First ionization potentials of amines and electronic effects in their radical cations

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The possibility of application of linear free energy relationships for studying the effects of substituents on the first vertical ionization potentials of amines, $I(n_N)$, was substantiated. The $I(n_N)$ values depend on the inductive, resonance, and polarizability effects of substituents and are also affected by hyperconjugation. The σ_R^+ resonance parameters of substituents MR_3 (M = Si, Ge, Sn) and CH_2SiMe_3 bound to the $N^{\bullet+}$ radical cation center were calculated for the first time.

Key words: amines, ionization potential, radical cation, conjugation, polarizability, electronic effects of organometallic substituents.

The concept of ionization potential (IP) considered as the energy necessary for detachment of an electron from the valence energy level of a molecule is widely used in theoretical chemistry. The IP values of organic, organoelement, and inorganic compounds are listed in monographs (see, *e.g.*, Refs. 1—3) and continuously accumulated. Until recently, no detailed studies on the mechanisms of the influence of substituents X on the IPs of $R_\pi X$ and ZX_n compounds in which ionization is due to abstraction of an electron from the reaction center of the π-type (R_π = aryl, hetaryl, CH_2=CH, HC≡C, *etc.*) or n-type (Z is a fragment containing an atom Y with at least one lone electron pair and bound to X substituents) has been carried out. Establishment of this mechanism would allow rigorous determination of the inductive effect of X substituents on the IP values, quantitative estimation of conjugation between MR_3 (M = Si, Ge, Sn) substituents and the radical cation centers $R_\pi^{\bullet+}$ and $Z^{\bullet+}$, as well as contributing to further development of modern concept of conjugation in compounds of the silicon subgroup elements.[4]

Recently, we found correlations between the IPs of $R_\pi X$ [5—7] and ZX_n ($S(X_i)_2$,[8] $P(X_i)_3$ [9]) molecules and the nature of X substituents whose interaction with the radical cation centers $R_\pi^{\bullet+}$, $S^{\bullet+}$, and $P^{\bullet+}$ involves not only the inductive and resonance, but also polarizability, mechanisms. The contribution of polarizability interaction (*i.e.*, electrostatic attraction between the positive charge and the induced dipole moment of the X substituent) to the IP value is comparable with those of the inductive and resonance effects while their ratio is determined by the nature of R_π and Z groups.[5—9]

Establishing the applicability of the known approach[5—9] to investigation of ionization potentials and conjugation in the $Z^{\bullet+}$ radical cations requires the use of new series of ZX_n compounds. The aim of this work was to study the effect of substituents bound to N atom on the IP of amines, to obtain quantitative estimates of the inductive, resonance, and polarizability contributions to IPs, and to calculate the σ_R^+ resonance parameters of Si-, Ge-, and Sn-containing substituents bound to the radical cation center $N^{\bullet+}$.

Calculation Procedure

The first vertical IPs corresponding to detachment of an electron from the highest occupied MO (HOMO) localized mainly on the N atom of ammonia derivatives $N(X_i)_3$ (X is an organic or inorganic substituent) are listed in Table 1. The IP values were determined by photoelectron spectroscopy with an accuracy of 0.01 eV. The notation of the IPs of molecules **1—57**, $I(n_N)$, emphasizes similarity between the corresponding HOMOs and the lone electron pair orbital of N atom.[1,3]

Photoelectron spectroscopy uses a gas-phase ionization process initiated by photons with the energy $h\nu$

$$M \xrightarrow{h\nu} M^{\bullet+} + e^-, \qquad (1)$$

where M is the neutral molecule, $M^{\bullet+}$ is the radical cation, and e^- is an electron.

The ionization potential (I) is equal to the difference between the total energies of the radical cation $M^{\bullet+}$ and the molecule M [1]:

$$I = E_{tot}^{\bullet+} - E_{tot}. \qquad (2)$$

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Table 1. First vertical ionization potentials $I(n_N)$ of $(X_i)_3N$ molecules and the sums of σ parameters of substituents X_i

