

Correlation Analysis of Data of Quantum-Chemical Calculations on Stabilization Energy. Polarization Effect in Cations

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Abstract—Effects of substituents X on stabilization energy (*SE*) of 31 series of cations containing fragment XC^+ , $\text{XCH}=\text{CHC}^+$, and XSi^+ were investigated. *SE* values calculated by quantum-chemical procedures or measured experimentally depend on induction, resonance, and polarization effects of X. The polarization effect contribution into the overall *SE* variation under X influence amounts to 10–44%.

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Nowadays data accumulate indicating that chemical [1, 2] and physical [3–9] properties *P* of electron-deficient XBR_c^+ , $\text{XBR}_c^{\delta+}$ and electron-excessive XBR_c^- , $\text{XBR}_c^{\delta-}$ reaction series are governed by the character of the B bridge connecting the substituents X to the reaction center R_c . We shall consider series where chemical and physical processes involve only R_c and not B or X. These series may be divided into classic and nonclassical. In the classic series 1,4- $\text{XC}_6\text{H}_4\text{R}_c^q$ the substituent X and center R_c bearing a positive or a negative charge *q* are separated by a *para*-phenylene bridge. The properties *P* of these series are described by equation (1).

$$P = P_H + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-) \quad (1)$$

Here P_H is *P* value at X = H, σ_I is the inductive constant of substituent X, σ_R , σ_R^+ , and σ_R^- are parameters describing the resonance effect of X at a small, large positive and negative charge *q* respectively.

In nonclassical series XBR_c^q and XR_c^q B bridge (for instance, $-\text{CH}=\text{CH}-$, $-\text{C}\equiv\text{C}-$ etc.) is smaller than the *para*-phenylene moiety, or is absent. The properties *P* of nonclassical series are described by equation (2).

$$P = P_H + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-) + C\sigma_\alpha \quad (2)$$

Here σ_α is the constant characterizing the polarization effect of substituent X, and the other terms are the same as in equation (1).

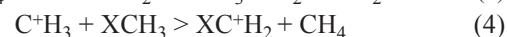
The important influence of the polarization effect

should be taken into account, firstly, in a detailed analysis of such properties *P* of nonclassical systems as ionization potentials [3, 4], electron affinities [4], electrochemical reduction potentials [5], and oxidation potentials [6] and, secondly, for understanding the impact of the substituents X on the spectral, geometric, and other parameters of H-complexes [3, 7], charge-transfer complexes [8], and the other donor-acceptor complexes [9] involving the nonclassical systems.

Quite a number of publications concern the stabilization energy of organic cations [10–19]. As far as we know, organic cations as nonclassical systems has not drawn sufficient attention up till now.

The goal of the present study is the investigation of substituents effect on the stabilization energy of carbocations and silylium cations. We believe that this problem has not only its proper interest but it is important for the development of the existing concepts of the polarization effect.

The convenient procedure for solving this problem is the consideration of isodesmic reactions. In these reactions the initial compounds and reaction products have equal numbers of molecules, valence bonds of every type, and also cations or anions [10–20]. Processes (3) and (4) are examples of this type reactions.



The enthalpy $\Delta_r H^\circ$ of isodesmic reactions is called stabilization energy (SE).

The SE values for reactions of type (3) involving neutral molecules depend on the inductive and resonance effects of substituents X [12] and can be calculated with an accuracy up to 5 kcal mol⁻¹ by ab initio methods of the quantum chemistry [20].

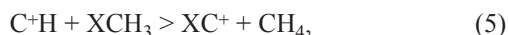
For reactions of (4) type involving cations the SE values contain information on the ability of substituents X to stabilize the cation [10, 13–16]. Reaction (4) is exothermic ($SE < 0$) when X are resonance donors (R_2N , RO , Hlg , ...). These substituents stabilize cations XC^+H_2 to a greater degree than neutral molecules XCH_3 . The resonance stabilization originates from the donation of n - or π -electrons of X to the vacant p -orbital of the cationic center [10, 13–16]. Reaction (4) becomes as a rule endothermic ($SE > 0$) when X are resonance acceptors (CN , COH , NO_2 , ...). These substituents destabilize cations XC^+H_2 [10, 13–16]. At the same time cations XC^+H_2 resemble nonclassical electron-deficient systems [3–9] obeying the three-parameter equation (2). It is therefore hardly possible that in cations XC^+H_2 the interaction of X with reaction center C^+ is limited to the resonance effect.

