

## Gaseous-phase proton affinity of anilines: A quantum chemical evaluation and discussion in view of aqueous basicity

ALEXEI N. PANKRATOV, INNA M. UCHAEVA, SERGEI YU. DORONIN and  
RIMMA K. CHERNOVA

Department of Chemistry, N. G. Chernyshevskii Saratov State University, 83 Astrakhanskaya  
Street, Saratov 410026, Russia

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Using the PM3 method, enthalpies and free energies of the gaseous-phase proton affinity ( $PA$ ) have been computed for aniline and 62 of its derivatives with different kinds of electron-donor and electron-acceptor substitution in the aromatic ring and at the nitrogen atom. Linear correlations of the type  $pK_a$  vs.  $PA$  have been found. Deviations of the data for *ortho* substituted anilines from the above relationships was discussed in view of possible hydrophobic hydration of the molecular fragments adjacent to the protonation centre. Linear dependences  $P_{\text{exper}} = bP_{\text{theor}}$  (where  $P$  is standard entropy, heat or Gibbs energy of formation, first ionization potential, molecular dipole moment) were found.

*Keywords:* anilines, proton affinity, basicity, quantum chemical computation, theory-experiment correlation, hydrophobic hydration.

### INTRODUCTION

The reactivities of aniline and its derivatives are influenced by their protolytic properties. Directive synthesis of anilines with a given basicity requires *a priori* theoretical estimation of the  $pK_a$  values for amines conjugate acids. It would be reasonable to assume that in aqueous solutions, the basicity of anilines (characterized by the  $pK_a$  values) is determined to a significant extent by the molecular electronic structure, by electronic effects of substituents in aromatic ring and at the nitrogen atom. An integral measure of intramolecular factors involved in the basicity of amines could be proton affinity ( $PA$ ), which is the reaction enthalpy for a proton breaking-off in the gaseous phase:



The  $PA$  is calculated using semiempirical quantum chemical methods by the formula:<sup>1,2</sup>

$$PA = H_f(\text{B}) + H_f(\text{H}^+) - H_f(\text{BH}^+)$$

where  $H_f(\text{H}^+)/4.184$  is the experimental value of the proton heat of formation, which is equal to 367.163 kJ/mol.<sup>1–5</sup>

The present work is aimed at the quantum chemical computation of the proton affinity of aniline and 62 of its derivatives (Table I) with different kinds of electron-donor and electron-acceptor substitution in the aromatic ring and at the nitrogen atom, as well as at establishing the interrelations between the  $pK_a$  and  $PA$  values.

TABLE I. Experimental (at 298 K)  $pK_a$  values<sup>6-10</sup> for aqueous solutions and PM3-computed gas-phase proton affinities ( $PA$ )

Compound	$pK_a$	Methods of $pK_a$ determination	$PA/4.184$ ; kJ/mol	
			$H_f$	$G_f$
Aniline	4.58	Potentiometric	213.39	204.46
2-Methylaniline	4.39	Potentiometric; thermodynamic; method of calculation	214.59	205.81
3-Methylaniline	4.69	"	214.38	205.54
4-Methylaniline	5.12	"	215.13	206.21
<i>N</i> -Methylaniline	5.02	Potentiometric	211.98	203.71
2,6-Dimethylaniline	3.89	"	216.18	207.38
<i>N,N</i> -Dimethylaniline	5.21	"	210.51	201.37
<i>N,N</i> -Dimethyl-2-methylaniline	5.86	Potentiometric; thermodynamic	212.21	204.87
4-Ethylaniline	5.05	Potentiometric	215.03	206.46
<i>N</i> -Ethylaniline	5.11	"	214.69	206.32
<i>N,N</i> -Diethylaniline	6.56	"	213.94	205.47
<i>N,N</i> -Diethyl-2-methylaniline	7.18	"	216.33	208.37
4-Isopropylaniline	5.02	"	215.21	206.44
<i>N</i> -Isopropylaniline	5.50	"	215.98	207.02
2- <i>tert</i> -Butylaniline	3.78	"	217.31	209.73
<i>N-tert</i> -Butylaniline	7.10*	"	218.56	210.28
2-Aminobiphenyl	3.78	"	217.88	209.45
3-Aminobiphenyl	4.18	"	214.96	206.06
4-Aminobiphenyl	4.27	"	215.87	206.85
1,2-Phenylenediamine	4.47**	"	216.42	207.70
1,3-Phenylenediamine	4.88**	"	214.99	206.08
1,4-Phenylenediamine	6.08**	"	219.22	210.27
<i>N,N,N',N'</i> -Tetramethyl-1,4-phenylenediamine	6.35**	Potentiometric; thermodynamic	216.76	207.79
2-Aminophenol	4.72 <sup>+</sup>	Potentiometric	219.14	210.11
3-Aminophenol	4.17 <sup>+</sup>	"	213.13	204.18
4-Aminophenol	5.50*	"	215.92	206.87
2-Methoxyaniline	4.49	Potentiometric; thermodynamic; method of calculation	220.16	211.09
3-Methoxyaniline	4.20	"	214.26	205.03
4-Methoxyaniline	5.29	"	216.92	207.68

