Charge control of the complex formation of phenol with unsaturated compounds containing organoelement substituents from group IV

8.* Furan derivatives

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The frequency shifts ($\Delta\nu$ (OH)) of phenol and the resonance components ($\Delta\nu_R$) of these shifts in the IR spectra of forty H-complexes of phenol with furan derivatives containing organic, organosilicon, organogermanium, and organotin substituents are studied. The values of $\Delta\nu$ and $\Delta\nu_R$ are linearly related to quantum chemical parameters of the variation of the effective charges of the furan ring atoms affected by σ- and π-interactions with organic substituents. The effect of the conjugation between an organoelement substituent and the furan ring on the effective charges is estimated. The resonance parameters (σ_R) of organoelement substituents in derivatives of benzene, thiophene, and furan and the reasons for the non-versatility of σ_R are considered.

Key words: furan derivatives, H-complexes, charge control of complex formation, effective charge, non-versatility of resonance parameters.

Previously, based on studies of H-complexes formed by organic and organoelement derivatives of benzene, thiophene, ethylene, and acetylene[1—4] (molecule-donors X_i—D) with phenol, new opportunities were found for applying IR spectroscopy to the study of the nature of weak intramolecular hydrogen bonds and to estimating the variation in the effective charges at donor centers (D) during intramolecular resonance interactions of organoelemental substituents (X_i) with D in X_i—D. These possibilities arise when the simplest spectroscopic parameters ($\Delta\nu$ and $\Delta\nu_R$) of H-complexes and the quantum chemical parameters of the σ- and π-interactions of the organic substituents (X_i) and D in individual molecule-donors (X_i—D) are considered in combination. The use of this approach allowed us, first, to experimentally check the statement that charge interaction predominates over orbital interaction in the formation of hydrogen bonds;[5,6] second, to quantitatively estimate the effect of conjugation between the organoelemental substituents and the π-system on the effective charge of the C-atoms of the D donor centers (benzene and thiophene rings, double and triple bonds); third, to calculate the resonance parameters (σ_R) of organoelemental substituents in a series of benzene, thiophene, ethylene, and acetylene derivatives; fourth, to collect the actual data for finding the versatility of σ_R parameters of organoelemental substituents.

The purpose of this work is to study in terms of the approach mentioned, H-complexes of phenol with furan derivatives containing organic and organoelemental substituents.

Experimental

IR spectra of H-complexes were obtained on a UR-20 spectrophotometer, CCl_4 was used as the solvent, the concentration of furan derivatives was 1.5—2.0 mol L^{-1}, and the concentration of phenol was 0.01—0.02 mol L^{-1}. A cuvette with a CCl_4 solution of the substituted furan to be studied was placed in the reference channel of the instrument. The concentrations of the compound studied in both channels of the spectrophotometer were nearly the same. Absorption layers of 0.1- or 0.4-cm width were used. The accuracy of $\Delta\nu$ was ~3 cm^{-1}.

An IBM PC AT personal computer with the standard package of STAT-GRAPHICS Vers. 3.0 programs was used to calculate the correlation equations.

The values of σ_p, σ_I, and σ_R for the organic substituents were taken from a review (see Ref. 7), and the values of σ_I for the organoelemental substituents were taken from a previously published work.[8]

Results and Discussion

Shifts in the frequency $\Delta\nu$ of the stretching vibration of the phenol O—H bond in IR spectra are known for a few H-complexes of phenol with furan derivatives.[9,10]

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* For report 7, see Ref. 1.

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Based on the IR spectral data of H-complexes, in particular, those in which phenol is the molecule-acceptor,

$$X_i - D + H - OPh \rightleftharpoons X_i - D \ldots H - OPh, \quad (1)$$

several empirical dependences have been established (Refs. 11 and 12). When the molecule-acceptor (phenol) and the π- or n-type donor center D (benzene ring, double bond, oxygen atom in ethers, *etc.*) remain constant, the IR spectroscopic parameters ($\Delta\nu$) 1) are reliably characterized by the electron-donating capability and the relative basicity of the X_i—D molecule-donors; 2) are related by linear dependences to the enthalpy changes and Gibb's energy of process (1); and 3) correlate linearly with the Hammett σ_p-constants of the substituents X_i

$$\Delta\nu = a\sigma_p + b. \quad (2)$$

The numerical values of *a* and *b* depend on the type of donor center D and can be established for a particular D by two methods. The first method is to vary the X_i substituents over a sufficiently wide range of σ_p, which can be realized only with a rather large series of X_i—D molecule-donors. For example, for 12 thiophene derivatives, correlation (2) takes the form[1]

$$\Delta\nu^T = -57\Sigma\sigma_p + 54, \quad (3)$$

$S_a = 2$, $S_b = 1$, $S_y = 2$, $r = 0.996$, $n = 12$.

