Journal of Organometallic Chemistry, 344 (1988) 49–60
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Hyperconjugation in phenyl and benzyl derivatives of the Main Group IV elements

A.N. Egorochkin[★], **G.A. Razuvaev, M.A. Lopatin**
Institute of Chemistry, U.S.S.R. Academy of Sciences, Gorky (U.S.S.R.)

(Received June 17th, 1987)

Abstract

The σ_p and σ_p^+ constants for 63 $ER_{3-n}X_n$ and $CR_{3-n-m}X_n$ $[E(CH_3)_3]_m$ substituents in $C_6H_5ER_{3-n}X_n$ (I) (E = Si, Ge, Sn, Pb, Hg, B, P, As, Sb; R = H, Alk; X = π-donor group or groups having lone electron pairs) have been analyzed, and for $C_6H_5CR_{3-n-m}X_n[E(CH_3)_3]_m$ (II), (E = Si, Ge, Sn, Pb). The $\sigma_p^+ - \sigma_p$ difference characterizes the strengthening of donor (or weakening of acceptor) properties of substituents towards C_6H_5 group (i.e. hyperconjugation strengthening when the positive charge appears on the aromatic ring). It has been shown that hyperconjugation increases with increase in chemical bond polarizability, i.e. with bond refraction, R_D. Linear relationships of $\sigma_p^+ - \sigma_p$ with ΣR_D for compounds I and II were found. It was found that the two resonance effects by the $ER_{3-n}X_n$ (E = Si, Ge, Sn, Pb) substituents towards the aromatic ring are opposite directions. These substituents are donors at hyperconjugation and acceptors at $(p-d)\pi$-interaction.

Introduction

The role of hyperconjugation (σ,π-conjugation) presents important problems in the physical organometallic chemistry of silicon subgroup elements in general, as well as the possibility of its being an alternative to $(p-d)\pi$-interaction. Though these problems presented themselves 15 years ago [1,2], they remain a current issue. It was unambiguously found, by use of a number of experimental and quantum chemical methods [3], that the R_3E fragments (E = Si, Ge, Sn; R = H or Alk) compared to the substituents X (atoms with lone electron; π-donor moieties such as phenyl, alkenyl or thienyl type etc.) appear to be typical acceptors when regarded in terms of the resonance mechanism. Traditional interpretation of these resonance-acceptor properies of E atoms is based on the concept of $(p-d)\pi$-conjugation or interaction. The latter is considered to be a partial transfer of lone electron pairs or π-electrons X to vacant nd-orbitals of E atom. With such $(p-d)\pi$-conjugation, E–X

0022-328X/88/$03.50

bond multiplicity is increased and the R_3E fragment shows resonance π-acceptor properties towards X. A quantitative indication of the ability of X to undergo conjugation with R_3E, as found for those compounds with E = Si or Ge [3], is the resonance constant σ_R ($\sigma_R = \sigma_p - \sigma_I$, where σ_p is Hammett's *para*-substituent constant, and σ_I the inductive constant), which characterises the conjugation of the same substituent X, having lone pairs of electrons or π-electrons together with an aromatic ring or a multiple bond [4]. In addition a profound analogy between conjugation effects in organic and organometallic chemistry was pointed out for the first time [5], and this means that the effects of conjugation in R_3EX compounds have not been ruled out yet by the existence $(p\text{–}d)\pi$-interaction. The second resonance effect in these compounds is σ,π-conjugation [2]. We consider the compounds R_3EX (E = Si, Ge and X = C_6H_5) to be convenient objects for the qualitative evaluation of the relative contributions by $(p\text{–}d)\pi$-interaction and σ,π-conjugation, because these compounds can be regarded as benzene derivatives so use can be made of good experimental techniques for the investigation of ER_3 fragment resonance effects.

On the basis of the perturbation theory of molecular orbitals it was shown [2] that the perturbation energy δE, due to σ,π-conjugation in $R_3EC_6H_5$, such that $\delta E = \pm \dfrac{a^2(\pi) \cdot a^2(\sigma) \cdot p^2}{\Delta E}$,
where $\Delta E = E(\pi) - E(\sigma)$, the energy difference between the energy levels of the unperturbed aromatic ring π-orbitals and the σ-orbitals of the E–R bonds; $a^2(\pi)$ and $a^2(\sigma)$ are the electron densities in the p-orbitals of the bonding atoms in the HOMO of the π- and σ-systems; and p is the perturbation integral, which includes overlap of the p-orbitals connecting the π- and σ-systems. Several factors influencing σ,π-conjugation with varying E and R (alkyl groups, halogen atoms etc.) not only make the estimation of σ,π-conjugation value difficult but they also raise certain doubts about the direction of this effect. Thus based only on the formal quantum-chemical approach, one may see the σ,π-conjugation in $R_3EC_6H_5$ as a transfer of electron density from R_3E to the C_6H_5 group and vice versa.

Approximate calculations of the MO energy for phenyl derivatives of the silicon subgroup elements were carried out by use of semiempirical methods of quantum chemistry [6,7]. It follows from these calculations that, just as for the inductive effect in phenyl derivatives, two oppositely directed resonance effects occur, viz. $(p\text{–}d)\pi$-interaction and σ,π-conjugation. These calculations are approximate and thus require clarification.