TABLE I. (Continued)

Compound	$pK_a$	Methods of $pK_a$ determination	$PA/4.184$ ; kJ/mol	
			$H_f$	$G_f$
2-Ethoxyaniline	4.47	Potentiometric; thermodynamic	219.48	209.55
3-Ethoxyaniline	4.17	"	214.73	205.83
4-Ethoxyaniline	5.25	"	217.58	208.64
3-Methylthioaniline	4.05	Potentiometric	213.46	203.88
4-Methylthioniline	4.40	"	213.79	205.31
2-Fluoroaniline	3.20	Spectrophotometric; thermodynamic	210.31	201.37
3-Fluoroaniline	3.59	"	208.50	199.62
4-Fluoroaniline	4.65	"	209.81	200.90
2-Chloroaniline	2.64	Indicator method; spectrophotometric; thermodynamic	211.54	202.63
3-Chloroaniline	3.34	"	211.02	202.07
4-Chloroaniline	3.98	"	211.81	202.86
2-Bromoaniline	2.60	Distribution method	211.08	202.12
3-Bromoaniline	3.51	"	210.35	201.41
4-Bromoaniline	3.91	"	210.19	201.23
2-Iodoaniline	2.60	Spectrophotometric; thermodynamic	213.67	204.26
3-Iodoaniline	3.61	"	211.96	202.98
4-Iodoaniline	3.78	"	212.13	203.18
3-Trifluoromethylaniline	3.5	Potentiometric	205.39	196.40
4-Trifluoromethylaniline	2.6	"	203.69	194.74
3-Aminobenzonitrile	2.76	Spectrophotometric; thermodynamic	206.19	197.35
4-Aminobenzonitrile	1.74	"	205.67	196.96
2-Aminobenzoic acid	2.11	Potentiometric	215.30	207.51
3-Aminobenzoic acid	3.12	"	209.36	200.34
4-Aminobenzoic acid	2.41	"	207.05	198.26
Methyl 2-aminobenzoate	2.23	Catalytic	216.93	209.11
Methyl 3-aminobenzoate	3.64	"	210.28	201.52
Methyl 4-aminobenzoate	2.38	"	208.50	200.01
2-Nitroaniline	-0.29	Indicator method; thermodynamic; method of calculation	205.35	196.55
3-Nitroaniline	2.50	"	202.24	193.11
4-Nitroaniline	1.02	"	198.78	190.16
3-Methylsulphonylaniline	2.68	Potentiometric	208.01	199.43
4-Methylsulphonylaniline	1.48	"	202.62	194.11
3-Aminobenzenesulphonic acid	3.65	"	207.40	198.67
4-Aminobenzenesulphonic acid	3.12	"	203.56	194.86