Correlation (3) can be transformed[1] into the following equation:

$$\Delta\nu^T = -57\Sigma\sigma_I - 56\Sigma\sigma_R + 54, \quad (4)$$

$S_a = 3$, $S_b = 7$, $S_c = 1$, $S_y = 2$, $r = 0.995$, $n = 12$,

where $\Sigma\sigma_I$ and $\Sigma\sigma_R$ are the sums of the inductive and resonance constants of the X_i substituents linked to the thiophene ring. The second method is based on the existence of linear dependences between the $\Delta\nu$ values in different series of X_i—D. It follows from correlation (2) that for X_i—D_1 (series 1) $\Delta\nu_1 = a_1; \sigma_p + b_1$, and for X_i—D_2 (series 2) $\Delta\nu_2 = a_2; \sigma_p + b_2$. Hence,

$$\Delta\nu_1 = \frac{a_1}{a_2}\Delta\nu_2 - \frac{a_1 b_2}{a_2} + b_1. \quad (5)$$

Therefore, if the form of dependence (5) is known for a limited number of compounds of series 1 and 2 and correlations (3) and (4) are established for series 1, linear equations of types (2) and (4) can also be calculated for series 2.

The second method is used for establishing the forms of correlations (2) and (4) for furan derivatives. The values of $\Delta\nu$ in eight furan derivatives (furan, 2-methylfuran, 2,5-dimethylfuran, dimethyl(2-furyl)silane, trimethyl(2-furyl)silane, dimethyldi(2-furyl)silane, tri(2-furyl)silane, and methyltri(2-furyl)silane) are related to the $\Delta\nu^T$ values of the corresponding thiophene derivatives[10] by the linear dependence

$$\Delta\nu^T = 0.68\Delta\nu + 18, \quad (6)$$

$S_a = 0.04$, $S_b = 3$, $r = 0.989$, $n = 8$.

Combining (6) with (3) and (4), we obtain

$$\Delta\nu = -84\Sigma\sigma_p + 53, \quad (7)$$

$$\Delta\nu = -84\Sigma\sigma_I - 82\Sigma\sigma_R + 53. \quad (8)$$

It follows from a comparison of correlations (3) and (7) and Eqs. (4) and (8) that furans are more sensitive than thiophenes to the influence of the inductive and resonance effects of substituents on their electron-donating capability in the formation of H-complexes.

Only general assumptions can be made concerning the mutual orientation of furan derivatives and furan in H-complexes. It is known[3] that the values of $\Delta\nu$ for H-complexes of benzene derivatives with phenol are related to their proton affinity (PA) by a linear dependence (the enthalpy of the attachment of a proton to the carbon atom of the benzene ring with the maximum basicity and effective charge is negative). For a few furan derivatives with known values of $\Delta\nu$ and PA a direct correlation is observed between these quantities. For furan, 2-methylfuran, 2,5-dimethylfuran, and 2,5-di-*tert*-butylfuran the $\Delta\nu$ values are equal to 50, 66, 83, and 87 cm^{-1}, and those of PA are equal to 819,[13] 864, 869, and 891 [14] kJ mol^{-1}, respectively. Furan[13] and its mono-, di-, and tetraalkyl derivatives[14] are known to be protonated at the α-position of the ring. Protonation at the β-carbon atoms or at the oxygen atom is less thermodynamically favorable by approximately 60—65 and 80—160 kJ mol^{-1}.[13,14] Therefore, in the H-complexes of the furans studied with phenol the donor center can be assumed to be located at the α-carbon atoms of the ring. Additional arguments in favor of this assumption are presented below.

