Comparison Study for the Physical and Chemical Properties of Aniline and its Derivatives

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Abstract

The aim of the present study was to investigate the effect of substituents on the phenyl ring of aniline which influence the amino pK_b depending on their position and electron-donating or electron-withdrawing nature. Theoretical physical properties of these substituents have been calculated by (AM1) and (PM3) method. These physical properties are steric energy, dipole moment, nitrogen charge, bond length, heat of formation, ionization potential, LUMO and electronic energy. The pK_b values have been correlated with the calculated parameters. Clearly showed that the ionization potential and bond length parameters are affected directly on the pKb values (R= 0.97).

الخلاصة

ان الهدف من هذه الدراسة هو تشخيص تاثير المعوضات على حلقة البنزين لمركب الانيلين من حيث تاثير قيمة (pK_b) بالاعتماد على الموقع ومن حيث طبيعة المجاميع الدافعة والساحبة. ان الصفات الفيزياوية النظرية للمعوضات تم حسابها بالاعتماد على طريقتي (AM1) و (PM3)، هذه الصفات المحسوبة هي طاقة الاعاقة وعزم القصور وشحنة ذرة النتروجين وطول الاصرة وحرارة التكوين وجهد التأين وقيمة (LUMO) والطاقة الالكترونية. تم ايجاد علاقة بين قيمة (pK_b) العملية مع القيم المحسوبة نظريا، اذ وجد ان جهد التأين وطول الاصرة ذات تاثير مباشر على قيمة (pK_b) العملية (R= 0.97).

Introduction

Acids, according to the Bronsted-Lowry theory of acids and bases; an acid is a substance capable of donating a proton, or hydrogen ion (H^+) to a base. While, a base is a substance that is capable of accepting a proton from an acid. The lone pair availability, is more a stronger bases. So, the amide ion is the strongest base since it has two pairs of non-bonding electrons compared to ammonia which only has one. Ammonium ion is not basic since no lone pair to donate as a base [1].

Basicity constant for amine can be measured its ability to accept the proton hydrogen atom from water as shown in the next equation:

$$R\text{-}\overset{\bullet\bullet}{N}H_2 + H\text{-}OH \rightleftharpoons R\text{-}NH_3^{+} + OH^{-} \qquad (1)$$

Then, the basicity constant (Kb) is calculated from:

$$Kb = \frac{[RNH_3^{+}][OH]}{[RNH_2]} \qquad (2)$$

AM1 and PM3 are the most methods used in the calculation because they gives the best relation with laboratories measurements especially for bond length. These calculations are not needed for a long time in comparison with ab initio method which has required sometimes several days to completing its calculations [2-4].

The basicity constant is defined as Kb (expressed similarly to the Ka) and it is a measure of base strength. So, pKa and pKb are used as a measure of the amine's basicity as pKa + pKb = pKw , where Kw is the ionization constant of water.

In previews studies, it have investigated the effect of several electron-donating and electron-withdrawing substituents on the basicity of a number of compounds contain amino group [5-8]. So, in this paper; we have studied the effect of the physical properties of (Cl, CH_3, NO_2, OCH_3 and NH_2) groups on the basicity of aniline; when they are ortho, meta or para to the original amino group. Theoretical foundation for modern chemistry was laid more than 70 years ago; and at this time it becomes possible to use this for understanding how electrons, atoms and molecules interact. Theoretical and empirical calculation methods like experimental or spectroscopic ones are helpful tools for elucidating structure and behavior of molecules, atoms and electrons [9].

Hammett constant (σ) [see equation (3)] have been relating the nature of substituents to their effects on chemical reactivity and other properties. The application of the Hammett equation is to the prediction of unknown rate and equilibrium constant, characterize the electronic behavior of substituents and give information about the mechanism of reactions. The pKb, rate of reaction and proton NMR shift have predicting by (σ) constant [10,11]. Potentiometric titration in non-aqueous media gives valuable information about the basicity or acidity of a compound [12-15].

