Charge control of phenol complexation with unsaturated compounds containing organosilicon substituents.*
Thiophene derivatives

A. N. Egorochkin and S. E. Skobeleva*

Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (0831) 235 6480

The frequency shifts $\Delta\nu$ of the O—H stretching modes and the resonance components $\Delta\nu_R$ of these shifts in the IR spectra of H-complexes of phenol with thiophene derivatives having organic and organosilicon substituents have been analyzed. Relationship of $\Delta\nu$ and $\Delta\nu_R$ parameters to values calculated by nonempirical methods that characterize the electronic effect of organic substituents on the effective charges of the thiophene ring atoms has been established. It has been shown that in the complexation of phenol (hard acid) with thiophene derivatives charge control prevails over frontier orbital control. The changes in the effective charges of the thiophene ring atoms due to the effect of organosilicon substituents have been calculated.

Key words: thiophene derivatives; silylthiophenes; H-complexes; effective charges; charge control in complexation; σ,π-conjugation; d,π-conjugation.

The use of IR spectroscopy in studies of intramolecular electronic interactions in organic and organometallic compounds is very effective.[1—6] Two approaches can be noted. The first one initially developed on an empirical basis. An analysis of the extensive experimental data[1—6] on the IR spectra of H-complexes of electron-acceptor molecules (phenol, pyrrole, methanol, *etc.*) and electron-donor molecules of the n-type (ethers $(R_i)_2O$, amines $(R_i)_3N$, sulfides $(R_i)_2S$, *etc.*) or of the π-type (derivatives of benzene, $C_6H_{6-n}(R_i)_n$, ethylene, $H_2C{=}CHR_i$, and acetylene, $R_iC{\equiv}CR_i$) showed that if the organic or organometallic substituents R_i were bound to donor centers (O, N, and S atoms, benzene ring, double, or triple bond), then for the same acceptor (for example, phenol H-complexes) the following correlations were fulfilled

$$\Delta\nu(\mathrm{OH}) = a\Delta G + b, \qquad (1)$$

$$\Delta\nu(\mathrm{OH}) = c\Delta H + d, \qquad (2)$$

$$\Delta\nu(\mathrm{OH}) = k\sigma_p(R_i) + l, \qquad (3)$$

$$\Delta\nu(\mathrm{OH}) = m\sigma_I(R_i) + n\sigma_R(R_i) + p. \qquad (4)$$

In Eqs. (1)—(4), $\Delta\nu$(OH) is the shift in the frequency of the stretching mode ν(O—H) in the IR spectrum of phenol due to H-complexation, ΔG and ΔH are the changes in Gibbs energy and enthalpy due to complexation, σ_p, σ_I and σ_R are the Hammett, inductive, and resonance constants of the substituents R_i at the donor center, and the coefficients *a—p* in the general case depend on the type of acceptor A and donor D (for the phenol complexes under consideration, they depend only on the type of donor).

Eqs. (3) and (4) can be used for determining the unknown constants σ from the experimentally measured values of $\Delta\nu$(OH). In particular, it has been confirmed that the values of σ_R for organometallic substituents of group IV are not universal. In fact, the σ_R constants for MR_3 substituents (M = Si, Ge, Sn; R is an organic radical) depend on the type of donor-center (benzene ring,[5] double bond,[6] or triple bond[4]), to which they are bound.

From the above statement it is clear that the empirical approach does not provide, in an explicit form, any information on mechanism of the interaction between A and D during H-complexation. Such important features of the intramolecular interactions in compounds D as π-electron exchange in the conjugation of the organometallic substituents R_i with the donor center remain beyond the given approach.