\*At 292 K, \*\*At 293 K, <sup>+</sup>At 294 K

## METHODS

The computations by means of the PM3 method<sup>11</sup> were performed using software from the MOPAC package<sup>12,13</sup> with complete geometric optimization (Broyden – Fletcher – Goldfarb – Shanno function minimizer)<sup>14</sup> involving the Thiel fast minimization algorithm.<sup>15</sup> The preliminary optimization was realized by the molecular mechanics (the MMX procedure)<sup>16</sup> using software from the PCMODEL package.<sup>16</sup> In the quantum chemical computations, a condition in the gradient norm not exceeding 0.084 kJ/mol Å was preset. In some cases, the sufficient decrease in gradient norm was achieved by means of abandonment of the Thiel fast minimization routine (the keyword NOTHIEL of the MOPAC package was applied) or by optimization with the Davidon – Fletcher – Powell method (keyword DFP),<sup>14</sup> as well as using combined approaches involving the keywords NOTHIEL and DFP.

In calculating the rotational contributions to the thermodynamic functions, the symmetry number was taken as unity. Linear regression analysis was performed at the confidence level of 0.95.

For computing clusters with water molecules included, the PM3 method was used, the HyperChem package HyperChem (TM), Hypercube Inc., 1115 NW 4th Street, Gainesville, Florida 32601, U. S. A. , and just the same computer. A minimal distance of 1.7 Å was assumed between the solute and water molecules.

## RESULTS AND DISCUSSION

It is reasonable to use semi-empirical quantum chemical methods to obtain rather simplified predictive quantitative relations.

For series of organic compounds belonging to different classes and possessing various functional groups, we validated a correctness of the most important thermodynamic and molecular characteristics reproduction the use of the MNDO, AM1 and PM3 methods,<sup>17–23</sup> as well as of electronegativity, inductive and mesomeric parameters of atomic groups.<sup>24,25</sup> Among the mentioned methods, the PM3 method seems to provide satisfactory results for obtaining the heats of formation of nitro derivatives<sup>11,17,19</sup> and dimethylsulphone.<sup>19</sup> Some of the molecular systems under study contain NO<sub>2</sub> or SO<sub>2</sub> groups. For this reason the PM3 method was selected for the purposes of this work.

The correctness of the quantum chemical computations performed in the present work was also confirmed by the reproduced standard gaseous-phase heats of formation ( $H_f^\circ$ ), entropies ( $S$ ), Gibbs energies of formation ( $G_f^\circ$ ), ionization potentials ( $I$ ), molecular dipole moments ( $\mu$ ) of anilines (Tables II–IV).

Furthermore, computations adequately convey the trends in the changes of the above properties over the aniline series. Thus, linear dependences were found:

$$P_{\text{exper}} = bP_{\text{theor}} \quad (1)$$

where  $P$  is any of the above mentioned values ( $m$  is the number of considered points,  $r$  is the correlation coefficient):

$P$	$m$	$b$		$r$
$H_f$	5	0.9797	0.0478	0.9909
$S$	5	0.9448	0.0525	0.9794
$G_f$	5	1.0238	0.0357	0.9980
$I$	13	0.8814	0.0118	0.9457
	43	1.0515	0.0639	0.9513

The correlations  $P_{\text{exper}} = bP_{\text{theor}}$  for  $P = H_f, S, \Delta G_f$  are not well substantiated, since each of them was established using only five points. That is why the meaning of the above dependences is not predictive. They provide an evidence for the correctness of the PM3 method evaluations made in this work.

TABLE II. Experimental<sup>3</sup> and PM3-computed values of standard heats of formation

Compound	$H_{f \text{ exper}}/4.184$ ; kJ/mol	$H_{f \text{ theor}}/4.184$ ; kJ/mol
Aniline	20.76	21.30
<i>N</i> -Methylaniline	20.4	20.68
<i>N,N</i> -Dimethylaniline	20.10	20.03
<i>N</i> -Ethylaniline	13.40	14.79
<i>N,N</i> -Diethylaniline	9.6	9.13

