituent	σ_p^+	Method of determination	Refs.
SiH_3	[−0.01]	UV-2	[119*]
SiH_3	+0.03	UV-3	[119*]
$SiH(CH_3)_2$	−0.16	UV-3	[120*]
$SiH(CH_3)_2$	−0.14	UV-2	[120*]
$Si(CH_3)_3$	[−0.22]	UV-1	[121]
$Si(CH_3)_3$	−0.15	UV-3	[120*]
$Si(CH_3)_3$	−0.14	IP	[114*]
$Si(CH_3)_3$	[−0.13]	UV-2	[120*]
$Si(CH_3)_3$	−0.03	X	[122]
$Si(CH_3)_3$	0.0	NMR-H-P	[59]
$Si(CH_3)_3$	[+0.02]	X	[15]
$Si(C_2H_5)_3$	−0.16	UV-3	[119*]
$Si(C_2H_5)_3$	−0.14	UV-2	[119*]
$Si(n\text{-}C_4H_9)_3$	−0.18	UV-3	[120*]
$Si(n\text{-}C_4H_9)_3$	−0.16	UV-2	[120*]
$Si(t\text{-}C_4H_9)_3$	−0.18	UV-3	[119*]
$Si(t\text{-}C_4H_9)_3$	−0.16	UV-3	[119*]
$SiH_2C_6H_5$	−0.02	UV-2	[119*]
$SiH_2C_6H_5$	~0	UV-3	[119*]
$SiH_2C_6H_5$	~0	IP	[123*]
$SiH(CH_3)(C_6H_5)$	−0.06	UV-2	[120*]
$SiH(CH_3)(C_6H_5)$	−0.05	UV-3	[120*]
$SiH(C_2H_5)(C_6H_5)$	−0.06	UV-2	[120*]
$SiH(C_6H_5)(C_6H_5)$	−0.05	UV-3	[120*]
$Si(CH_3)_2C_6H_5$	−0.09	UV-2	[119*]
$Si(CH_3)_2C_6H_5$	−0.09	UV-3	[119*]
$SiH(C_6H_5)_2$	−0.09	IP	[123*]
$SiH(C_6H_5)_2$	−0.01	UV-2	[119*]
$SiH(C_6H_5)_2$	+0.01	UV-3	[119*]
$Si(CH_3)(C_6H_5)_2$	−0.05	UV-2	[119*]
$Si(CH_3)(C_6H_5)_2$	−0.04	UV-3	[119*]
$Si(C_2H_5)(C_6H_5)_2$	−0.06	UV-2	[120*]
$Si(C_2H_5)(C_6H_5)_2$	−0 05	UV-3	[120*]
$Si(C_6H_5)_3$	−0.18	UV-3	[119*]
$Si(C_6H_5)_3$	−0.15	UV-2	[119*]
$Si(C_6H_5)_2OH$	−0.04	UV-2	[120*]
$Si(C_6H_5)_2OH$	−0.03	UV-3	[120*]
$Si(OC_2H_5)_3$	+0.01	UV-2	[124*]
$Si(OCH_2CH_2)_3N$	−0.21	UV-2	[90*]
$Si[OCH(CH_3)CH_2]_3N$	−0.24	UV-2	[90*]
$Si(CH_3)F_2$	+0.37	IP	[125*]
SiF_3	~+0.7	IP	[125*]
SiH_2Cl	[+0.09]	UV-2	[119*]
SiH_2Cl	+0.16	UV-3	[119*]
$Si(CH_3)_2Cl$	+0.05	UV-2	[116]
$Si(CH_3)_2Cl$	+0.05	IP	[125*]
$Si(CH_3)Cl_2$	[+0.13]	UV-2	[120*]
$Si(CH_3)Cl_2$	+0.21	IP	[125*]
$Si(CH_3)Cl_2$	+0.22	UV-3	[120*]