Compound	$I(n_N)$ /eV	$\Sigma\sigma_P^+$	$\Sigma\sigma_I$	$\Sigma\sigma_R^+$	$\Sigma\sigma_\alpha$
NH_3 (**1**)	10.90	0	0	0	0
$MeNH_2$ (**2**)	9.64	−0.31	−0.05	−0.26	−0.35
$EtNH_2$ (**3**)	9.46	−0.30	−0.05	−0.25	−0.49
$PrNH_2$ (**4**)	9.34	−0.30	−0.05	−0.25	−0.54
Pr^iNH_2 (**5**)	9.36	−0.28	−0.03	−0.25	−0.62
cyclo-$PrNH_2$ (**6**)	9.43	−0.41	0.02	−0.43	−0.62
$BuNH_2$ (**7**)	9.29	−0.30	−0.05	−0.25	−0.57
Bu^iNH_2 (**8**)	9.28	−0.28	−0.03	−0.25	−0.61
Bu^sNH_2 (**9**)	9.27	−0.28	−0.03	−0.25	−0.68
Bu^tNH_2 (**10**)	9.25	−0.26	−0.07	−0.19	−0.75
$C_5H_{11}NH_2$ (**11**)	9.30	−0.30	−0.05	−0.25	−0.58
$Bu^tCH_2NH_2$ (**12**)	9.25	−0.28	−0.03	−0.25	−0.67
Me_2EtCNH_2 (**13**)	9.20	−0.26	−0.07	−0.19	−0.82
$H_2C{=}CHCH_2NH_2$ (**14**)	9.44	−0.22	−0.06	−0.16	−0.57
$N{\equiv}CNH_2$ (**15**)	10.65	0.66	0.51	0.15	−0.46
$HONH_2$ (**16**)	10.64	−0.92	0.33	−1.25	−0.03
$MeONH_2$ (**17**)	10.25	−0.78	0.29	−1.07	−0.17
$ClNH_2$ (**18**)	10.52	0.11	0.42	−0.31	−0.43
$BrNH_2$ (**19**)	10.18	0.15	0.45	−0.30	−0.59
Me_2NH (**20**)	8.94	−0.62	−0.10	−0.52	−0.70
Et_2NH (**21**)	8.67	−0.60	−0.10	−0.50	−0.98
Pr_2NH (**22**)	8.55	−0.60	−0.10	−0.50	−1.08
$Pr^i{}_2NH$ (**23**)	8.42	−0.56	−0.06	−0.50	−1.24
Bu_2NH (**24**)	8.49	−0.60	−0.10	−0.50	−1.14
$Bu^i{}_2NH$ (**25**)	8.47	−0.56	−0.06	−0.50	−1.22
$(C_5H_{11})_2NH$ (**26**)	8.45	−0.60	−0.10	−0.50	−1.16
MeEtNH (**27**)	8.73	−0.61	−0.10	−0.51	−0.84
$(H_2C{=}CHCH_2)_2NH$ (**28**)	8.79	−0.44	−0.12	−0.32	−1.14
Me(HO)NH (**29**)	9.82	−1.23	0.28	−1.51	−0.38
Me(MeO)NH (**30**)	9.49	−1.09	0.24	−1.33	−0.52
F_2NH (**31**)	12.38	−0.14	0.90	−1.04	0.26
Me(Cl)NH (**32**)	9.80	−0.20	0.37	−0.57	−0.78
Cl_2NH (**33**)	10.56	0.22	0.84	−0.62	−0.86
Br_2NH (**34**)	10.10	0.30	0.90	−0.60	−1.18
Me_3N (**35**)	8.51	−0.93	−0.15	−0.78	−1.15
Et_3N (**36**)	8.09	−0.90	−0.15	−0.75	−1.47
Pr_3N (**37**)	7.94	−0.90	−0.15	−0.75	−1.62
Bu_3N (**38**)	7.88	−0.90	−0.15	−0.75	−1.71
$Bu^i{}_3N$ (**39**)	7.98	−0.84	−0.09	−0.75	−1.83
$(C_5H_{11})_3N$ (**40**)	7.85	−0.90	−0.15	−0.75	−1.74
Me_2EtN (**41**)	8.39	−0.92	−0.15	−0.77	−1.19
$MeEt_2N$ (**42**)	8.22	−0.91	−0.15	−0.76	−1.33
$(H_2C{=}CHCH_2)_3N$ (**43**)	8.30	−0.66	−0.18	−0.48	−1.71
$Me_2(NCCH_2)N$ (**44**)	9.22	−0.46	0.07	−0.53	−1.25
$Et_2(N{\equiv}C)N$ (**45**)	9.32	0.04	0.41	−0.37	−1.44
$Me_2(O{=}CH)N$ (**46**)	9.40	0.11	0.23	−0.12	−1.16
$Me_2(F_3C)N$ (**47**)	9.99	−0.01	0.28	−0.29	−0.95
$(F_3C)_3N$ (**48**)	12.52	1.83	1.14	0.69	−0.75
$Me_2(HO)N$ (**49**)	9.18	−1.54	0.23	−1.77	−0.73
$Me_2(MeO)N$ (**50**)	8.81	−1.40	0.19	−1.59	−0.87
$F(F_3C)_2N$ (**51**)	12.45	1.15	1.21	−0.06	−0.37
$F_2(F_3C)N$ (**52**)	12.62	0.47	1.28	−0.81	0.01
F_3N (**53**)	13.73	−0.21	1.35	−1.56	0.39
$Me_2(Cl)N$ (**54**)	9.31	−0.51	0.32	−0.83	−1.13
$Cl(F_3C)_2N$ (**55**)	11.45	1.33	1.18	0.15	−0.93
$MeCl_2N$ (**56**)	10.01	−0.09	0.79	−0.88	−1.21
Cl_3N (**57**)	10.69	0.33	1.26	−0.93	−1.29

Note. The $I(n_N)$ of compounds **12**, **13**, and **42** were taken from Ref. 10 and those of compounds **27**, **44**, **45**, **47**, **48**, **51**, **52**, and **55** were taken from Ref. 11. The ionization potentials of other compounds were taken from Refs. 1 and 3. Standard sets of the σ_I, σ_R^+, and σ_α constants, as well as the sums $\sigma_P^+ = \sigma_I + \sigma_R^+$, are the same as those used previously.[5—9]

Currently, the use of relationship (2) for comparative analysis of substituent effects (in particular, conjugation) in M and $M^{\bullet+}$ faces some computational problems associated with incorrect quantum-chemical calculations of total energies. The accuracy of energy (E_{tot} and $E_{tot}{}^{\bullet+}$) calculations comparable with the experimental error of determination of the IP values can be achieved only for the simplest molecules (*e.g.*, CF and CF_2 [12]); therefore, the IP values are interpreted using approximate methods.