The second approach to the study of intramolecular interactions by IR spectroscopy is practically devoid of any of the abovementioned restrictions. The H-complexes are considered from the more general position of donor-acceptor bonding theory on the basis of the modern concepts of hard and soft acids and bases.[7—9] As was shown earlier,[9] the change in the total energy ΔE upon the interaction of molecules A and D (derivatives of

---

* For the previous publication of this series see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2163—2168, December, 1994.

thiophene, benzene,[5] ethylene,[6] and acetylene[4] as π-bases) at a distance r_{DA} in a polar medium with dielectric constant ε is described by the equation

$$\Delta E = -\frac{q_D q_A}{r_{DA}\varepsilon} + 2\sum_D\sum_A \frac{\left(C_D^m C_A^n \Delta\beta_{DA}\right)^2}{E_m - E_n}. \quad (5)$$

The first term of Eq. (5) characterizes the electrostatic interaction of hard acids (phenol, for example[7,8]) with hard bases, which are controlled by the effective charges at the donor (q_D) and acceptor (q_A) centers of molecules D and A. For H-complexes of π-bases with phenols, the carbon atoms with multiple bonds or in the benzene ring are the donor centers,[4–6] and the hydrogen atom of the phenol OH group is the acceptor center. Covalent interactions of soft acids with soft bases correspond to the second term of Eq. (5). These interactions are orbital-controlled, since an increase in the coefficients $C_D{}^m$ and $C_A{}^n$ at the atomic orbitals in the frontier and near-frontier molecular orbitals of the donor (m) and the acceptor (n), as well as a decrease in the difference between the energies E_m and E_n of the orbitals and an increase in the resonance integral $\Delta\beta_{DA}$, strengthen them.

In general, both electrostatic and covalent interactions occur between D and A, but in extreme cases[9–11] one of the two terms of Eq. (5) prevails. Electrostatic interaction dominates in the formation of H-complexes of phenol with derivatives of benzene, ethylene, and acetylene[4–6] (the first term of Eq. (5) distinctly prevails over the second term). In these cases, the predominance of charge control over orbital control is reflected, in particular, by the linear correlations[4–6]

$$\Delta\nu(\mathrm{OH}) = a'q_\pi + b'q_\sigma + c', \quad (6)$$

$$\Delta\nu_R(\mathrm{OH}) = k'q_\pi + l', \quad (7)$$

where $\Delta\nu_R(\mathrm{OH})$ is the resonance component of the frequency shift $\Delta\nu(\mathrm{OH})$, defined according to Eq. (4) as $\Delta\nu_R(\mathrm{OH}) = n\sigma_R(R_i)$; q_π and q_σ are the changes in the effective charges at the donor center due to π- and σ-interactions, respectively, between this center and the substituents R_i in the donor molecules D; the coefficients a', b', c', k', and l' depend on the type of donor center.

Thus, the second approach to the study of H-complexes by IR spectroscopy allows one to get information on the mechanism of intermolecular interactions between the partners of the H-bond, and, in principle, to quantitatively evaluate the effect of intramolecular interactions between the substituents and the donor center on the effective charge distribution in the donor molecules.

In the present work we used both of these approaches to study inter- and intramolecular interactions in thiophene derivatives with organic and organosilicon substituents.

Experimental

To solve the problem mentioned we used all of the available literature values of $\Delta\nu$ (see Refs. 2, 12, and 13) for H-complexes of thiophene derivatives with phenol and $\Delta\nu$ obtained in the present work as well. IR spectra of the H-complexes were recorded under the following conditions: CCl_4 as the solvent, concentration of phenol 0.01—0.02 M, concentration of thiophene derivatives 1.5—2 M; the reference cell of the spectrophotometer contained a solution of the substance under study in CCl_4 at the same concentration as in the analytical cell. The absorbing layer thickness was 0.1 or 0.4 cm. The values of $\Delta\nu$ were measured with an accuracy of *ca.* 3 cm^{-1}.

The correlations were established using the standard software package Statgraphics 3.0 with an IBM PC AT. Processing was carried out by the mean-least-square method at a confidence level of 95 %. We used the values of σ_p, σ_I, and σ_R from Ref. 14 for organic substituents and the values of σ_I from Refs. 3 and 15 for organosilicon substituents.