We think that unambiguous conclusions on the direction of σ,π-conjugation and $(p\text{–}d)\pi$-interaction effects in $R_3EC_6H_5$ can be obtained by use of an independent method, by analysing both the Hammett σ-constants of ER_3 fragments and the Brown-Okamoto σ^+-constants, so that the electronic effects of some fragments, in cases when positive charge exists on aromatic ring can be characterized. It is well known, for example [8,9], that in benzyl derivatives $C_6H_5CH_2ER_3$, the σ,π-conjugation effect of the C–E σ-bonds with the π-electron system of the aromatic ring, firstly it originates in the CH_2ER_3 fragment and is directed towards the π-system, secondly it increases with increase in atomic number of element E and, thirdly it increases sharply with the presence of positive charge at the π-system. Such an increase in σ,π-conjugation effect in particular, is manifested by the substantial increase in the absolute values of $CH_2E(CH_3)_3$ substituent σ-constants on going from σ°-constants ($\sigma^{\circ} = \sigma_R^{\circ} + \sigma_I$ determined by NMR spectroscopy in the ground electronic state to be between -0.25 and -0.3 [8]) to σ^+-constants ($\sigma^+ = \sigma_R^+ + \sigma_I$ determined by UV-spectroscopy of charge transfer complexes with tetracyanoethylene; under experimental conditions positive charge develops on π-system, σ^+ values for E = Si, Ge, Sn, Pb are -0.54; -0.63; -0.81 and -1.03, respectively [10]). Thus, an increase in the $CH_2E(CH_3)_3$-moiety donor properties relative to phenyl group with increasing positive charge on this group is manifested in the appearance of $\sigma_p^+ - \sigma$ differences. These differences are by corollary an indication that an increase in σ,π-conjugation causes an increase in the $CH_2E(CH_3)_3$-substituent donor properties. We thought that if $ER_{3-n}X_n$ substituents with a silicon subgroup E-element, analogous to $CH_2E(CH_3)_3$, take part in σ,π-conjugation with the benzene ring, then a positive charge at the π-system should lead to obvious $\sigma_p^+ - \sigma_p$ differences, including those for ($ER_{3-n}X_n$) substituents. All of the constants, σ_p and σ_p^+ as well as the $\sigma_p^+ - \sigma_p$ differences for organometallic and organic substituents drawn from the literature or calculated by procedures described therein to support this assumption, have been collected in Tables 1–4. The notes regarding charge influence which have been included are important for the analysis of these differences which become apparent upon conjugation in benzyl organic derivatives.

Table 1

σ_p and σ_p^+ values and sums of the bond refractions ΣR_D for the compounds $C_6H_5SiR_{3-n}X_n$

Compound No.	Substituent $SiR_{3-n}X_n$	σ_p	σ_p^+	$\sigma_p^+ - \sigma_p$	ΣR_D
1	SiH_3	+0.10 [a]	−0.01 [b]	−0.11	12.5
2	$SiH(CH_3)_2$	+0.05 [c]	−0.06 [b]	−0.11	11.1
3	$Si(CH_3)_3$	−0.10 [a]	−0.13 [b]	−0.03	10.5
4	$Si(C_2H_5)_3$	−0.14 [d]	−0.14 [b]	0	10.5
5	$Si(CH_3)_2C_6H_5$	~ −0.09 [e]	−0.10 [b]	−0.01	10.9
6	$Si(CH_3)(C_6H_5)_2$	~ −0.09 [e]	−0.06 [b]	+0.03	11.3
7	$Si(C_6H_5)_3$	−0.08 [f]	−0.15 [b]	−0.07	11.7
8	$Si(OC_2H_5)_3$	−0.01 [f]	+0.01 [g]	~ +0.02	8.3
9	$Si[OSi(CH_3)_3]_3$	+0.02 [h]	~ 0 [i]	~ −0.02	8.3
10	$\overline{Si(OCH_2CH_2)_3N}$	−0.18 [j]	−0.21 [k]	−0.03	10.5
11	$Si(CH_3)F_2$	+0.42 [l]	+0.37 [m]	−0.05	8.8
12	SiF_3	+0.66 [f]	+0.7 [m]	+0.04	8.0
13	SiH_2Cl	+0.26 [l]	+0.09 [b]	−0.17	16.4
14	$Si(CH_3)_2Cl$	+0.21 [n]	+0.05 [m]	−0.16	15.0
15	$Si(CH_3)Cl_2$	+0.39 [n]	+0.13 [b]	−0.26	19.6
16	$SiCl_3$	+0.56 [o]	+0.16 [b]	−0.40	24.2
17	$Si(CH_3)Br_2$	+0.30 [p]	−0.08 [q]	−0.38	25.9
18	$SiBr_3$	+0.57 [o]	−0.11 [r]	−0.68	33.6

[a] Ref. 11. [b] Calculated from frequencies of CT bands (ν_{CT}) in UV spectra of charge transfer complexes with tetracyanoethylene [12] by a method described previously [10]. [c] Ref. 13. [d] Ref. 14. [e] Taken close to σ_p for $Si(CH_3)_3$ and $Si(C_6H_5)_3$. [f] Ref. 15. [g] Calculated from ν_{CT} [16] by use of a method described previously [10]. [h] Ref. 17. [i] Calculated from ν_{CT} (26200 cm^{-1}) by use of a method described previously [10]. [j] $\sigma_p = \sigma_I(-0.20$ [18]$) + \sigma_R(+0.02$ [15]$)$. [k] Calculated from ν_{CT} [19] by use of a method described previously [10]. [l] Evaluated from the data in ref. [20] for substituents of related structures. [m] Calculated from ionization potentials [21] by use of the equation $IP = 1.31\sigma^+ + 9.24$ [22]. [n] Ref. 23. [o] Ref. 24. [p] Ref. 25. [q] Calculated from ν_{CT} (25300 cm^{-1}) by use of a method described previously [10]. [r] Calculated from ν_{CT} (25000 cm^{-1}) by use of a method described previously [10].

