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A novel approach to the analysis of substituent effects: Quantitative description of ionization energies and gas basicity of amines

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In this work, a new topological approach based on simple matrix algebra is introduced to explore substituent effects at the level of atomic additivity in the absence of significant resonance contributions. In the framework of the suggested method, all atoms are classified according to element and valence state. The sums of the inverse squared distances between the substituent atoms and the reaction centre of the molecule are used as operational parameters in the present method. The approach implies atomic level of consideration of inductive and steric effects and allows for quantification of substituent effects without the use of pre-established group substituent constants. The practical application of the model is illustrated by the quantitative interpretation of ionization energies and gas basicity of a broad range of amines. Further development of the elaborated approach is also discussed. © 1999 by Elsevier Science Inc.

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INTRODUCTION

The elucidation of relationships between structure and reactivity of compounds is one of the major challenges in modern chemistry. Mono- and multiparametric free energy relationships (LFERs) allow mathematical formalization of quantitative structure–activity relationships in the framework of Hammett–Taft-type equations. The variables used in such equations are usually group substituent constants. A wide range of substituent parameters, extensively used in modern QSAR for drug design and molecular modeling and for studies of reactivity, physicochemical properties, and bioactivity, have been presented in numerous comprehensive reviews and monographs.[1–8] A large number of inductive (field), steric, and resonance constants for hundreds of diverse functional groups have been determined. These constants form many of the most commonly used substituent scales for studies of substituent effects at the group additivity level.

Relationships based on discrete distance-dependent atomic contributions have been derived, e.g., the model of the frontier steric effect and the additive model of inductive effect, which allow accurate theoretical calculation of steric and inductive constants of substituents through electronegativities and radii of the constituent atoms and intramolecular distances. A relevant description of these approaches and aspects of their application can be found in Refs. 2, 3, 9, and 10.

In this work we have combined these models into a unified topological technique for quantification of substituent effects in terms of discrete distance-dependent atomic contributions.

RESULTS AND DISCUSSION

Within the framework of the models mentioned in the introduction we have proposed that the steric and inductive effects can be described as follows.

Steric constants

The model assumes the frontal character of steric interactions.[3] The basis for this model is simple mechanical screening of the reaction center by the substituent atoms:

$$R'_S = \sum_{i=1}^{n} \frac{R_i^2}{4r_i^2} \quad (1)$$

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In Eq. (1), R_S is the steric substituent constant, n is the number of atoms in the substituent, R_i is the radius of the ith atom, and r_i is the direct distance between the ith atom and the reaction center.

The model allows for accurate evaluation of the steric effect solely on the basis of atomic radii and interatomic distances. Calculated R_S substituent parameters correlate well with empirical scales: for instance, for a wide variety of substituents, the calculated R'_S values and the corresponding Taft E_S steric constants correlate well ($N = 35$, $R = 0.9854$, $S = 0.141$).[4]

Inductive constants

In the framework of this approach we have explored the Taft inductive substituent constants at the level of atomic additivity:[2,9]

$$\sigma^* = \sum_{i=1}^{n} \frac{\sigma_{A_i}}{r_i^2} \tag{2}$$

where σ^* is the inductive substituent constant, n is the number of atoms in the substituent, r_i is the distance from the ith atom to the reaction center, and σ_A is an empirical parameter reflecting the ability of an atom to attract (or donate) electrons, depending on its nature and valence state. Values of σ_A have been established for a wide range of elements in various valence states by substitution of the empirical Taft σ^* constants in Eq. (2).

Inductive constants calculated by Eq. (2) also correlate well with the corresponding Taft empirical values ($N = 426$, $R = 0.9910$, $S = 0.190$).[10]

The practical use of these approaches for quantitative interpretation of reactivity and physicochemical properties and for investigation of reaction mechanisms has been quite successful. Many important theoretical questions concerning the physical nature of the inductive effect and its mechanism have also been clarified.[11,12]

Resonance contributions

The present models concern only steric and inductive interactions and resonance effects cannot be directly accounted for. However, our previous investigations show that the additive model for the inductive effect, on the whole, describes fairly well substituent effects also in conjugated systems and only some of them can be treated as exceptional owing to strong direct polar conjugation or saturation effects.[2]

General approach for the analysis of substituent effects

The fact that both the steric and inductive effects of substituents, explored at the atomic level, have been established as functions of the inverse square of the distance between the reaction center and the substituent atom can be useful. As a result, the two-parameter Taft equation:

$$Y = \rho \sum_i \sigma^* + \delta \sum_i E_s \tag{3}$$

explored in terms of distance-dependent constant atomic contributions, can be written as

$$Y - Y^0 = \sum_{i \neq rc}^{N-1} \frac{e_i}{r_{rc-i}^2} \tag{4}$$

where N is the number of atoms in the molecule, rc is the atom of the molecule chosen as the reaction center, and r_{rc-i} is the distance between atom i and the reaction center.

Y can be the logarithm of a rate or equilibrium constant, energy of reaction, energy of activation, or any other quantitative characteristics that in principle can be treated by correlation analysis; Y^0 corresponds to the (unsubstituted) standard compound of the reaction series and e_i is the ability of an atom of a certain type to contribute to the $(Y - Y^0)$ difference between the explored quantitative characteristics of a given compound and the standard.

This approximation enables us to check if there exists an overall operational e_i parameter for a given atom. If it exists, the next question is to analyze its possible physical meaning.

The formalism of the proposed technique suggests that each atom common for all molecules of a reaction series can be explored as a hypothetical reaction center (rc). In this case, for every single compound of a series, all its $N - 1$ atoms, except rc, can be taken as one subsubstituent, which can be treated by Eqs. (1)–(4).

r^{-2} Matrixes

The next step is the composition of the r^{-2} matrix containing sums of the corresponding $\sum_k 1/r_{rc-m_k}^2$ terms, related to certain types of atoms.

In Table 1, n are the rows of the matrix corresponding to the molecules of the reaction series, m are the columns of the matrix related to the types of atoms composing the molecules of the series, k is the number of atoms of type m in molecule n, and r_{rc-m_k} is the direct distance between atoms of the m type in molecules n and rc (the atom chosen as reaction center of the series).

In the absence of atom(s) of the m type in molecule n, the corresponding $1/r_{rc-m_k}^2$ matrix element is set equal to 0.

For instance, if we treat N-methylaniline ($C_6H_5NHCH_3$), chloramine (Cl–NH_2), and dimethylamine [$(CH_3)_2NH$], where the nitrogen atom is the reaction center, then the example of the corresponding r^{-2} matrix can be seen in Table 2.

The columns of such a matrix can be taken as the sets of independent X variables while the corresponding $(Y - Y^0)$ values form the set of dependent Y parameters.

The final step in this procedure is the estimation of accurate additive contributions, where the explored $(Y - Y^0)$ data set can be treated as dependent parameters of a multilinear regression without intercept.

If an acceptable multiple regression exists, its linear coeffi-

Table 1. General view of r^{-2} matrix

Compounds/ atomic type	$Atom_1$	...	$Atom_m$	...
$Compound_1$				
$Compound_n$			$\sum_k \frac{1}{r_{rc-m_k}^2}$	

Table 2. r^{-2} matrix for $(CH_3)_2NH$, $Cl–NH_2$, and $C_6H_5–NH–CH_3$ molecules

Molecule/atom	H	C sp^3	Cl	C_{arom}
$(CH_3)_2NH$	$\frac{1}{1.01^2} + \frac{6}{2.10^2}$	$\frac{2}{1.47^2}$	0	0
$Cl–NH_2$	$\frac{2}{1.01^2}$	0	$\frac{1}{1.74^2}$	0
$C_6H_5–NH–CH_3$	$\frac{1}{1.01^2} + \frac{3}{2.10^2} + \frac{2}{2.61^2} + \frac{2}{4.50^2}$	$\frac{1}{1.47^2}$	0	$\frac{1}{1.32^2} + \frac{2}{2.35^2} + \frac{2}{3.63^2} + \frac{1}{4.12^2}$

cients can be taken as the operational atomic e_i parameters, corresponding to certain types (nature and valence state) of atoms.

Clearly, the suggested approach should work well for any reaction series that in principle can be quantitatively described by inductive and steric constants, since σ^* and R'_S parameters calculated by Eqs. (1) and (2) are in excellent agreement with the literature data.[2,10]

Analysis of the physical meaning of the operational atomic contributions

There are certain merits in the use of the elaborated topological approach, although there are some drawbacks that should also be mentioned. The resonance effect cannot be directly taken into account. Thus, strongly conjugated systems can hardly be treated within the suggested scheme (provided that conjugation has a large effect on the property of interest). A more significant problem when exploring quantitative characteristics, Y, of molecules of a reaction series by Eq. (4) is that the physical meaning of the corresponding atomic e parameters remains unclear and the overall substituent effects cannot be divided into particular electronic and steric components. Thus, once the atomic e parameters are established, further interpretation of their physical meaning is the actual goal.

Simple treatment of e parameters can be performed on the basis of previously established correlations.

It has been found that, for a broad range of elements, σ_A constants correlate with the difference in electronegativity between a given element and the reaction center, $\Delta\chi_{i-rc}$, reflecting the driving force for the electron density displacement, and with the square of the covalent radius of the element, R_i^2, reflecting the ability to delocalize the charge ($\sigma_A = 7.84\Delta\chi_{i-rc}R_i^2$).[10] Thus, the Taft inductive constant can be written as

$$\sigma^* = 7.84 \sum_i \frac{\Delta\chi R_i^2}{r_i^2} \qquad (5)$$

Therefore, if we combine Eqs. (1), (4), and (5), the atomic e parameters can be explored in the general form

$$e_i = a\Delta\chi_{i-rc}R_i^2 + bR_i^2 \qquad (6)$$

where the increments reflect possible contributions of inductive and steric effects, respectively. Thus, if correlation (6) is established, then Eq. (4) can be divided into the inductive and steric components, presented in Eqs. (1) and (5), respectively. If necessary, R_S can easily be transformed into the scale of Taft E_s parameters and Eq. (4) will then have the exact form of the two-parameter Taft Eq. (3).

If the electronegativity of the atom chosen as the reaction center is not available, then e can simply be explored as a two-parameter correlation of the following form:

$$e_i = a'\chi_i R_i^2 + b'R_i^2 \qquad (7)$$

where coefficient b' contains the electronegativity of the reaction center.