Results and Discussion

The values of $\Delta\nu$ for the thiophene derivatives depend on the nature and the number of organic substituents (Table 1). For these derivatives, a general relation (3), which is valid for H-complexes of substituted benzene, ethylene, and acetylene with phenol,[4–6] has the following form

$$\Delta\nu = -57\Sigma\sigma_p + 54 \quad (8)$$

$$(S_a = 2,\ S_b = 1,\ S_Y = 2,\ r = 0.996,\ n = 12).$$

The high quality of correlation (8) attests to the absence of steric effects in the complexation of phenol with thiophenes, *i.e.*, $\Delta\nu$ depends only on electronic factors (inductive and resonance effects). The sensitivity of $\Delta\nu$ to these effects is almost the same, which can be seen from the of equation

$$\Delta\nu = -57\Sigma\sigma_I - 56\Sigma\sigma_R + 54 \quad (9)$$

$$(S_a = 3,\ S_b = 7,\ S_c = 1,\ S_Y = 2,\ r = 0.995,\ n = 12).$$

The parameters in Eqs. (8) and (9) and in the corresponding equations

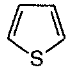
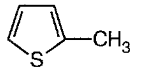
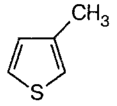
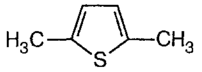
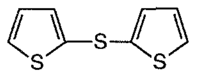
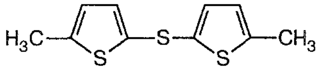
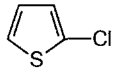
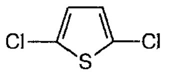
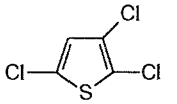
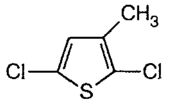
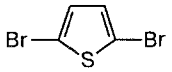
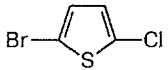
$$\Delta\nu^b = -50\Sigma\sigma_p + 50, \quad (10)$$

$$\Delta\delta^b = -54\Sigma\sigma_I - 48\Sigma\sigma_R + 51 \quad (11)$$

for the H-complexes of benzene derivatives with phenol are similar. In addition to the obvious conclusion that the electron-donor ability of benzene and thiophene are similar (similar values of $\Delta\nu^b$ and $\Delta\nu$), one can also conclude that the sensitivities of the aromatic and heteroaromatic systems of benzene and thiophene to the electronic effects of substituents on the reaction center during complexation with phenol differ only slightly.

However, position selectivity (the position of the reaction center) in the formation of complexes of substituted benzenes and thiophenes with phenol has not yet

Table 1. Frequency shifts $\Delta\nu$ in the IR-spectra of thiophene derivatives caused by the formation of H-complexes and the σ-constants of the substituents

Compound	$\Delta\nu$/cm^{-1}	$\Sigma\sigma_p$	$\Sigma\sigma_I$	$\Sigma\sigma_R$
	53	0	0	0
	64	−0.17	−0.05	−0.12
	66	−0.17	−0.05	−0.12
	74	−0.34	−0.10	−0.24
	49*	0.07	0.25	−0.18
	59*	−0.10	0.20	−0.30
	39	0.23	0.47	−0.24
	26	0.46	0.94	−0.48
	15	0.69	1.41	−0.72
	35	0.29	0.89	−0.60
	31	0.46	0.90	−0.44
	29	0.46	0.92	−0.46