Similar to the σ,π-conjugated systems discussed above, the difference $\sigma_p^+ - \sigma_p$ for typical n-donor +M-substituents (NH_2,OR, ...), taking part in the n,π-conjugation with aromatic ring have high negative values, for example [11,38]. In particular, the σ_p^+ constants were derived [35] so as to characterize the increase in n-donor properties in substituents on going from a mesomeric +M-effect (constants σ_p) to one which is total (constants σ_p^+) and includes mesomeric and electromeric +E constituents [38]. The behaviour of the typical π-acceptor organic +M-substituents (NO_2, COH, ...) that participate in n,π-conjugation with aromatic ring is of a different character. Usually it is assumed that the presence of positive charge at the π-system or at the *para*-substituent does not have a pronounced influence of the electronic effects of the −M-substituents. It is necessary to point out that this conclusion is general and not a strict rule, i.e. with an extremely strong influence of positive charge in $YCH_2{}^+$ cations, +M-substituents, can actually lose their π-acceptor properties [39]. The σ_p and σ_p^+ constants of organic −M-substituents differ very little from each other, i.e. $\sigma_p^+ - \sigma_p$ approaches zero. On the assumption that $ER_{3-n}X_n$ substituents (E-silicon subgroup elements) possess a $(p\text{–}d)\pi$-interaction single resonance π-acceptor effect, instead of assuming the analogy with organic −M-substituents, one can conclude that $\sigma_p^+ - \sigma_p$ should be close to zero. If the second but oppositely directed π-donor effect of σ,π-conjugation plays an appreciable role along with $(p\text{–}d)\pi$-interaction, the $\sigma_p^+ - \sigma_p$ differences should be negative. The σ_p and σ_p^+ values for organosilicon compounds, which are discussed below, are listed in Table 1.

Discussion

Phenylsilanes

The literature data on the σ_p and σ_p^+ values are limited and in some cases lack reliability. Some σ-values are doubtful owing to the presence of side reactions occurring during determination of σ by the use of chemical methods. Obviously, for the determination of σ-constants preference should be given to physical methods. Furthermore, in an effort to choose the most reliable σ-constant values, (Tables 1–4) we could not avoid subjective estimation in some cases. This is related to difficulties in correctly evaluating the accuracy of the σ value owing to possible uncontrollable errors, which are admitted in the determination of the σ constants.

The σ_p-constants of silyl substituents quantitatively characterize the total electronic effect (inductive and resonance) of $SiR_{3-n}X_n$ substituents. Thus, σ_p constants for SiH_3 (+0.10), $SiH(CH_3)_2$ (+0.05) and $Si(CH_3)_3$ (−0.10) are larger, than those for CH_3 (−0.17), $CH(CH_3)_2$ (−0.15) and $C(CH_3)_3$ (−0.20) [11]. This is definitely indicative of the resonance π-acceptor properties of organosilicon substituents, because in the case of only inductive effect being present, rather large σ_p values would be shown for organic substituents in the opposite direction. Another characteristic is the increase in σ_p constants with the increase in acceptor properties of X in SiX_3 (for example in series $C_6H_6 < OC_2H_5 < Br \approx Cl < F$). This is also true for an increase in n in $SiR_{3-n}X_n$. Larger σ_p constant values are a result of an increase in both inductive and resonance π-acceptor components.

The σ_p^+ constants quantitatively characterize the total electronic effect of the $SiR_{3-n}X_n$ substituents towards the electron-deficient reaction center bearing positive charge. As with σ_p values σ_p^+ constants for silyl substituents SiH_3 (−0.01),

$SiH(CH_3)_2$ (~ 0.06) and $Si(CH_3)_3$ (−0.13) have higher values than the corresponding alkyl groups CH_3 (−0.31), $CH(CH_3)_2$ (−0.28) and $C(CH_3)_3$ (−0.26) [11]. However there is no clearly defined dependence of the $SiR_{3-n}X_n$ substituent σ_p constants on the quantity of, and acceptor properties of, X substituents during the transition to σ_p^+ constants in general. At first sight it would seem that there is no agreement at all between σ_p and σ_p^+ organosilicon substituent values. For example for halogen derivatives $SiHlg_3$, depending on which halogen is bound to the silicon, both a maximum value for σ_p^+ (for SiF_3) and very small one (for $SiBr_3$) were observed.

From Table 1 it can be seen that there is no correlation of the $\sigma_p^+ - \sigma_p$ differences to the donor-acceptor properties of the three halogen substituents on the silicon atom.

Actually, large negative values ($SiCl_3$, $SiBr_3$) and small positive $\sigma_p^+ - \sigma_p$ differences were observed for substituents $SiHlg_3$. The $\sigma_p^+ - \sigma_p$ differences for the rest of the silyl substituents spread between these boundary values. Along with all the data presented above it follows that the $\sigma_p^+ - \sigma_p$ differences are an indication the strengthening of the $SiR_{3-n}X_n$ substituent σ,π-conjugation with the benzene ring on going from a molecule in the ground electronic state to the charge-transfer state in which an aromatic ring has a positive charge. According to the value and sign of these differences, strengthening of σ,π-conjugation varies over a wide range, depending on the nature of R and X in $SiR_{3-n}X_n$, but it is quite clearly not related to the donor-acceptor properties of R and X.

It is important that future studies are carried out to detail the differences between mesomeric +M and electromeric +E effects. It is known (for example [38]) that the total conjugation effect (+K-mechanism [38], a quantitative measure of the σ_p^+-constant) comprises the mesomeric +M-effect and the electromeric +E-effect. The +M-effect, a quantitative measure of the σ_p constant is an indication of molecular polarization in the ground electronic states. The +E-effect, a quantitative measure of the difference $\sigma_p^+ - \sigma_p$ is an indication of the additional conjugation in the mesomeric system which is transferred from the ground to the excited state (in our case such a transition takes place with the appearance of the positive charge on the aromatic ring). The most important electromeric effect is that of polarizability which is closely related to the energy gained by an electron undergoing transition from the ground to the excited state [38,40], in addition it can be characterized by the $\sigma_p^+ - \sigma_p$ value. It follows from the above that an increase in σ,π-conjugation together with the appearance of positive charge on the aromatic ring should be greater, the higher the polarizability of $SiR_{3-n}X_n$ fragment chemical bonds taking part in this type of conjugation with aromatic π-system. For $C_6H_5SiR_{3-n}X_n$ compounds these bonds are C_{ar}–Si, Si–R and Si–X. R_D bond refraction is a quantitative measure of the polarizability of the chemical bonds and the lability of the electrons which take part in bond formation [40]. The refraction system developed by Vogel is one which is most commonly used. We found that there was a linear relationship between $\sigma_p^+ - \sigma_p$ and ΣR_D values for $C_6H_5SiR_{3-n}X_n$ compounds at a 95% confidence level:

$$\sigma_p^+ - \sigma_p = -(0.0260 \pm 0.0029)\sum R_D + (0.238 \pm 0.045) \qquad (1)$$

$$r = 0.979 \qquad n = 18$$

It is noteworthy that as opposed to the differences $\sigma_p^+ - \sigma_p$, the value of σ_p or σ_p^+

when taken individually do not show satisfactory linear correlations with ΣR_D, which is evident from the above. The σ,π-conjugation effect depends on many factors [2], and not only in bond polarizability. But strengthening of σ,π-conjugation under developing positive charge on the aromatic ring depends mostly upon polarizability of bonds. A comparatively low correlation coefficient (I) which is related to errors in the determination of the σ_p and σ_p^+ constants as well as to errors in the R_D values used. Firstly, R_D values for particular compounds may differ from tabulated data owing to intramolecular interactions and, secondly, they are only approximate for the branched R groups and X in $SiR_{3-n}X_n$, because we assumed that the Si–R and Si–X refractions represent silicon atom bond refraction with first atom of the R group or X, bound to it.

Thus, bond polarizability is the main factor which determines the strength of σ,π-conjugation in the organosilicon compounds studied. So, the strongest acceptor, the organosilicon substituent SiF_3 ($\sigma_p = +0.66$), practically does not change its acceptor properties when positive charge is present on the aromatic ring in $C_6H_5SiF_3$, this is be cause of the slight polarizability of Si–F bonds. Polarizability of Si–Br bonds is considerably higher, so the acceptor, $SiBr_3$ ($\sigma_p = +0.57$), when positive charge is present on the ring, becomes a donor-type substituent ($\sigma_p^+ = -0.11$). The data obtained unambiguously support the fact that the two $SiR_{3-n}X_n$ substituent resonance effects are towards aromatic ring in the opposite direction. The $SiR_{3-n}X_n$ substituent is a π-acceptor under $(p-d)\pi$-interaction, and a σ-donor under σ,π-conjugation.

Phenyl derivatives of germanium, tin and lead

It follows from the data on phenylsilanes, that $(p-d)\pi$-interactions and σ,π-conjugation effects act in opposite directions. Characteristically, the order with which these values change with change in the atomic number of element E in silicon subgroup is also opposite [3,9]. According to traditional ideas [3,6], the $(p-d)\pi$-interaction effect decreases with increase in the atomic number of the elements of the silicon subgroup. This effect is of maximum importance for organosilicon compounds relative to lead derivatives, particularly because up to now the existence of $(p-d)\pi$-interaction has been doubtful. In contrast the σ,π-conjugation effect increases with increase of atomic number of elements of the silicon subgroup. Markedly higher values of σ,π-conjugation in organosilicon compounds occur compared with organic ones and are found to increase progressively towards organogermanium, -tin and -lead compounds [9]. Thus, of these resonance effects acting in opposite directions, the $(p-d)\pi$-interaction should prevail in silicon compounds, and σ,π-conjugation should predominate in the lead compounds. Resonance effects in germanium and tin compounds should include contributions from both $(p-d)\pi$-interaction and σ,π-conjugation. Before we consider the $\sigma_p^+ - \sigma_p$ values for germanium, tin and lead compounds (Table 2), it would be useful to consider $\sigma_R = \sigma_p - \sigma_I$ values for the simplest substituents of $E(CH_3)_3$ (Table 3). It follows from Table 3 that σ_p values are higher for organometallic substituents than σ_p for $C(CH)_3$ group. This suggests that, according to the total electronic effect, organometallic substituents are generally in the ground electronic state, less of a donor type than $C(CH_3)_3$ group. However, when positive charge is present on the aromatic ring, donor properties of all organometallic substituents increase, and as the difference between σ_p and σ_p^+ increases, the greater the atomic weight of the

Table 2

σ_p and σ_p^+ values and sums of the bond refractions ΣR_D for the $C_6H_5ER_{3-n}X_n$ compounds (E = Ge, Sn, Pb)

Compound No.	Substituent $ER_{3-n}X_n$	σ_p	σ_p^+	$\sigma_p^+ - \sigma_p$	ΣR_D
19	$Ge(CH_3)_3$	~ −0.10 [a]	−0.21 [b]	−0.11	14.0
20	$GeH(C_6H_5)_2$	+0.16 [c]	−0.07 [d]	−0.23	18.0
21	$Ge(C_6H_5)_3$	+0.16 [c]	−0.07 [e]	−0.23	19.0
22	$GeCl_3$	+0.79 [f]	+0.33 [g]	−0.46	27.6
23	$Ge(C_6H_5)_2Br$	+0.35 [h]	−0.05 [d]	−0.40	25.4
24	$Ge(C_6H_5)Br_2$	+0.60 [h]	+0.09 [i]	−0.51	31.8
25	$Sn(CH_3)_3$	−0.12 [j]	−0.34 [k]	−0.22	17.5
26	$SnH(C_6H_5)_2$	+0.20 [l]	−0.10 [d]	−0.30	19.8
27	$Sn(C_6H_5)_3$	+0.21 [m]	−0.07 [n]	−0.28	20.0
28	$Sn(C_6H_5)_2Cl$	+0.40 [o]	+0.04 [d]	−0.36	23.9
29	$SnCl_3$	+0.95 [m]	+0.41 [p]	−0.54	30.5
30	$Pb(C_6H_5)_3$	+0.21 [m]	−0.07 [n]	−0.28	21.0

[a] Averaged values [13,14,20]. [b] Calculated from ν_{CT} (23800 cm^{-1}) by use of a method described previously [10]. [c] Averaged value [11,26]. [d] Calculated from *IP* [27] by use of a method described previously [22]. [e] Calculated from ν_{CT} [28] by use of a method described previously [10]. [f] Ref. 24. [g] Calculated from ν_{CT} (29500 cm^{-1}) by use of a method described previously [10]. [h] Evaluated from the data in ref. 20 for substituents of related structures. [i] Calculated from ν_{CT} (27000 cm^{-1}) by use of a method described previously [10]. [j] Ref. 9, 11. [k] Calculated from ν_{CT} (22500 cm^{-1}) by use of a a method described previously [10]. [l] Taken to be equal to σ_p for $Sn(C_6H_5)_3$. [m] Ref. 29. [n] Calculated from ν_{CT} [28] by use of a method described previously [10]. [o] Evaluated from the data in ref. 29 for substituents of related structures. [p] Calculated from *IP* [30] by use of a method described previously [30].