$SiCl_3$	[+0.16]	UV-2	[120*]
$SiCl_3$	+0.24	IP	[125*]
$SiCl_3$	+0.26	UV-3	[120*]
$SiH_2(CH_2Cl)$	−0.04	UV-2	[120*]
$SiH_2(CH_2Cl)$	−0.03	UV-3	[120*]
$Si(CH_3)_2Si(CH_3)_3$	−0.62	UV-1	[121]
$Si(CH_3)_2Si(CH_3)_3$	[−0.55]	UV-2	[67, 121*]
$Si(CH_3)_2Si(CH_3)_3$	−0 23	NMR-H-P	[59]
1-$Si_3(CH_3)_7$	−0.77	UV-1	[121]
1-$Si_3(CH_3)_7$	[−0.67]	UV-2	[67, 121*]
2-$Si_3(CH_3)_7$	−0.81	UV-1	[121]
2-$Si_3(CH_3)_7$	[−0.70]	UV-2	[67, 121*]
CH_2SiH_3	−0.27	UV-2	[49]
CH_2SiH_3	−0.15	UV-2	[124*]
$CH_2Si(CH_3)_3$	[−0.66]	UV-1	[121]
$CH_2Si(CH_3)_3$	−0.66; −0.63	UV-1	[65]
$CH_2Si(CH_3)_3$	−0.63	IP	[114*]
$CH_2Si(CH_3)_3$	−0.62	UV-1	[126]
$CH_2Si(CH_3)_3$	−0.61	X	[65]
$CH_2Si(CH_3)_3$	−0.56	X	[49]
$CH_2Si(CH_3)_3$	−0.55	UV-2	[67][a]
$CH_2Si(CH_3)_3$	−0.50	UV-2	[119*]
$CH_2Si(CH_3)_3$	−0.54	X	[130]
$CH_2Si(CH_3)_3$	−0.54	UV-2	[49]
$CH_2Si(CH_3)_3$	[−0.54±0.01]	UV-2	[67][b]
$CH_2Si(CH_3)_3$	−0.4	NMR-C-B	[55]
$CH_2SiH(C_6H_5)_2$	−0.55	UV-2	[109*]
$CH_2Si(C_6H_5)_3$	−0.57	X	[49]
$CH_2Si(C_6H_5)_3$	−0.57	UV-2	[49]
$CH_2SiH_2(n\text{-}C_3H_7)$	−0.57	UV-2	[67, 120*]
$CH_2Si(n\text{-}C_3H_7)_3$	−0.58	UV-2	[49]
$CH_2Si(n\text{-}C_3H_7)_3$	−0.57	X	[49]
$CH_2Si(n\text{-}C_4H_9)_3$	−0.55	UV-2	[67, 120*]
$CH_2SiH(t\text{-}C_4H_9)_2$	−0.49	UV-2	[109*]
$CH_2Si(t\text{-}C_4H_9)_3$	−0.54	UV-2	[119*]
$CH_2Si(C_6H_5)_3$	−0.42	UV-1	[66]
$CH_2Si(C_6H_5)_3$	−0.4	UV-1	[126]
$CH_2Si(C_6H_5)_3$	[−0.38±0.02]	UV-2	[67][b]
$CH_2Si(C_6H_5)_2$	−0.36	UV-2	[67][a]
$CH_2Si(CH_3)_2OCH_3$	−0.45	UV-2	[49]
$CH_2Si(CH_3)(OCH_3)_2$	−0.40	UV-2	[49]
$CH_2Si(OCH_3)_3$	−0.24	UV-2	[49]
$CH_2Si(OCH_3)_3$	−0.14	UV-2	[90*]
$CH_2Si(OC_2H_5)_3$	−0.19	UV-2	[124*]
$CH_2Si(OCH_2CH_2)_3N$	−0.49	UV-2	[90*]