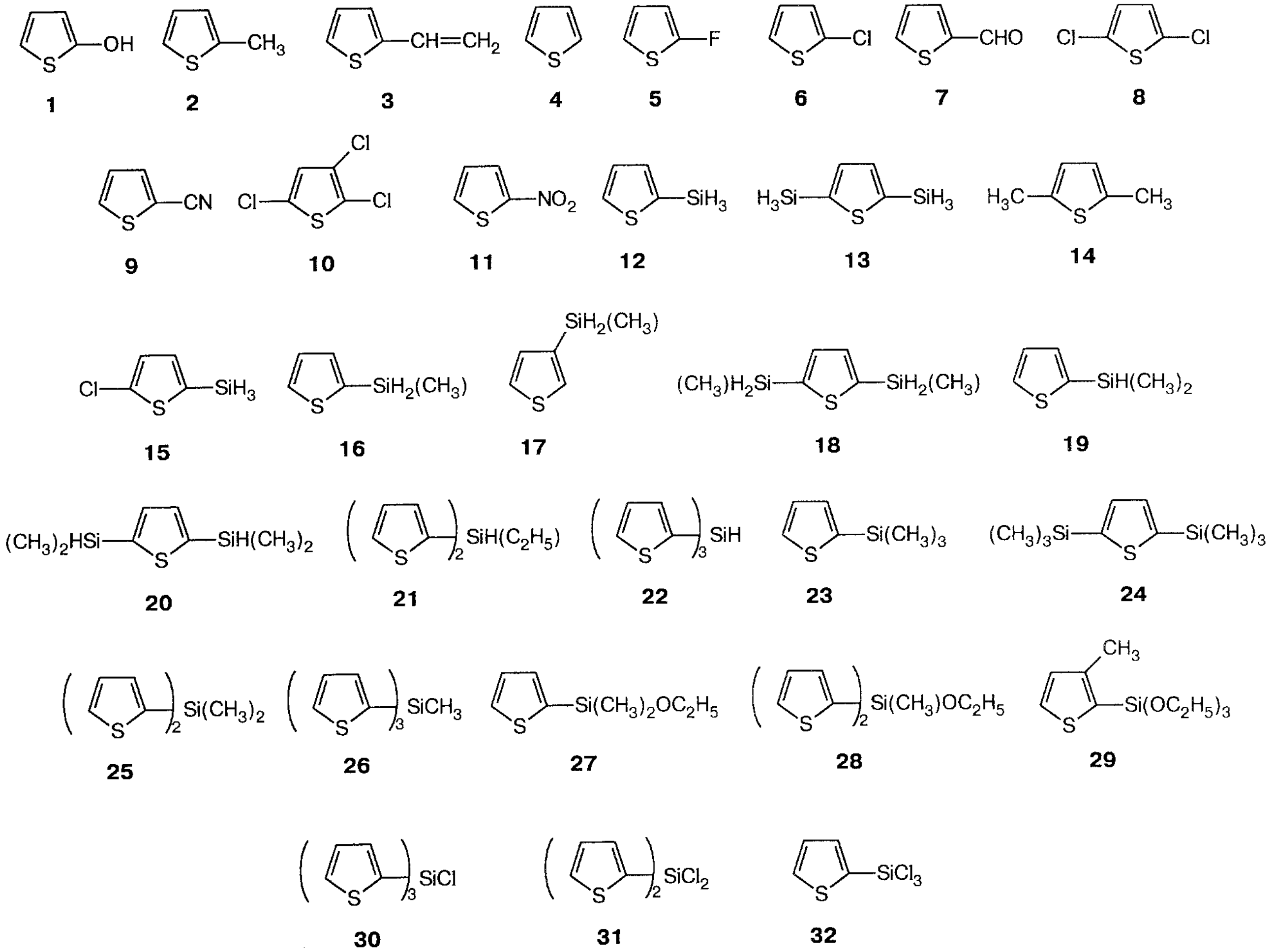
* In the H-binding between phenol and the S atom that is not included in the thiophene ring $\Delta\nu$ = 130 to 280 cm^{-1}.

been adequately studied, although the similarity between H-complexation and protonation has been established.[5] As has been shown earlier,[16] protonation of monosubstituted benzenes containing resonance donor and acceptor substituents occurs at the *para-* and, probably, *meta*-positions, respectively, *i.e.*, at the carbon atoms with the largest negative charge. Thus, one can assume that the formation of H-complexes between monosubstituted benzenes and phenol that occurs with charge control at the donor and acceptor centers exhibits position selectivity similar to that observed in protonation.[5]

Making a similar assumption for H-complexes of thiophene derivatives is more problematic, as H-bonding and protonation in thiophenes have not been studied as much as in benzenes. In the case of thiophene[17—19] and its various monochloro- and dichloroderivatives[17,18] it is established that protonation occurs at the α-position of the ring. According to quantum-chemical evaluations,[18] α-protonation of thiophene is 48 kJ mol^{-1} thermodynamically more favorable than β-protonation. It is significant that in thiophene and in monochloro-, and dichlorothiophenes the negative charge at the α-carbon atoms is higher than at the β-carbon atoms (the sulfur atom is charged positively).[18]

These facts are consistent with the conclusion[19] that position selectivity in the reaction of simple heteroaromatic compounds with typical electrophiles (in particular, in protonation) is controlled by electrostatic factors, *i.e.*, by the charges at the donor and acceptor centers (the first term in Eq. (5)). If we assume the priority of charge control in the complexation of thiophene derivatives with phenol, this assumption can be confirmed by using both the values of $\Delta\nu$ and the non-empirical quantum-chemical data[18,20] for various thiophenes. These data are available[18,20] for compounds **1—11** (Table 2).