Consideration of IPs in the framework of quantum-chemical approaches allows separation of the relaxation (R) and correlation (C) energies which characterize the changes in the composition of the wave functions of M due to its transformation into $M^{\bullet+}$. In particular, for the first IP, I_1, we get[13]

$$I_1 = I_1{}^0 - R + C. \quad (3)$$

The Koopmans approximation[1]

$$I_1{}^0 = -E_{HOMO} \quad (4)$$

ignores the R and C contributions to I_1, which is not always true. For instance, the Koopmans approximation was found to be valid for none of the series of $R_\pi X$ and ZX_n compounds we studied previously.[5—9]

It has been of our main interest here to use the thermodynamic approach for studying the substituent effect on IP. The standard Gibbs free energy, $\Delta_r G^\circ(T)$, of process (1) can be calculated using the Gibbs—Helmholtz equation[14]:

$$\Delta_r G^\circ(T) = \Delta_r H^\circ(T) - T\Delta_r S^\circ(T). \quad (5)$$

The standard enthalpy $\Delta_r H^\circ(T)$ and entropy $\Delta_r S^\circ(T)$ of a chemical reaction proceeding at temperature T can be found from the relationships

$$\Delta_r H^\circ(T) = \Delta H_f^\circ(T, M^{\bullet+}) + \Delta H_f^\circ(T, e^-) - \Delta H_f^\circ(T, M) \quad (6)$$

and

$$\Delta_r S^\circ(T) = S^\circ(T, M^{\bullet+}) + S^\circ(T, e^-) - S^\circ(T, M), \quad (7)$$

where ΔH_f° and S° are respectively the standard enthalpy of formation and the absolute entropy of reagents. By definition,[14] the energy of ionization (a more correct term for ionization potential, $I(M)$) is the thermal effect, $\Delta_r H^\circ(T)$, of process (1). Therefore,

$$\Delta_r G^\circ(T) = I(M) - T\Delta_r S^\circ(T). \quad (8)$$

Let us estimate the entropy contribution, $T\Delta_r S^\circ(T)$, to $\Delta_r G^\circ(T)$ for $T = 0$, 298.15, and 500 K. For $T = 0$ K, this contribution equals zero, so that

$$\Delta_r G^\circ(T) = I(M). \quad (9)$$

Table 2. Thermodynamic parameters of ionization process (1)

T/K	$S°(M^+) - S°(M)$	$S°(e^-)$	$T\Delta_r S°$	min $\Delta_r G°(T)$	max $(T\Delta_r S°)/\Delta_r G°(T)$
	cal mol^{-1} K^{-1}		kcal mol^{-1}		
298.15	−3—3.5	5.0	0.6—2.5	112.5	0.02
500	−3—4	7.5	2.3—5.7	109.3	0.05

Note. $S°(T, e^-)$ is the entropy of electron gas at temperature T; min $\Delta_r G°$ is the minimum standard free energy of ionization; and max $(T\Delta_r S°)/\Delta_r G°(T)$ is the maximum entropy contribution to the free energy of ionization. For both temperatures, the I(M) values lie between 115 and 360 kcal mol^{-1} (see Refs. 1—3, 14).

For T = 298.15 and 500 K, we obtained numerical estimates of the entropy contribution for ionization of more than 20 of the simplest M systems such as H_2O, CO_2, CO, NO, NH, CN, oxides, hydroxides, and metal halides. Tabulated values of the standard thermodynamic quantities[14] were taken as initial data for calculations. We found that the entropy contribution does not exceed 5% (Table 2) and, hence, relationship (9) is valid for the ionization process (1) over a wide temperature range. Therefore, the influence of substituents on IPs (including the $I(n_N)$ ionization potentials of molecules **1—57**, see Table 1) can be considered using the linear free energy relationship (LFER, see, *e.g.*, Ref. 4). In practice, this relationship is used in the form of the Hammett—Taft correlation equations.

It is convenient to re-write relationship (9) as follows

$$\delta_X(\Delta G) = \delta_X I(M), \qquad (10)$$

where δ_X characterizes the differences between the changes in the free energy and ionization potential of the molecule containing the X substituent and the unsubstituted molecule (X = H). The contributions of different intramolecular effects to $\delta_X(\Delta G)$ are independent and additive.[4] In studying the substituent effects on IPs this allows representation of $\delta_X(\Delta G)$ as the sum of the contributions of the inductive (Ind), resonance (Res), and polarizability (Pol) effects:

$$\delta_X(\Delta G) = \delta_X(\Delta G_{Ind}) + \delta_X(\Delta G_{Res}) + \delta_X(\Delta G_{Pol}). \qquad (11)$$

The linear free energy relationship is separately applied to each component rather than the overall change $\delta_X(\Delta G)$.[4] It should be remembered that in this case the inductive, resonance, and polarizability effects of X substituents are characterized by the σ_I, σ_R^+, and σ_α parameters, respectively. Hence dependences (10) and (11) are reduced to the following relationship

$$I = I_H + a\sigma_I + b\sigma_R^+ + c\sigma_\alpha, \qquad (12)$$

where the origins of all the scales of the σ parameters listed in Table 1 are chosen in such a way that σ = 0 for X = H (therefore, the notation δ_X can be omitted) and I_H is the I value for X = H.