Table 7 (continued).

Substituent	σ_p^+	Method of determination	Refs.
$CH_3SiH(CH_3)(CH_2C_6H_5)$	−0.57	UV-2	[109*]
$CH_3Si(CH_3)_2(CH_2C_6H_5)$	−0.56	UV-2	[67, 120*]
$CH_3SiH(C_6H_5)(CH_2C_6H_5)$	−0.54	UV-2	[109*]
$CH_3SiH(CH_2C_6H_5)_2$	−0.45	UV-2	[67, 120*]
$CH_3Si(CH_3)(CH_2C_6H_5)_2$	−0.56	UV-2	[120*]
$CH_3Si(CH_3)_2Si(CH_3)_3$	−0.72	UV-1	[121]
$CH_3Si(CH_3)_2Si(CH_3)_3$	−0.62	UV-2	[67, 121*]
$CH[Si(CH_3)_3]_2$	(−1.06)	UV-2	[67, 131*]
$CH[Si(CH_3)_3]_3$	−0.76	UV-1	[121]
$CH[Si(CH_3)_3]_2$	[−0.65]	UV-2	[67, 121*]
$CH[Si(CH_3)_3]_3$	−0.62	X	[130]
$C[Si(CH_3)_3]_3$	(−0.79)	UV-1	[121]
$C[Si(CH_3)_3]_2$	[−0.68]	UV-2	[67, 121*]
$C[Si(CH_3)_3]_3$	−0.62	UV-2	[49]
$C[Si(CH_3)_3]_3$	(−0.52)	X	[130]
CH_2SiF_2	−0.03	UV-2	[124*]
CH_2SiCl_2	−0.08	UV-2	[124*]

Notation: UV-1—analysis of the frequency ν_{CT} of the charge-transfer bands in the UV spectra of the CTC of monosubstituted benzenes with tetracyanoethylene using the relation $\nu_{CT} = 9300\,\sigma^+ + 26\,200$;[65,66] UV-2—the same method as UV-1 but using the relation $\sigma^+ = 9.46 \times 10^{-5}\,\nu_{CT} - 2.466$;[67] UV-3—the same method as UV-1 but using the relation $\nu_{CT} = 7600\,\sigma^+ + 25\,800$;[38] IP—on the basis of the ionisation potentials (IP) of monosubstituted benzenes using the relation $IP = 1.31\,\sigma^+ + 9.24$;[66] NMR-H-P—analysis of the chemical shifts of the signals of the OH group in ^1H NMR spectra of phenol derivatives;[59] for the significance of the remaining designations of the methods, see the footnote to Table 1.

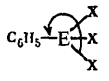
[a] Taking into account the data in Refs. 65 and 127–129.

[b] Taking into account the data in Refs. 65, 113, 131, and 132.

4. The Electrophilic Constants σ_p^+

The constants σ_p^+ reflect the overall influence of the electronic structure of the substituents EX_3 or CH_2EX_3 on the electron-deficient reaction centre. For the majority of the systems investigated hitherto (Tables 7 and 8), such a centre is the benzene ring, which has a positive charge. Analysis of the values of these constants constitutes an even more complex task than the interpretation of the Hammett constants σ_p. At first sight, it may turn out that there is altogether no correspondence between the values of the constants σ_p and σ_p^+ for organoelemental substituents (in contrast to organic substituents). For example, it is known[19] that, in the presence of a positive charge on the benzene ring, the p,π conjugation of the electron-donating organic substituents of the $+M$ type with the ring intensifies (the constants σ_p^+ and σ_p are negative and $\sigma_p^+ > \sigma_p$), while the conjugation remains unchanged for the electron-accepting substituents of the $-M$ type (the constants σ_p^+ and σ_p are positive and $\sigma_p^+ \cong \sigma_p$).

The values of σ_p^+ found for organoelemental compounds show that any groups EX_3 should exhibit stronger electron-donating properties (or weaker electron-accepting properties) than would follow from the estimates based on the σ_p constants. This is caused by the enhancement of the σ,π conjugation



when a positive charge arises on the ring.[116] [The second resonance effect—the $(p-d)\pi$ interaction—hardly depends on the charge on the ring.]

Table 8. The constants σ_p^+ of germanium-, tin-, and lead-containing substituents.