It is well known that two major factors influence the basicity or acidity of molecules which are structure and solvent [16-21]. It is well known, that electron-withdrawing substituents are favoring quinoid resonance structures, while electron-donating substituents are favoring Kekule-type structure as shown below (see Fig. 1):

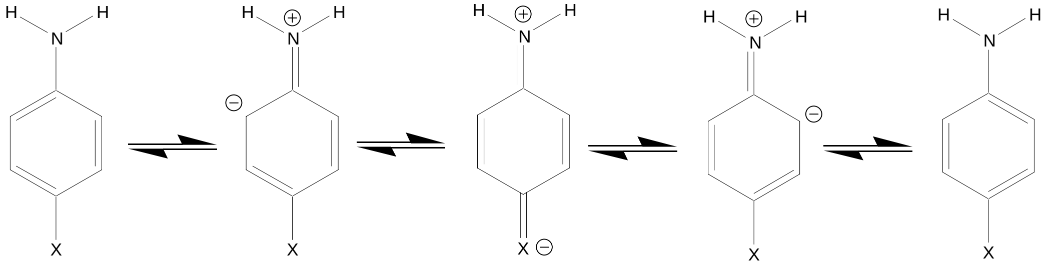

Fig. 1. Resonance structures of aniline compound

Methods

The AM1 and PM3 method has proved to be highly reliable for calculating the physical properties of molecules. The MOPAC program package, version 5.0 was used. In our semi-empirical AM1 and PM3 calculations we used each of these structures as the starting point for the energy minimization [22]. AM1 and PM3 method were used to calculate the physical properties of the substituents. MM2 method was used to find the steric energy of these substituents.

All calculations were performed on a Pentium IV, processor 2.4 MHz full cash computer. Hammett constants (σ) [23] and pKb[24] values were taken. The measurements and charts have been treated by using (spss version 11.0) and (Excel 2000). The regression sample expresses the relation between dependent variable and independent variable (or more). If the sample contains one independent variable, the regression is named simple regression, while it is named multiple regressions when containing more than one independent variable [25].

Results and Discussion

Generally, believed that the resonance effect in the para position is more grater that in the ortho position. It can be assumed that hydrogen-bonded ring formation makes the substances more stabilized. Clearly shown with comparing the steric energy between (o-CH_3) and (o-OCH_3).

Table 1 is the list of experimental pKb values for the substituted aniline, while Table 2 is the calculated parameters, steric energy (S.E.), heat of formation (H.F.), electronic energy (Elect.Ene.), dipole, ionization potential (ion.pot), LUMO level, nitrogen charge (Charge-N) and bond length [R(C-N)]. All the regressions statistics for ortho, meta and para were summered in Table 3.

Table 1. Hammett constants (σ) and experimental pKb of aniline derivatives

Substituents	K_b	pK_b	σ
H	4.2×10^{-10}	9.38	0
o-Cl	5.0×10^{-12}	11.30	0.20
m-Cl	3.0×10^{-11}	10.52	0.37
p-Cl	1.0×10^{-10}	10.00	0.23
o-CH_3	2.6×10^{-10}	9.59	-0.17
m-CH_3	5.0×10^{-10}	9.30	-0.07
p-CH_3	1.2×10^{-9}	8.92	-0.17
o-NO_2	6.0×10^{-14}	13.22	0.80
m-NO_2	2.9×10^{-12}	11.54	0.71
p-NO_2	1.0×10^{-13}	13.00	0.78
o-OCH_3	3.0×10^{-10}	9.52	-0.39
m-OCH_3	2.0×10^{-10}	9.70	0.12
p-OCH_3	2.0×10^{-9}	8.70	-0.27
m-NH_2	1.0×10^{-9}	9.00	-0.16
p-NH_2	1.4×10^{-8}	7.85	-0.66

The results show that electron-donating groups cause an increase of basicity compared with the pKb of the parent compound; the opposite holds for electron-withdrawing groups. The results of the calculated physical properties are presented in the table (2).

Table 2. Calculated results for substituents of aniline using AM1 (first row) and PM3 (second row) methods