Thus, correct separation of inductive and steric contributions to substituent effects in terms of the elaborated technique seems to be problematic without the knowledge of the nature (electronegativity) of the reaction center and requires some reasonable assumptions.

However, as mentioned above, even if correlations (6) and (7) do not exist, but the corresponding atomic e_i increments are well established, then these e_i values can be used as operational parameters for simple estimations of unknown Y values for similar molecular systems, composed by atoms with empirically determined e values.

The advantages of using this general approach are numerous:

- There are no limitations in the choice of appropriate substituent scales, since none are required.
- The approach operates by direct intramolecular distances and allows analysis of conformational aspects of substituent effects.
- In the framework of the elaborated procedure it is possible to perform a search over all possible reaction centers of a reaction series and, thus, suggest hypothetical "active molecular sites."

Apart from the resonance effect, there are no serious limitations of the applications of the elaborated technique and it has been found to successfully describe substituent effects even in systems where established empirical substituent scales fail.[13]

PRACTICAL APPLICATIONS

Previously, we have applied the approach for quantitative interpretation of substituent effects in nonaromatic radical systems,[13,14] where LFERs have been successfully used only for aromatic series.[1,15]

In the framework of Eq. (4) we have quantitatively interpreted redox properties of C-, N-, S-, and O-centered radicals in the gas phase.[13,14]

Here, the atoms carrying the unpaired electron (X ·) have been chosen as the corresponding reaction centers. The ionization potentials (IPs) and electron affinities (EAs) have been explored as

$$\mathrm{IP(EA)}_{R_nX\cdot} - \mathrm{IP(EA)}_{H_nX\cdot} = \sum_{i\subset R} \frac{e_i^{+/-}}{r_i^2} \tag{8}$$

where e^+ and e^- are operational atomic parameters for the ionization potentials and electron affinities, respectively.

Fairly good multilinear correlations were established for all types of free radicals explored. Statistical parameters of the estimated correlations are presented in Table 3 as an illustration.

Another example of the practical use of the elaborated technique is in the study of substituent effects on C–H bond dissociation enthalpies (BDEs). A wide set of C–H BDEs was described by multilinear regression[16]:

$$\mathrm{BDE}_{R_3CH} - \mathrm{BDE}_{CH_4} = \sum_i \frac{\mathrm{dh}_i}{r_{C-i}^2} \tag{9}$$

$$N = 72,\ R = 0.9773,\ S = 8.484\ \text{(kJ/mol)}$$

where the carbon atom of the C–H bond was chosen as the reaction center and dh is the operational atomic increment, introduced for this particular series [corresponding to the *e* atomic parameter in the general Eq. (4)] and reflecting the ability of a certain type of atom to contribute to the relative C–H bond dissociation enthalpy.

In the present work we have applied the elaborated approach to the quantitative interpretation of adiabatic $\mathrm{IE_{ad}}$ and vertical $\mathrm{IE_{vert}}$ ionization energies and gas basicities, Gb, for a broad range of amines.

We have composed a [421 × 11] r^{-2} matrix for 422 different amines, containing 11 types of substituent atoms. For simplicity, the interatomic distances, *r*, were determined by using the Hyperchem software package, which allows simple estimation of the standard geometries of the corresponding hydrocarbons. The accuracy of this procedure would probably be improved if optimized structures were used; however, this would make the approach more difficult and time consuming and thereby less attractive.

Values of $\mathrm{IE_{ad}}$, $\mathrm{IE_{vert}}$, and Gb, taken from Ref. 17, have then been analyzed in terms of the general Eq. (4).

Table 3. Statistical parameters of correlation (4) estimated for various types of free radicals

Type of radical	Property	Number of observations	*R*	*F*	*S* (eV)
C centered	IP	48	0.9768	62.5	0.2345
	EA	20	0.9816	39.8	0.1995
S centered	IP	7	0.9278	3.7	0.6105
	EA	12	0.8697	18.8	0.2675
O centered	IP	10	0.9938	20.0	0.3557
	EA	12	0.9836	14.9	0.1150
N centered	IP	5	0.968	2.5	1.041
	EA	6	0.9744	3.1	0.2179

On the basis of the r^{-2} matrix, three multiple regressions of high quality have been found:

$$\mathrm{IE}_{R_3N}^{\mathrm{vert}} = \sum_i^{N-1} \frac{\mathrm{ie}_i^{\mathrm{vert}}}{r_i^2} + \mathrm{const}_1 \tag{10}$$

$$\mathrm{IE}_{R_3N}^{\mathrm{ad}} = \sum_{i=1}^{N-1} \frac{\mathrm{ie}_i^{\mathrm{ad}}}{r_i^2} + \mathrm{const}_2 \tag{11}$$

$$\mathrm{Gb}_{R_3N} = \sum_{i=1}^{N-1} \frac{\mathrm{gb}_i}{r_i^2} + \mathrm{const}_3 \tag{12}$$

where *N* is the number of atoms in the amine molecule; and $\mathrm{ie}_i^{\mathrm{vert}}$, $\mathrm{ie}_i^{\mathrm{ad}}$, and gb_i are the corresponding atomic operational parameters, reflecting the ability of an atom to contribute to the overall $\mathrm{IE_{ad}}$, $\mathrm{IE_{vert}}$, and Gb value, respectively.

Statistical parameters of the correlations are presented in Table 4; the corresponding estimated ionization energies and gas basicities of the amines are collected in Table 5; and the operational atomic parameters $\mathrm{ie}^{\mathrm{vert}}(X)$, $\mathrm{ie}^{\mathrm{ad}}(X)$, and gb(*X*) taken as the multiple coefficients of Eqs. (10)–(12) are collected in Table 6.

It should be pointed out that the intercepts of correlations (9)–(12) have been estimated close to the corresponding $\mathrm{IE}^{\mathrm{ad/vert}}$ and Gb parameters of the ammonia molecule, which is in complete agreement with the basic Eq. (4) of the elaborated algorithm.

Interrelations between estimated and experimental $\mathrm{IE_{ad}}$, $\mathrm{IE_{vert}}$, and Gb values are presented graphically in Figures 1–3.

Thus, the suggested approach allows for a reasonably accurate quantitative interpretation of redox properties and basicity data of a wide range of aliphatic and aromatic amines. The values of the estimated atomic operational contributions in Eqs. (10)–(12) can, hence, be used for prediction of unknown values of $\mathrm{IE_{ad}}$, $\mathrm{IE_{vert}}$, and Gb for amines, constituted from the atom types presented in Table 6.

The large uncertainties in the operational parameters $\mathrm{ie}^{\mathrm{ad/vert}}$ and gb, estimated for C *sp*, Cl, Br, and I, are due to the lack of the data (column elements of the r^{-2} matrix) for these atoms, which leads to significant statistical deviations.

The possible contributions of inductive and steric components to the estimated $\mathrm{ie}^{\mathrm{ad/vert}}$ and gb parameters have then been analyzed terms of Eq. (7).

Table 4. Statistical parameters of the correlations (10)–(12) estimated

Statistics/ correlation	(10)	(11)	(12)
Multiple *R*	0.954	0.96	0.9722
Standard error	0.331	0.341	11.422
F	251.09	234.17	271.76
Observations	287	231	177

Table 5. Experimental and predicted adiabatical ionization energies IE_{ad}, vertical ionization energies IE_{vert}, and gas basicities Gb of amines