For the study of substituents effect on the stabilization energy SE of cations from series **I–XXXI** (Table 1–7) we employed the correlation analysis. Correlation equations were computed by standard programs Statgraphics 3.0. The treatment by the least-squares method was performed on the confidence level 95%.

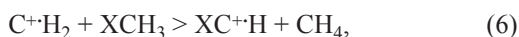
A standard set of constants σ_I , σ_R , σ_R^+ , σ_α (Table 8) used before [3–9] was applied.

Alongside process (4) (series **I–VIII**) isodesmic reactions (5–13) were considered:

For series **IX–XI**



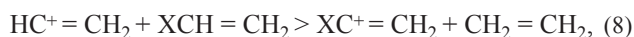
for series **XII** and **XIII**



for series **XIV**



for series **XV–XX**



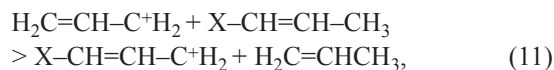
for series **XXI**



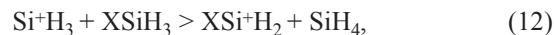
for series **XXII**



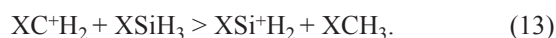
for series **XXIII–XXVII**



for series **XXVIII** and **XXIX**



for series **XXX** and **XXXI**



In Table 9 three-parameter equations of (2) kind are presented for experimental and calculated stabilization energies ($P = SE$). The absolute terms of the equations, except for the expressions for series **XXX** and **XXXI**, are zero. In going from two-parameter equations of (1) kind to three-parameter ones the standard error of approximation S_γ decreases, and the correlation factor r increases. These findings indicate an essential impact of the polarization effect of substituents X on the stabilization energy of cations.

By three-parameter equations we calculated the inductive ($Ind = a\sigma_I$), resonance [$Res = b\sigma_R(\sigma_R^+)$], and polarization ($Pol = c\sigma_\alpha$) contributions into the overall change in the stabilization energy SE produces by substituents X (Table 10).

As seen from Tables 9 and 10, stabilization energies SE of cations (and also of cation-radicals of series **XII** and **XIII**) depend on the inductive, resonance, and polarization effects of substituents. Therefore carbocations and silylium cations of series **I–XXXI** are typical representatives of nonclassical electron-deficient systems. The characteristic features of these systems is the presence of the polarization effect lacking in classic systems. As a rule the neglect of the polarization effect impedes even approximate estimation of the substituents influence on properties P of nonclassical systems. This effect affects versatile systems [3–9], in particular, the stabilization energy SE .

In series **I–XXXI** containing fragments XC^+ , $X-CH=CH-C^+$, XSi^+ the charge q^+ polarizes substituent X inducing a dipole in it. The energy of electrostatic ion-dipole interaction E_{es} is described by expression (14) [1–9, 21].

Table 1. Stabilization energies SE (kcal mol⁻¹) of carbocations XC^+H_2 [reaction (4)]