Substituents	Method	S.E. (kcal/mol)	Dipole (Debye)	Charge(N)	R (C-N)A°
H	AM1	2.712	1.542	-0.3273	1.3998
	PM3	4.137	1.296	0.0708	1.4300
o-Cl	AM1	4.753	1.760	-0.3320	1.3929
	PM3	6.774	1.468	0.0771	1.4259
m-Cl	AM1	3.192	2.325	-0.3302	1.3971
	PM3	5.119	1.792	0.0752	1.4280
p-Cl	AM1	3.089	2.631	-0.3302	1.3966
	PM3	4.999	1.966	0.0753	1.4282
o-CH_3	AM1	4.124	1.560	-0.3252	1.4003
	PM3	6.082	1.334	0.0610	1.4308
m-CH_3	AM1	2.843	1.469	-0.3268	1.4005
	PM3	4.326	1.256	0.0698	1.4303
p-CH_3	AM1	2.859	1.445	-0.3255	1.4003
	PM3	4.336	1.227	0.0708	1.4303
o-NO_2	AM1	14.320	5.288	-0.3703	1.3634
	PM3	24.434	5.071	0.0819	1.4148
m-NO_2	AM1	23.509	5.942	-0.3329	1.3942
	PM3	22.787	5.696	0.0825	1.4274
p-NO_2	AM1	20.304	7.298	-0.3580	1.3783
	PM3	20.405	6.639	0.0968	1.4155
o-OCH_3	AM1	16.085	0.630	-0.3196	1.3979
	PM3	17.874	0.240	0.0758	1.4284
m-OCH_3	AM1	14.992	1.382	-0.3314	1.3973
	PM3	17.539	1.310	0.0717	1.4283
p-OCH_3	AM1	15.220	1.884	-0.3172	1.4041
	PM3	20.289	1.381	0.0704	1.4326
m-NH_2	AM1	8.077	0.770	-0.3294	1.4000
	PM3	11.011	0.459	0.0682	1.4297
p-NH_2	AM1	8.373	2.798	-0.3145	1.4049
	PM3	10.214	0.009	0.0693	1.4326

Continue….

Substituents	Method	H.F. (kca/mol)	Ion.Pot (eV)	LUMO (eV)	Elect.Energ (eV)
H	AM1	20.41	8.521	0.640	-4358.96
	PM3	21.22	8.609	0.418	-4358.96
o-Cl	AM1	13.02	8.622	0.286	-5613.10
	PM3	14.606	8.663	0.128	-5613.10
m-Cl	AM1	13.19	8.731	0.263	-5553.99
	PM3	14.32	8.760	0.119	-5553.99
p-Cl	AM1	12.99	8.576	0.293	-5540.48
	PM3	14.33	8.583	0.104	-5540.48
o-CH3	AM1	13.08	8.434	0.601	-5532.02
	PM3	12.92	8.542	0.409	-5532.02
m-CH3	AM1	12.91	8.470	0.607	-5473.52
	PM3	11.91	8.562	0.412	-5473.52
p-CH3	AM1	12.85	8.354	0.616	-5460.06
	PM3	11.94	8.465	0.395	-5460.06
o-NO2	AM1	20.60	9.070	-0.794	-8238.41
	PM3	13.36	9.289	-0.914	-8238.41
m-NO2	AM1	23.88	9.253	-0.950	-8094.73
	PM3	12.41	9.285	-1.053	-8094.73
p-NO2	AM1	21.42	9.266	-0.783	-8063.45
	PM3	10.56	9.423	-1.008	-8063.45
o-OCH3	AM1	-17.13	8.542	0.419	-7002.62
	PM3	-14.94	8.575	0.279	-7002.62
m-OCH3	AM1	-17.66	8.518	0.614	-6889.01
	PM3	-17.03	8.597	0.392	-6889.01
p-OCH3	AM1	-16.66	8.202	0.517	-6869.49
	PM3	-16.28	8.345	0.351	-6869.49
m-NH2	AM1	18.75	8.263	0.748	-5562.43
	PM3	18.84	8.402	0.458	-5562.43
p-NH2	AM1	19.89	7.906	0.643	-5546.30
	PM3	19.40	8.060	0.420	-5546.30

1. The Relations of pKb Values:

1.1 Hammett Constant (σ)

From the table (1), the electron donating substituents decrease the pKb's values while electron withdrawing substituents increase the pKb's. The Hammett substituents parameter (σ) quite well in predicting pKb for this set of aniline with:

$pKb = 3.312 (\pm 0.36) \times \sigma + 9.811 (\pm 0.15)$……(3)

$n = 15, \quad R = 0.929, \quad F = 82$

Here, [n] is the number of data included in the correlation, [R] is the correlation coefficient and [F] is the Fisher ratio. There were two substituted outliers from these set, o-Cl-aniline and o-OCH3-aniline (R= 0.959). A better relationship was obtained for the ortho position (R=0.939), meta (R=0.998) and para (R=0.971).