Experimental<sup>3</sup> and PM3-computed values of standard entropies

Compound	$S_{\text{exper}}/4.184$ ; J/mol K	$S_{\text{theor}}/4.184$ ; J/mol K
Aniline	76.28	75.83
<i>N</i> -Methylaniline	81.6	83.84
<i>N,N</i> -Dimethylaniline	87.5	91.09
<i>N</i> -Ethylaniline	84.1	91.04
<i>N,N</i> -Diethylaniline	92.4	103.02

Experimental<sup>3</sup> and PM3-computed values of standard Gibbs energies of formation

Compound	$G_{f \text{ exper}}/4.184$ ; kJ/mol	$G_{f \text{ theor}}/4.184$ ; kJ/mol
Aniline	39.84	40.51
<i>N</i> -Methylaniline	47.61	47.22
<i>N,N</i> -Dimethylaniline	55.26	54.12
<i>N</i> -Ethylaniline	49.58	48.89
<i>N,N</i> -Diethylaniline	62.72	59.09

The interrelation  $I_{\text{exper}} = bI_{\text{theor}}$  links experimental adiabatic and Koopmans theoretical ionization potentials. Thus it is not surprising that  $b$  value differs from unity considerably. The advantage of the last equation consists in the possibility to evaluate easily adiabatic potentials, the measurement of which is often difficult.

The relationship  $P_{\text{exper}} = b P_{\text{theor}}$  may be used for the prediction of dipole moments for newly synthesized anilines. On one hand, the accuracy of such correlations is

comparable to the semiempirical method errors. The latter are not random, but determined by the given molecules specificity differing from the peculiarities of the whole series of compounds. However, in this instance the sample comprises 43 single-type molecules, the dipole moments of which vary in the wide range from 0 to 6.33 D. So the correlation  $I_{\text{exper}} = b \cdot I_{\text{theor}}$  is statistically notable and reliable for prognosis.

TABLE III. Ionization potentials:measured adiabatically by the photoionization technique<sup>26</sup> and Koopmans<sup>27</sup> ones computed using the PM3 method

Compound	$I_{\text{exper}}/\text{eV}$	$I_{\text{theor}}/\text{eV}$
Aniline	7.70	8.61
2-Methylaniline	7.44	8.54
3-Methylaniline	7.50	8.57
4-Methylaniline	7.24	8.47
<i>N</i> -Methylaniline	7.34	8.53
<i>N,N</i> -Dimethylaniline	7.14	8.44
<i>N,N</i> -Diethylaniline	7.51*	8.37
3-Fluoroaniline	7.90	8.86
4-Fluoroaniline	7.82	8.74
2-Nitroaniline	8.27	9.16
3-Nitroaniline	8.31	9.29
4-Nitroaniline	8.34	9.42

\*Photoelectron spectroscopy

TABLE IV. Measured by the second Debye method<sup>28</sup> and PM3-computed values of dipole moments

Compound	$\mu_{\text{exper}}/\text{D}$	Conditions	$\mu_{\text{theor}}/\text{D}$
Aniline	1.54	Benzene; 298 K	1.30
2-Methylaniline	1.61	Benzene; 298 K	1.33
3-Methylaniline	1.49	Benzene; 298 K	1.26
4-Methylaniline	1.30	Benzene; 298 K	1.22
<i>N</i> -Methylaniline	1.64	Benzene; 298 K	1.24
2,6-Dimethylaniline	1.63	Benzene; 298 K	1.34
<i>N,N</i> -Dimethylaniline	1.55	Benzene; 298 K; hexane; 293 K 1.18	
<i>N,N</i> -Dimethyl-2-methylaniline	0.88	Benzene; 298 K	0.914
<i>N</i> -Ethylaniline	1.68	Benzene; 293 K	1.25
<i>N,N</i> -Diethylaniline	1.65	Benzene; 291 K	1.33
2-Aminobiphenyl	1.42	Benzene	1.23
4-Aminobiphenyl	1.74	Benzene; 298 K	1.39
1,2-Phenylenediamine	1.45	Benzene; 298 K	0.220
1,3-Phenylenediamine	1.8	Benzene; 298 K	0.457

TABLE IV. (Continued)