central element. As this takes place, judging from σ_p^+ values, donor properties of $Sn(CH_3)_3$ group are increased compared with those of $C(CH_3)_3$ group. Owing to the high carbon electronegativity among all Group IVB elements [44] inductive σ_I constants have lower values compared with that for $C(CH_3)_3$ group. Resonance constants $\sigma_R = \sigma_p - \sigma_I$ for organometallic substituents are positive, while the σ_R value for $C(CH)_3$ is −0.13. Once σ,π-conjugation has become the only possible resonance effect for $C(CH_3)_3$ group, two resonance effects act on the organometallic substituents: $(p\text{–}d)\pi$-interaction and σ,π-conjugation.

In accordance with the general ideas, the decrease of σ_R on going from $Si(CH_3)_3$ to $Ge(CH_3)_3$ and to $Sn(CH_3)_3$ can be seen as a result of the simultaneous strengthening of σ,π-conjugation and weakening of $(p\text{–}d)\pi$-interaction. But in

Table 3

σ constants for substituents $E(CH_3)_3$ (E = C, Si, Ge, Sn) in $C_6H_5E(CH_3)_3$

	$C(CH_3)_3$	$Si(CH_3)_3$	$Ge(CH_3)_3$	$Sn(CH_3)_3$
σ_p	−0.20 [a]	−0.10 [b]	−0.10 [c]	−0.12 [c]
σ_p^+	−0.26 [a]	−0.13 [b]	−0.21 [c]	−0.34 [c]
σ_I	−0.07 [a]	−0.15 [d]	−0.11 [e]	−0.13 [e]
σ_R	−0.13 [a]	+0.05 [f]	+0.01 [f]	+0.01 [f]
σ_R^+	−0.19 [a]	+0.02 [g]	−0.10 [g]	−0.21 [g]

[a] Ref. 11; [b] Table 1; [c] Table 2; [d] Ref. 42; [e] Ref. 43; [f] $\sigma_R = \sigma_p - \sigma_I$. [g] $\sigma_R^+ = \sigma_p^+ - \sigma_I$.

principle there can be another explanation for the decrease of σ_R in the given series. Thus $(p-d)\pi$-interaction (σ,π-conjugation) increases with the increase in atomic number of the element in the silicon subgroup so that σ,π-conjugation increase occurs to a greater extent than that of $(p-d)\pi$-interaction. In such a situation, the σ_R constants which characterize the total resonance effect of the organometallic substituents must also decrease on going from $Si(CH_3)_3$ to $Sn(CH_3)_3$. However this alternative is contrary traditional views on $(p-d)\pi$-interaction [3]. Nevertheless it seem that such an alternative can be rejected with assurance only on the basis of results of quantum-chemical investigations have yet to be carried out.

As comprehensively discussed above, σ,π-conjugation is strengthened when positive charge exists on the aromatic ring and this is reflected in lower σ_R^+ values relative to σ_R. Thus the σ_R^+ values for organometallic substituents differ greatly. For $Si(CH_3)_e$ the σ_R^+ value is positive, which indicates that $(p-d)\pi$-interaction prevails over σ,π-conjugation. However, for $Sn(CH_3)_3$ the σ_R^+ constant is large and negative which indicates obvious domination of σ,π-conjugation over $(p-d)\pi$-interaction.

To come back to the discussed data given in Table 2, some of typical features can be seen. Firstly, a regular increase in $\sigma_p^+ - \sigma_p$ for each type of substituent structure with increase of the central element atomic number takes place so that in the three series of substituents 3,19,25;7,21,27,30;16,22,29. Secondly, in each of the three substituent series given above the increase in $\sigma_p^+ - \sigma_p$ is associated with an increase in the atomic number of the central element. Thirdly, negative σ_p^+ values are seen for some substituents, which from their σ_p values are acceptors in their ground electronic state, e.g. $Ge(C_6H_5)_2Br$. These features (analogous to those observed for silicon-containing substituents) are quite clearly explained in terms of the polarizability effect. So for substituents **19**–**30** a linear relationship at a 95% confidence level is valid:

$$\sigma_p^+ - \sigma_p = -(0.0234 \pm 0.0025)\sum R_D + (0.196 \pm 0.058) \qquad (2)$$
$$r = 0.989 \qquad n = 12$$

For substituents **1**–**30**, comprising silicon subgroup elements, a unitary relationship is observed

$$\sigma_p^+ - \sigma_p = -(0.0249 \pm 0.0017)\sum R_D + (0.226 \pm 0.032) \qquad (3)$$
$$r = 0.985 \qquad n = 30$$

Phenyl derivatives of group II, III and V elements

It follows from the above, that the $\sigma_p^+ - \sigma_p$ difference becomes apparent for $ER_{3-n}X_n$ substituents in the compounds $C_6H_5ER_{3-n}X_n$ (E-silicon subgroup element) after the strengthening of the σ,π-conjugation for these substituents with benzene ring. The strengthening of σ,π-conjugation with increasing positive charge on the ring, a quantitative indication of this is the difference $\sigma_p^+ - \sigma_p$ and is related to polarizability of the bonds by the linear relationship (3). We thought that eq. 3 would not impose notable restrictions on the nature of substituents connected to aromatic ring. The only restriction is that substituents **1**–**30** provide two oppositely directed effects. In this case resonance donor effect (σ,π-conjugation) in the ground electronic state is comparatively small. So when checking the suitability of relationship (3) for substituents not associated with silicon subgroup, one should avoid those substituents (for example, NH_2, OR type n-donors) which are already in the

Table 4

σ_p and σ_p^+ values and sums of the bond refractions ΣR_D for the $C_6H_5EX_n$ compounds (E = Hg, B, P, As, Sb, Bi)