The inductive effect of substituents is quantitatively characterized by universal σ_I constants, which are "insensitive" to the type of reaction center.[4] The resonance effect of substituents cannot be characterized by a set of universal σ_R constants. For instance, the σ_R parameters of benzene derivatives C_6H_5X depend on the magnitude and sign of the charge induced on the benzene ring.

Out of several types of σ_R parameters let us dwell on the σ_R^0 and σ_R^+ constants. The σ_R^0 parameter is a quantitative characteristic of conjugation between the substituent X and the reaction center in the neutral molecule which is in the ground electronic state. The σ_R^0 constants of $R_\pi X$ (R_π = Ph, CH_2=CH, HC≡C) compounds are related to q_π values (q_π is the π-electron exchange in the case of resonance interaction between R_π and X and its values are obtained from *ab initio* quantum-chemical calculations) by linear dependences.[15] The σ_R^+ parameter quantitatively characterizes conjugation between the substituent X and electron-deficient reaction center of any type formed in the final or transition state of a chemical process.[16] Reaction (1) results in the appearance of such a positively charged center in the radical cation $M^{\bullet+}$. Therefore, the σ_R^+ constants of substituents X should be used for estimation of the resonance contributions to the changes in the free energy, $\delta_X(\Delta G_{Res})$, and ionization potential, $b\sigma_R^+$, using Eqs. (11) and (12), respectively. The σ_R^0 and σ_R^+ parameters of substituents X differ appreciably.[16] Impossibility of description of the resonance effect of substituents X on the IP values using the σ_R^0 parameters characterizing conjugation in neutral molecules is the first indicator of a failure of the Koopmans approximation (4).

The polarizability effect of substituents can be taken into account[5—9] using universal σ_α constants[17] which characterize the $\delta_X(\Delta G_{Pol})$ contributions to the changes in the free energy of gas-phase reactions (in particular, process (1)). In $R_\pi^{\bullet+}X$ and $Z^{\bullet+}X_n$ systems, the energy of electrostatic attraction between the charge q of the radical cation center $R_\pi^{\bullet+}$ or $Z^{\bullet+}$ and the induced dipole of the substituent X stabilizing the charge is calculated by the formula

$$E_{es} = -q^2\alpha/(2\varepsilon r^4), \qquad (13)$$

where α is the polarizability of the substituent X, ε is the dielectric constant, and r is the distance between the charge and induced dipole.

The polarizability contribution (13) to the changes in $\delta_X(\Delta G)$ and I can be taken into account using LFER. This requires introduction of yet another parameter into correlation equations of the type (12). The new parameter (σ_α) characterizes the polarizability of substituent X.[17] In neutral $R_\pi X$ and ZX_n molecules, the polarizability effect is absent. Therefore, a nonzero polarizability contribution in relationship (12) is the second indicator of the failure of the Koopmans approximation (Eq. (4)).

Correlation equations were obtained using the "Statgraphics 3.0" program package on an AT 286 personal computer. The data were processed by the least squares method at a 95% confidence level.

Results and Discussion

The following correlation equations obtained for R_nNH_{3-n} compounds (**1—57**, see Table 1)

$$I(n_N) = 10.05 + 1.43\Sigma\sigma_P^+, \qquad (14)$$

S_a = 0.14, S_b = 0.21, S_Y = 0.95, r = 0.683, n = 57;

$$I(n_N) = 9.20 + 2.55\Sigma\sigma_I + 0.34\Sigma\sigma_R^+, \quad (15)$$

$S_a = 0.13$, $S_b = 0.18$, $S_c = 0.18$, $S_Y = 0.61$, $r = 0.881$, $n = 57$;

$$I(n_N) = 11.27 + 1.12\Sigma\sigma_P^+ + 1.56\Sigma\sigma_\alpha, \quad (16)$$

$S_a = 0.15$, $S_b = 0.13$, $S_c = 0.16$, $S_Y = 0.58$, $r = 0.893$, $n = 57$

are unsatisfactory since the correlation coefficients r are less than 0.90. However, the r value increases on going from Eq. (14) to Eqs. (15) and (16). In the former case, this is due to the large difference between the inductive ($2.55\Sigma\sigma_I$) and resonance ($0.34\Sigma\sigma_R^+$) contributions to the overall electronic effect of substituents on the IP value, while in the latter case this is due to inclusion of the polarizability contribution ($1.56\Sigma\sigma_\alpha$). As should be expected, the dependence

$$I(n_N) = 10.35 + 2.04\Sigma\sigma_I + 0.38\Sigma\sigma_R^+ + 1.21\Sigma\sigma_\alpha, \quad (17)$$

$S_a = 0.09$, $S_b = 0.08$, $S_c = 0.07$, $S_d = 0.07$, $S_Y = 0.24$, $r = 0.982$, $n = 57$

differs from Eqs. (14)—(16) by better statistical characteristics.