Compound	exper/D	Conditions	theor/D
1,4-Phenylenediamine	0	Benzene; 298 K	0.00544
<i>N,N,N',N'</i> -Tetramethyl-1,4-phenylene-diamine	1.33	Carbon tetrachloride; 293 K	1.93
2-Aminophenol	1.86	Dioxane; 298 K	1.39
3-Aminophenol	2.19	Dioxane	1.41
2-Methoxyaniline	1.50	Benzene; 198 K	1.66
3-Methoxyaniline	1.76	Benzene; 298 K	1.31
4-Methoxyaniline	1.80	Benzene; 298 K	1.60
4-Methylthioaniline	2.54	Benzene; 303 K	2.16
3-Fluoroaniline	2.22	Benzene; 298 K	2.30
4-Fluoroaniline	2.34	Benzene; 298 K	2.47
2-Chloroaniline	1.84	Benzene; 298 K	1.47
3-Chloroaniline	2.91	Benzene; 298 K	1.79
4-Chloroaniline	3.00	Benzene; 298 K	1.97
2-Bromoaniline	1.77	Benzene; 293 K	1.57
3-Bromoaniline	2.85	Benzene;p298 K	1.99
4-Bromoaniline	2.85	Benzene; 298 K	2.15
4-Iodoaniline	2.82	Benzene; 298 K	1.83
4-Aminobenzonitrile	5.02	Benzene; 298 K	4.65
2-Aminobenzoic acid	1.51	Dioxane	1.62
3-Aminobenzoic acid	2.70	Dioxane	2.35
4-Aminobenzoic acid	3.29	Dioxane	3.27
Methyl 2-aminobenzoate	1.0	Benzene; 293 K and 323 K; liquid; 373 K	1.36
Methyl 3-aminobenzoate	2.4	Benzene; 293–323 K; liquid; 373 K	1.77
Methyl 4-aminobenzoate	3.3	Benzene; 293–323 K; liquid; 373 K	2.70
2-Nitroaniline	4.38	Benzene; 298 K	4.88
3-Nitroaniline	4.91	Benzene; 298 K	5.70
4-Nitroaniline	6.33	Benzene; 298 K	6.64
3-Methylsulphonylaniline	5.11	Benzene; 298 K	4.99
4-Methylsulphonylaniline	6.09	Benzene; 298 K	5.69

The proton affinity was computed in accordance with the aforesaid formula<sup>1,2</sup> ( $PA = H_f$ ), as well as using the following expression ( $PA = G_f$ ):

$$PA = G_f(B) + G_f(H^+) - G_f(BH^+),$$

where the free energy of proton formation  $G_f(H^+)/4.184$  has the value 362.570 kJ/mol.<sup>3-5</sup>

To establish the relationships  $pK_a$  vs.  $PA$  and to evaluate the medium contribution to the anilines basicity, one should be sure that protonation of all the surveyed molecules occurs *via* the amine nitrogen. The latter is assumed usually, often by default.<sup>6–10</sup>

Aimed at more detailed elucidation of the anilines protonation site, proton affinities were computed for a few typical arylamines protonation by alternative basic centres (Table V). As one can see, even in the gas phase protonation by the amino group is preferential. Although, for 4-aminobenzoic acid and 4-nitroaniline the differences in enthalpies and free energies of proton affinity at the protonation *via* nitrogen and oxygen are comparatively small.

For the cations of 4-methoxyaniline (**I**), 4-aminobenzoic acid (**II**) and 4-nitroaniline (**III**) conjugate acids, by means of the PM3 method clusters were computed including the aforesaid molecular systems along with 107 water molecules.

The greater number ( $n$ ) of water molecules built in the cluster, up to 729 in cubic cell with 28.00 Å side, what corresponds to liquid water density,<sup>29</sup> the more adequately hydration is considered. The results presented in Table V show (similarly to Refs. 30 and 31) that at sufficiently large  $n$  quantity (107) a density of water molecules distribution in a cell approaches to this value for liquid state, even if the partial occupation of the cell volume by the species **I** – **III** is disregarded.