		IE_{ad}			IE_{vert}			Gb		
No.	Compound	Predic.	Exp.	Resid.	Predic.	Exp.	Resid.	Predic.	Exp.	Resid.
1	NH_3	9.10	10.07	*0.97*	9.69	10.82	*1.13*	844.46	819.00	*−25.46*
2	CH_3NH_2	8.83	8.90	*0.07*	9.43	9.65	*0.22*	866.73	864.50	*−2.23*
3	$C_2H_5NH_2$	8.66	8.90	*0.24*	9.24	9.50	*0.26*	877.76	878.00	*0.24*
4	$(CH_3)_2NH$	8.56	8.24	*−0.32*	9.16	8.95	*−0.21*	889.00	896.50	*7.50*
5	$C_2H_5NHCH_3$	8.39	8.15	*−0.24*	8.97	8.73	*−0.24*	900.03	909.20	*9.17*
6	$C_3H_7NH_2$	8.58	8.54	*−0.04*	9.15	9.37	*0.22*	882.65	883.90	*1.25*
7	*iso*-$C_3H_7NH_2$	8.49	8.63	*0.14*	9.06	9.31	*0.25*	888.79	889.00	*0.21*
8	$(CH_3)_3N$	8.30	7.85	*−0.45*	8.89	8.54	*−0.35*	911.27	918.10	*6.83*
9	*tert*-$C_4H_9NH_2$	8.32	8.46	*0.14*				899.83	899.90	*0.07*
10	$C_4H_9NH_2$	8.53	8.73	*0.20*	9.10	9.40	*0.30*	885.67	886.60	*0.93*
11	$(C_2H_5)_2NH$	8.22	8.01	*−0.21*	8.79	8.68	*−0.11*	911.06	919.40	*8.34*
12	*sec*-$C_4H_9NH_2$	8.41	8.46	*0.05*				893.68	895.70	*2.02*
13	*iso*-$C_4H_9NH_2$	8.44	8.50	*0.06*				891.52	890.80	*−0.72*
14	$C_2H_5N(CH_3)_2$	8.13	7.74	*−0.39*	8.70	8.40	*−0.30*	922.30	929.10	*6.80*
15	*iso*-$C_3H_7NHCH_3$							911.06	919.40	*8.34*
16	$C_5H_{11}NH_2$	8.50	8.70	*0.20*	9.07	9.30	*0.23*	887.59	889.50	*1.91*
17	$(C_2H_5)_2NCH_3$	7.96	7.50	*−0.46*	8.52	8.32	*−0.20*	933.33	940.00	*6.67*
18	*neo*-$C_4H_{11}NH_2$	8.29	8.50	*0.21*	8.83	9.30	*0.47*	900.38	894.00	*−6.38*
19	C_2H_5NH-*iso*-C_3H_7							922.10	926.70	*4.60*
20	$C_2H_5(CH_3)_2C$-NH_2	8.24	8.46	*0.22*				904.71	903.60	*−1.11*
21	*iso*-$C_3H_7N(CH_3)_2$	7.96	7.30	*−0.66*	8.52	8.20	*−0.32*	933.33	939.60	*6.27*
22	$C_3H_7NH_2$	8.58	8.24	*−0.34*	9.15	9.37	*0.22*	882.65	883.90	*1.25*
23	$(C_2H_5)_3N$	7.79	7.53	*−0.26*	8.33	8.03	*−0.30*	944.36	951.00	*6.64*
24	(*iso*-$C_3H_7)_2NH$	7.89	7.59	*−0.30*				933.13	938.60	*5.47*
25	$(C_3H_7)_2NH$	8.07	7.76	*−0.31*	8.62	8.59	*−0.03*	920.84	929.30	*8.46*
26	$C_6H_{13}NH_2$	8.48	8.60	*0.12*				888.96	893.50	*4.54*
27	$C_4H_9N(CH_3)_2$	8.00	8.35	*0.35*				930.21	938.20	*7.99*
28	*tert*-$C_4H_9N(CH_3)_2$	7.79	8.08	*0.29*				944.36	948.60	*4.24*
29	*sec*-$C_4H_9N(CH_3)_2$							938.22	945.10	*6.88*
30	$C_7H_{15}NH_2$							889.97	889.30	*−0.67*
31	$(C_2H_5)_2NC_3H_7$	7.71	7.70	*−0.01*	8.25	8.32	*0.07*	949.25	947.90	*−1.35*
32	*neo*-$C_5H_{11}N(CH_3)_2$							944.92	935.90	*−9.02*
33	*tert*-$C_5H_{11}N(CH_3)_2$							949.25	951.50	*2.25*
34	*iso*-$C_3H_7N(C_2H_5)_2$							955.40	965.60	*10.20*
35	$(C_4H_9)_2NH$	7.97	7.69	*−0.28*				926.88	935.30	*8.42*
36	$C_8H_{16}NH_2$	8.41	8.50	*0.09*				892.90	895.00	*2.10*
37	(*iso*-$C_4H_9)_2NH$	7.78	7.80	*0.02*	8.29	8.45	*0.16*	938.57	925.10	*−13.47*
38	(*sec*-$C_4H_9)_2NH$	7.66	7.60	*−0.06*	8.17	8.28	*0.11*	946.88	947.50	*0.62*
39	(*iso*-$C_3H_7)_2NC_2H_5$							966.43	963.50	*−2.93*
40	(*tert*-$C_4H_9)_2NH$							955.19	954.70	*−0.49*
41	$(C_3H_7)_3N$	7.49	7.40	*−0.09*	8.00	8.04	*0.04*	963.01	960.10	*−2.91*
42	(*tert*-$C_5H_{11})_2NH$(*tert*-C_4H_9)	7.52	7.81	*0.29*				955.75	958.20	*2.45*
43	$C_{10}H_{21}NH_2$	8.43	8.50	*0.07*				891.87	896.50	*4.63*
44	$(C_4H_9)_3N$	7.41	7.40	*−0.01*	7.91	7.86	*−0.05*	968.09	967.60	*−0.49*
45	*cyclo*-C_3H_6-NH_2	8.61	8.80	*0.19*	9.20	9.41	*0.21*	882.78	869.90	*−12.88*
46	H_2C=CH-NH_2	8.45	8.10	*−0.35*	8.73	8.60	*−0.13*	867.67	866.50	*−1.17*
47	Azetidine	8.48	8.63	*0.15*	9.08	9.04	*−0.04*	897.76	908.60	*10.84*
48	Aziridine, 1-methyl-	8.47	8.70	*0.23*	9.10	9.21	*0.11*	903.87	904.10	*0.23*
49	Aziridine, 2-methyl-	8.59	9.00	*0.41*	9.20	9.57	*0.37*	891.36	892.10	*0.74*
50	H_2C=CH-NH-CH_3	8.18	8.00	*−0.18*						
51	Pyrrolidine	8.30	8.41	*0.11*	8.88	8.82	*−0.06*	908.46	915.30	*6.84*

(*continued*)

Table 5. (*Continued*)

No.	Compound	IE_{ad}			IE_{vert}			Gb		
		Predic.	Exp.	Resid.	Predic.	Exp.	Resid.	Predic.	Exp.	Resid.
52	*cyclo*-C_4H_8-NH_2	8.47	8.60	*0.13*						
53	H_2C=$C(CH_3)CH_2$-NH_2	8.41	8.80	*0.39*				886.22	883.50	*−2.72*
54	Aziridine, 2,2-dimethyl-	8.44	8.94	*0.50*	9.04	9.29	*0.25*			
55	H_2C=CH-$N(CH_3)_2$							912.21	924.40	*12.19*
56	Piperidine	8.17	8.03	*−0.14*	8.74	8.65	*−0.09*	915.99	921.00	*5.01*
57	H_2C=CH-CH_2-$N(CH_3)_2$	8.03	7.84	*−0.19*				921.01	926.80	*5.79*
58	Pyrrolidine, 1-methyl-				8.61	8.41	*−0.20*	930.73	934.80	*4.07*
59	(*E*)-CH_3-HC=CH-$N(CH_3)_2$							917.36	934.50	*17.14*
60	*cyclo*-C_6H_{12}-NH_2	8.30	8.41	*0.11*				901.21	899.60	*−1.61*
61	Piperidine, 1-methyl-	7.90	7.80	*−0.10*	8.47	8.35	*−0.12*	938.26	940.10	*1.84*
62	(*E*)-C_2H_5-HC=CH-$N(CH_3)_2$	7.78	7.57	*−0.21*						
63	Piperidine, 4-methyl-	8.11	8.06	*−0.05*						
64	CH_3-C≡C-NH_2							842.06	853.50	*11.44*
65	1*H*-Pyrrole, 2,5-dihydro-	8.28	8.00	*−0.28*	8.73	8.61	*−0.12*			
66	Aziridine, 1-ethenyl-	8.08	8.20	*0.12*	8.39	8.75	*0.36*			
67	$(CH_3)_2$N-CH_2-C≡CH	8.12	8.29	*0.17*				910.69	909.50	*−1.19*
68	1,2,3,6-Tetrahydropyridine	8.15	8.00	*−0.15*	8.61	8.64	*0.03*			
69	Aziridine, 1-(1-propenyl)-, (*Z*)-	7.92	8.00	*0.08*	8.21	8.39	*0.18*			
70	Aziridine, 1-(1-propenyl)-, (*E*)-	7.99	7.90	*−0.09*	8.30	8.34	*0.04*			
71	2,5-Dihydro-1-methylpyrrole				8.46	8.21	*−0.25*			
72	1*H*-Pyrrole, 1-methyl-	7.60	7.99	*0.39*						
73	1*H*-Pyrrole, 2-methyl-	7.71	8.01	*0.30*						
74	1*H*-Pyrrole, 3-methyl-	7.78	7.90	*0.12*						
75	Pyridine,1,4-dihydro-				7.73	7.46	*−0.27*			
76	1,2,2-Trimethylaziridine				9.04	8.68	*−0.36*			
77	Piperidine, 2-methyl-	8.00	7.90	*−0.10*						
78	Piperidine, 3-methyl-	8.09	8.03	*−0.06*						
79	$(CH_3)_2$HC=CH-$N(CH_3)_2$	7.68	8.15	*0.47*				926.97	934.50	*7.53*
80	*cyclo*-C_7H_{14}-NH_2	8.10	8.50	*0.40*	8.63	8.41	*−0.22*	913.38	923.50	*10.12*
81	$(CH_2$=CH-CH_2-$)_2$NH	8.04	8.20	*0.16*	8.41	8.79	*0.38*	908.47	916.30	*7.83*
82	Aziridine, 1-(1-butenyl)-, (*E*)-	7.94	7.70	*−0.24*	8.24	8.26	*0.02*			
83	Aziridine, 1-(1-butenyl)-, (*Z*)-	7.86	7.90	*0.04*	8.15	8.26	*0.11*			
84	Aziridine, 1-(2-methyl-1-propenyl)-	7.84	7.60	*−0.24*	8.13	8.20	*0.07*			
85	1-Methyl-1,2,3,6-tetrahydropyridine				8.34	8.67	*0.33*			
86	7-Azanorbornane	8.01	8.40	*0.39*	8.58	9.00	*0.42*			
87	2-Azabicyclo[2.2.1]heptane				8.62	8.50	*−0.12*			
88	1*H*-Pyrrole, 2,5-dimethyl-	7.55	7.69	*0.14*				908.65	887.10	*−21.55*
89	(*E*)-HC≡C-C=CH-$N(CH_3)_2$	7.83	7.70	*−0.13*						
90	1*H*-Pyrrole, 2,4-dimethyl-	7.68	7.54	*−0.14*						
91	1*H*-Pyrrole, 2-ethyl-	7.75	7.97	*0.22*						
92	Pyridine,1,4-dihydro-1-methyl-				7.60	7.39	*−0.21*			
93	7-Azanorbornene	7.97	8.30	*0.33*	8.38	8.75	*0.37*			
94	2-Azabicyclo[2.2.1]hept-5-ene				8.48	8.60	*0.12*			
95	C_6H_5-NH_2	8.00	7.72	*−0.28*	8.38	8.05	*−0.33*	858.21	850.60	*−7.61*
96	$(HC$≡C-$CH_2)_2$NH							887.84	876.90	*−10.94*
97	7-Azanorbornadiene	7.93	8.25	*0.32*	8.20	8.65	*0.45*			
98	*cyclo*-C_6H_{12}-CH_2-NH_2							904.19	895.80	*−8.39*
99	3,3-Dimethylpiperidine	7.95	8.05	*0.10*						
100	2,6-Dimethylpiperidine	7.83	7.93	*0.10*						
101	1,2-Dimethylpiperidine	7.74	7.63	*−0.11*						
102	1,3-Dimethylpiperidine	7.76	7.76	*0.00*						
103	1,4-Dimethylpiperidine	7.84	7.79	*−0.05*						

(*continued*)

Table 5. (*Continued*)