Substituent	σ_p^+	Method of determination	Refs.
GeH_3	−0.04	UV-2	[119*]
GeH_3	−0.03	UV-3	[119*]
$Ge(CH_3)_3$	−0.21	UV-2	[116]
$Ge(CH_3)_3$	−0.19	IP	[114*]
$Ge(CH{=}CHC_4H_9)_3$	−0.12	UV-3	[116]
$Ge(CH{=}CHC_4H_9)_3$	−0.11	UV-2	[116]
$GeH_2(C_6H_5)$	−0.04	UV-2	[120*]
$GeH_2(C_6H_5)$	−0.03	UV-3	[120*]
$Ge(CH_3)_2C_6H_5$	−0.17	UV-3	[120*]
$Ge(CH_3)_2C_6H_5$	−0.15	UV-2	[120*]
$Ge(n\text{-}C_6H_{13})_2C_6H_5$	−0.13	UV-3	[109*]
$Ge(n\text{-}C_6H_{13})_2C_6H_5$	−0.12	UV-2	[109*]
$GeH(C_6H_5)_2$	−0.07	IP	[123*]
$Ge(n\text{-}C_6H_{13})(C_6H_5)_2$	−0.12	UV-3	[109*]
$Ge(n\text{-}C_6H_{13})(C_6H_5)_2$	−0.11	UV-2	[109*]
$Ge(C_6H_5)_2CH_2CH{=}CHCH_3$	−0.11	UV-3	[109*]
$Ge(C_6H_5)_2CH_2CH{=}CHCH_3$	−0.10	UV-2	[109*]
$Ge(C_6H_5)_3$	−0.07	UV-2	[133*]
$GeH(n\text{-}C_6H_{13})Cl$	−0.06	UV-2	[109*]
$GeH(n\text{-}C_6H_{13})Cl$	−0.05	UV-3	[109*]
$GeH(C_6H_5)Cl$	−0.05	UV-2	[109*]
$GeH(C_6H_5)Cl$	−0.04	UV-3	[109*]
$GeCl_3$	+0.33	UV-2	[116]
$Ge(C_6H_5)_2Br$	−0.05	IP	[116,123*]
$Ge(C_6H_5)Br_3$	+0.09	UV-2	[116]
$Ge(C_6H_5)_2Ge(C_6H_5)_3$	−0.26	UV-3	[116]
$Ge(C_6H_5)_2Ge(C_6H_5)_3$	−0.22	UV-2	[116]
$CH_3Ge(CH_3)_3$	−0.65	UV-2	[109*]
$CH_3Ge(CH_3)_3$	−0.64	IP	[114*]
$CH_3Ge(CH_3)_3$	[−0.63±0.02]	UV-2	[67]
$CH_3Ge(CH_3)_3$	−0.61	UV-2	[67,120*]
$CH_3Ge(CH_3)_3$	−0.4	NMR-C-B	[55]
$CH_3GeH_2(C_6H_5)$	−0.64	UV-2	[109*]
$CH_3Ge(C_6H_5)_3$	−0.67	UV-2	[67,120*]
$CH_3Ge(C_6H_5)_3$	−0.67	UV-2	[49]
$CH_3Ge(C_6H_5)_3$	(−0.60)	UV-1	[66]
$CH_3Ge(C_6H_5)_3$	−0.6	UV-1	[126]
$CH_3Ge(C_6H_5)_3$	−0.52	UV-2	[67,120*]
$CH_3Ge(C_6H_5)_3$	[−0.52±0.02]	UV-2	[67]
$CH_3Ge(OC_6H_5)_3$	−0.39	UV-2	[67,120*]
$CH_3GeH_2(CH_2C_6H_5)$	−0.59	UV-2	[109*]
$CH_3GeH(CH_2C_6H_5)_2$	−0.59	UV-2	[67,120*]
$CH_3Ge(CH_2C_6H_5)_3$	−0.57	UV-2	[67,120*]
$CH_3CH_2Ge(OC_2H_5)_3$	−0.16	UV-2	[120*]
$Sn(CH_3)_2$	[−0.34]	UV-2	[116]
$Sn(CH_3)_3$	−0.30	IP	[114*]
$Sn(CH_3)_3$	(−0.12)	X	[122]
$SnH(C_6H_5)_3$	−0.11	IP	[123*]
$Sn(C_6H_5)_3$	−0.07	UV-2	[116,133*]
$Sn(C_6H_5)_3Cl$	+0.04	IP	[116,123*]
$SnCl_3$	+0.41	IP	[134]
$CH_3Sn(CH_3)_3$	(−0.92)	UV-1	[126]
$CH_3Sn(CH_3)_3$	−0.91	UV-1	[66]
$CH_3Sn(CH_3)_3$	−0.9	UV-1	[65]
$CH_3Sn(CH_3)_3$	−0.82	UV-2	[67,135*]
$CH_3Sn(CH_3)_3$	[−0.81±0.02]	UV-2	[67]
$CH_3Sn(CH_3)_3$	−0.78	IP	[114*]
$CH_3Sn(CH_3)_3$	−0.76	X	[65]
$CH_3Sn(CH_3)_3$	−0.45	NMR-C-B	[55]
$CH_3Sn(C_6H_5)_3$	(−0.81)	UV-1	[66]
$CH_3Sn(C_6H_5)_3$	−0.75	UV-1	[126]
$CH_3Sn(C_6H_5)_3$	[−0.73±0.02]	UV-2	[67]
$CH_3Sn(C_6H_5)_3$	−0.69	UV-2	[65*,67]
$OSn(C_6H_5)_3$	−1.55 (CH_2Cl_2)	IR-NB	[61]
$OSn(C_6H_5)_3$	−2.34 (DMSO)	IR-NB	[61]
$SSn(C_6H_5)_3$	−0.08 (CH_2Cl_2)	IR-NB	[61]
$SSn(C_6H_5)_3$	−0.35(DMSO)	IR-NB	[61]
$Pb(C_6H_5)_3$	−0.07	UV-2	[116,133*]
$CH_3Pb(CH_3)_3$	−1.03±0.03	UV-2	[67][a]
$CH_3Pb(CH_3)_3$	−0.52	NMR-C-B	[55]
$CH_3Pb(C_6H_5)_3$	(−1.08)	UV-1	[65]
$CH_3Pb(C_6H_5)_3$	−1.0	UV-1	[126]
$CH_3Pb(C_6H_5)_3$	−1.0	UV-1	[66]
$CH_3Pb(C_6H_5)_3$	−0.92	UV-2	[65*,67]
$CH_3Pb(C_6H_5)_3$	[−0.90±0.02]	UV-2	[67]
$CH_3CH_2Pb(C_6H_5)_3$	(−0.5)	X	[65]
$CH_3CH_2Pb(C_6H_5)_3$	−0.22	UV-1	[65]
$CH_3CH_2Pb(C_6H_5)_3$	[−0.08]	UV-2	[65*,67]
$OPb(C_6H_5)_3$	−1.79 (CH_2Cl_2)	IR-NB	[61]
$OPb(C_6H_5)_3$	−3.13 (DMSO)	IR-NB	[61]
$SPb(C_6H_5)_3$	−0.28 (CH_2Cl_2)	IR-NB	[61]
$SPb(C_6H_5)_3$	−0.52 (DMSO)	IR-NB	[61]