As Table V shows, for aqueous solutions the conclusion on preferential anilines protonation by the nitrogen atom remains valid. Moreover, the medium increases the difference between the anilines' **I** – **III** conjugate acids heats of formation (or which is just the same, between enthalpies of the compounds' **I** – **III** proton affinity) as compared to the gaseous phase.

Provided that the differences in the basicities of anilines are due to intramolecular factors, and the medium makes a constant contribution, the  $pK_a$  vs.  $PA$  dependences must be linear.

However, for the whole set of considered substances, the dependences  $pK_a$  vs.

$H_f$  and  $pK_a$  vs.  $G_f$  was not linear. Obviously, the medium has a differentiating effect upon the protolytic properties of the aniline series.

At the same time, if one excludes the experimental and computed data deviating most significantly from the linear trend toward positive (for *N,N*-dimethyl-2-methylaniline, *N,N*-diethylaniline, *N,N*-diethyl-2-methylaniline, *N-tert*-butylaniline) and negative (for  $XC_6H_5NH_2$  with  $X = 2-I, 2-COOH, 2-COOCH_3, 2-NO_2$ ) direction so the relations between  $pK_a$  and  $PA$  become noticeably closer to linear:

$$\begin{aligned} pK_a &= A + B \quad H_f \text{ (kJ/mol)} \\ m &= 55, \quad A = -35.24 \quad 8.33 \\ 4.184B &= 0.1848 \quad 0.0393 \text{ (mol/kJ)} \\ r &= 0.7919 \end{aligned} \quad (2)$$



$$\begin{aligned}
 \text{p}K_{\text{a}} &= A + B \quad G_{\text{f}} \text{ (kJ/mol)} \\
 m &= 55, \quad A = -33.56 \quad 8.15 \\
 4.184B &= 0.1846 \quad 0.0401 \text{ (mol/kJ)} \\
 r &= 0.7853
 \end{aligned} \tag{3}$$

The subsequent rejection of the data deviating substantially from the trend: toward positive direction for *N*-methylaniline, *N,N*-dimethylaniline, *N,N,N',N'*-tetramethyl-1,4-phenylenediamine, 4-fluoroaniline, toward negative direction for the systems  $\text{XC}_6\text{H}_5\text{NH}_2$  with  $\text{X} = 2,6\text{-(CH}_3)_2, 2\text{-tert-C}_4\text{H}_9, 2\text{-C}_6\text{H}_5, 2\text{-OCH}_3, 2\text{-OC}_2\text{H}_5, 2\text{-Cl}, 2\text{-Br}, 4\text{-CN}, 4\text{-COOCH}_3$ , results in rather improved linearity:

$$\begin{aligned}
 \text{p}K_{\text{a}} &= A + B \quad H_{\text{f}} \text{ (kJ/mol)} \\
 m &= 42, \quad A = -37.83 \quad 6.35 \\
 4.184B &= 0.1974 \quad 0.0300 \text{ (mol/kJ)} \\
 r &= 0.9031
 \end{aligned} \tag{4}$$

$$\begin{aligned}
 \text{p}K_{\text{a}} &= A + B \quad G_{\text{f}} \text{ (kJ/mol)} \\
 m &= 42, \quad A = -37.68 \quad 5.93 \\
 4.184B &= 0.2054 \quad 0.0292 \text{ (mol/kJ)} \\
 r &= 0.9135
 \end{aligned} \tag{5}$$

As can be seen, the molecules deviating from the linear correlations  $\text{p}K_{\text{a}}$  vs.  $PA$ , are predominantly those having *ortho* substituents in the aromatic ring.

The positive deviations of the data for *N*-alkyl anilines from the trend line can be explained by the considerable structural difference of the above compounds from primary aromatic amines.

If the effect of *ortho* substituents on the basicity of anilines can be explained by intramolecular steric factors, negative deviations from the dependences  $\text{p}K_{\text{a}}$  vs.  $PA$  should not occur. In addition, the  $\text{NH}_2$  group is relatively small and so the atomic groups in the *ortho* positions of the aromatic ring do not disturb considerably the orientation of the unshared electron pair of the amine nitrogen atom, favourable for conjugation with the  $\pi$ -system of the ring. On the other hand, steric demands of the proton are extremely low.<sup>32</sup>

Allowing for the discussion above, a reason for the *ortho*-effect may be thought of as an increase in the hydrophobicity of molecular fragments in the vicinity of the reaction centre, *i.e.*, the amine nitrogen atom.