No.	Compound	IE_{ad}			IE_{vert}			Gb		
		Predic.	Exp.	Resid.	Predic.	Exp.	Resid.	Predic.	Exp.	Resid.
104	1-Cyclobuten-1-amine, *N,N*-dimethyl-	7.77	7.61	*−0.16*						
105	*cyclo*-C_7H_{14}-NH-CH_3				8.36	8.29	*−0.07*			
106	Cyclopentanamine, *N,N*-dimethyl-				8.32	8.34	*0.02*			
107	Quinuclidine	7.80	7.50	*−0.30*	8.37	8.00	*−0.37*	947.13	952.50	*5.37*
108	Exo-2-aminonorbornane	8.22	8.40	*0.18*				907.58	901.30	*−6.28*
109	Piperidine, 1-methyl, 4-methylene-				8.35	8.36	*0.01*			
110	(*E*)-1-Azetidino-1-butene	7.67	7.10	*−0.57*	7.94	7.62	*−0.32*			
111	1-Azetidino-isobutene	7.57	6.90	*−0.67*	7.83	7.56	*−0.27*			
112	$(H_2C{=}CH\text{-}CH_2)_2N\text{-}CH_3$				8.14	8.41	*0.27*			
113	1,3-Cyclopentadien-1-amine, *N,N*-dimethyl-				8.29	8.17	*−0.12*			
114	1-Cyclopenten-1-amine, *N,N*-dimethyl-				7.91	7.46	*−0.45*			
115	1-Azabicyclo[2.2.2]oct-2-ene	7.54	8.02	*0.48*				940.22	938.60	*−1.62*
116	2-Azabicyclo[3.2.1]oct-6-ene				8.36	8.60	*0.24*			
117	2-Azabicyclo[2.2.2]oct-5-ene				8.26	8.35	*0.09*			
118	Pyrrole, 1,3,4-trimethyl-	7.43	7.30	*−0.13*						
119	2-CH_3-C_6H_4-NH_2	7.86	7.47	*−0.39*	8.21	7.84	*−0.37*	867.45	859.10	*−8.35*
120	C_6H_5-CH_2-NH_2	8.23	8.49	*0.26*	8.70	9.10	*0.40*	877.60	879.40	*1.80*
121	C_6H_5-NH-CH_3	7.74	7.32	*−0.42*	8.11	7.73	*−0.38*	880.48	890.10	*9.62*
122	4-CH_3-C_6H_4-NH_2	7.97	7.37	*−0.60*	8.34	7.81	*−0.53*	860.53	864.80	*4.27*
123	3-CH_3-C_6H_4-NH_2	7.95	7.54	*−0.41*	8.32	7.82	*−0.50*	861.31	864.00	*2.69*
124	*cyclo*-C_6H_{12}-N$(CH_3)_2$	7.63	7.50	*−0.13*	8.16	8.09	*−0.07*	954.68	952.60	*−2.08*
125	1,4,4-Trimethylpiperidine	7.74	7.77	*0.03*				948.18	934.70	*−13.48*
126	1,3,5-Trimethylpiperidine, *trans*-, *trans*-							951.96	947.20	*−4.76*
127	Piperidine, 1,2,6-trimethyl-, *cis*-	7.57	7.77	*0.20*						
128	1-Methyloctahydroazocine				8.47	8.02	*−0.45*			
129	1,3,5-Trimethylpiperidine, *cis*-, *cis*-	7.75	7.63	*−0.12*						
130	1,3,5-Trimethylpiperidine, *cis*-, *trans*-	7.62	7.66	*0.04*						
131	Pyrrolidine, 1-(2-methylpropyl)-				8.27	8.17	*−0.10*			
132	1-Azabicyclo[2.2.2]octane,4-methyl-				8.30	8.06	*−0.24*	951.37	948.60	*−2.77*
133	Pyrrolidine, 1-(2-methyl-1-propenyl)-	7.41	6.80	*−0.61*	7.65	7.75	*0.10*			
134	Pyrrolidine, 1-(1-butenyl)-	7.51	6.70	*−0.81*	7.76	7.24	*−0.52*			
135	Azetidine, 1-(1-ethyl-1-propenyl)-				7.73	7.48	*−0.25*			
136	Tropane				8.42	8.21	*−0.21*			
137	2-Azabicyclo[2.2.2]octane, 2-methyl-				8.13	7.78	*−0.35*			
138	9-Azabicyclo[4.2.1]nonane				8.17	8.50	*0.33*			
139	$(C_2H_5)_2$N-CH=CH-C≡CH-, (*E*)-	7.49	8.00	*0.51*						
140	C_6H_5-N$(CH_3)_2$	7.47	7.12	*−0.35*	7.84	7.35	*−0.49*	902.74	909.20	*6.46*
141	C_6H_5-NH-C_2H_5	7.57	7.56	*−0.01*	7.92	7.67	*−0.25*	891.51	892.90	*1.39*
142	2,6-Dimethylaniline	7.71	7.33	*−0.38*	8.05	7.78	*−0.27*	876.69	869.80	*−6.89*
143	Pyrrolidine, 1-(1-buten-3-ynyl)-	7.67	7.50	*−0.17*						
144	C_6H_5-C_2H_4-NH_2	8.36	8.50	*0.14*	8.88	8.99	*0.11*	883.35	902.30	*18.95*
145	CH_3NH-CH_2-C_6H_5	7.96	8.65	*0.69*	8.43	8.73	*0.30*			
146	2,5-Dimethylaniline	7.81	7.50	*−0.31*	8.16	7.78	*−0.38*			
147	2-C_2H_5-C_6H_4-NH_2							871.26	866.10	*−5.16*
148	2-CH_3NH-C_6H_4-CH_3	7.59	7.25	*−0.34*						
149	3,5-Dimethylaniline	7.90	7.61	*−0.29*	8.27	7.75	*−0.52*			
150	*para*-$C_2H_5C_6H_4NH_2$	7.93	7.62	*−0.31*						
151	*meta*-CH_3NH-C_6H_4-CH_3	7.69	7.26	*−0.43*						
152	2,3-Dimethylaniline	7.80	7.51	*−0.29*	8.16	7.77	*−0.39*			
153	2,4-Dimethylaniline	7.82	7.40	*−0.42*	8.17	7.65	*−0.52*			

(*continued*)

Table 5. (*Continued*)

No.	Compound	IE_{ad}			IE_{vert}			Gb		
		Predic.	Exp.	Resid.	Predic.	Exp.	Resid.	Predic.	Exp.	Resid.
154	*para*-CH_3-NH-C_6H_4-CH_3	7.70	7.58	*−0.12*						
155	3,4-Dimethylaniline				8.28	7.68	*−0.60*			
156	*ortho*-C_2H_5-C_6H_4-NH_2	7.79	7.57	*−0.22*						
157	Aziridine, 1-phenyl-	7.63	8.00	*0.37*	8.04	8.19	*0.15*	896.27	895.70	*−0.57*
158	Piperidine, 2,2,6,6-tetramethyl-	7.49	7.59	*0.10*	7.99	8.14	*0.15*	960.18	953.90	*−6.28*
159	*cyclo*-C_6H_5-$N(CH_3)_2$	7.63	7.50	*−0.13*	8.16	8.09	*−0.07*	954.68	952.60	*−2.08*
160	Octahydroazocine,1-ethyl-				7.92	7.93	*0.01*			
161	Piperidine, 1-(1-butenyl)-				7.62	7.46	*−0.16*			
162	Piperidine, 1-(2-methyl-1-propenyl)-				7.50	8.00	*0.50*	954.49	949.40	*−5.09*
163	(*E*)-1-Pyrrolidino-2-pentene				7.97	7.29	*0.68*			
164	$(CH_2$=CH-CH_2-$)_3N$	7.51	7.60	*0.09*	7.76	8.30	*0.54*	940.48	941.30	*0.82*
165	1-Azetidinocyclohexene				7.69	7.46	*−0.23*			
166	4-$(CH_3)_2N$-C_6H_4-CH_3	7.43	6.93	*−0.50*	7.80	7.48	*−0.32*	905.07	918.10	*13.03*
167	3-$(CH_3)_2N$-C_6H_4-CH_3	7.42	7.02	*−0.40*	7.78	7.24	*−0.54*	905.85	915.70	*9.85*
168	$(CH_3)_2N$-C_2H_4-C_6H_5	7.83	7.69	*−0.14*				927.88	937.40	*9.52*
169	2-$(CH_3)N$-C_6H_4-CH_3	7.32	7.42	*0.10*	7.67	7.92	*0.25*	911.99	925.30	*13.31*
170	H_2N-C_3H_6-C_6H_5				8.90	8.89	*−0.01*			
171	$CH_3(C_2H_5)N$-C_6H_5	7.30	7.37	*0.07*				913.78	912.40	*−1.38*
172	4-H_2N-C_6H_4-C_3H_7	7.91	7.41	*−0.50*						
173	CH_3NH-C_2H_4-C_6H_5	8.09	8.40	*0.31*	8.61	8.66	*0.05*			
174	H_2N-$CH(CH_3)CH_2$-C_6H_5				8.69	8.99	*0.30*			
175	2,4,6-Trimethylaniline	7.67	7.15	*−0.52*						
176	4-H_2N-C_6H_4-*iso*-C_3H_7	7.90	7.68	*−0.22*						
177	C_3H_7-NH-C_6H_5	7.49	7.54	*0.05*						
178	*iso*-C_3H_7-NH-C_6H_5	7.40	7.50	*0.10*						
179	*N*-2,6-Trimethylaniline	7.44	7.34	*−0.10*						
180	Isoquinoline, 1,2,3,4-tetrahydro-				8.38	8.57	*0.19*			
181	*N*-Phenylazetidine	7.36	7.10	*−0.26*	7.74	7.61	*−0.13*	912.93	902.40	*−10.53*
182	*N*-(4-Methylphenyl)aziridine				7.99	8.30	*0.31*			
183	$(HC\equiv C$-$CH_2)_3N$							909.53	894.40	*−15.13*
184	Pempidine	7.23	7.23	*0.00*						
185	1-Methyldecahydroazecine				7.73	7.99	*0.26*			
186	(*Z*)-3-Piperidino-2-pentene				7.41	7.61	*0.20*			
187	Pyrrolidine, 1-cyclohexyl-				8.04	7.96	*−0.08*			
188	Piperidine, 1-(1-cyclopenten-1-yl)-	7.25	7.00	*−0.25*	7.48	7.40	*−0.08*			
189	Pyrrolidine, 1-(1-cyclohexen-1-yl)-	7.28	7.14	*−0.14*	7.51	7.15	*−0.36*			
190	$(C_2H_5)_2N$-C_6H_5	7.13	6.98	*−0.15*	7.47	7.51	*0.04*	924.81	927.90	*3.09*
191	3-$(CH_3)_2N$-C_6H_4-CH_3	7.42	6.95	*−0.47*				905.85	924.30	*18.45*
192	2-$(CH_3)_2N$-C_6H_4-CH_3	7.32	7.30	*−0.02*	7.67	7.83	*0.16*	911.99	923.20	*11.21*
193	4-H_2N-C_6H_4-C_4H_9	7.90	7.61	*−0.29*						
194	4-H_2N-C_6H_4-*tert*-C_4H_9	7.87	7.35	*−0.52*						
195	$(CH_3)_2N$-C_2H_4-C_6H_5	7.83	7.70	*−0.13*	8.34	8.35	*0.01*			
196	4-$(CH_3)_2N$-CH_2-C_6H_4-CH_3	7.66	7.61	*−0.05*						
197	3-H_2N-C_6H_4-C_4H_9	7.88	7.51	*−0.37*						
198	2,6-Diethylaniline				7.91	7.77	*−0.14*			
199	C_4H_9-NH-C_6H_5	7.44	7.53	*0.09*						
200	CH_3NH-$CH(CH_3)$-CH_2-C_6H_5				8.43	8.60	*0.17*			
201	$(CH_3)_2N$-2,4-$(CH_3)_2$ C_6H_3	7.28	7.17	*−0.11*	7.63	7.79	*0.16*			
202	CH_3-NH-2,4,6-$(CH_3)_3$-C_6H_2	7.40	7.22	*−0.18*						
203	4-$(CH_3)_2N$-C_6H_4-C_2H_5	7.40	7.38	*−0.02*						
204	*N*-Phenylpyrrolidine	7.20	6.80	*−0.40*	7.56	7.23	*−0.33*	922.55	915.10	*−7.45*
205	*N*-(2-Methylphenyl)azetidine	7.05	7.10	*0.05*	7.39	7.67	*0.28*			