Now let us consider H-complexes of furans with phenol on the basis of the general principles of donor-acceptor interaction[15] using the modern concept of hard and mild bases.[16]

Based on the data presented previously,[15] the change in the total energy (ΔE) in the interaction of a donor "d" (in our case, "d" are furan derivatives as π-bases) and an acceptor "a" (phenol) at a distance r_{da} in a medium with dielectric constant ε is determined by the equation:

$$\Delta E = -\frac{q_d q_a}{r_{da}\varepsilon} + 2\sum_{d}\sum_{a}\frac{(C_d^m C_a^n \Delta\beta_{da})^2}{E_m - E_n}, \quad (9)$$

whose first term characterizes electrostatic interactions of hard acids (including phenol[16]) with hard bases. Coulomb interactions are determined by the charges on the donor (q_d) and acceptor (q_a) centers. The second term characterizes covalent interactions of weak acids with weak bases. These interactions are enhanced by increasing the C_d^m and C_a^n coefficients of the atomic orbitals in the boundary molecular orbitals and in the molecular orbitals of the donor ("m") and the acceptor ("n") that have similar energy, by changing the resonance integral $\Delta\beta_{da}$ for the interaction of "m" and "n", and when the energies E_m and E_n of the orbitals orbitals of "m" and "n" are similar.

Of the two types of interaction mentioned the first one predominates in the formation of a complex of a strong acid (phenol) with benzene,[3] thiophene,[1] ethylene,[4] and acetylene[2] derivatives. This is indicated by the fulfillment of the linear correlations

$$\Sigma\nu = kq_\sigma + lq_\pi + h, \tag{10}$$

$$\Delta\nu_R = pq_\pi + t, \tag{11}$$

where $\Delta\nu_R$ is the resonance component of the frequency shift (see below); q_σ and q_π are the portions of the change in the effective charge on the atoms of the D donor center (benzene, thiophene rings, or triple bond) caused by the σ- and π-interactions of X_i and D in X_i—D, respectively; and the numerical values of k, l, h, p, and t coefficients depend on the type of D.

To prove that the correlations of the form (10) and (11) are fulfilled, compounds **1—22** of the furan series (Table 1) were used. For these compounds, the values of q_σ and q_π, which are the σ- and π-components, respectively, of the changes in the effective charges on the atoms of the furan ring affected by the electronic interaction of substituents with the ring, were calculated *ab initio*[17] within the STO-3G basis. Negative values of q_σ and q_π correspond to electron donation from the substituent to the ring.

The following linear dependence is fulfilled for compounds **1—18***

$$\Delta\nu = -232q_\sigma - 819q_\pi + 41, \tag{12}$$

$S_a = 46,\ S_b = 89,\ S_y = 11,\ r = 0.919,\ n = 18.$

Dependence (12), which is similar to the corresponding dependences for benzenes, thiophenes, and ethylenes[1,3,4] testifies, according to the modern hydrogen bond theory,[5,6] that Coulomb interactions predominate in the formation of H-complexes.

The q_π values for compounds **23—40** are of considerable interest from the viewpoint of organometallic chemistry. As a rule, calculational and methodological difficulties arise in the direct calculations (even by non-empirical quantum chemical methods) of these values for organometallic compounds.[18,19] Therefore, we used the following method for the calculation of q_π for organoelemental furans.

It is clear from correlation (8) that the following value can be introduced within the accuracy of the constant, to characterize the resonance component of the free term of this correlation:

$$\Delta\nu_R = -82\Sigma\sigma_R. \tag{13}$$

This value is the contribution of the conjugation between the substituents and the furan ring to Δν. The $\Delta\nu_R$ and q_π values for compounds **1—22** are related by the correlation

$$\Delta\nu_R = -490q_\pi + 3, \tag{14}$$

$S_a = 27,\ S_b = 1,\ S_y = 6,\ r = 0.971,\ n = 22,$

which in the form

$$q_\pi = -0.00193\Delta\nu_R + 0.006, \tag{15}$$

$S_a = 0.00011,\ S_b = 0.002,\ S_y = 0.011,\ r = 0.971,\ n = 22$

is used for the calculation of q_π for compounds with organoelemental substituents. Then the q_σ values (see Table 1) are calculated by Eq. (12) from the Δν and q_π values for these compounds.