Concerning the vicinity of the protonation centre, hydrophobic hydration is possible (observed commonly for molecular systems as a whole), which is related to the fact that due to the size of solute particles, the solute exerts a retarding effect on the translation movement of water molecules.<sup>33,34</sup> The space occupied by such a particle (in our case by bulky substituents and neighbouring atomic basins, including the reaction centre), the reaction centre becomes inaccessible for water molecules, which lead to so the called "barrier effect" and the particle is surrounded by a layer of more struc-

tured water (iceberg).<sup>33,34</sup> Hydrophobic hydration induces diminution of the medium polarity in the vicinity of the molecules (in our case, in the vicinity of molecular fragments), as well as a change in the prototropic properties of the medium within the local microenvironment of molecules (fragments). This change hinders proton transfer to the heteroatom.<sup>34,35</sup> The aforesaid effects cause the acid-base equilibrium in the system substituted aniline–anilinium ion to be displaced.

The decline of the hydrophilicity of the groups  $X = 2\text{-COOH}$ ,  $2\text{-COOCH}_3$ ,  $2\text{-NO}_2$  could be explained therewith by their involvement in intramolecular hydrogen bonds (IHB).<sup>8,9</sup> For example, the occurrence of IHB in 2-nitroaniline is the reason for the feasibility of its steam distillation, in contrast to the 4-nitro isomer.<sup>9</sup>

The data for  $X = 2\text{-COOH}$ ,  $2\text{-COOCH}_3$ ,  $2\text{-NO}_2$  do not obey the linear dependences  $\text{p}K_a$  vs.  $PA$  due, in part, to the obviously non-comprehensive suitability of the PM3 method for describing hydrogen-bonded molecular systems.

Within the set of data under question, there are linear relationships involving the  $\text{p}K_a$  and  $PA$  values for the compounds  $\text{XC}_6\text{H}_5\text{NH}_2$ , where  $X = \text{H}$ ,  $2\text{-CH}_3$ ,  $3\text{-CH}_3$ ,  $4\text{-CH}_3$ ,  $4\text{-C}_2\text{H}_5$ ,  $4\text{-CH}(\text{CH}_3)_2$ ,  $3\text{-C}_6\text{H}_5$ ,  $4\text{-C}_6\text{H}_5$ ,  $2\text{-NH}_2$ ,  $3\text{-NH}_2$ ,  $4\text{-NH}_2$ ,  $4\text{-H}$ ,  $3\text{-OH}$ ,  $4\text{-OH}$ ,  $3\text{-OCH}_3$ ,  $4\text{-OCH}_3$ ,  $3\text{-OC}_2\text{H}_5$ ,  $4\text{-OC}_2\text{H}_5$ ,  $3\text{-SCH}_3$ ,  $4\text{-SCH}_3$ ,  $2\text{-F}$ ,  $2\text{-Cl}$ ,  $3\text{-Cl}$ ,  $4\text{-Cl}$ ,  $2\text{-Br}$ ,  $3\text{-Br}$ ,  $4\text{-Br}$ ,  $3\text{-I}$ ,  $4\text{-I}$ ,  $3\text{-CN}$ ,  $4\text{-CN}$ ,  $3\text{-COOH}$ ,  $4\text{-COOH}$ ,  $3\text{-COOCH}_3$ ,  $4\text{-COOCH}_3$ ,  $3\text{-SO}_2\text{CH}_3$ ,  $4\text{-SO}_2\text{CH}_3$ , as well as for *N*-ethylaniline, *N*-isopropylaniline, *N,N,N',N'*-tetramethyl-1,4-phenylenediamine:

$$\begin{aligned} \text{p}K_a &= A + B \quad H_f \text{ (kJ/mol)} \\ m &= 39, \quad A = -58.26 \quad 8.74 \\ 4.184B &= 0.2929 \quad 0.0411 \text{ (mol/kJ)} \\ r &= 0.9209 \end{aligned} \tag{6}$$

$$\begin{aligned} \text{p}K_a &= A + B \quad G_f \text{ (kJ/mol)} \\ m &= 39, \quad A = -56.80 \quad 8.46 \\ 4.184B &= 0.2985 \quad 0.0415 \text{ (mol/kJ)} \\ r &= 0.9226 \end{aligned} \tag{7}$$