(*continued*)

Table 5. (*Continued*)

No.	Compound	IE_{ad}			IE_{vert}			Gb		
		Predic.	Exp.	Resid.	Predic.	Exp.	Resid.	Predic.	Exp.	Resid.
206	*N*-(2,6-Dimethylphenyl)aziridine				7.70	7.88	*0.18*			
207	*N*-(2,4-Dimethylphenyl)aziridine				7.83	7.80	*−0.03*			
208	*N*-Methyl-1,2,3,4-tetrahydroisoquinoline				8.11	8.60	*0.49*			
209	2-Naphthylamine				8.20	7.55	*−0.65*			
210	1-Naphthylamine	7.68	7.26	*−0.42*	7.99	7.48	*−0.51*	864.06	875.10	*11.04*
211	$4\text{-}(C_2H_5)_2N\text{-}C_6H_4\text{-}CH_3$	7.09	6.84	*−0.25*				927.13	931.00	*3.87*
212	$3\text{-}(C_2H_5)_2N\text{-}C_6H_4\text{-}CH_3$	7.08	6.90	*−0.18*				927.91	932.20	*4.29*
213	$2,4,6\text{-}(CH_3)_2N\text{-}C_6H_2(CH_3)_3$	6.79	7.24	*0.45*						
214	$C_5H_{11}NHC_6H_5$	7.41	7.50	*0.09*						
215	*N*-Phenylpiperidine	7.07	7.10	*0.03*				930.28	926.40	*−3.88*
216	*N*-(2,6-Dimethylphenyl)azetidine	7.06	7.00	*−0.06*	7.41	7.76	*0.35*			
217	*N*-(2-Methylphenyl)pyrrolidine	7.05	6.80	*−0.25*	7.39	7.73	*0.34*			
218	*N*-(2,4-Dimethylphenyl)azetidine				7.53	7.48	*−0.05*			
219	*cyclo*-$C_5H_{10}\text{-}NH\text{-}C_6H_5$	7.29	7.45	*0.16*						
220	$(H_2C\text{-}C(CH_3)\text{-}CH_2)_3N$	7.08	7.80	*0.72*				964.26	949.40	*−14.86*
221	$(CH_3)_2N$-1-Adamantyl-							966.96	963.00	*−3.96*
222	$(C_3H_7)_2N\text{-}C_6H_5$	6.98	6.93	*−0.05*				934.58	931.10	*−3.48*
223	$4\text{-}(CH_3)_2NC_6H_4$, *tert*-C_4H_9	7.33	6.90	*−0.43*						
224	$C_6H_{13}\text{-}NH\text{-}C_6H_5$	7.39	7.50	*0.11*						
225	*N*-(2-Methylphenyl)piperidine	6.92	7.10	*0.18*	7.25	7.84	*0.59*			
226	*N*-(2,6-Dimethylphenyl)pyrrolidine	6.90	7.00	*0.10*	7.23	7.67	*0.44*			
227	*cyclo*-$C_6H_2\text{-}NH\text{-}C_6H_5$	7.21	7.45	*0.24*						
228	$(CH_3)_2$N-Naphthyl-1,	7.15	7.00	*−0.15*	7.45	7.59	*0.14*			
229	$(CH_3)_2$N-Naphthyl-2,				7.66	7.12	*−0.54*			
230	$(C_6H_5)_2NH$	6.91	7.19	*0.28*	7.06	7.44	*0.38*			
231	[1,1′-Biphenyl]-2-amine	7.34	7.28	*−0.06*						
232	4-Aminobiphenyl	7.85	7.49	*−0.36*						
233	Carbazol-1	7.03	7.57	*0.54*	7.21	7.50	*0.29*			
234	*N*-Methyl-carbazol	6.77	7.50	*0.73*						
235	Acridine, 9, 10-dihydro-	6.87	7.24	*0.37*	7.02	7.33	*0.31*			
236	4-Aminofluorene	7.51	7.25	*−0.26*	7.78	7.60	*−0.18*			
237	$(C_6H_5)_2N\text{-}CH_3$	6.65	6.94	*0.29*	6.79	7.33	*0.54*			
238	Benzenamine, 4-(phenylmethyl)-	7.81	7.61	*−0.20*						
239	$C_7H_{15}\text{-}NH\text{-}C_6H_5$	7.11	7.50	*0.39*						
240	9-Aminophenanthrene	7.53	7.19	*−0.34*						
241	5*H*-Dibenz[*b*,*f*]azepine,10, 11-dihydro-				6.88	7.25	*0.37*			
242	$4\text{-}H_2N\text{-}C_6H_4\text{-}C_2H_4\text{-}C_6H_5$	7.84	7.55	*−0.29*						
243	1-(3-Aminophenyl)-2-phenylethene	7.81	7.60	*−0.21*	8.13	7.90	*−0.23*			
244	$NH(CH_2\text{-}C_6H_5)_2$	7.35	8.22	*0.87*						
245	1-(4-Aminophenyl)-2-phenylethene	7.84	7.70	*−0.14*						
246	$C_6H_5(CH_3)N\text{-}CH_2\text{-}C_6H_5$	6.87	7.44	*0.57*						
247	$4\text{-}H_2N\text{-}C_6H_4\text{-}C_8H_{17}$							867.10	862.00	*−5.10*
248	$(C_4H_9)_2N\text{-}C_6H_5$	6.88	6.95	*0.07*						
249	$C_8H_{17}\text{-}NH\text{-}C_6H_5$	7.36	7.50	*0.14*						
250	4-Aminofluorene	7.51	7.10	*−0.41*	7.78	7.50	*−0.28*			
251	$CH_3\text{-}N(CH_2\text{-}C_6H_5)_2$	7.09	7.85	*0.76*						
252	2,3-Benzocarbazole	6.89	7.05	*0.16*						
253	1,2-Benzocarbazole	6.75	7.10	*0.35*						
254	1-Aminopyrene	7.48	6.82	*−0.66*						
255	$C_6H_5\text{-}NH$-Naphthyl-2,	6.76	7.15	*0.39*						
256	$(CH_3)_2N\text{-}C_6H_3$ ($tert$-$C_4H_9)_2$, 2,4-							943.06	942.40	*−0.66*
257	$(C_5H_{11})_2N\text{-}C_6H_5$	6.63	7.10	*0.47*						

(*continued*)

Table 5. (*Continued*)