The π-electronic charges $q_\pi(5)$ on the carbon atoms at position 5 of compounds **1—22** are also calculated by the non-empirical quantum chemical method (STO-3G basis).[17] The $\Delta\nu_R$ and $q_\pi(5)$ values are related by the linear dependence

$$\Delta\nu_R = 9667q_\pi(5) - 1033, \tag{16}$$

$S_a = 75,\ S_b = 80,\ S_y = 8,\ r = 0.945,\ n = 22.$

The fulfillment of dependence (16) additionally confirms the assumption that the donor centers of H-complexes with phenol are localized on the α-carbon atoms of the furan rings. Correlation (16) in the form

$$q_\pi(5) = 0.00092\Delta\nu_R + 1.068, \tag{17}$$

$S_a = 0.00007,\ S_b = 0.002,\ S_y = 0.008,\ r = 0.945,$

is used for the calculation of $q_\pi(5)$ in compounds with organoelemental substituents.

It should be mentioned that correlations (12), (14), and (16) are approximate because the q and Δν parameters correspond to somewhat different electronic states of the furan derivatives. The q_π and $q_\pi(5)$ parameters characterize the interaction of X_i substituents with the π-system of the D ring in the ground electronic state of the individual X_i—D molecules. The Δν and $\Delta\nu_R$ parameters characterize the similar interaction in H-complexes of furans with phenol. In addition to the predominant Coulomb interaction in H-complexes, there is always some charge transfer from the X_i—D molecule-donors to the molecule-acceptors,[1—6,20] resulting in a partial positive charge δ^+ on the D donor center. In

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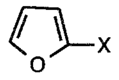
* Compounds **19—22** are excluded from the correlation, because their calculated Δν values are negative, apparently, owing to the absence of π-donating properties due to the influence of the electron-acceptor substituents CN, COF, NO_2, and NO.

Table 1. Frequency shifts (Δν and $\Delta\nu_R$) in the IR spectra of H-complexes with phenol, σ_p and σ_R constants of the X substituents, the values of the charge transfer (q_σ and q_π) from the substituents to the furan ring, and the π-electronic charges $q_\pi(5)$ on the carbon atoms at position 5 of 2-substituted furans 

Compound	X	Δν cm^{-1}	σ_p	$\Delta\nu_R$ /cm^{-1}	σ_R	q_σ /au	q_π /au	$q_\pi(5)$ /au
1	NH_2	108	−0.66	61	−0.74	+0.133	−0.112	1.126
2	OH	84	−0.37	57	−0.70	+0.153	−0.094	1.114
3	OMe	76	−0.27	46	−0.56	+0.150	−0.096	1.107
4	Me	66	−0.17	10	−0.12	−0.035	−0.007	1.087
5	Et	66	−0.15	8	−0.10	−0.042	−0.006	1.088
6	$CH=CH_2$	57	−0.05	8	−0.10	−0.028	+0.006	1.077
7	H	50	0	0	0	−0.082	0	1.078
8	CH_2OH	53	−0.00	2	−0.03	−0.023	+0.007	1.078
9	F	48	+0.06	32	−0.39	+0.183	−0.071	1.095
10	CH_2F	44	+0.11	3	−0.04	−0.030	+0.006	1.075
11	$C\equiv CH$	34	+0.23	−1	+0.01	+0.022	+0.011	1.065
12	CHF_2	26	+0.32	−2	+0.03	−0.021	+0.011	1.070
13	$CONH_2$	23	+0.36	−8	+0.10	−0.024	+0.027	1.064
14	CHO	18	+0.42	−7	+0.09	−0.029	+0.038	1.058
15	COOH	15	+0.45	−9	+0.11	+0.001	+0.037	1.051
16	NC	12	+0.49	−2	+0.02	+0.206	−0.014	1.065
17	COMe	11	+0.50	−14	+0.17	−0.036	+0.032	1.058
18	CF_3	8	+0.54	−13	+0.16	−0.010	+0.013	1.062
19	CN	—	—	−12	+0.15	+0.070	+0.027	1.048
20	COF	—	—	−18	+0.22	−0.003	+0.040	1.049
21	NO_2	—	—	−11	+0.13	+0.198	+0.034	1.037
22	NO	—	—	−27	+0.33	+0.081	+0.044	1.044
23	SiH_3	48	+0.06	−7	+0.09	−0.101	+0.020	1.062
24	$SiHMe_2$	62	−0.11	4	−0.05	−0.083	−0.002	1.072
25	$SiHBu^n{}_2$	62	−0.11	~4	~−0.05	−0.083	−0.002	1.072
26	SiHMeEt	60	−0.08	~2	~−0.02	−0.075	+0.002	1.070
27	$SiHMe(n\text{-}C_{12}H_{25})$	63	−0.12	~5	~−0.06	−0.081	−0.004	1.073
28	$SiMeCHCl_2$	59	−0.07	—	—	—	—	—
29	CMe_3	70	−0.20	11	−0.13	−0.072	−0.015	1.078
30	$SiMe_3$	67	−0.17	2	−0.02	−0.119	+0.002	1.070
31	$GeMe_3$	70	−0.20	7	−0.09	−0.096	+0.008	1.074
32	$GeEt_3$	72	−0.23	8	−0.10	−0.102	−0.009	1.075
33	$SnMe_3$	79	−0.31	15	−0.18	−0.083	−0.023	1.082
34	SiH_2R	50	+0.04	—	—	—	—	—
35	SiHMeR	60	−0.08	—	—	—	—	—
36	$SiMe_2R$	62	−0.11	—	—	—	—	—
37	$SiHR_2$	50	+0.04	—	—	—	—	—
38	$SiMeR_2$	54	−0.01	—	—	—	—	—
39	$SiEtR_2$	55	−0.02	—	—	—	—	—
40	$SiBu^nR_2$	54	−0.01	—	—	—	—	—