1.2 Nitrogen Charge (N):

The amino nitrogen charge was give a good correlation with aniline pKb's :

$pKb = -95.92 (\pm 12.54) \times [\text{Charge-N}] - 21.68 (\pm 4.16)$……….[AM1] (4)

n = 15, R= - 0.904, F = 58

Only o-Cl-aniline and m-NO_2-aniline substituents were outliers in this series. It was showed that the relationship were better for ortho and para derivatives (R= -0.937 and R= -0.989) than for the meta position (R= -0.756).

pKb = 152.87 (±30.15) × [Charge-N] – 1.277 (±2.25)...…….[PM3] (5)
n = 15, R= 0.814, F = 25

The author found a good correlation by excluding substituents of
o-NO2-aniline and o-CH3-aniline (R= 0.911).

1.3 LUMO Energy :

A better correlation was showed between LUMO energy with pKb values:

pKb = -2.339 (±0.34) × LUMO + 10.68 (±0.21)……………[AM1]
(6)
n = 15, R= - 0.884, F = 46

In this fit, m-NO_2-aniline, p-NH_2-aniline and p-OCH_3-aniline are out from this fit. The regression considered to (R= -0.950), (R= -0.945) and (R= -0.956) for ortho, meta and para derivatives.

pKb = -2.448 (±0.35) × LUMO + 10.25 (±0.19)…………….[PM3]
(7)
n = 15, R= - 0.884, F = 46

The same result has been found for m-NO_2-aniline, p-NH_2-aniline and p-OCH-aniline.

1.4 Ionization Potential Energy :

A good correlation between ionization potential and the pKb values of the substituents is found:

pKb = 3.796 (±0.43) × ion.pot. - 22.48 (±3.73)……………..[AM1] (8)
n = 15, R= 0.924, F = 76

We notice from the correlation that o-Cl-aniline, o-NO_2-aniline and p-NO_2-aniline substituents were not fit in with the other substituent. Meta and para substituents show a much better correlation with ionization potential (R= 0.976) and (R= 0.984) respectively than do the ortho substituents (R= 0.945).

pKb = 3.878 (±0.37) × ion.pot. – 23.54 (±3.24)……………..[PM3] (9)
n = 15, R= 0.944, F = 107

We notice that o-Cl-aniline and m-NO_2-aniline were not fit in with the other substituents (R= 0.983).

1.5 Bond Length:

Correlation of the bond length [R(C-N)] for all the substituted with pKb's values are:

pKb = -129.73 (±17.10) × [R(C-N)] + 191.10 (±23.86)………….[AM1]
(10)
n = 15, R= - 0.903, F = 57

The o-NO_2-aniline substituted was the only substituent which outlier from this fit. Ortho and meta substituents show a fair correlation (R= -0.950) and (R= -0.946) respectively in comparison with para substituted (R= -0.988).

pKb = -268.31 (±29.77) × [R(C-N)] + 393.13 (±42.50)…………[PM3]
(11)
n = 15, R= - 0.928, F = 81

o-Cl-aniline and m-NO_2-aniline were been showed outlier from this fit it. The overall correspondences are shown bellow (see Fig. 2).