No.	Compound	IE_{ad}			IE_{vert}			Gb		
		Predic.	Exp.	Resid.	Predic.	Exp.	Resid.	Predic.	Exp.	Resid.
258	$C_{10}H_{21}NH\text{-}C_6H_5$	7.34	7.50	*0.16*						
259	6-Aminochrysene	7.41	6.99	*−0.42*						
260	$(C_6H_5)_3N$	5.82	6.75	*0.93*	5.74	7.00	*1.26*	885.69	876.60	*−9.09*
261	$H_2N\text{-}C_6H_2\text{-}(tert\text{-}C_4H_9)_3$, 2,4,6-	6.80	6.90	*0.10*	7.04	7.30	*0.26*			
262	$C_{12}H_{25}\text{-}NH\text{-}C_6H_5$	7.33	7.50	*0.17*						
263	$(C_6H_{13})_2N\text{-}C_6H_5$	6.77	7.10	*0.33*						
264	$HC(O)\text{-}NH_2$	9.86	10.16	*0.30*	10.10	9.95	*−0.15*	827.30	791.20	*−36.10*
265	$CH_3\text{-}C(O)\text{-}NH_2$	9.69	9.69	*0.00*	9.92	10.00	*0.08*	838.11	832.60	*−5.51*
266	$CH_3\text{-}NH\text{-}HCO$	9.59	9.83	*0.24*				849.57	820.30	*−29.27*
267	$HC{\equiv}C\text{-}C(O)\text{-}NH_2$	9.68	9.85	*0.17*	9.85	9.85	*0.00*			
268	$H_2N\text{-}C(O)\text{-}CH{=}CH_2$	9.59	9.50	*−0.09*	9.71	10.00	*0.29*	837.24	839.80	*2.56*
269	$(CH_3)_2\text{-}N\text{-}HCO$	9.32	9.13	*−0.19*	9.56	9.14	*−0.42*	871.84	856.60	*−15.24*
270	$H_2N\text{-}C(O)\text{-}C_2H_5$							843.20	845.30	*2.10*
271	$CH_3C(O)\text{-}NH\text{-}CH_3$	9.43	9.70	*0.27*	9.65	9.85	*0.20*	860.38	857.60	*−2.78*
272	$H_2C{=}CH\text{-}C(O)\text{-}NH_2$							843.96	849.40	*5.44*
273	$H_2C{=}CH\text{-}NH\text{-}C(O)\text{-}CH_3$	9.22	8.95	*−0.27*						
274	$(CH_3)_2N\text{-}C(O)\text{-}CH_3$							882.70	877.00	*−5.70*
275	$(CH_3)_2CH\text{-}C(O)\text{-}NH_2$							854.26	846.70	*−7.56*
276	$CH_3\text{-}NH\text{-}C(O)\text{-}C_2H_5$							865.47	889.40	*23.93*
277	$CH_3\text{-}C(O)\text{-}NH\text{-}C_2H_5$				9.46	8.71	*−0.75*	871.41	867.00	*−4.41*
278	$C_3H_7\text{-}NH\text{-}HCO$							865.49	847.40	*−18.09*
279	$tert\text{-}C_4H_9\text{-}C(O)\text{-}NH_2$							859.73	857.20	*−2.53*
280	$HCO\text{-}N(C_2H_5)_2$	8.98	8.89	*−0.09*						
281	$CH_3\text{-}NH\text{-}C(O)\text{-}C_3H_7$	9.19	9.68	*0.49*						
282	$(CH_3)_2N\text{-}C(O)\text{-}CH{=}CH_2$							884.66	873.40	*−11.26*
283	Caprolactam	9.12	9.07	*−0.05*	9.31	9.19	*−0.12*			
284	2-Piperidinone,1-methyl-				9.15	8.92	*−0.23*	898.56	892.60	*−5.96*
285	$(CH_3)_2N\text{-}C(O)\text{-}CH{=}CH\text{-}CH_3$	8.92	9.00	*0.08*				888.50	899.40	*10.90*
286	4-Piperidinone, 1-methyl-	8.25	8.30	*0.05*	8.74	8.82	*0.08*			
287	Acetylpyrrolidine							891.65	894.40	*2.75*
288	$(C_2H_5)_2N\text{-}C(O)CH_3$	8.68	8.60	*−0.08*				913.58	894.40	*−19.18*
289	$(CH_3)_2N\text{-}C(O)\text{-}C_3H_7$							890.76	890.80	*0.04*
290	$iso\text{-}C_3H_7\text{-}C(O)\text{-}N(CH_3)_2$							896.00	891.80	*−4.20*
291	Ethanone, 1-(1*H*-pyrrol-2-yl)-	9.06	8.72	*−0.34*						
292	2*H*-Azepin-2-one, hexahydro-1-methyl-	8.75	9.00	*0.25*	8.93	8.73	*−0.20*			
293	Hexahydro-2(1*H*)-azocinone				8.76	9.19	*0.43*			
294	$tert\text{-}C_4H_9\text{-}C(O)\text{-}NH_2$							904.27	895.20	*−9.07*
295	$H_2N\text{-}C(O)\text{-}C_6H_5$	9.27	9.25	*−0.02*	9.39	9.45	*0.06*	837.68	861.20	*23.52*
296	$H_2N\text{-}C_6H_4\text{-}HCO$	8.11	8.25	*0.14*				855.64	878.60	*22.96*
297	$C_6H_5\text{-}NH\text{-}HCO$				8.78	8.60	*−0.18*			
298	2-Cyclohexenone, 3-amino, 5,5-dimethyl-				8.39	8.55	*0.16*	890.59	915.90	*25.31*
299	Hexahydro-1-methyl-2(1*H*)-azocinone				8.93	8.76	*−0.17*			
300	1-Methylhexahydroazocin-5-one				8.50	8.13	*−0.37*			
301	$tert\text{-}C_4H_9\text{-}CH_2\text{-}C{=}CH_2\text{-}N(CH_3)_2$							899.76	896.70	*−3.06*
302	$(CH_3)_2CH\text{-}C(O)\text{-}N(C_2H_5)_2$				8.77	8.80	*0.03*			
303	$CH_3\text{-}C(O)\text{-}NH\text{-}C_6H_5$	8.60	8.30	*−0.30*	8.60	8.46	*−0.14*			
304	$4\text{-}CH_3\text{-}C(O)\text{-}C_6H_4\text{-}NH_2$	8.08	7.80	*−0.28*	8.42	8.27	*−0.15*	857.49	877.00	*19.51*
305	$3\text{-}CH_3\text{-}C(O)\text{-}C_6H_4\text{-}NH_2$	8.07	8.56	*0.49*						
306	$CH_3\text{-}NH\text{-}C(O)\text{-}C_6H_5$	9.00	9.33	*0.33*						
307	$4\text{-}H_2N\text{-}C(O)\text{-}C_6H_4\text{-}CH_3$				9.35	9.14	*−0.21*	839.44	869.90	*30.46*
308	$3\text{-}H_2N\text{-}C(O)\text{-}C_6H_4\text{-}CH_3$				9.35	9.11	*−0.24*	839.65	869.90	*30.25*
309	$(CH_3)_2N\text{-}C(O)\text{-}C_6H_5$				8.85	9.04	*0.19*	882.22	901.80	*19.58*

(*continued*)

Table 5. (*Continued*)

No.	Compound	IE_{ad}			IE_{vert}			Gb		
		Predic.	Exp.	Resid.	Predic.	Exp.	Resid.	Predic.	Exp.	Resid.
310	4-$(CH_3)_2$N-C_6H_4-HCO	7.58	7.30	*−0.28*	7.92	7.81	*−0.11*	900.18	898.30	*−1.88*
311	2-CH_3-C(O)-NH-C_6H_4-CH_3	8.45	8.03	*−0.42*	8.43	8.34	*−0.09*			
312	4-CH_3-C(O)-NH-C_6H_4-CH_3	8.56	8.33	*−0.23*						
313	3-CH_3-C(O)-NH-C_6H_4-CH_3	8.55	8.29	*−0.26*						
314	CH_3-C(O)-N$(CH_3)C_6H_5$				8.33	8.81	*0.48*			
315	2-Cyclohexenone,3-(*N*-methylamino), 5,5-dimethyl				8.12	8.11	*−0.01*			
316	C_6H_5-NH-C(O)-CH=CH_2	8.50	8.70	*0.20*						
317	*N*,*N*-4-Trimethyl benzamide				8.73	8.90	*0.17*	888.74	896.00	*7.26*
318	$(CH_3)_2$N-C_6H_4-C(O)-CH_3				7.88	7.69	*−0.19*	902.03	900.30	*−1.73*
319	3-$(CH_3)_2$N-C(O)-C_6H_4-CH_3							885.08	896.00	*10.92*
320	3-CH_3-C(O)-C_6H_4-N$(CH_3)_2$							903.23	901.50	*−1.73*
321	2,6-CH_3-C(O)-NH-C_6H_3, $(CH_3)_2$				8.26	8.70	*0.44*			
322	C_3H_7-C(O)-C_6H_4-NH_2	8.05	8.01	*−0.04*						
323	3-CH_3-C(O)-N(CH_3)-C_6H_4-CH_3				8.28	8.82	*0.54*			
324	H_2N-C_6H_4-C(O)-C_3H_7	8.02	8.06	*0.04*						
325	2(1*H*)-Quinolinone, 1-methyl-	8.26	8.00	*−0.26*	8.16	8.25	*0.09*			
326	2-Butenamide, *N*-(phenylmethyl)- Acetamide, *N*-(2,6-dimethylphenyl)-*N*-	8.67	8.60	*−0.07*						
327	methyl-				7.98	8.80	*0.82*			
328	5,5-Dimethyl-3-(*n*-propylamino)cyclohex-2-en-1-one				7.85	8.03	*0.18*			
329	5,5-Dimethyl-3-(isopropylamino)cyclohex-2-en-1-one				7.75	7.94	*0.19*			
330	2-Aminobenzophenone	8.55	8.25	*−0.30*						
331	3-Aminobenzophenone	8.05	8.45	*0.40*						
332	4-Aminobenzophenone	7.97	8.40	*0.43*						
333	C_6H_5-NH-C(O)-C_6H_5	8.18	8.10	*−0.08*						
334	9,I0-Dihydro-9-oxoacridine	7.23	7.60	*0.37*						
335	9-Hydro-IO-methyl-9-oxoacridine	6.96	7.53	*0.57*						
336	9-Hydro-IO-ethyl-9-oxoacridine	6.79	7.49	*0.70*						
337	$(CH_3)_2$N-C_6H_4-C(O)-C_6H_5	7.44	7.50	*0.06*						
338	CH_3-C(O)-C(O)-NH_2				10.10	9.71	*−0.39*			
339	2,5-Pyrrolidinedione				10.14	10.01	*−0.13*			
340	Glutarimide				10.10	9.87	*−0.23*			
341	Phthalimide				9.65	9.90	*0.25*			
342	H_2N-C≡N	9.94	10.40	*0.46*	10.29	10.65	*0.36*	756.76	774.90	*18.14*
343	H_2N-CH_2-C≡N							822.78	791.00	*−31.78*
344	$(CH_3)_2$N-C≡N	9.41	9.00	*−0.41*	9.75	9.44	*−0.31*	801.29	821.40	*20.11*
345	H_2N-C_2H_4-C≡N							856.13	832.50	*−23.63*
346	CH_3-NH-CH_2-C≡N							845.05	830.70	*−14.35*
347	$(CH_3)_2$N-CH_2-C≡N	8.77	8.86	*0.09*				867.32	853.70	*−13.62*
348	F-NH_2	10.22	10.83	*0.61*	10.87	11.62	*0.75*			
349	4-H_2N-C_6H_4-F	8.07	7.87	*−0.20*				852.18	839.70	*−12.48*
350	2-H_2N-C_6H_4-F	8.26	8.50	*0.24*	8.63	8.18	*−0.45*			
351	3-H_2N-C_6H_4-F				8.46	8.33	*−0.13*	850.17	835.50	*−14.67*
352	F-C_3H_6-NH_2							874.96	886.90	*11.94*
353	F-C_2H_4-NH_2	8.80	9.10	*0.30*				864.23	858.00	*−6.23*
354	F_2CH-CH_2-NH_2	9.04	9.40	*0.36*				841.72	836.60	*−5.12*
355	2,6-F,F-C_6H_3-NH_2				8.89	8.58	*−0.31*			
356	2,4-F,F-C_6H_3-NH_2				8.70	8.54	*−0.16*			
357	2,5-F,F-C_6H_3-NH_2				8.72	8.41	*−0.31*			