The above series contains many compounds included in the previous one, for which the equalities (4) and (5) are valid. The species belonging exclusively to the series described by the Eqs. (4) and (5) are: *N*-ethyl, 2-OH, 3-F, 4-F, 3-CF<sub>3</sub>, 4-CF<sub>3</sub>, 3-SO<sub>3</sub>H, 4-SO<sub>3</sub>H anilines. In contrast, *N,N,N',N'*-tetramethyl-1,4-phenylenediamine, along with 2-Cl, 2-Br, 4-CN, 4-COOCH<sub>3</sub> anilines enter only when the relations (6) and (7) are true.

For the Eqs. (4)–(7), the values of the correlation coefficient  $r$  can be regarded as satisfactory, since the comparison is made between the  $\text{p}K_a$  values in aqueous media and the characteristics of isolated molecules in the gaseous phase ( $H_f$ ,  $G_f$ ). The discrepancy in data originates mainly from just the neglect of the medium in the quantum chemical consideration.

The occurrence of alternative linear correlations of  $pK_a$  with  $PA$  confirms a differing contribution of the medium to the basicity of anilines and, at the same time, proves the existence of series, within which the medium contribution is more or less constant.

A measure of influence of constant medium component upon anilines basicity can be presented as: i) deviation of  $B$  value in the Eqs. (4)–(7) from a theoretical slope of dependence  $pK_a$  vs.  $G_f$  equal to  $4.184 (\ln 10 RT)^{-1} = 0.7330 \text{ mol/kJ}$  and being referred to gaseous phase; ii) absolute  $A$  value (equal to zero for gaseous phase).

#### CONCLUSION

Using the relations (1) and (4)–(7), the  $I$ ,  $\Delta$  and  $pK_a$  values for anilines can be predicted and so construct the compounds with the desired polar, acid-base properties and capability for ionization. The approach proposed in the present work for evaluating the  $pK_a$  values of *N*- and *ortho*-unsubstituted anilines, aimed at their molecular design, can be extended to other classes of compounds.

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#### ИЗВОД

##### АФИНИТЕТ ПРЕМА ПРОТОНУ АНИЛИНА У ГАСОВИТОЈ ФАЗИ: КВАНТНО ХЕМИЈСКА ПРОЦЕНА И ДИСКУСИЈА У СВЕТЛУ ЊЕГОВЕ БАЗИЧНОСТИ У ВОДИ

ALEXEI N. PANKRATOV, INNA M. UCHAEVA, SERGEI YU. DORONIN и RIMMA K. CHERNOVA

*Department of Chemistry, N. G. Chernyshevskii Saratov State University, 83 Astrakhanskaya Street, Saratov 410026, Russia*

Коришћењем РМЗ методе израчунате су енталпије и Гибсове енергије афинитета према протону ( $PA$ ) у гасовитој фази за анилин и његових 62 деривата који имају различите врсте електрон-донорских и електрон-акцепторских супституената у ароматском прстену и на атому азота. Нађено је да важе линеарне корелације типа  $pK_a$  vs.  $PA$ . Одступање података од линеарне релације за *ortho*-супституисане анилине дискутовано је у светлу могуће хидрофобне хидратације делова молекула уз центар протонације. Нађено је да важе линеарне зависности  $P_{\text{експ}} = bB_{\text{теор}}$  где је  $P$  стандардна ентропија, топлота стварања, Гибсова енергија стварања, први јонизациони потенцијал и молекулски диполни момент.

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