Thus, Eq. (12) is valid for any organic amines, sulfides,[8] and phosphines.[9] The coefficients of Eq. (12) depend on the type of the radical cation center. Conjugation between substituents X and the radical cation centers $N^{\bullet+}$, $S^{\bullet+}$,[8] and $P^{\bullet+}$ [9] is characterized by the σ_R^+ resonance parameters. It seems likely that specific features of these centers manifest themselves only in the magnitude of the resonance contribution, $b\sigma_R^+$, which depends on the b coefficient rather than σ_R^+ constant. However, yet another interpretation cannot also be ruled out. Probably, each radical cation center of the n-type ($N^{\bullet+}$, $S^{\bullet+}$, and $P^{\bullet+}$) and π-type $R_\pi^{\bullet+}$ (see Refs. [5—7]) is characterized by its own set of σ_R^+ parameters. The σ_R^+ constants of all such centers are related to one another by linear dependences and, hence, the resonance contribution, $b\sigma_R^+$, depends on the σ_R^+ value rather than b coefficient. Currently, it is hard to give preference to any of the two viewpoints.

In this connection, let us refer to the results of *ab initio* quantum-chemical calculations of π-electron transfer, q_π, in the XCH_2^+ (q_π^C), 4-$XC_6H_4CH_2^+$ (q_π^B), and $XCH{=}CHCH_2^+$ (q_π^E) cations.[18] Using these results, we found[8] that the q_π^C, q_π^B, and q_π^E values are related by linear dependences. This suggests the absence of fundamental differences between the resonance interactions in the XCH_2^+ cations and those in typical conjugated systems irrespective of different q_π values. Taken together with the aforesaid, this points to the similarity of the manifestations of conjugation between substituents X and electron-deficient reaction centers of diverse nature including radical cation reaction centers.

The absolute term of Eq. (17) denoted below as I_H similarly to that of relationship (12) differs appreciably from the IP of ammonia molecule (10.90 eV). Rationalization of this fact requires a separate consideration of the correlation equations for primary ($I(n_N)$, p; compounds **2—19**), secondary ($I(n_N)$, s; compounds **20—34**), and tertiary ($I(n_N)$, t; compounds **35—57**) amines given below:

$$I(n_N),\ p = 10.14 + 1.92\sigma_I + 0.16\sigma_R^+ + 1.10\sigma_\alpha, \quad (18)$$

$S_a = 0.13$, $S_b = 0.12$, $S_c = 0.10$, $S_d = 0.19$, $S_Y = 0.08$, $r = 0.987$, $n = 18$;

$$I(n_N),\ s = 10.78 + 1.87\Sigma\sigma_I + 0.62\Sigma\sigma_R^+ + 1.61\Sigma\sigma_\alpha, \quad (19)$$

$S_a = 0.21$, $S_b = 0.11$, $S_c = 0.16$, $S_d = 0.14$, $S_Y = 0.14$, $r = 0.992$, $n = 15$;

$$I(n_N),\ t = 11.08 + 1.71\Sigma\sigma_I + 0.57\Sigma\sigma_R^+ + 1.53\Sigma\sigma_\alpha, \quad (20)$$

$S_a = 0.28$, $S_b = 0.16$, $S_c = 0.11$, $S_d = 0.16$, $S_Y = 0.26$, $r = 0.990$, $n = 23$.

Compare Eqs. (18)—(20) with the general equation for amines **2—57**:

$$I(n_N) = 10.27 + 2.07\Sigma\sigma_I + 0.35\Sigma\sigma_R^+ + 1.16\Sigma\sigma_\alpha, \quad (21)$$

$S_a = 0.09$, $S_b = 0.08$, $S_c = 0.07$, $S_d = 0.07$, $S_Y = 0.23$, $r = 0.984$, $n = 56$.

The I_H value of Eq. (21) is much smaller than the IP of ammonia, which is due to the small I_H (10.14 eV) of Eq. (18) for primary amines.

It is noteworthy that statistical characteristics of the correlation equations for eight primary (**2—4**, **7**, **8**, **11**, **14**, and **18**), secondary (**20—22**, **24—26**, **28**, and **33**), and tertiary (**35—40**, **43**, and **57**) amines containing the same substituents X are much better

$$I(n_N),\ p = 10.80 + 2.33\sigma_I + 1.78\sigma_R^+ + 1.65\sigma_\alpha, \quad (22)$$

$S_a = 0.08$, $S_b = 0.05$, $S_c = 0.22$, $S_d = 0.08$, $S_Y = 0.02$, $r = 0.999$, $n = 8$;

$$I(n_N),\ s = 10.97 + 2.12\Sigma\sigma_I + 1.95\Sigma\sigma_R^+ + 1.14\Sigma\sigma_\alpha, \quad (23)$$

$S_a = 0.03$, $S_b = 0.01$, $S_c = 0.05$, $S_d = 0.02$, $S_Y = 0.01$, $r = 0.999$, $n = 8$;

$$I(n_N),\ t = 11.28 + 1.88\Sigma\sigma_I + 1.68\Sigma\sigma_R^+ + 1.07\Sigma\sigma_\alpha, \quad (24)$$

$S_a = 0.35$, $S_b = 0.07$, $S_c = 0.30$, $S_d = 0.13$, $S_Y = 0.07$, $r = 0.997$, $n = 8$.