Table 2. Frequency shifts Δν, the constants σ of substituents, and charges q localized in the thiophene ring



Compound	$\Delta\nu$/cm^{-1}	$\Sigma\sigma_p$	$\Delta\nu_R$/cm^{-1}	$\Sigma\sigma_R$	q_π/a.u.	q_σ/a.u.
1	75	−0.37	35	−0.62	−0.098	0.169
2	64	−0.17	7	−0.12	−0.007	−0.018
3	57	−0.05	6	−0.10	0.011	−0.010
4	53	0	0	0	0	−0.071
5	50	0.06	26	−0.46	−0.073	0.196
6	39	0.23	13	−0.24	−0.032	0.168
7	28	0.45	−15	0.27	0.038	−0.018
8	26	0.46	27	−0.48	−0.069	0.309
9	15	0.69	−12	0.21	0.028	0.092
10	15	0.69	40	−0.72	−0.102	0.494
11	8	0.81	−11	0.20	0.037	0.216
12	44	0.19	−12	0.22	0.036	–
13	40	0.26	−18	0.32	0.053	–
14	57	−0.03	−6	0.11	0.020	–
15	28	0.46	−1	0.02	0.007	–
16	54	0.02	−4	0.07	0.015	–
17	55	0.01	−3	0.06	0.012	–
18	54	0.02	−7	0.12	0.023	–
19	59	−0.06	0	0	0.004	–
20	64	−0.15	2	−0.03	−0.001	–
21	59	−0.06	–	–	–	–
22	50	0.09	–	–	–	–
23	63	−0.13	−1	0.02	0.007	–
24	70	−0.25	−3	0.05	0.012	–
25	59	−0.06	–	–	–	–
26	55	0.01	–	–	–	–
27	59	−0.06	–	–	–	–
28	65	−0.16	–	–	–	–
29	73	−0.30	7	−0.12	−0.015	–
30	38	0.29	–	–	–	–
31	28	0.46	–	–	–	–
32	20	0.60	−12	0.21	0.036	–

Notes. The values of Δν for compounds **1**, **3**, **5**, **7**, **9**, and **11** were calculated by Eq. (8); for the other compounds they were experimental. $\Sigma\sigma_p$: for **1**—**11** see Ref. 14, for **12**—**32** they were calculated by Eq. (15). $\Sigma\sigma_R$: for **1**—**11** see Refs. 5, 14, for **12**—**20**, **23**, **24**, **29**, and **32** they were calculated using the relationship $\Sigma\sigma_R = \Sigma\sigma_p - \Sigma\sigma_I$, where $\Sigma\sigma_I$ have been determined earlier.[3,5] $\Delta\nu_R$ were calculated by Eq. (13). For q_π and q_σ for **1**—**11** see Refs. 18, 20; q_π for **12**—**20**, **23**, **24**, **29**, and **32** were calculated by Eq. (16).

We showed that for these compounds linear correlation (6) had the following form

$$\Delta\nu = -463q_\pi - 165q_\sigma + 50 \qquad (12)$$

$(S_a = 70,\ S_b = 22,\ S_c = 4,\ S_Y = 9,\ r = 0.924,\ n = 11)$.

In Eq. (12), q_π and q_σ (see Refs. 18, 20) quantitatively characterize the increments of the effective charges at the thiophene ring atoms due to π- and σ-interaction, respectively, between the substituent and the ring in compounds **1—11**. The values q_π and q_σ were calculated *ab initio* in the STO-3G basis (see Refs. 18, 20), and the minus signs on q_π and q_σ correspond to the transfer of an electron from the substituent to the ring.