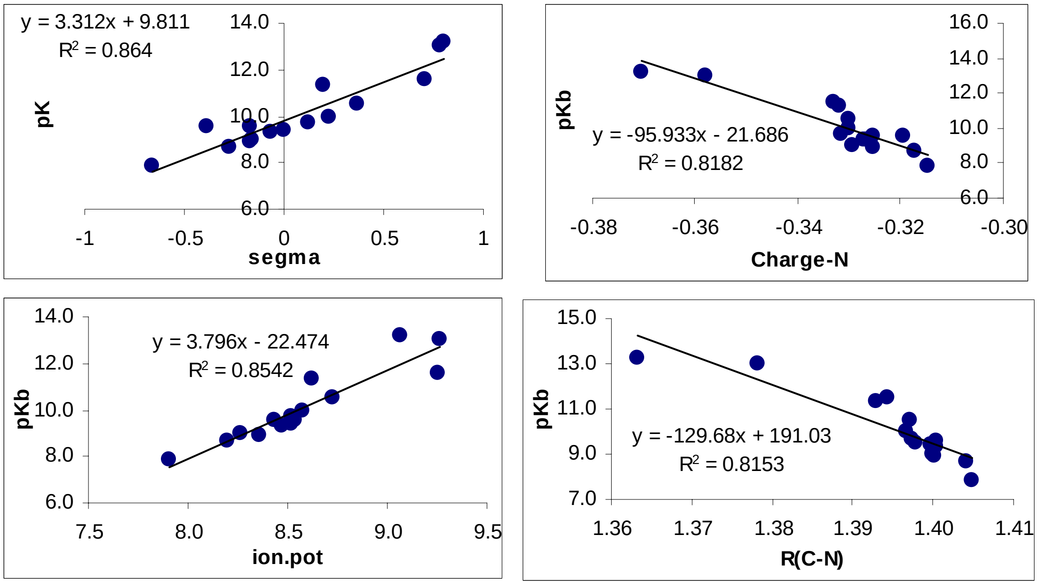

Fig. 2. Plots of pKb versus some physical parameters calculate by (AM1) method

2. The Relation of Hammett Constant (σ):

2.1 Bond Length R(C-N)

A fair correlation is found between the bond length R(C-N) and the (σ) values:

R(C-N) = -0.019 (±0.004) × σ + 1.396 (±0.001)…………….[AM1] (12)

n = 15, R= - 0.785, F = 20

The electron donating substituents (except o-OCH3) and the electron withdrawing (except m-NO2) show a better correlation with bond length R(C-N) (R= -0.900) and (R= -0.897) respectively.

R(C-N) = -0.009 (±0.002) × σ + 1.428 (±0.001)…………….[PM3] (13)

n = 15, R= - 0.807, F = 24

The same result were noticed for o-OCH$_3$-aniline and m-NO$_2$-aniline were not in fit with other substituents.

2.2 Ionization Potential Energy:

The ionization potential value was represent the lowest energy found to withdrawing the electron. A good correlation was found between (σ) and the ionization potential values of the amino group for this set of compounds:

Ion. Pot. = 0.814 (±0.08) × σ + 8.510 (±0.03)………[AM1] (14)

n = 15, R= 0.938, F = 96

Here, o-OCH$_3$-aniline was the only substituent which outlier from this fit, the correlation became better by removing its parameter from the correlation (R= 0.976).

Ion. Pot. = 0.816 (±0.08) × σ + 8.605 (±0.03)…………….[PM3] (15)

n = 15, R= 0.940, F = 100

The same result was shown for o-OCH$_3$-aniline (R= 0.966).

2.3 LUMO Energy:

LUMO value was representing the lowest energy found to accept the electron. The determined gave a LUMO values fair correlation with (σ) values:

LUMO = -1.159 (±0.19) × σ + 0.350 (±0.08)…………….[AM1]
(16)
n = 15, R= - 0.860, F = 37

The correlation was better (R= -0.933) by removing the (o-OCH_3) and (p-NH_2) substituents.

LUMO = -1.112 (±0.17) × σ + 0.158 (±0.07)……….[PM3]
(17)
n = 15, R= - 0.864, F = 38

The same result has been shown by remove o-CH_3-aniline and p-NH_2-aniline (R= - 0.932).

2.4 Nitrogen Charge (N):

The charge of nitrogen atom (Charge-N) exhibited good correlation with the Hammett constants (σ):

(Charge-N) = -0.028 (±0.004) × σ - 0.328 (±0.002)…...[AM1]
(18)
n = 15, R= - 0.845, F = 32

The m-NO_2-aniline substituent was outlier from this fit, and gave good correlation this value (R= -0.908).

(Charge-N) = 0.014 (±0.003) × σ + 0.073 (±0.001)…….[PM3]
(19)
n = 15, R= 0.760, F = 17

The correlation was better by removing o-OCH_3-aniline, p-NO_2-aniline and o-CH_3-aniline (R= 0.903).

3. Nitrogen Charge (N):

3.1 Ionization Potential Energy:

The fair correlation was obtained between the charge of nitrogen with ionization potential

Ion. Pot. = -19.87 (±4.57) × (Charge-N) + 1.995 (±1.51)…[AM1] (20)
n = 15, R= -0.769, F = 18

Both of (o-NO_2) and (m-NO_2) substituents were outlier from this fit, the correlation was better by removing these parameters (R= -0.891).

Ion. Pot. = 37.70 (±7.16) × (Charge-N) + 5.870 (±0.53)…….[PM3] (21)
n = 15, R= 0.825, F = 27

While (o-CH_3) and (p-NH_2) substituents were outlier from the fit, the correlation was better by removing these parameters (R= 0.895).