No.	Substituent EX_n	σ_p	σ_p^+	$\sigma_p^+ - \sigma_p$	ΣR_D
31	HgCl	+0.35 [a]	+0.16 [b]	−0.19	18.7
32	HgBr	+0.35 [a]	+0.07 [b]	−0.28	21.7
33	$B(C_6H_5)_2$	+0.1 [c]	−0.01 [d]	−0.11	8.3
34	$P(CH_3)_2$	+0.03 [a]	−0.03 [e]	−0.06	11.1
35	$P(C_6H_5)_2$	+0.16 [a]	∼ 0 [e]	−0.16	13.2
36	PCl_2	+0.61 [a]	+0.35 [e]	−0.26	21.2
37	$PSCl_2$	∼ +0.90 [a]	+0.53 [e]	∼ −0.4	27.7
38	$As(C_6H_5)_2$	+0.18 [f]	−0.01 [d]	−0.19	14.8
39	$Sb(C_6H_5)_2$	+0.19 [g]	−0.07 [d]	−0.26	16.2
40	$Bi(C_6H_5)_2$	+0.18 [g]	−0.13 [d]	−0.31	20.7

[a] Ref. 11. [b] Calculated from *IP* [31] by the use of a method described previously [22]. [c] Evaluated from the data in ref. 11 for substituents of related structures. [d] Calculated from ν_{CT} [28] by the use of a method described previously [10]. [e] Calculated from *IP* [32] by the use of a method described previously [22]. [f] Taken to be equal to σ_p for $Sb(C_6H_5)_2$ and $Bi(C_6H_5)_2$. [g] Ref. 33, $\sigma_p = \sigma_I + \sigma_R$.

ground electronic state enter into strong conjugation with aromatic ring. Such a restriction, and the need to know the exact σ_p and σ_p^+ values, appreciably narrow the range of substituents for which eq. 3 can be expected to be satisfaction (Table 4). We assumed on the basis of a previous report [45] that in the phosphorus subgroup compounds the conjugation effects with participation of lone-pairs electrons of central elements are small, i.e. the elements have diffuse *p*-orbitals. In addition, the central atoms of substituents **31**–**40** have vacant *np*- or *nd*-orbitals. Thus substituents **31**–**40** should exhibit π-acceptor properties towards aromatic ring, i.e. taking part in $(p\text{–}p)\pi$- or $(p\text{–}d)\pi$-interactions. Furthermore substituents **31**–**40** comprise polarizable bonds and hence show an increase in the degree of σ,π-conjugation with the aromatic ring having positive charge present on it. This is indicated by large $\sigma_p^+ - \sigma_p$ and ΣR_D values. Thus compounds **31**–**40** follow relationship (3) and for compounds **1**–**40** the linear relationship (4) is true at 95% confidence level.

$$\sigma_p^+ - \sigma_p = -(0.0235 \pm 0.0019)\sum R_D + (0.198 \pm 0.036) \qquad (4)$$

$$r = 0.971 \qquad n = 40$$

Phenyl derivatives of the type $C_6H_5CR_{3-n}X_n$ *and* $C_6H_5CH_{3-n}[E(CH_3)_3]_n$

It follows from eq. 4 that the linear relationship between $\sigma_p^+ - \sigma_p$ and ΣR_D is true for all investigated phenyl derivatives of main group elements $C_6H_5ER_{3-n}X_n$ (E = Hg, B, P, As, Sb, Bi, Si, Ge, Sn, Pb). Now let us consider carbon derivatives $C_6H_5CR_{3-n}X_n$. These derivatives differ significantly from organometallic compounds by impracticable participation of vacant carbon atom *nd*-orbitals in $(p\text{–}d)\pi$-interaction, for example [3]. Thus the only resonance effect in carbon derivatives studied is σ,π-conjugation. Details of σ,π-conjugation with participation of alkyl groups has been described previously [46], but it seems that the presence of positive charge at the reaction center leads to strengthening of the σ,π-conjugation [46,47]. Thus for substituents **41**–**48**, the $\sigma_p^+ - \sigma_p$ differences are negative (Table 5). Substituents **49**–**52**, as they are electron donors, and in the ground state, with the appearance of positive charge on the aromatic ring, the relation concerned is similar

Table 5

σ_p and σ_p^+ values and sums of the bond refractions for the compounds $C_6H_5CR_{3-n}X_n$ and $C_6H_5CH_{3-n}[E(CH_3)_3]_n$

No.	Substituent $CR_{3-n}X_n$	σ_p	σ_p^+	$\sigma_p^+ - \sigma_p$	ΣR_D
41	CH_3	−0.17 [a]	−0.31 [a]	−0.14	6.3
42	C_2H_5	−0.15 [a]	−0.29 [a]	−0.14	6.0
43	i-C_3H_7	−0.15 [a]	−0.28 [a]	−0.13	5.6
44	t-C_4H_9	−0.20 [a]	−0.26 [a]	−0.06	5.2
45	$CH_2C(CH_3)_3$	−0.16 [a]	−0.33 [a]	−0.17	6.0
46	cyclo-C_4H_7	−0.14 [a]	−0.29 [a]	−0.15	5.8
47	cyclo-C_5H_9	−0.13 [a]	−0.30 [a]	−0.17	5.6
48	cyclo-C_6H_{11}	−0.13 [a]	−0.28 [a]	−0.15	5.6
49	$CH_2C_6H_5$	−0.09 [a]	−0.25 [a]	−0.16	5.0
50	CH_2OCH_3	−0.05 [a]	−0.30 [b]	−0.25	6.2
51	$C(OCH_3)_3$	−0.04 [a]	−0.16 [c]	−0.12	5.9
52	CH_2CO_2R	−0.07 [a]	−0.15 [a]	−0.08	6.0
53	CF_3	+0.53 [a]	+0.61 [d]	+0.08	5.6
54	CH_2Cl	+0.12 [a]	−0.01 [a]	−0.13	11.2
55	CCl_3	+0.46 [a]	~ +0.2 [e]	~ −0.25	20.8
56	CH_2Br	+0.14 [a]	−0.06 [a]	−0.20	14.1
57	$CH_2Si(CH_3)_3$	−0.27 [f]	−0.54 [g]	−0.27	7.2
58	$CH[Si(CH_3)_3]_2$	−0.28 [h]	−0.65 [g]	−0.37	8.0
59	$C[Si(CH_3)_3]_3$	−0.28 [h]	−0.68 [g]	−0.40	8.3
60	$CH_2Ge(CH_3)_3$	−0.25 [i]	−0.63 [g]	−0.38	7.8
61	$CH_2Sn(CH_3)_3$	−0.29 [i]	−0.81 [g]	−0.52	8.9
62	$CH[Sn(CH_3)_3]_2$	~ −0.3 [j]	−1.06 [g]	~ −0.75	11.2
63	$CH_2Pb(CH_3)_3$	−0.29 [i]	−1.03 [g]	−0.74	10.0