(*continued*)

Table 5. (*Continued*)

No.	Compound	IE_{ad}			IE_{vert}			Gb		
		Predic.	Exp.	Resid.	Predic.	Exp.	Resid.	Predic.	Exp.	Resid.
358	F_2NH	11.35	11.60	*0.25*	12.04	12.38	*0.34*			
359	F-C_2H_4-NH_2	8.80	9.10	*0.30*	9.39	9.86	*0.47*	864.23	858.00	*−6.23*
360	F_3C-CH_2-NH_2	9.27	9.70	*0.43*	9.86	10.35	*0.49*	819.21	812.90	*−6.31*
361	F_3C-C_2H_4-NH_2	8.87	9.30	*0.43*	9.45	9.70	*0.25*	854.79	853.20	*−1.59*
362	F_3C-$N(CH_3)_2$	9.36	9.20	*−0.16*	9.98	9.99	*0.01*			
363	F_3C-CH_2-$NHCH_3$							841.48	848.00	*6.52*
364	F_3C-CH_2-$N(CH_3)_2$	8.74	8.42	*−0.32*	9.33	8.98	*−0.35*	863.75	871.90	*8.15*
365	F_3C-C_3H_6-NH_2	8.72	9.10	*0.38*				867.53	869.60	*2.07*
366	3-F_3C-C_6H_4-NH_2							842.79	825.10	*−17.69*
367	3-F_3C-C_6H_4-$N(CH_3)_2$							887.41	881.80	*−5.61*
368	4-F_3C-C_6H_4-$N(CH_3)_2$							891.26	876.80	*−14.46*
369	F_3N	12.48	12.94	*0.46*	13.21	13.60	*0.39*	539.27	538.60	*−0.67*
370	2,3,5,6-, H_2N-C_6H, F,F,F,F				9.06	8.90	*−0.16*			
371	2,3,5,4-, H_2N-C_6H, F,F,F,F				8.87	8.70	*−0.17*			
372	F_2CH-NF_2	11.79	11.50	*−0.29*	12.50	12.33	*−0.17*			
373	C_6F_5-NH_2	8.74	8.40	*−0.34*	9.13	8.90	*−0.23*			
374	C_6F_5-NH-CH_3				8.86	8.65	*−0.21*			
375	C_6F_5-N-$(CH_3)_2$				8.59	8.48	*−0.11*			
376	CF_3NF_2	12.15	11.90	*−0.25*	12.86	12.62	*−0.24*			
377	$(CHF_2)_3N$	10.43	11.20	*0.77*	11.07	11.65	*0.58*			
378	3,5-, $(CH_3)_2$-N-C_6H_3 $(CF_3)_2$							872.00	858.40	*−13.60*
379	$(CF_3CH_2)_2$-NH							793.96	805.10	*11.14*
380	3,5-, H_2N-$C_6H_3(CF_3)_2$	8.29	8.59	*0.30*						
381	$(CF_3)_2N$-C_6H_5				10.03	10.00	*−0.03*			
382	C_2H_5-NF_2	12.24	11.60	*−0.64*	12.94	12.45	*−0.49*			
383	F_3C-$N(CHF_2)_2$	10.78	11.40	*0.62*	11.44	12.08	*0.64*			
384	$(CF_3)_2NF$	11.82	11.60	*−0.22*	12.51	12.45	*−0.06*			
385	$(CF_3)_3N$	11.50	11.70	*0.20*	12.17	12.55	*0.38*			
386	$(CF_3)_3C$-NH_2	10.15	10.40	*0.25*	10.74	11.10	*0.36*			
387	$(C_2H_5)_2N$-C≡N	9.07	8.97	*−0.10*	9.38	9.32	*−0.06*			
388	Cl-NH_2	9.45	9.85	*0.40*	10.06	10.60	*0.54*			
389	4-$(C_2H_5)_2N$-C_6H_4-Cl							919.44	899.20	*−20.24*
390	(*E*)-4-(2-(4-Chlorophenyl)ethenyl) benzenamine-*N*,*N*-dimethyl				7.63	7.05	*−0.58*			
391	$(CH_3)_2NCl$	8.92	8.75	*−0.17*	9.52	9.25	*−0.27*			
392	Cl_3C-CH_2-$N(CH_3)_2$							870.45	882.00	*11.55*
393	H_2N-C_6H_3, Cl,Cl, 2,6	8.13	7.60	*−0.53*						
394	4-H_2N-C_6H_4-Cl	8.02	7.77	*−0.25*	8.39	8.18	*−0.21*	852.84	842.00	*−10.84*
395	3-H_2N-C_6H_4-Cl	8.03	8.09	*0.06*				851.06	836.30	*−14.76*
396	2-H_2N-C_6H_4-Cl	8.07	7.90	*−0.17*						
397	4-Chloro-1-azabicyclo[2.2.2]octane				8.40	8.55	*0.15*	937.02	918.60	*−18.42*
398	3-Chloro-1-azabicyclo[2.2.2]octane				8.41	8.80	*0.39*	933.70	923.50	*−10.20*
399	2-Chloro-1-azabicyclo[2.2.2]octane							919.99	920.00	*0.01*
400	$(CH_3)_2N$-C_6H_5-Cl	7.49	7.20	*−0.29*				897.37	896.40	*−0.97*
401	CH_3-NCl_2	9.53	9.52	*−0.01*	10.15	10.06	*−0.09*			
402	CH_3-NH-Cl	9.18	9.19	*0.01*	9.79	9.70	*−0.09*			
403	NCl_3	10.15	10.12	*−0.03*	10.79	10.70	*−0.09*			
404	Cl_2NH	9.80	9.98	*0.18*	10.42	10.52	*0.10*			
405	$(C_4F_9)_3N$	12.14	11.30	*−0.84*	12.75	11.70	*−1.05*			
406	$(CF_3)_2N$-CHF_2	11.14	11.70	*0.56*	11.80	12.35	*0.55*			
407	$(C_2F_5)_3N$	11.75	11.70	*−0.05*						
408	4-$(C_2H_5)_2N$-C_6H_4-Br	7.13	6.96	*−0.17*						

(*continued*)

Table 5. (*Continued*)

No.	Compound	IE_{ad} Predic.	IE_{ad} Exp.	IE_{ad} Resid.	IE_{vert} Predic.	IE_{vert} Exp.	IE_{vert} Resid.	Gb Predic.	Gb Exp.	Gb Resid.
409	(*E*)-4-(2-(4-Bromophenyl)ethenyl) benzenamine-*N*,*N*-dimethyl				7.63	7.04	*−0.59*			
410	$(CH_3)_2N$-Br	8.74	8.61	*−0.13*	9.34	9.15	*−0.19*			
411	2-H_2N-C_6H_4-Br	8.01	8.45	*0.44*						
412	4-H_2N-C_6H_4-Br	8.00	7.74	*−0.26*						
413	4-$(CH_3)_2N$-C_6H_4-Br	7.47	7.33	*−0.14*						
414	CH_3-NBr_2	9.19	9.15	*−0.04*	9.79	9.68	*−0.11*			
415	CH_3-NH-Br	9.01	9.12	*0.11*	9.61	9.67	*0.06*			
416	NH_2Br				9.88	10.18	*0.30*			
417	$NHBr_2$				10.06	10.10	*0.04*			
418	1-Azabicyclo[2.2.2]octane,4-iodo-				8.35	8.35	*0.00*			
419	4-H_2N-C_6H_4-I	8.06	7.51	*−0.55*						
420	2-H_2N-C_6H_4-I	8.21	8.35	*0.14*						
421	3-H_2N-C_6H_4-I							846.80	846.80	*0.00*

The following correlations between the estimated atomic operational parameters and χR^2 and R^2 quantities have been obtained:

$$ie^{ad} = (4.55 \pm 0.76)\chi R^2 - (12.71 \pm 2.24)R^2 \quad (13)$$

$$R = 0.9015,\ S^0 = 1.0704,\ N = 10,\ F = 17.3655$$

$$ie^{vert} = (4.38 \pm 0.50)\chi R^2 - (13.06 \pm 1.47)R^2 \quad (14)$$

$$R = 0.9527,\ S^0 = 0.7049,\ N = 10,\ F = 39.1897$$

$$gb = (-311.97 \pm 33.03)\chi R^2 + (701.58 \pm 96.98)R^2 \quad (15)$$

$$R = 0.9153,\ S^0 = 83.3409,\ N = 11,\ F = 23.2475$$

(the values of the corresponding "inductive" atomic electronegativities used in the correlations and covalent radii are given in Table 6).

The O sp^2 atom has been excluded from the correlations since the corresponding inductive electronegativity value is probably overestimated.

If we suggest that there is no major influence of the steric and resonance effects on the ionization energies of the treated amines, then we can evaluate the electronegativity of the reaction center chosen (in this particular case, nitrogen):

$$ie^{ad} = 4.55(\chi - 2.79)R^2$$

$$ie^{vert} = 4.38(\chi - 2.98)R^2$$

The estimated values 2.79 ± 0.7 and 2.98 ± 0.7 are close to each other and to the corresponding inductive electronegativity of $N = 2.56$.

Thus, the established equations can be used for the calculation of unknown operational atomic parameters, which in turn allow for the calculation of ionization energies and gas basicities of any amine.