Although the authors of Ref. 20 found that the approximate character of the calculations in the minimum basis STO-3G resulted in pronounced differences between the dipole moments of unsubstituted thiophene calculated in the minimum basis (STO-3G) and in the expanded basis (44-31G), the use of the calculated values q_π and q_σ allows one to answer the important question about the type of interaction between phenol and thiophene. The existence of correlation (12) indicates that apparently charge effects prevail over orbital effects during the formation of H-complexes between a hard acid (phenol) and thiophene derivatives. This conclusion agrees both with the abovementioned conclusions obtained in the study of benzene, ethylene, and acetylene H-complexes[4—6] and with modern theoretical concepts on H-bonding.[21,22]

The values of q_π for organosilicon derivatives of thiophene are of great interest for the development of the existing concepts of conjugation in organosilicon compounds.[3,23] These values have not yet been calculated directly by nonempirical quantum-chemical methods, probably because of the considerable increase of the computational difficulties on going from carbon compounds to their silicon analogs.[24] In addition, the interpretation of the quantum-chemical data on the conjugation effects in organosilicon compounds is questionable.[23] In this connection, the correlations that permit one to estimate the values of q_π for silylthiophenes are useful. From (9) we can obtain the value

$$\Delta\nu_R = -56\Sigma\sigma_R. \qquad (13)$$

This value defines the contribution to $\Delta\nu$ from conjugation of substituents with the thiophene ring and is as accurate as the constant characterizing the resonance contribution to the free term of correlation (9).

For structures **1—11** (with organic substituents) $\Delta\nu_R$ and q_π are linked by the linear dependence:

$$\Delta\nu_R = -358q_\pi + 2 \qquad (14)$$

$(S_a = 21,\ S_b = 1,\ S_Y = 3,\ r = 0.985,\ n = 11)$.

Using transformed correlations (8) and (14)

$$\Sigma\sigma_p = -0.017\Delta\nu + 0.94 \qquad (15)$$

$(S_a = 0.0005,\ S_b = 0.02,\ S_Y = 0.03,\ r = 0.996,\ n = 12)$,

$$q_\pi = -0.0027\Delta\nu_R + 0.004 \qquad (16)$$

$(S_a = 0.0001,\ S_b = 0.003,\ S_Y = 0.0097,\ r = 0.985,\ n = 11)$

the values of $\Sigma\sigma_p$ and q_π for compounds **12—32** with organosilicon substituents were obtained (see Table 2). Then, based on them, the mean values of σ_p, the Hammett constants for SiR_3 substituents in the thiophene ring, were calculated. For example, the mean σ_p for SiH_3 (0.17) was calculated with the use of $\Sigma\sigma_p$ of structures **12—15** (see Table 2). Taking into account σ_p for CH_3 and Cl, the obtained values of σ_p for SiH_3 in compounds **12—15** are 0.19, 0.13, 0.14, and 0.23, respectively. The mean values of σ_p for SiR_3 are given in Table 3 along with $\sigma_R = \sigma_p - \sigma_I$, used for the calculation of q_π by correlations (13) and (16).

The approximate character of the σ-constants and the charges q_π given in Table 3 is worth noting. At least three sources of errors may decrease the accuracy of their determination. First, the absolute error of the values of σ_p calculated by Eq. (15) using the experimental shifts $\Delta\nu$ after averaging is no less than 0.03. Second, the accuracy of the inductive constants σ_I, taken for the substituents SiR_3 from the literature,[3,5] has not yet been determined and, depending on the R type, lies in the range 0.01—0.03. Therefore, the absolute error in the values of σ_R, *i.e.*, in the difference $\sigma_p - \sigma_I$, can be up to 0.04—0.06. Third, correlation (16) for the estimation of charges q_π of the substituents SiR_3 is of a lower quality than correlation (15). This is reflected in the correlation coefficients and increases the error in the calculation of q_π from σ_R.