[a] Ref. 11. [b] Calculated from *IP* [34] by use of a method described previously [22]. [c] Calculated from *IP* [30] by use of a method described previously [22]. [d] Ref. 35. [e] Calculated from ν_{CT} [16] by use of a method described previously [10]. [f] Ref. 36. [g] Ref. 10. [h] $\sigma_p = \sigma_I(-0.06) + \sigma_R(-0.22$ [37]). The σ_I values are taken to be equal to σ_I for $CH_2Si(CH_3)_3$ [8]. [i] Ref. 8, $\sigma_p = \sigma_I + \sigma_R$. [j] Taken close to σ_p for $CH_2Sn(CH_3)_3$ [8].

to that for alkyl groups. Substituents **57–63**, as is well known [9] and as discussed above, take part in the strong σ,π-conjugation with aromatic ring. Thus a characteristic feature of substituents **41–52**,**57–63** is their typical donor nature both according to the total electronic effect (negative σ_p and σ_p^+ values) and resonance effect of σ,π-conjugation.

An opposite situation exists for substituents **53–56**. Firstly, in the ground electronic state these substituents are typical acceptors and two of them (CF_3 and CCl_3) retain their acceptor properties in the presence of positive charge on aromatic ring. Secondly, resonance constants σ_R of the substituents, CH_2Cl (−0.03), CCl_3 (+0.02), CH_2Br (−0.03) [48] do not deviate much from zero and for CF_3 $\sigma_R = +0.10$, which suggests that direction of σ,π-conjugation in $C_6H_5CF_3$ is reversed [48]. The presence of electronic effects, which act in opposite directions, imparts to compounds **53–56** features analogous to compounds **1–40**. So that compounds **53–56** obey relationship (4). For compounds **1–40**,**53–56** the linear relationship (5) is true at 95% confidence level:

$$\sigma_p^+ - \sigma_p = -(0.0233 \pm 0.0019)\sum R_D + (0.192 \pm 0.034) \qquad (5)$$

$$r = 0.969 \qquad n = 44$$

As to the other compounds from Table 5 (**41–52,57–63**), linear relationship (6) is true

$$\sigma_p^+ - \sigma_p = -(0.117 \pm 0.015)\sum R_D + (0.53 \pm 0.11) \qquad (6)$$

$$r = 0.968 \qquad n = 19$$

Of considerable significance is the large angle coefficient of eq. 6 compared with that of eq. 5. The angle coefficient clearly reflects the well-known regularity associated with any conjugation effects [9], in other words the conjugation energy increases with an increase in the difference in donor-acceptor properties of chemical bonds participating in conjugation. Such a difference is larger (same ΣR_D, $\sigma_p^+ - \sigma_p$ values larger) for compounds, that obey relationship (6). As already mentioned above, the direction of the total substituent electronic effect in these compounds coincides with the direction of the substituent donor resonance effect towards the aromatic ring under σ,π-conjugation. In contrast to compounds obeying relationship (5), there are one or two electronic effects (inductive, resonance) that act in a direction opposite to σ,π-conjugation. Thus the compounds for which relationship (5) is valid because of an unfavourable influence by other electronic effects, σ,π-conjugation and its strengthening becomes less, which is to be expected in light of ΣR_D values and relationship (6).

Experimental

Three types of σ_p and σ_p^+ constants are listed in Tables 1–5. Values of the first type are literature data. Values of the second type were calculated from literature data by use of published methods. Values of the third type (σ_p^+) were calculated by use of the method by Davis [10]; for the calculation of ν_{CT} values, the frequencies of the charge transfer bands in the UV spectra of the CT complexes of compounds **9,17,18,22,24** and **25** with tetracyanoethylene were used. Spectra were recorded on a Perkin–Elmer 402 spectrophotometer. The cell path was 1 cm. CH_2Cl_2 was used as solvent. Donor concentration was about 1.10^{-1} mole/l^{-1}, that of tetracyanoethylene was about 2.10^{-2} mole/l^{-1}.

References

1 C.G. Pitt, Chem. Commun., (1971) 816.
2 C.G. Pitt, J. Organomet. Chem., 61 (1973) 49.
3 A.N. Egorochkin and S.Ya. Khorshev, Usp. Khim., 49 (1980) 1687; D.B. Beach and W.L. Jolly, Inorg. Chem., 23 (1984) 4774; E. Magnusson, Tetrahedron, 41 (1985) 2945; D.W.J. Cruickshank and M. Eisenstein, J. Mol. Struct., 130 (1985) 143; D.W.J. Cruickshank, J. Mol. Struct., 130 (1985) 177 and references cited therein
4 S. Marriott and R.D. Topsom, J. Mol. Struct., 106 (1984) 277
5 A.N. Nesmeyanov, Uch. Zap. Moskov. Univ., No. 132 (1950) 5
6 P.K. Bischof, M.J.S. Dewar, D.W. Goodman and T.B. Jones, J. Organomet. Chem., 82 (1974) 89
7 T. Veszprémi and J. Nagi, J. Organomet. Chem., 255 (1983) 41
8 W. Adcock, D.P. Cox and W. Kitching, J. Organomet. Chem., 133 (1977) 393
9 A.N. Egorochkin, Usp. Khim., 53 (1984) 772
10 D.D. Davis, J. Organomet. Chim., 206 (1981) 21
11 O. Exner in A. Chapman and J. Shorter (Eds.), Correlation Analysis in Chemistry. Recent Advances, Plenum Press, New York, 1978, p. 439
12 T.A. Zakomoldina, P.G. Sennikov, V.A. Kuznetsov, A.N. Egorochkin and V.O. Reikhsfel'd, Zh. Obshch. Khim., 50 (1980) 898