Substituent X	Number of cations series							
	I ^a	II ^b	III ^c	IV ^d	V ^e	VI ^f	VII ^g	VIII ^h
H	0	0	0	0	0	0	0	0
Mf	-37.0	-26.9	-29.0	-18.3	-29.5	-36.0	-34.1	-40.6
Ph	-55.0	-53.4	-56.3	-22.9	–	–	–	–
H ₂ N	-96.0	-78.8	-80.2	-74.5	-86.5	-98.8	-97.8	-100.5
HO	-62.0	-42.8	-51.4	-46.7	-53.7	-64.7	-62.7	-66.3
MeO	-69.0	-51.3	-57.6	-44.8	–	–	–	–
F	-27.0	-19.8	-5.5	-14.3	-14.9	-23.9	-21.5	-25.3
N=C	10.0	2.1	-5.0	4.2	12.8	–	–	–
H ₂ C=CH	–	–	-43.3	-27.2	–	–	–	–
HC=C	–	–	-34.4	-18.4	–	–	–	–
H(Me)N	-99.0	–	–	–	–	–	–	–
Me ₂ N	-106.0	–	–	–	–	–	–	–
HS	-64.0	–	–	–	–	–	-60.9	-63.6
MeS	-74.0	–	–	–	–	–	–	–
Cl	-32.0	–	–	–	–	–	-26.6	-29.2
Br	-51.0	–	–	–	–	–	–	–
H(O)C	–	–	-1.7	5.4	–	–	–	–
HO(O)C	–	–	11.5	14.2	–	–	–	–
O ₂ N	–	–	30.8	27.8	–	–	–	–

^a Experimental values [10, 15].^b Calculated by semiempirical method AM1 [15].^c PMH [15].^d PMH with H₂O [15].^e ab initio 6-31G* [13].^f ab initio CI [13].^g MPH/6-31G*//HF/6-31G* [14].^h MP2(fc)/6-31G*//MP2(fc)/6-31G* [16].**Table 2.** Stabilization energies SE (kcal mol⁻¹) of carbocations XC^+ [reaction (5)] and cation-radicals XC^+H [reaction (6)]

Substituent X	XC ⁺		XC ⁺ H		
	number of cations series				
	IX ^a	X ^b	XI ^c	XII ^b	XIII ^c
H	0	0	0	0	0
Me	-58.0	-57.6	-65.0	-35.9	-42.3
Et	-66.0	–	–	–	–
H ₂ C=CH	-78.0	–	–	–	–
HC=C	-61.0	–	–	–	–
H ₂ N	–	-114.6	–	-89.6	–
			126.6		101.5
HO	-112.0	-112.1	–	-60.8	-72.5
			123.1		
F	-48.0	-70.8	-82.0	-17.6	-27.6

^a Calculated by ab initio method 4-31G [11].^b ab initio 6-31G* [13].^c ab initio CI [13].**Table 3.** Stabilization energies SE (kcal mol⁻¹) of carbocations XC^+HCH_3 [series XIV, reaction (7)] and $XC^+=CH_2$ [series XV, reaction (8)]^a

Substituent X	Number of cations series		Substituent X	Number of cations series	
	XIV	XV		XIV	XV
H	0	0	H ₂ N	-65.0	-53.5
Me	-18.6	-25.9	HO	-37.4	-25.9
Ph	-36.8	-54.1	HS	-36.4	-38.2
H ₂ C=CH	-32.0	-32.6	F	-7.0	9.2
HC=C	-18.2	-25.6	Cl	-9.8	-11.2
NCCH ₂	2.1	-4.8	Br	-9.5	-12.7
HOCH ₂	-15.3	-21.7	HOC	10.2	4.5
F ₃ C	23.6	16.4	HOOC	8.4	5.9
ClCH ₂	-5.6	-12.9	N=C	16.0	11.7
BrCH ₂	-8.7	-14.0	O ₂ N	23.1	25.4

^a Calculated by method CBS-Q [19].

Table 4. Stabilization energies SE (kcal mol⁻¹) of carbocations $XC^+=CH_2$ [reaction (8)] [17]

Substituent X	Number of cations series				
	XXVI ^a	XXVII ^b	XXVIII ^c	XXIX ^d	XX ^e
H	0	0	0	0	0
Me	-24.5	-30.6	-24.0	-23.6	-25.9
H ₂ C=CH	-33.5	-38.1	-32.2	-31.3	-32.6
F	6.7	7.7	8.6	9.3	9.2
Cl	-11.4	-11.5	-10.4	-10.5	-11.2