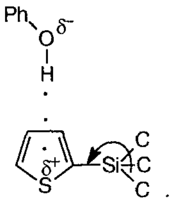
There is a more fundamental reason for the approximate character of correlations (6) and (7), which hold for substituted thiophenes as correlations (12), (14), and (16). The charges q_π and q_σ characterize intramolecular interactions between the substituents and the ring in the electronic ground state of isolated thiophene derivatives, whereas the frequency shifts $\Delta\nu$ and $\Delta\nu_R$ characterize

Table 3. The σ-constants of the substituents and the charges q_π for benzene (in the numerator) and thiophene (in the denominator) derivatives

Substiuent	σ_p	σ_I	σ_R	q_π/a.u.
$Si(CH_3)_3$	$\frac{-0.10}{-0.13}$	−0.15	$\frac{0.05}{0.02}$	$\frac{0.004}{0.007}$
$SiH(CH_3)_2$	$\frac{0}{-0.07}$	−0.06	$\frac{0.06}{0}$	$\frac{0.007}{0.004}$
SiH_2CH_3	$\frac{\text{—}}{0.01}$	−0.05	$\frac{\text{—}}{0.06}$	$\frac{\text{—}}{0.012}$
SiH_3	$\frac{0.10}{0.17}$	−0.03	$\frac{0.13}{0.20}$	$\frac{0.017}{0.034}$
$SiCl_3$	$\frac{0.56}{0.60}$	−0.39	$\frac{0.17}{0.21}$	$\frac{0.023}{0.036}$

Notes. For the values of σ_p for benzene derivatives see Refs. 3, 5; σ_p for thiophene derivatives are the average values from Table 2. For σ_I see Refs. 3, 5, σ_I for SiH_2CH_3 are the average values between the values for $SiH(CH_3)_2$ and SiH_3. $\sigma_R = \sigma_p - \sigma_I$. For the charges q_π for the benzene derivatives see Ref. 5; they were also calculated by the method given in Ref. 5. For the thiophene derivatives they were calculated by Eq. (16).

these interactions for their H-complexes with phenol. Despite the predominance of electrostatic binding between the H-complex components, some charge transfer from D (thiophene derivatives) to A (phenol) always occurs, as, for example, in the following structure[25]



The appearance of a partial positive charge δ^+ at D enhances the resonance interactions of both +M-type donors (OH, SR, and F) prone to n,π-conjugation, and the substituents SiR_3, for which σ,π-conjugation is typical, with the ring. A peculiar channel of direct polar conjugation that corresponds to the passage from $\sigma_R{}^\circ$ to σ_R in terms of the Hammett system is formed. The effective charges q_π and q_σ are determined without direct polar conjugation, and the frequency shifts $\Delta\nu$ are determined in the presence of this conjugation. Therefore, the values of q and $\Delta\nu$ characterize somewhat different electron distributions in the molecules of D, and correlations (6), (7), (12), (14), and (16) are approximate.

Consider now the data given in Table 3, taking into account the comments made. As follows from these data, within the errors of their estimation the constants σ_p and σ_R for SiR_3 practically coincide for analogous thiophenes and benzenes. (As is known,[23] the constant σ_I is a versatile quantitative parameter of the inductive effect of a substituent.) The signs of the σ_R-constants are positive. This implies that of the two components of the overall resonance effect of the substituents SiR_3, the acceptor component (d,π-conjugation, *i.e.*, the cooperative effect of the vacant 3d-orbitals of the Si atom and the antibonding σ*-orbitals of the Si—R bonds) and the donor component (σ,π-conjugation),[23] the former prevails. The values of σ_R and q_π increase as the donor properties of R in SiR_3 decrease (acceptor properties increase). The substituents SiR_3 are arranged in this order in Table 3. For instance, $Si(CH_3)_3$ is a relatively weak π-acceptor, and the characteristics of $SiCl_3$ are similar to those of typical organic resonance acceptors (CN, NO_2, CHO).

Despite the mentioned similarity in the conjugation of the SiR_3 substituents with the benzene and thiophene rings, differences are also observed in the resonance interactions in silylbenzenes and silylthiophenes. The SiR_3 substituents affect the effective charges q_π more profoundly in thiophenes than in benzenes. This concerns, first of all, the $Si(CH_3)_3$, SiH_3, and $SiCl_3$ groups, for which the values of q_π are more precise because of the low errors in determining of σ_I values.

This work was supported by the Russian Foundation for Basic Research, Project No. 93-03-18372.