13 Vo Kim Yen, Z. Papouskova, J. Schraml and V. Chvalovsky, Coll. Czech. Chem. Commun., 38 (1973) 3167
14 G.A. Razuvaev, A.N. Egorochkin, S.E. Skobeleva, V.A. Kuznetsov, M.A. Lopatin, A.A. Petrov, V.S. Zavgorodny and E.T. Bogoradovsky, J. Organomet. Chem., 222 (1981) 55
15 M.G. Voronkov, V.I. Glukhikh, V.M. D'yakov, V.V. Keiko, G.A. Kuznetsov and O.G. Yarosh, Dokl. Akad. Nauk SSSR, 258 (1981) 382
16 R. Ponec and V. Chvalovsky, Coll. Czech. Chem. Commun., 39 (1974) 1185
17 Z. Plzak, F. Mares, J. Hetflejs, J. Schraml, Z. Papouskova, V. Bazant, E.G. Rochow and V. Chvalovsky, Coll. Czech. Chem. Commun., 36 (1971) 3115
18 M.G. Voronkov and V.M. D'yakov, Silatrani, Nauka, Novosibirsk, 1978
19 A. Daneshrad, C. Eaborn and D.R.M. Walton, J. Oranomet. Chem., 85 (1975) 35
20 A.N. Egorochkin and G.A. Razuvaev, Dokl. Akad. Nauk SSSR, 293 (1987) 129
21 T. Veszprémi, Y. Harada, K. Ohno and H. Mutoh, J. Organomet. Chem., 226 (1984) 9
22 T.G. Traylor, H.J. Berwin, J.M. Jerkunica and M.L. Hall, Zh. VKhO im.Mendeleeva, 17 (1972) 392
23 J. Lipowitz, J. Am. Chem. Soc., 94 (1972) 1582
24 N.V. Kondratenko, G.P. Syrova, V.I. Ionov, Yu.N. Sheinker and L.M. Yagupolski, Zh. Obshch. Khim., 41 (1971) 2056
25 F. Mares, Z.P. Plzak, J. Hetflejs and V. Chvalovsky, Coll. Czech. Chem. Commun., 36 (1971) 2957
26 R.A. Benkeser and H.R. Krysiak, J. Am. Chem. Soc., 75 (1953) 2421
27 G. Distefano, S. Pignataro, L. Szepes and J. Borossay, J. Organomet. Chem., 104 (1976) 173
28 J.E. Frey, R.D. Cole, E.C. Kitchen, L.M. Suprenant and M.S. Sylwestrzak, J. Am. Chem. Soc., 107 (1985) 748
29 J.M. Angelelli, M.A. Delmas, J.C. Maire and J.P. Zahra, J. Organomet. Chem., 128 (1977) 325
30 B.G. Ramsey, J. Organomet. Chem., 135 (1977) 307
31 V.N. Baidin, I.I. Kritskaya, M.M. Timoshenko, Yu.A. Ustynyuk and Yu.V. Chizhov, in M.E. Akopyan (Ed.), Uspekhi fotoniki. Sbornik 8. Leningrad, Izd. Leningradskogo Universiteta, 1983, p. 8
32 V.J. Vovna and F.I. Vilesov, in F.I. Vilesov (Ed.) Uspekhi fotoniki. Sbornik 5. Leningrad, Izd. Leningradskogo Universiteta, 1975, p. 3
33 A.N. Nesmeyanov, D.N. Kravtsov, B.A. Kvasov, S.I. Pombrik and E.I. Fedin, J. Organomet. Chem., 47 (1973) 367
34 K. Watanabe, J. Chem. Phys., 26 (1957) 542
35 H.C. Brown and Y. Okamoto, J. Am. Chem. Soc., 80 (1958) 4979
36 R.W. Taft, E. Price, I.R. Fox, I.C. Lewis, K.K. Anderson and G.T. Davis, J. Am. Chem. Soc., 85 (1963) 3146
37 C. Eaborn, A.R. Hancock and W.A. Stanzyk, J. Organomet. Chem., 218 (1981) 147
38 C.K. Ingold, Structure and Mechanism in Organic Chemistry, (1969), Cornell University Press, Ithaca, London, Ch. 2, Ch. 16
39 W.F. Reynolds, P. Dais, D.W. MacIntyre, R.D. Topsom, S. Marriott, E. VonNagy-Felsobuki and R.W. Taft, J. Am. Chem. Soc., 105 (1983) 378
40 S.S. Batsanov, Strukturnaya refraktometriya, Izd. Vyshaya Shkola, Moskva, 1960
41 A.I. Vogel, W.T. Cresswell and J. Leicester, J. Phys. Chem., 58 (1954) 174
42 A.N. Egorochkin, S.Ya. Khorshev, N.S. Vyazankin and E.N. Gladyshev, Izv. Akad. Nauk. SSSR, Ser. Khim., (1969) 1863
43 A.N. Egorochkin, Yu.D. Semchikov, N.S. Vyazankin and S.Ya. Khorshev, Izv. Akad. Nauk SSSR. Ser. Khim., (1970) 152
44 J. Marrot and J.C. Maire, J. Organomet. Chem., 157 (1978) 7
45 A.R. Katritzky and R.D. Topsom, Chem. Revs., 77 (1977) 639
46 R. Taylor, J. Chem. Res. (S), (1985) 318
47 P.B.D. de la Mare, Pure Appl. Chem., 56 (1984) 1755
48 L.M. Yagupolski, A.Ya. Il'chenko and N.V. Kondratenko, Usp. Khim., 43 (1974) 64