The I_H values of Eqs. (22)—(24) differ slightly from the IP of ammonia and increase on going from primary to secondary and then to tertiary amines as is the case of Eqs. (18)—(20). The number of primary amines can be increased from eight (compounds **2—4**, **7**, **8**, **11**, **14**, and **18**; Eq. (18)) to fourteen (compounds **2—5**, **7—14**, **18**,

and **19**) without a significant decrease in the I_H value of Eq. (25) compared to that of Eq. (22):

$$I(n_N),\ p = 10.65 + 2.14\sigma_I + 2.01\sigma_R^+ + 1.22\sigma_\alpha, \quad (25)$$

$$S_a = 0.27,\ S_b = 0.16,\ S_c = 0.79,\ S_d = 0.20,\ S_Y = 0.07,\ r = 0.982,\ n = 14.$$

Calculations for the amines containing no alkyl substituents (compounds **15—19**, **31**, **33**, **53**, and **57**) lead to a substantial decrease in the I_H value of the correlation equation:

$$I(n_N) = 10.23 + 2.36\Sigma\sigma_I + 0.29\Sigma\sigma_R^+ + 1.74\Sigma\sigma_\alpha, \quad (26)$$

$$S_a = 0.08,\ S_b = 0.09,\ S_c = 0.08,\ S_d = 0.07,\ S_Y = 0.09,\ r = 0.997,\ n = 10.$$

The amine molecules for which particular correlation equations (19), (20), and (22)—(26) are valid contain different number of the H—C—$N^{\bullet+}$ fragments (m). The m/n ratio characterizes the proportion of these fragments in the series of n compounds (Table 3). The I_H and m/n values for the series described by Eqs. (19), (20), and (22)—(26) are related by a linear dependence:

$$I_H = 10.35 + 0.17m/n, \quad (27)$$

$$S_a = 0.07,\ S_b = 0.02,\ S_Y = 0.10,\ r = 0.965,\ n = 7.$$

Increasing the sample size by including the compounds described by Eq. (18) leads to a decrease in the correlation coefficient:

$$I_H = 10.23 + 0.19m/n, \quad (28)$$

$$S_a = 0.11,\ S_b = 0.03,\ S_Y = 0.17,\ r = 0.921,\ n = 8.$$

It is believed that the interrelation between the I_H and m/n values indicates a weaker hyperconjugation of C—H bonds of the alkyl groups in the —CH_2—$N^{\bullet+}$ fragments compared to the corresponding —CH_2—$C^{\bullet+}$ fragments in which the radical cation center is mainly localized on the C atom. The ability of the C—H bonds to be involved in hyperconjugation with the electron-deficient reaction center localized on the C atom (including that of the $R_\pi^{\bullet+}$ type) is taken into account in the standard values of the σ_R^+ parameters of alkyl groups.[19] Therefore, resonance interactions in the $R_\pi^{\bullet+}X$ radical cations with any X (including X = Alk) are similar.[5—7] Hyperconjugation in fragments of the H—C—$S^{\bullet+}$ [8] and H—C—$P^{\bullet+}$ [9] radical cations is stronger than in $R_\pi^{\bullet+}$Alk. The increase in the resonance donor properties of alkyl groups toward the $S^{\bullet+}$ and $P^{\bullet+}$ radical cation centers cannot be adequately taken into account by using the standard σ_R^+ values. Therefore, increasing the number of alkyl groups bound to these centers (*i.e.*, strengthening of hyperconjugation) leads to a decrease in the absolute terms, I_H, of correlation equations similar to Eq. (12).

Table 3. Parameters I_H and m/n of correlation equations and the inductive (Ind), resonance (Res), and polarizability (Pol) contributions to the changes in ionization potentials of unsubstituted molecules caused by replacement of H atoms bound to the N atom by X substituents in the series of molecules described by different correlation equations

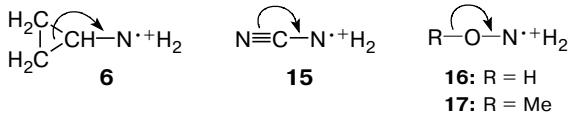
Equation	I_H	m/n	Ind	Res	Pol
			%		
(18)	10.14	1.11	50	10	40
(19)	10.78	3.07	28	32	40
(20)	11.08	4.65	35	19	46
(22)	10.80	1.88	61	15	24
(23)	10.97	3.75	64	18	18
(24)	11.28	5.62	65	18	17
(25)	10.65	1.36	56	15	29
(26)	10.23	0	42	8	50

Just the opposite is observed for amines. From Eqs. (27) and (28) it follows that the absolute terms I_H in equations of the type (12) increase as the number of alkyl groups bound to the $N^{\bullet+}$ radical cation center increases. This is due to weak hyperconjugation in radical cations containing the H—C—$N^{\bullet+}$ fragment compared to that in $R_\pi^{\bullet+}$Alk. Adequate characterization of conjugation between alkyl groups and the $N^{\bullet+}$ radical cation center requires a decrease of absolute values of the standard negative σ_R^+ constants of these substituents.

Consideration of Eqs. (18)—(20) revealed an important feature of the radical cations of primary amines, that is, the degree of delocalization of the unpaired electron and positive charge in the $XN^{\bullet+}H_2$ radical cations is lower than in the $X_2N^{\bullet+}H$ and $X_3N^{\bullet+}$ cations containing a larger number of the same substituents X (*e.g.*, X = Me).