^a Experimental data.^b Calculated by method C3LYP, basis 6-311+G(d,p);^c MP2, basis 6-311+G(d,p);^d QCISD(T);^e CCS-Q.**Table 5.** Stabilization energies SE (kcal mol⁻¹) of carbocations XC^+PhH [series XXI, reaction (9)] and XC^+Ph_2 [series XXII, reaction (10)] (calculation by method PMC [15])

Substituent X	Number of cations series		Substituent X	Number of cations series	
	XXI	XXII		XXI	XXII
H	0	0	MeO	-19.1	-15.2
Me	-12.6	-6.6	F	-4.3	-0.8
Ph	-18.8	-10.6	N=C	9.4	6.9
H ₂ C=CH	-13.3	-8.4	HOC	1.7	5.5
HC=C	-13.0	-7.1	HOOC	8.7	7.5
H ₂ N	-40.6	-29.7	O ₂ N	12.9	18.8
HO	-24.1	-16.7			

Table 6. Stabilization energies SE (kcal mol⁻¹) of carbocations $XCH=CH-C^+H_2$ [reaction (11)] [18]

Substituent X	Number of cations series				
	XXIII ^a	XXIV ^b	XXV ^c	XXVI ^d	XXVII ^e
H ₂ N	-46.7	-52.4	-50.1	-51.4	-51.1
MeO	-30.8	-34.6	-33.9	-34.8	-34.7
Me	-13.4	-14.4	-16.4	-15.2	-15.3
F	-2.7	-5.6	-6.6	-5.8	-5.2
H	0	0	0	0	0
Cl	0.7	-5.7	-6.2	-7.9	-8.2
HOC	13.4	9.4	9.9	10.4	10.4
F ₃ C	16.6	14.8	12.0	15.8	15.0
N=C	19.7	14.8	12.3	12.2	14.2
O ₂ N	31.7	20.7	19.3	19.4	19.9

^a Calculation by method RHF, 6-31G*;^b MP2, 6-31G*;^c C3LYP, 6-31G*;^d CBS-Q;^e G3.**Table 7.** Stabilization energies SE (kcal mol⁻¹) of silylium cations XSi^+H_2

Substituent X	Reaction (12)		Reaction (13)	
	Number of cations series			
	XXVIII ^a	XXIX ^b	XXX ^a	XXXI ^b
H	0	0	-54.9	-57.4
Me	-15.1	-15.1	-35.9	-31.8
H ₂ N	-36.8	-37.5	6.1	5.6
HO	-17.9	-19.1	-10.1	-10.1
HS	-18.4	-18.5	-12.4	-12.2
F	2.3	1.1	-31.1	-31.0
Cl	-2.0	-2.2	-30.3	-30.3

^a Calculated by method MPC/6-31G*//HF/6-31G* [14]^b MP2(fc)/6-31G*//MP2(fc)/6-31G* [16].

$$E_{es} = -q^2\alpha/(2\epsilon r_q^4) \quad (14)$$

Here α is the polarizability of substituent X, ϵ is the dielectric constant, r_q is the distance between the charge q and the induced dipole. Energy E_{es} sharply decreases

Table 8. Inductive σ_I , resonance σ_R , σ_R^+ , and polarization σ_α constants of substituents X in cations of series I-XXXI

Substituent X	σ_I	σ_R	σ_R^+	σ_α
H	0	0	0	0
Me	-0.05	-0.12	-0.26	-0.35
Et	-0.05	-0.10	-0.25	-0.49
H ₂ C=CH	0.13	-0.17	-0.29	-0.50
HC=C	0.22	0.01	-0.04	-0.60
Ph	0.12	-0.13	-0.30	-0.81
NCCH ₂	0.17	0.01	-0.01	-0.55
HOCH ₂	0.03	-0.03	-0.07	-0.36
F ₃ C	0.38	0.16	0.23	-0.25
ClCH ₂	0.13	-0.01	-0.14	-0.54
BrCH ₂	0.14	0.00	-0.12	-0.61
HOC	0.33	0.09	0.40	-0.46
HOOC	0.34	0.11	0.08	-0.34
N=C	0.51	0.15	0.15	-0.46
H ₂ N	0.08	-0.74	-1.38	-0.16
HMeN	-0.03	-0.73	-1.78	-0.30
Me ₂ N	0.15	-0.98	-1.85	-0.44
O ₂ N	0.65	0.13	0.14	-0.26
HO	0.33	-0.70	-1.25	-0.03
MeO	0.29	-0.56	-1.07	-0.17
HS	0.30	-0.15	-0.33	-0.55
MeS	0.23	-0.23	-0.83	-0.68
F	0.45	-0.39	-0.52	0.13
Cl	0.42	-0.19	-0.31	-0.43
Br	0.45	-0.22	-0.30	-0.59