References

1. A. N. Egorochkin, S. E. Skobeleva, E. T. Bogoradovskii, and T. P. Zubova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 2069 [*Russ. Chem. Bull.*, 1993, **42**, 1982 (Engl. Transl.)].
2. M. D. Joesten and L. J. Schaad, *Hydrogen Bonding*, M. Dekker, New York, 1974.
3. A. N. Egorochkin and G. A. Razuvaev, *Usp. Khim.*, 1987, **56**, 1480 [*Russ. Chem. Rev.*, 1987, **56** (Engl. Transl.)].
4. A. N. Egorochkin, S. E. Skobeleva, V. L. Tsvetkova, E. T. Bogoradovskii, and V. S. Zavgorodnii, *Metalloorg. Khim.*, 1992, **5**, 818 [*Organomet. Chem. USSR*, 1992, **5** (Engl. Transl.)].
5. A. N. Egorochkin, S. E. Skobeleva, and V. L. Tsvetkova, *Metalloorg. Khim.*, 1993, **6**, 131 [*Organomet. Chem. USSR*, 1993, **6** (Engl. Transl.)].
6. A. N. Egorochkin, S. E. Skobeleva, and V. L. Tsvetkova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1383 [*Russ. Chem. Bull.*, 1993, **42**, 1316 (Engl. Transl.)].
7. P. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533.
8. P. G. Pearson, *J. Mol. Struct. (Theochem.)*, 1992, **255**, 261.
9. G. Klopman, in *Chemical Reactivity and Reaction Paths*, Ed. G. Klopman, Wiley, New York, 1974, Ch. 4.
10. T. L. Ho, *Hard and Soft Acids and Bases*, Academic Press, New York, 1977.
11. T. L. Ho, *Tetrahedron*, 1985, **41**, 3.
12. A. N. Egorochkin, N. S. Vyazankin, S. E. Skobeleva, S. Ya. Khoroshev, E. A. Chernyshev, V. I. Savushkina, and O. V. Kuz'min, *Khim. Geterotsikl. Soedin.*, 1972, 1057 [*Chem. Heterocycl. Compd.*, 1972 (Engl. Transl.)].
13. A. N. Egorochkin, M. A. Lopatin, S. E. Skobeleva, N. P. Erchak, L. N. Khokhlova, and E. Lukevits, *Izv. AN Latv. SSR, Ser. Khim.*, 1988, 220.
14. C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
15. A. N. Egorochkin, S. E. Skobeleva, V. L. Tsvetkova, E. T. Bogoradovskii, and V. S. Zavgorodnii, *Metalloorg. Khim.*, 1991, **4**, 362 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
16. V. A. Koptyug, *Arenonievye iony. Stroenie i reaktsionnaya sposobnost'* [*Areneonium Ions. Structure and Reactivity*], Nauka, Novosibirsk, 1983 (in Russian).
17. Y. Yokoyama, Y. Yamashita, K. Takahashi, and T. Sone, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 2208.
18. Y. Yamashita, H. Kobayashi, A. Yoshino, K. Takahashi, and T. Sone, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 1312.
19. G. Angelini, G. Laguzzi, C. Sparapani, and M. Speranza, *J. Am. Chem. Soc.*, 1984, **106**, 37.
20. J. Kao and L. Radom, *J. Am. Chem. Soc.*, 1979, **101**, 311.
21. P. Hobza and R. Zahradnik, *Intermolecular Complexes*, Academia, Prague, 1988.
22. S. Scheiner, in *Reviews in Computational Chemistry*, Eds. K. B. Lipkowitz and D. B. Boyd, VCH Publishers, New York, 1991, **2**, 165.
23. A. N. Egorochkin, *Usp. Khim.*, 1992, **61**, 1092 [*Russ. Chem. Rev.*, 1992, **61** (Engl. Transl.)].
24. Y. Apeloig, in *The Chemistry of Organic Silicon Compouds*, Eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1989, P. 1, 57.
25. M. C. Moreau-Descoings, G. Goethals, J. P. Sequin, and J. P. Doncet, *J. Mol. Struct.*, 1988, **177**, 407.

Received December 14, 1993