Among three series of eight amines containing the same substituents and described by Eqs. (22)—(24), the polarizability contribution, Pol, was found to be the largest for primary amines (24%, see Table 3). This can be rationalized by larger positive charge q of the $N^{\bullet+}$ radical cation center (and, hence, greater Pol contribution according to formula (13)) in the $XN^{\bullet+}H_2$ radical cations in which the degree of delocalization of this charge is lower than in $X_2N^{\bullet+}H$ and $X_3N^{\bullet+}$ radical cations. In turn, the larger charge q in $XN^{\bullet+}H_2$ compared to $X_2N^{\bullet+}H$ and $X_3N^{\bullet+}$ with the same X seems to be responsible for better conditions for hyperconjugation of the only substituent X in the radical cations of primary amines. Therefore, the change in the ionization potential, ΔIP, in the series of XNH_2 compounds on going from X = Me to X = HO and MeO (1.00 and 0.61 eV, respectively) is more pronounced than in X_2NH compounds on going from X_2 = Me_2 to X_2 = Me(HO) and Me(MeO) (ΔIP = 0.88 and 0.55 eV, respectively) and in X_3N compounds on going from X_3 = Me_3 to X_3 = Me_2(HO) and Me_2(MeO) (ΔIP = 0.67 and 0.30 eV, respectively).

It can be assumed that in the radical cations of primary amines **6** and **15—17** hyperconjugation



6 **15** **16:** R = H **17:** R = Me

is stronger than in radical cation containing the H—C—$N^{\bullet+}N_2$ fragment. For a detailed consideration of the dependence between hyperconjugation involving R—O bonds and the character of the reaction center see, *e.g.*, Ref. 20. The absolute terms, I_H, of correlation equations of the type (12) decrease as hyperconjugation strengthens. Therefore, the I_H value in Eq. (18) for primary amines containing, in particular, the HO, MeO, NC, and *cyclo*-Pr substituents is appreciably smaller than the absolute term of Eq. (25) which was obtained without these compounds (10.14 *vs.* 10.65 eV, respectively).

Using Eqs, (19), (20), and (25), we calculated unknown values of the $\sigma_R^+(N)$ resonance parameters of organoelement substituents MR_3 (M = Si, Ge, Sn) and CH_2SiMe_3 bound to the $N^{\bullet+}$ radical cation center (Table 4). As was mentioned above, these equations are characterized by different absolute terms I_H and m/n ratios (see Table 3). This indicates different contributions of hyperconjugation in corresponding series of compounds. Because of this, the $\sigma_R^+(N)$ constant of a particular substituent (*e.g.*, CH_2SiMe_3) can likely be dependent on the type of the equation used for its calculation (Eqs. (19), (20), or (25)) along with other factors. Therefore, we restrict ourselves to consideration of general trends of changes in the $\sigma_R^+(N)$ parameters listed in Table 4.

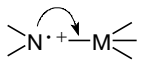
The magnitudes of the $\sigma_R^+(N)$ parameters are much larger than those of the standard $\sigma_R^+(B)$ constants of the MR_3 and CH_2SiMe_3 substituents bound to the benzene ring. On the other hand, the $\sigma_R^+(N)$ constants seem to be somewhat closer to the $\sigma_R^+(P)$ parameters characterizing the SiH_3, $SiMe_3$, GeH_3, and $SnMe_3$ substituents bound to the $P^{\bullet+}$ radical cation center. The signs of the $\sigma_R^+(N)$ parameters alternate. Positive $\sigma_R^+(N)$ values indicate that the organoelement substituent in the $N^{\bullet+}—MR_3$ or $N^{\bullet+}—CH_2SiMe_3$ fragment is a resonance acceptor toward $N^{\bullet+}$. According to modern concept of conjugation in compounds of the silicon subgroup elements,[4] the resonance acceptor effect of MR_3 (M = Si, Ge, Sn; R = H, Alk) substituents toward $N^{\bullet+}$ (d,n-conjugation) is due to the interaction between the n-AO of N on which the unpaired electron is localized and the nd-AO of the M atom and σ^*-orbitals of the M—R bonds. The resonance donor effect (σ,n-conjugation) is due to the interaction between the σ-orbitals of the M—R bonds and the n-AO of N on which the unpaired electron is localized. As is known,[4] d,n-conjugation in molecules of compounds of the silicon subgroup ele-

Table 4. Calculated $\sigma_R^+(N)$ parameters of MR_3 (M = Si, Ge, Sn) and CH_2SiMe_3 substituents