Note. The Δν values for compounds **1—3**, **5**, **6**, and **8—18** were calculated by Eq. (7), the values for the other compounds were experimentally obtained. The σ_p values for the substituents in compounds **1—18** and **29** are taken from Ref. 7, the values for the substituents in compounds **23—28** and **30—40** were calculated by Eq. (7). The σ_R values for the substituents in compounds **1—22** and **29** are taken from Ref. 9, those for the substituents in compounds **23—27** and **30—33** were calculated from the correlation $\sigma_R = \sigma_p - \sigma_I$; the σ_I constants are taken from Ref. 10. The values of $\Delta\nu_R$ were calculated by Eq. (13). The values of q_σ, q_π, and $q_\pi(5)$ for substituents in compounds **1—22** are taken from Ref. 17, those for organoelemental substituents were calculated by Eqs. (15), (12), and (17). The negative signs of q_σ and q_π correspond to electron donation from the substituent to the furan ring. The mean σ_R value (0.33) of the values presented previously[9] (0.42 and 0.25) is taken for the NO substituent. In the substituents of compounds **34—40** R = 2-furyl. For compounds **28** and **34—40** the calculations of all values except σ_p are impossible, because the σ_I values for substituents are scarce.

H-complexes, the stronger the +M-type resonance electron-donor in the ground electronic state of the X_i—D isolated molecules, the stronger the conjugation between X_i and D. In terms of the Hammett—Taft system, the transition from individual X_i—D to their H-complexes corresponds to the transition from $\sigma_R{}^0$ to σ_R constants for the characterization of the conjugation of the X_i substituents with D (see Refs. 1—4).

Now let us compare the values of σ_p, σ_R, q_π, and $q_\pi(5)$ for silyl-, germyl-, and stannylfurans to those for 2-*tert*-butylfuran (compounds **23**—**40**).

The values $\sigma_p = \sigma_I + \sigma_R$ reflect the joint influence of the effects of induction and conjugation. The values of σ_p increase as the electron-acceptor properties of the three substituents at the Si atom increase, *e.g.*, when alkyl groups are replaced by H atoms (on going from compound **30** to **24**—**27** and then to **23**) or furyl moieties (on going from compound **30** to **36** and then to **38**—**40**). The values of σ_R increase and the values of $q_\pi(5)$ decrease on going from compound **30** to **23**, which attests that the resonance accepting properties of SiH_3 are greater than those of $SiMe_3$. Organoelemental substituents have significantly lower values of q_σ than organic groups. This is quite clear from the values of the inductive constants σ_I, which, *e.g.*, for EMe_3 moieties (E = C, Si, Ge, and Sn) are equal to −0.07, −0.15, −0.11, and −0.13, respectively.[10]