Table 6. Operational atomic parameters, estimated on the basis of r^{-2} analysis of IE and Gb data

Atom	χ_i	R	IEad ie^{ad}	IEad +/−	IEvert ie^{vert}	IEvert +/−	Gb gb	Gb +/−
Intercept			9.99	0.19	10.78	0.20	838.48	9.50
H	2.10	0.3	−0.30	0.06	−0.37	0.06	13.95	2.92
C sp^3	2.10	0.77	−0.78	0.04	−0.82	0.05	54.84	1.97
C sp^2	2.25	0.67	−1.05	0.09	−1.51	0.10	38.50	4.81
C *sp*	2.65	0.60	−0.90	0.41	−1.23	1.37	6.08	10.50
C ar	2.45	0.67	−1.10	0.05	−1.33	0.06	16.16	2.62
N≡	6.76	0.55	6.55	1.77	5.73	4.91	−496.58	51.60
O=	4.59	0.62	5.50	0.37	4.80	0.36	−151.58	16.50
F	3.93	0.64	1.53	0.11	1.50	0.11	−165.91	8.35
Cl	3.09	0.99	0.17	0.30	0.01	0.32	−170.58	36.53
Br	2.97	1.14	−0.42	0.55	−0.63	0.46		
I	2.80	1.33	1.59	3.28	−1.03	7.44	−319.35	337.84

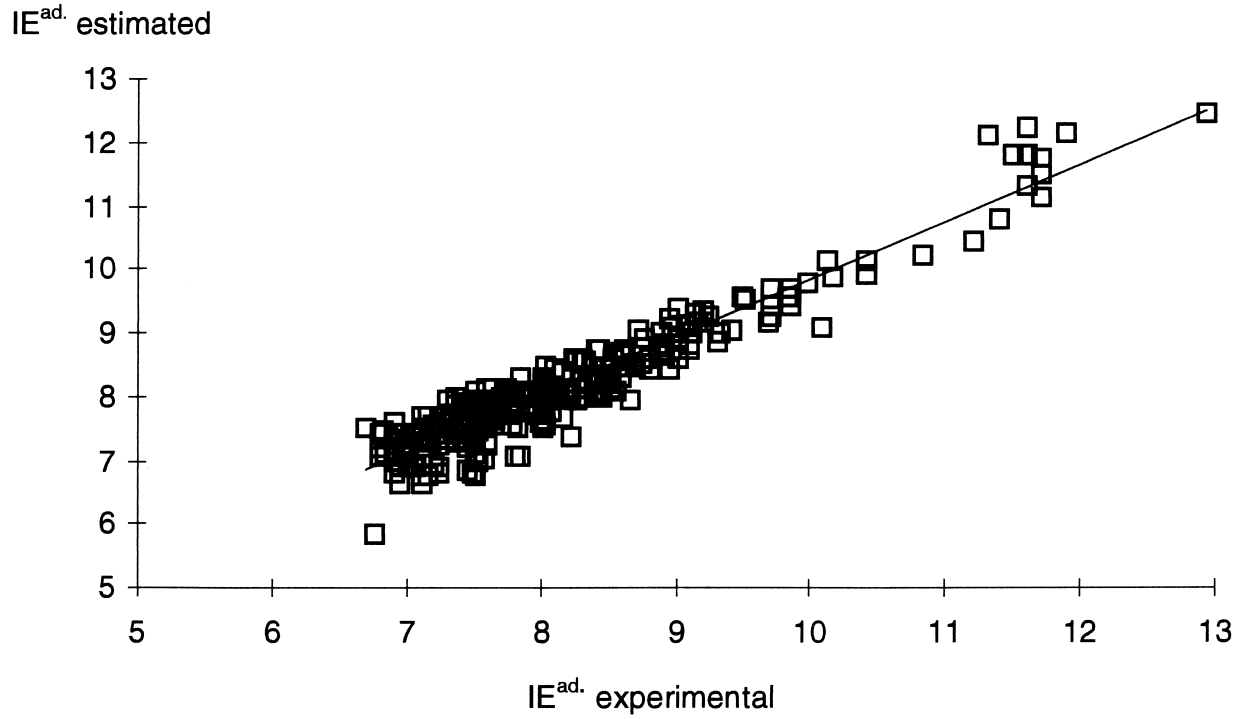

Figure 1. Experimental vs. estimated adiabatic ionization energies IE_{ad} of amines.

FUTURE DEVELOPMENT AND PROSPECTIVE

The suggested approach is suitable for implementation in a computer program and further development of the corresponding program, written on the MATLAB platform, is underway.

The advantages of a program based on the method presented in this article are as follows:

- The procedure for establishing structure–activity relationships would be fast, since the method is based on simple matrix algebra.

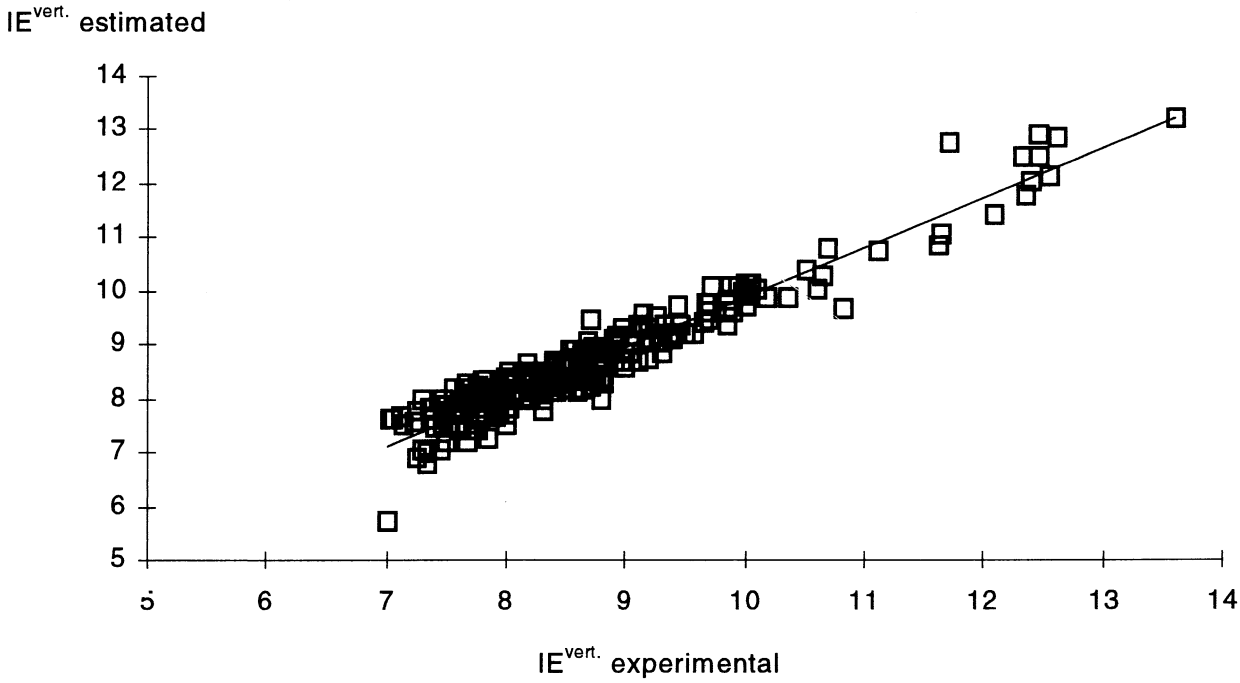

Figure 2. Experimental vs. estimated vertical ionization energies IE_{vert} of amines.

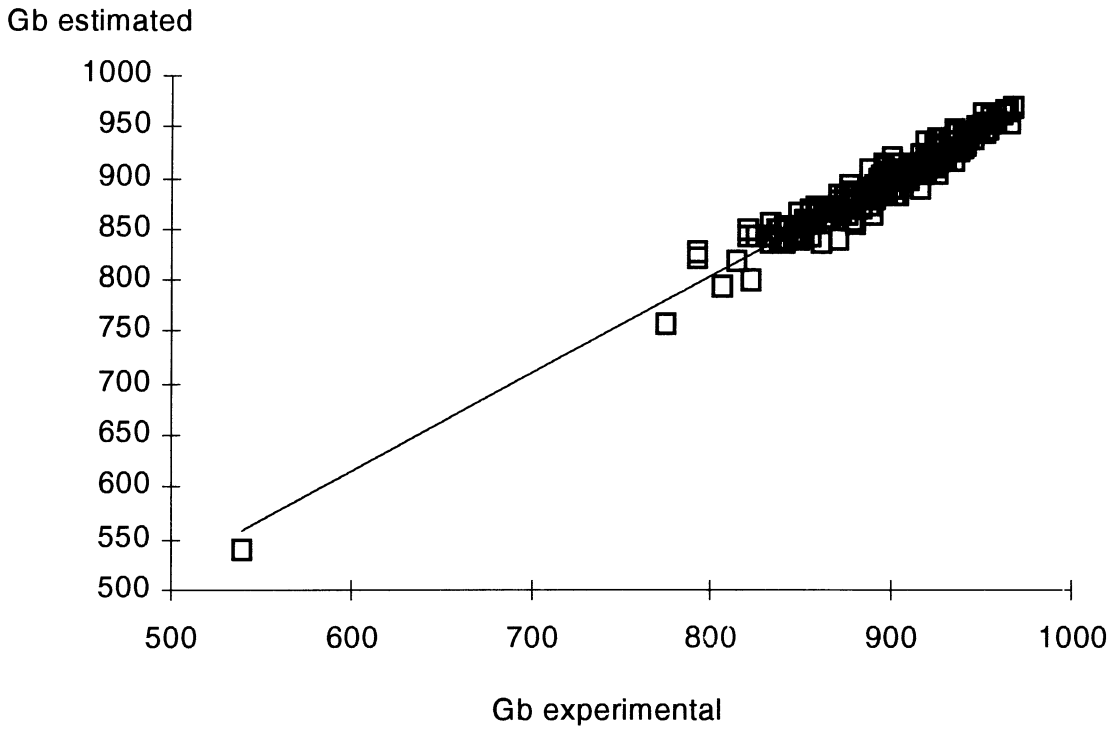

Figure 3. Experimental vs. estimated gas basicities Gb of amines.

- Practically useful structure–activity relationships could be obtained without the use of known substituent constants and without full physical understanding of the substituent effects.
- When the choice of reaction center is not obvious, several possible reaction centers could be screened and the quality of the correlations could give some guidance as to which part of the molecule is the reaction center.
- It is often possible to extract the physical meaning of the substituent effects in terms of steric and inductive contributions from the empirical relationships obtained by the present method.
- The method is sensitive to conformational differences, which is usually not the case when using conventional substituent constants.

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