Notation: IR-NB—analysis of the intensities of the stretching vibration bands of the NO_2 group in the IR spectra of *para*-substituted nitrobenzenes;[61] for the significance of the remaining designations of the methods, see the footnotes to Tables 1 and 7.

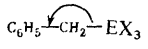
Note: The solvents are indicated in brackets.

[a] Taking into account the data in Refs. 65, 113, 131, and 132.

The enhancement of the σ,π conjugation, characterised by the difference $\sigma_p^+ - \sigma_p$ is greater the greater the polarisability of the chemical bonds of the $C_{Ar}EX_3$ fragment of the $C_6H_5EX_3$ fragment of the $C_6H_5EX_3$ molecule and hence the greater the bond refraction ΣR_D, which is a quantitative measure of the polarisability. Therefore linear relations between $\sigma_p^+ - \sigma_p$ and ΣR_D hold for silicon and the germanium compounds and also for any other phenyl derivatives of non-transition Group II–V elements.[116]

The constants σ_p^+ of the groups $E(CH_3)_3$ reflect the influence of oppositely directed effects—the $(p-d)\pi$ interaction and the σ,π conjugation. The former effect is most significant for E = Si or Ge and the corresponding values of σ_p^+ (−0.13 and −0.21) are therefore greater than for $C(CH_3)_3$ (−0.26). On passing to $Sn(CH_3)_3$, the σ,π conjugation intensifies and σ_p^+ diminishes (to −0.34). With enhancement of the electron-accepting properties of X in EX_3, the constants σ_p^+ increase.