Table 9. Coefficients and their standard deviations ($a \pm S_a$, $b \pm S_b$, $c \pm S_c$) of equation $SE = (a \pm S_a)\sigma_I + (b \pm S_b)\sigma_R(\sigma_R^+) + (c \pm S_c)\sigma_\omega$, standard errors of approximation S_Y , correlation factors r , and array size n for series **I–XXXI**

Reaction no.	Series no.	$a \pm S_a$	$b \pm S_b$	σ^a	$c \pm S_c$	S_Y^b	r^b	n
(4)	I	29.6 ± 17.5	98.3 ± 10.6	σ_R	58.8 ± 12.5	12(20)	0.942(0.819)	14
	I^c	37.6 ± 11.1	114.7 ± 7.6	σ_R	53.4 ± 8.6	6(18)	0.986(0.869)	8
	II^c	27.7 ± 13.7	87.7 ± 9.4	σ_R	54.5 ± 10.6	7.5(18.4)	0.964(0.752)	8
	III	39.6 ± 10.1	100.9 ± 7.4	σ_R	71.0 ± 8.8	6.7(18.3)	0.978(0.826)	13
	III^c	25.4 ± 7.0	51.7 ± 2.7	σ_R^+	56.9 ± 5.2	3.8(19.0)	0.992(0.773)	8
	IV	29.3 ± 10.2	87.6 ± 7.4	σ_R	31.1 ± 8.8	6.7(9.8)	0.970(0.936)	13
	V	43.4 ± 11.2	103.9 ± 8.3	σ_R	52.9 ± 13.7	6.0(14.3)	0.986(0.921)	6
	VI	50.7 ± 39.3	120.9 ± 16.9	σ_R	48.3 ± 41.1	8.7(9.5)	0.974(0.968)	5
(5)	VII	0	59.5 ± 9.3	σ_R^+	62.7 ± 19.6	11.6(21.4)	0.934(0.755)	7
	VIII	0	60.3 ± 9.3	σ_R^+	64.7 ± 19.5	11.6(21.8)	0.937(0.751)	7
	IX	0	155 ± 3	σ_R	103 ± 2	1(27.3)	0.999(0.672)	7
(6)	X	−95.1 ± 15.0	111.9 ± 6.4	σ_R	137.5 ± 15.6	3.3(20.8)	0.998(0.897)	5
	XI	−115.3 ± 27.1	119.3 ± 11.6	σ_R	157.2 ± 28.3	6.0(24.0)	0.993(0.886)	5
	XII	44.3 ± 6.1	109.3 ± 4.5	σ_R	58.0 ± 7.4	3.3(15.0)	0.996(0.920)	5
(7)	XIII	30.9 ± 27.5	119.7 ± 11.8	σ_R	71.3 ± 28.8	6.1(11.5)	0.988(0.956)	5
	XIV	38.7 ± 9.8	81.1 ± 7.9	σ_R	36.3 ± 8.4	7.8(11.1)	0.940(0.872)	20
(8)	XV	50.5 ± 9.6	66.0 ± 7.8	σ_R	55.2 ± 8.3	7.6(14.4)	0.939(0.785)	20
	XVI	48.9 ± 18.5	59.2 ± 31.1	σ_R	54.2 ± 9.6	5.1(20.8)	0.951(0.000)	5
	XVII	65.5 ± 16.9	78.2 ± 28.4	σ_R	61.7 ± 8.7	4.7(23.6)	0.971(0.000)	5
	XVIII	48.9 ± 17.2	54.0 ± 28.9	σ_R	53.7 ± 8.9	4.8(20.6)	0.958(0.000)	5
	XIX	46.8 ± 15.6	49.6 ± 26.2	σ_R	53.4 ± 8.1	4.3(20.4)	0.966(0.000)	5
	XX	51.1 ± 13.1	55.4 ± 22.0	σ_R	55.8 ± 6.8	3.6(21.3)	0.978(0.000)	5
	XXI	22.3 ± 5.0	46.5 ± 3.6	σ_R	22.1 ± 4.3	3.3(6.2)	0.977(0.915)	13
	XXII	21.5 ± 4.3	36.6 ± 3.1	σ_R	15.0 ± 3.7	2.8(4.5)	0.974(0.934)	13
(9)	XXIII	39.5 ± 5.3	63.4 ± 4.1	σ_R	15.6 ± 6.4	3.4(4.4)	0.990(0.983)	10
	XXIV	29.0 ± 5.0	67.4 ± 3.9	σ_R	20.8 ± 6.0	3.2(5.1)	0.990(0.975)	10
	XXV	27.8 ± 3.8	34.6 ± 1.6	σ_R^+	15.4 ± 4.5	2.4(3.9)	0.994(0.984)	10
	XXVI	27.0 ± 3.8	36.4 ± 1.6	σ_R^+	17.9 ± 4.5	2.4(4.3)	0.994(0.982)	10
	XXVII	28.2 ± 4.1	36.3 ± 1.7	σ_R^+	17.7 ± 4.9	2.6(4.4)	0.993(0.982)	10
	XXVIII	30.1 ± 9.2	24.0 ± 3.7	σ_R^+	27.0 ± 7.7	4.6(8.9)	0.944(0.764)	7
(10)	XXIX	28.9 ± 9.2	24.5 ± 3.7	σ_R^+	25.8 ± 7.8	4.6(8.6)	0.944(0.783)	7
	XXX^d	0	−69.5 ± 10.0	σ_R	−44.8 ± 11.6	6.6(14.4)	0.944(0.696)	7
(11)	XXXI^e	0	−70.0 ± 9.4	σ_R	−48.1 ± 11.0	6.3(15.1)	0.951(0.667)	7