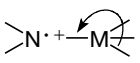
Compounds	$I(n_N)$ /eV	$\Sigma\sigma_I$	$\Sigma\sigma_\alpha$	$\Sigma\sigma_R^+(N)$	$\sigma_R^+(N)$	$\sigma_R^+(P)$	$\sigma_R^+(B)$
Me_2NSiH_3 (**58**)	8.5	−0.14	−1.29	−0.13	−0.13	—	—
$MeN(SiH_3)_2$ (**59**)	9.2	−0.13	−1.53	1.45	0.73	—	0.03
$N(SiH_3)_3$ (**60**)	9.7	−0.12	−1.77	2.68	0.89	0.49	—
Me_2NSiMe_3 (**61**)	8.03	−0.25	−1.42	−0.27	−0.27	—	—
$HN(SiMe_3)_2$ (**62**)	8.66	−0.30	−1.44	1.23	0.61	—	—
$MeN(SiMe_3)_2$ (**63**)	8.21	−0.35	−1.79	1.08	0.54	—	—
Et_2NSiMe_3 (**64**)	7.90	−0.25	−1.70	0.24	0.24	—	0.02
Pr_2NSiMe_3 (**65**)	7.93	−0.25	−1.80	0.38	0.38	—	—
$PrN(SiMe_3)_2$ (**66**)	8.18	−0.35	−1.98	1.53	0.76	—	—
$N(SiMe_3)_3$ (**67**)	8.60	−0.45	−2.16	2.79	0.93	0.18	—
$N(GeH_3)_3$ (**68**)	9.20	−0.12	−1.8	1.88	0.63	0.33	0.00
$N(SnMe_3)_3$ (**69**)	7.57	−0.39	−1.8	−0.16	−0.05	−0.11	−0.21
$H_2NCH_2SiMe_3$ (**70**)	9.07	−0.05	−0.66	−0.33	−0.33	—	—
$HN(CH_2SiMe_3)_2$ (**71**)	8.36	−0.10	−1.32	−0.18	−0.09	—	—
$HMeNCH_2SiMe_3$ (**72**)	8.55	−0.10	−1.01	−0.40	−0.40	—	—
$Me_2NCH_2SiMe_3$ (**73**)	8.20	−0.15	−1.36	−0.43	−0.43	—	—
$MeN(CH_2SiMe_3)_2$ (**74**)	7.86	−0.15	−1.67	−0.44	−0.22	—	−0.49
$HEtNCH_2SiMe_3$ (**75**)	8.46	−0.10	−1.15	−0.20	−0.20	—	—
$Et_2NCH_2SiMe_3$ (**76**)	7.93	−0.15	−1.64	−0.17	−0.17	—	—
$EtN(CH_2SiMe_3)_2$ (**77**)	7.82	−0.15	−1.81	−0.15	−0.08	—	—
$N(CH_2SiMe_3)_3$ (**78**)	7.66	−0.15	−1.98	−0.23	−0.08	—	—

Note. The $\sigma_R^+(N)$ parameters of MR_3 and CH_2SiMe_3 substituents in radical cations of primary, secondary, and tertiary amines were calculated using Eqs. (25), (19), and (20), respectively. The $I(n_N)$ values of compounds **58—63** and **67** were taken from Ref. 21 and that of compound **64** was taken from Ref. 22. The ionization potentials of compounds **65** and **66** were taken from Ref. 23, those of compounds **68** and **69** were taken from Ref. 24, and the $I(n_N)$ values of compounds **70—78** were taken from Ref. 25. The sets of parameters σ_I, σ_α, $\sigma_R^+(P)$, and $\sigma_R^+(B)$ were taken from Refs. 5—9.

ments weakens with increasing atomic number of the M element (Si, Ge, Sn) while σ,n-conjugation increases under the same conditions.



d,n-conjugation

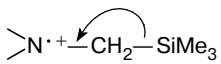


σ,n-conjugation

This is also valid for corresponding radical cations. Indeed, positive $\sigma_R^+(N)$ values suggest that d,n-conjugation in the $N^{\bullet+}MR_3$ radical cations of molecules **60** and **67—69** dominates over σ,n-conjugation for $MR_3 = SiH_3$ and $SiMe_3$ and weakens on going from $MR_3 = SiH_3$ to GeH_3, which is accompanied by a decrease in $\sigma_R^+(N)$. The $\sigma_R^+(N)$ constant of the $SnMe_3$ substituent was found to be negative owing to domination of σ,n-conjugation over d,n-conjugation.

Negative $\sigma_R^+(N)$ values of $Me_2N^{\bullet+}MR_3$ ($MR_3 = SiH_3$, $SiMe_3$) substituents indicate that σ,n-conjugation dominates over d,n-conjugation. σ,n-Conjugation increases with increasing positive charge of the reaction center (here, $N^{\bullet+}$).[4—9,19] In the case of $X_{3-n}N^{\bullet+}(MR_3)_n$ radical cations of compounds **58—67**, both passage from X = Me to Et and Pr and an increase in the number of the MR_3 substituents (SiH_3, $SiMe_3$) result in an increase in the degree of delocalization of the unpaired electron and positive charge of the N atom. This leads to weakening of σ,n-conjugation and to an increase in the contribution of the oppositely directed acceptor component (d,n-conjugation) to the overall resonance effect, which manifests itself as an increase in positive $\sigma_R^+(N)$ values.

Only the resonance donor effect (σ,n-conjugation) occurs in radical cations of compounds **70—78** (see Table 4)



Therefore the $\sigma_R^+(N)$ parameters of all CH_2SiMe_3 substituents are negative. σ,n-Conjugation weakens as the ability of the X and CH_2SiMe_3 substituents in the $X_{3-n}N^{\bullet+}(CH_2SiMe_3)_n$ radical cations to be involved in delocalization of the unpaired electron increases on going from X = Me to X = Et and with increasing *n*. This manifests itself in the decrease in the absolute values of the $\sigma_R^+(N)$ parameters of CH_2SiMe_3 substituents in the radical cations on going from compounds **72** to **75**, **73** to **76**, and **74** to **77**, as well as on going from compounds **70** to **71** and **78**, **73** to **74** and **78**, and from **76** to **77** and **78**.

Thus, in this work we found that linear free energy relationships can be used to study the effects of substituents on the first vertical ionization potentials of amines, $I(n_N)$.

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