The changes in the σ_p, σ_R, q_π, and $q_\pi(5)$ parameters on going from Me and CMe_3 groups to their organoelemental analogs provide a lot of information. Replacing the C atoms with Si in pairs of Me and SiH_3 compounds and also in CMe_3 and $SiMe_3$ is accompanied by increases in the values of σ_p, σ_R, and q_π, but a decrease in $q_\pi(5)$. This unambiguously attests to the resonance acceptor properties (the d,π-conjugation effect) of silyl moieties. According to the common conceptions,[19] the general resonance effect of Me_3E type substituents (E = Si, Ge, and Sn) with respect to the related π-systems includes acceptor and donor components. The acceptor component (d,π-conjugation decreases in the order Si > Ge > Sn) is the joint participation of the n,d-orbitals of E and the σ* antibonding orbitals of (E—C) in conjugation. The donor component (σ,π-conjugation increases in the order C < Si < Ge < Sn) is σ,π- and σ,π*-type superconjugation, *i.e.*, mixing of the σ(E—C)-orbitals of the Me_3E substituents with the π- and π*-orbitals.

Thus, on going from the Me_3Si substituent to Me_3Ge and Me_3Sn, the acceptor component (d,π-conjugation) of the total resonance effect of Me_3E with respect to the furyl group must decrease, while the donor component (σ,π-conjugation) must increase. Therefore, an increase in the atomic number of E in Me_3E (compounds **30**—**33**) results in a decrease in the σ_p, σ_R, and q_π values and an increase in $q_\pi(5)$.

Let us consider in more detail the σ_R values of the EMe_3 substituents in the series of benzene, furan, and thiophene derivatives (Table 2). A common tendency in the change in the σ_R parameters is observed for these series. The σ_R values increase on going from E = C to E = Si due to the effect of d,π-conjugation. This effect is absent for carbon compounds and is maximum in silicon compounds. On going from E = Si to Ge and Sn, the contribution of the acceptor effect of d,π-conjugation to σ_R decreases, and that of the donor effect of σ,π-conjugation increases; therefore, the σ_R values decrease. Despite the same qualitative tendency in the change in σ_R in the benzene, furan, and thiophene series, the numerical values of the σ_R parameters differ significantly in several cases. For example, if the σ_R value of the CMe_3 group remains unchanged (−0.13), the σ_R parameter for the $SnMe_3$ substituent in the benzene, furan, and thiophene series takes the values of +0.01, −0.18, and −0.15, respectively. Taking into account the data from Refs. 10, 19, and 21, we assumed that the dependence of the degree of σ,π-conjugation on the type of reaction center (benzene, furan, or thiophene ring) is the reason for the non-versatility of the σ_R values for organoelemental substituents.

Independent arguments in favor of this assumption can be obtained from the analysis of the energy of the highest occupied molecular orbitals (E_{HOMO}) of compounds **1**—**12** (see Table 2). According to MO perturbation theory (see, *e.g.*, Ref. 22), the HOMO is formed when the initial non-perturbed σ-MO of E—C (E(E—C) energy) of the EMe_3 moieties and the π-MO ($E(\pi)$ energy) of the benzene, furan, or thiophene rings are mixed. The perturbation energy $\delta E(\sigma, \pi)$ for σ,π-mixing can be determined, in addition to other methods, as the $E_{HOMO} - E(\pi)$ difference under the condition that a correction that takes into account the change in the energy of the π-MO caused by the inductive effect of the EMe_3 moieties is introduced to the $E(\pi)$ value. The values of $E(\pi)$ presented in Table 2 contain corrections that take into account the change in $E(\pi)$ of benzene (−9.24 eV), furan (−8.83 eV), and thiophene (−8.85 eV) when inductive electron-donors EMe_3 are involved in their structures. The method for taking into account the inductive effect of substituents on $E(\pi)$ in benzene derivatives has previously been described.[22]

The following correlation is fulfilled for compounds **1**—**12** (see Table 2):