^aType of resonance parameter in the summand ($b \pm S_b$) $\sigma_R(\sigma_R^+)$.

^bIn parentheses are given S_Y and r values of correlation equation $SE = (a \pm S_a)\sigma_I + (b \pm S_b)\sigma_R(\sigma_R^+)$ calculated without accounting for the influence of polarization effect on the stabilization energies SE .

^cEquations for series **I–III** were calculated at equal array size (n 8; X = H, Me, Ph, H₂N, HO, MeO, F, N≡C).

^dAbsolute term of equation equals -55.7 ± 5.3 .

^eAbsolute term of equation equals -56.4 ± 5.0 .

with growing distance r_q and therefore is close to zero in charged classic systems.

The polarization effect can be characterized both by energy E_{es} and by polarization constants σ_α of substituents X [1–9, 21]. Among the cations under study cations XCH=CH–C⁺H₂ (series **XXIII–XXVII**) stand

out for in these cations the distance r_q is maximal and therefore the polarization effect (contribution Pol) minimal.

The ratio of contributions Ind , Res , and Pol in series **I–XXXI** depends on the series type and on the size of the array n of the series. For instance, in the series **XV**

Table 10. Inductive *Ind*, resonance *Res*, and polarization *Pol* contributions (%) into the overall change in stabilization energy *SE* affected by substituents X in series **I–XXXI**