3.2 LUMO Energy :

The correlation between the charge of nitrogen with LUMO energy is calculated:

LUMO = 30.63 (±7.17) × (Charge-N) + 10.40 (± 2.37)………[AM1]
(22)
n = 15, R= 0.764, F = 18

Again, (m-NO_2) substituent was outlier from the fit, the correlation being better by removing this parameter (0.908).

LUMO = -57.78 (±9.81) × (Charge-N) + 4.36 (± 0.73)………[PM3] (23)
n = 15, R= - 0.852, F = 34

So, we notice that (o-CH_3), (o-NO_2) and (m-NO_2) were outlier from this fit (R= 0.986).

3.3 Bond Length R(C-N):

The charge of nitrogen atom served as a exceptionally good indicator of the aniline bond length R(C-N):

R(C-N) = 0.717 (±0.04) × (Charge-N) + 1.632 (± 0.01)………[AM1] (24)
n = 15, R= 0.972, F = 222

R(C-N) = - 0.532 (±0.10) × (Charge-N) + 1.467 (± 0.07)…….[PM3] (25)
n = 15, R= - 0.820, F = 26

Only (o-NO_2) substituent is outlier from this fit, the correlation was better by remove this parameter (R= -0.899).

Conclusions:

The electron donating substituents slightly increase the bond length R(C-N), whereas electron withdrawing substituents slightly decrease this bond length.

At the correlation between Hammett constant (σ) with the charge of nitrogen is calculated by AM1, the electron withdrawing substituents (except m-NO_2) gave better fit (R= -0.930) than the electron donating (except o-OCH_3) (R= -0.887).

Ortho value was having more value than meta and para values because the substituted was near to the amino group (-NH_2) which led to high steric. The steric energy value was arranged in the following for both AM1 and PM3 methods:

o-Cl-aniline > m-Cl-aniline ≈ p-Cl-aniline

o-CH_3-aniline > m-CH3-aniline ≈ p-CH_3-aniline

The basicity constant of nitro aniline value was arranged in the following:

m-NO_2 > p-NO_2 > o-NO_2

This means that the electron-withdrawing group was favoring meta position compared with ortho or para position. While, the basicity constant of methyl group is arranged as shown below:

p-CH_3 > m-CH_3

This means that the electron-donating group was favoring para position.

The multiple linear regression has been used for studying the effect of parameters on the basicity constant (pKb), by dependent (pKb) as a dependent variable and other physical properties parameters as independent variables. Using (Enter) method for the regression by entering two parameters (or more) from the physical properties parameters it is thought that these parameters were effected to the regression equation as shown below:

AM1

pKb = 438.64 + 2.973 (σ) + 1.25×10^{-2}(S.E.) + 3.59×10^{-2} (H.F.) – 5.66×10^{-4} (elect.ene) + 0.329 (dipole) + 2.850 (ion.pot.) + 4.167 (LUMO) + 188.1[Charge(N)] – 284.43[R(C-N)] -------- [R=0.986] (26)

PM3

pKb = 237.97 + 1.032 (σ) – 3.34×10^{-2}(S.E.) – 2.89×10^{-2} (H.F.) + 3.25×10^{-4} (elect.ene) – 0.314 (dipole) + 0.859 (ion.pot.) – 2.40 (LUMO) – 31.98 [Charge(N)] – 160.85 [R(C-N)] ---------[R=0.988] (27)

In general, decreasing the bond length led to decrease the speed of electron diffusion in the benzene rings. This phenomenon decreased the electron density around the nitrogen atoms of amino group ($-NH_2$), then led to increase the (pKb) value.

When using (stepwise) method which depends on entering all the variables to the regression equation at the calculations, then removing the inactive factor on the regression equation. The results show the same calculations depending on the (enter) method as shown in following equation:

AM1

pKb = 86.88 – 69.32 [R(C-N)] + 2.323 (ion.pot.) ------------[R=0.979] (28)

PM3

pKb = 176.66 – 130.66 [R(C-N)] + 2.300 (ion.pot.) -------- [R=0.974] (29)

The result by the two methods which are used in the regression, show that bond length [R(C-N)] and ionization potential (io.pot.) were effected directly in the regression equation on the pKb value. This means that two methods gives the same effect of the parameters on pKb values.

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