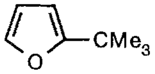
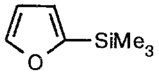
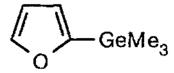
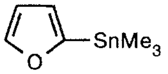
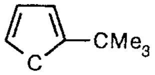
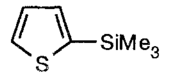
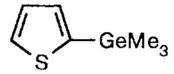
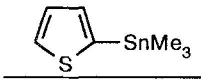
$$\sigma_R = -0.63\delta E(\sigma, \pi) + 0.08, \qquad (18)$$

$$S_a = 0.09,\ S_b = 0.02,\ S_y = 0.03,\ r = 0.920,\ n = 12.$$

Linear dependence (18) testifies that the change in the conditions for mixing the σ- and π-orbitals caused by a change in the type of reaction center (benzene, furan, or thiophene ring) is to a large extent responsible for the fact that the resonance parameters of the σ_R-substituents of Me_3E (E = Si, Ge, and Sn) do not retain their values unchanged.

The approximate character of dependence (18) should be emphasized. In the calculation of the $E(\pi)$ values, the influence of the inductive effect of the substituents on $E(\pi)$ in substituted furans and thiophenes is assumed to be approximately the same as that in benzene derivatives. The values of $\delta E(\sigma, \pi) = E_{HOMO} - E(\pi)$ characterize the single resonance effect of the σ,π-conjugation

Table 2. Parameter σ_R of the EMe_3 substituents and energetic parameters of molecular orbitals of benzene, furan, and thiophene derivatives

Compound	σ_R	E_{HOMO} /eV	$E(\pi)$ /eV	$\delta E(\sigma,\pi)$ /eV
$PhCMe_3$ (**1**)	−0.13	−8.83	−9.17	0.34
$PhSiMe_3$ (**2**)	+0.05	−9.05	−9.09	0.04
$PhGeMe_3$ (**3**)	+0.01	−9.00	−9.13	0.13
$PhSnMe_3$ (**4**)	+0.01	−8.94	−9.11	0.17
 (**5**)	−0.13	−8.38	−8.76	0.38
 (**6**)	−0.02	−8.53	−8.68	0.15
 (**7**)	−0.09	−8.47	−8.72	0.25
 (**8**)	−0.18	−8.33	−8.70	0.37
 (**9**)	−0.13	−8.44	−8.78	0.34
 (**10**)	+0.02	−8.61	−8.70	0.09
 (**11**)	−0.07	−8.52	−8.74	0.22
 (**12**)	−0.15	−8.49	−8.72	0.23

Note. The values for the σ_R for substituents in compounds **1—4**, **9**, and **10** are taken from Refs. 1 and 8, and those in **11** and **12** were calculated from Eqs. (6) and (3) using the $\Delta\nu$ values for analogous furan derivatives. The values of E_{HOMO} for compounds **1—6**, **8**, **10**, and **12** are taken from Refs. 23 and 24, those for **7**, **9**, and **11** were calculated from the frequencies (ν_{ct}) in the UV spectra of the complexes with tetracyanoethylene[25] by the known method.[24]

only in organic compounds **1**, **5**, and **9**. In the organoelemental derivatives, they reflect the total effect of σ,π- and d,π-conjugation on E_{HOMO} and hence, on $\delta E(\sigma, \pi)$ as well, which, seemingly, does not result in principle in restrictions to the fulfillment of Eq. (18), because both of the resonance effects (σ,π- and d,π-conjugation) affect both σ_R and $\delta E(\sigma, \pi)$. However, the contributions of σ,π- and d,π-conjugation to the σ_R and $\delta E(\sigma, \pi)$ values must differ somewhat quantitatively, because the resonance effects, especially the σ,π-conjugation, depend on the charge on the reaction center.[8,19] As shown above in the experiments on the determination of the σ_R parameters, a comparatively small partial positive charge is concentrated on the reaction center (benzene, furan, or thiophene ring). At the same time, the $\delta E(\sigma, \pi)$ values are calculated under the condition that Cupmans' theorem is fulfilled (see, *e.g.*, Ref. 23). According to this theorem, $E(\pi)$ and E_{HOMO} are the ionization potentials of MO with opposite signs. The large positive charge that appears on the reaction centers due to ionization stimulates the enhancement of σ,π-conjugation with the participation of organoelemental substituents Me_3E (E = Si, Ge, and Sn).[8,19]

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