Reaction no.	Series no.	Array size <i>n</i>	<i>Ind</i>	<i>Res</i>	<i>Pol</i>	
(4)	I	14	9±5	61±6	30±6	
	I	8	12±4	59±4	29±5	
	II	8	11±5	54±6	35±7	
	III	8	12±4	59±4	29±5	
	III	13	15±4	49±4	36±4	
	IV	13	16±6	61±5	23±6	
	V	6	16±4	63±5	21±6	
	VI	5	18±14	65±9	17±14	
	VII	7	0	66±10	34±11	
(5)	VIII	7	0	65±10	35±10	
	IX	7	0	60±1	40±1	
	X	5	24±4	42±2	34±4	
(6)	XI	5	26±6	40±4	34±6	
	XII	5	16±2	62±3	22±3	
(7)	XIII	5	11±10	64±6	25±10	
	XIV	20	20±5	54±5	26±6	
(8)	XV	20	24±5	41±5	35±5	
	XVI	5	30±11	28±15	42±7	
	XVII	5	32±8	30±11	38±5	
	XVIII	5	31±11	27±14	42±7	
	XIX	5	31±10	25±13	44±7	
	XX	5	31±8	26±10	43±5	
	(9)	XXI	13	20±4	53±4	27±5
		XXII	13	24±5	53±4	23±6
	(10)	XXIII	10	29±4	61±4	10±4
		XXIV	10	22±4	65±4	13±4
XXV		10	22±3	68±3	10±3	
XXVI		10	20±3	69±3	11±3	
XXVII		10	21±4	68±3	11±3	
(11)		XXVIII	7	22±7	50±8	28±8
		XXIX	7	22±7	51±8	27±8
(12)	XXX	7	0	63±9	37±10	
	XXXI	7	0	61±8	39±9	

for cations $\text{XC}^+ = \text{CH}_2$ (n 20) the contribution *Res* exceeds *Pol*. Yet in the series **XVI–XX** for the same cations (n 5) the contribution *Pol* exceeds *Res*.

Stabilization energies calculated by modern quantum-chemical procedures are well consistent with the experimental *SE* values. This is clear from the comparison of series **I** with series **VI–VIII** (Table 1), and also of series **XVI** with series **XVII–XX** (Table 4). Besides providing the array is the same (n 8) the contributions *Ind*, *Res*, and *Pol* in series **I** (calculated

from the experimental data), and **II**, **III** (quantum-chemical calculations) are identical. Analogously the contributions *Ind*, *Res*, and *Pol* in series **XVI** and series **XVII–XX** nearly coincide.

The contributions *Ind*, *Res*, and *Pol* vary in the range from 0 to 32%, from 25 to 69%, and from 10 to 44% respectively. In neither series the contribution *Ind* is the principal for the energy *SE*. In the series **I–XV** and **XXI–XXXI** the contribution *Res* dominates, in series **XVI–XX**, the contribution *Pol*. As follows from equation (14), the larger is the charge q^+ on reaction centers C^+ and Si^+ , the stronger is the polarization effect, other conditions being equal (the greater contribution *Pol*). At the same time the magnitude of the charge q^+ depends on the inductive and resonance interaction of the centers C^+ and Si^+ with substituents X. Therefore the contributions *Ind*, *Res*, and *Pol* are interdependent.

Series **III**, **XXI**, and **XXII** have arrays of the same size (n 13). Even so, the contributions *Pol* slightly decrease in going from XC^+H_2 (36±4%) to XC^+HPh (27±5%) and XC^+Ph_2 (23±6%). This fact is evidently caused by partial delocalization of the charge q^+ on the benzene rings. In keeping with equation (14) it should result in weakening of the polarization effect.

Silylium cations XSi^+H_2 are as a rule stronger stabilized by substituents X than their carbon analogs XC^+H_2 . This is shown by the negative values of the stabilization energy for series **XXX** and **XXXI** measured by reaction (13) (Table 7). Yet the negative *SE* values of series **VII** and **VIII** for cations XC^+H_2 [reaction (4)] are a lot larger than the *SE* values of series **XXVIII** and **XXIX** for XSi^+H_2 [reaction (12)] (Tables 1 and 7).