On passing from EX_3 to the substituents CH_2EX_3, the constants σ_p^+ diminish sharply, i.e. the negative values of these constants are significantly greater than the corresponding values of σ_p. This is caused by the intensification of the σ,π conjugation



in the present of a positive charge on the ring. The linear relation between $\sigma_p^+ - \sigma_p$ and $\sum R_D$, which holds for $C_6H_5.CH_2EX_3$, is also valid for alkylbenzenes, although the σ,π conjugation in the latter is comparatively weak.[116] It follows from the analysis of the values of σ_p^+ that the electron-donating properties of the substituents CH_2EX weaken following the enhancement of the electron-accepting properties of X and intensify with increase of the atomic number of E. These features of the σ,π conjugation have been discussed in greater detail in other communications.[44,67,116]

The properties of the σ_p^+ constants of organoelemental substituents reflect the dependence of σ_p^+ on the type of reaction series and on the degree of conjugation between the substituent and the reaction centre, which is familiar[19] for carbon compounds. Comparison of the constants σ_p^+, determined for the same substituent by methods based on the NMR and UV spectroscopy of CTC, indicates a marked discrepancy between the results. According to the UV spectroscopic data for CTC, the substituents $CH_2E(CH_3)_3$ are much stronger electron donors, the discrepancy between the results obtained by the two methods increasing with increase of the atomic number of E. Under the experimental conditions of the UV spectroscopic measurements for CTC, there is an appreciable positive charge on the aromatic ring, which leads to an increase of the degree of σ,π conjugation. The constants σ_p^+ then reach high negative values, which is inconsistent with the data obtained by the NMR method, where there is no positive charge on the ring in the ground electronic state.

Thus in the experiments involving the NMR and UV spectroscopic measurements for CTC, the substituent $CH_2E(CH_3)_3$ is in essence linked to different reaction centres (neutral and positively charged). The constants σ_p^+ therefore do not remain invariant, reflecting the unequal degrees of conjugation of the substituent $CH_2E(CH_3)_3$ with different reaction centres. Analogous situations have been discussed for organic compounds.[112,116]

5. Other σ Constants

Systematic studies of other constants of organoelemental substituents are only just beginning. Only scattered data are available on the constants σ_p^- of the substituents $Si_n.(CH_3)_{2n+1}$ (where $n = 1,2,3$),[59,69,121,136] $Si(C_6H_5)_3$, and $Ge(C_6H_5)_3$;[73] the constants σ_R^- and σ_R^+ of the silantranyl and trialkoxysilyl groups[52] and $COOCH_2SiF_3$,[83] $OE(C_6H_5)_3$, and $SE(C_6H_5)_3$, where E = Sn or Pb,[61] have also been obtained.

The steric effects in organoelemental compounds[45] are distinguished by a number of features. Therefore, together with the accumulation of data on the steric constants E_S of silyl substituents,[137] the constants $E_S(Si)$,[138] reflecting the specific features of the steric effects of the alkyl groups linked to the silicon atom, have also been introduced.

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In conclusion we may note that the correlation equations linking structure and reactivity have been developed for silicon subgroup compounds to a lesser extent than for carbon derivatives, which can be explained not only by the inadequate extent to which the organoelemental compounds have been investigated and the experimental difficulties in the determination of the σ constants of the element-containing substituents but also by the marked, even more pronounced than for carbon compounds, dependence of these constants on the type of reaction centre. Although, on the one hand, this factor does hold back the use of the σ constants as universal characteristics of the donor–acceptor properties of element-containing substituents, on the other hand, the correlation equations constitute an effective means for the investigation of intramolecular interactions between the silicon subgroup element and the variable reaction centre. Analysis of the accumulated information about the σ constants is therefore of independent interest and leads to prospects for further study of urgent theoretical problems in the organoelemental chemistry of non-transition elements.

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