As already mentioned, the resonance donor X stabilize cations XC^+H_2 to a considerable greater degree than molecules XCH_3 . Unlike that the energies *SE* of series **XXVIII** and **XXIX** are affected at least by three factors. Firstly, the involvement not only of ions XSi^+H_2 but also of neutral molecules into the conjugation with substituents X [22]; secondly, the increase in the acceptor quality of the silicon atom with respect to X when Si gets positively charged [22]; thirdly, the great stability of cation Si^+H_3 (Table 7).

REFERENCES

1. Taft, R.W. and Topsom, R.D., *Prog. Phys. Org. Chem.*, 1987, vol. 16, p. 1.
2. Hansch, C., Leo, A., and Taft, R.W., *Chem. Rev.*, 1991, vol. 91, p. 165.

3. Egorochkin, A.N. and Kuznetsova, O.V., *Zh. Org. Khim.*, 2006, vol. 42, p. 192.
4. Egorochkin, A.N. and Kuznetsova, O.V., *Zh. Obshch. Khim.*, 2007, vol. 77, p. 68.
5. Egorochkin, A.N., Kuznetsova, O.V., and Novikova, O.V., *Zh. Org. Khim.*, 2007, vol. 43, p. 1277.
6. Novikova, O.V., Kuznetsova, O.V., and Egorochkin, A.N., *Zh. Obshch. Khim.*, 2007, vol. 77, p. 1529.
7. Kuznetsova, O.V. and Egorochkin, A.N., *Izv. Akad. Nauk, Ser. Khim.*, 2006, p. 602.
8. Egorochkin, A.N., Zderenova, O.V., and Skobeleva, S.E., *Izv. Akad. Nauk, Ser. Khim.*, 2000, p. 1002.
9. Kuznetsova, O.V., Egorochkin, A.N., and Novikova, O.V., *Zh. Obshch. Khim.*, 2006, vol. 76, p. 584.
10. Taft, R.W., Martin, R.N., and Lampe, F.W., *J. Am. Chem. Soc.*, 1965, vol. 87, 2490.
11. Radom, L., Poppinger, D., and Haddon, R.C., *Carbonium Ions*, Olah, G.A. and von Schleyer, P.R., New York: Wiley, 1976, vol. 5, p. 2303.
12. Greenberg, A. and Stevenson, T.A., *J. Am. Chem. Soc.*, 1985, vol. 107, p. 3488.
13. Hopkinson, A.C. and Lien, M.N., *Canad. J. Chem.*, 1985, vol. 63, p. 3582.
14. Apeloig, Y., *Heteroatom Chem.*, Block, E., Ed., Weinheim: VCH, 1990, p. 27.
15. El-Nahas, A.M. and Clark, T. *J. Org. Chem.*, 1995, vol. 60, p. 8023.
16. Maerker, C. and von Schleyer, P.R., *The Chemistry of Organic Silicon Compounds*, Rappoport, Z., and Apeloig, Y., Eds., Chichester: Wiley, 1998, vol. 2, p. 513.
17. Van Alem, K., Lodder, G., and Zuilhof, H., *J. Phys. Chem. A*, 2000, vol. 104, p. 2780.
18. Han, I.S., Kim, C.K., Kim, Ch.K., Lee, H.W., and Lee, I. *J. Phys. Chem. A*, 2002, vol. 106, p. 2554.
19. Van Alem, K., Lodder, G., and Zuilhof, H., *J. Phys. Chem. A*, 2002, vol. 106, p. 10681.
20. Burshtein, K.Ya. and Shorygin, P.P., *Kvantovokhimicheskie raschety v organicheskoi khimii i molekulyarnoi spektroskopii* (Quantum-Chemical Computations in Organic Chemistry and Molecular Spectroscopy), Moscow: Nauka, 1989, p. 104.
21. Pacey, P.D. and Tan, Q.-T., *J. Phys. Chem.*, 1995, vol. 99, 17729.
22. Egorochkin, A.N. and Voronkov, M.G., *Elektronnoe stroenie organicheskikh soedinenii kremniya germaniya i olova* (Electronic Structure of Organic Compounds of Silicon, Germanium, and Tin), Novosibirsk: Izd SO RAN, 2000, 615 p.