Study The Effect of Factors on the Rate Constant (K) for Some Substituted Benzyl-amine Using Theoretical Calculations

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Abstract: The computational calculations methods are applied for the determination of some benzyl-amine substituents. The logK at temperature 303K are used as dependent variables. While the other variables like HOMO, LUMO, Dipole moment, chemical potential, hardness, softness and electrophilicity are independent variables. AM1, PM3 and HF/STO-3G methods have been utilized to portend (logK) parameters. The fisher values is taken as a criterion for our system to predict the (logK) parameters.

Keywords: Rate Constant, Benzyl-amine, HOMO, LUMO

1 Introduction:

Many compounds were synthesized by treated with benzyl-amine[1-3] or coupling with benzyl-amine[4]. The reactivity of some compounds in the presence of different amine like benzyl-amine have been determinate. And the mechanism of de-oxygenated for the product was exanimate[5]. Complexes of benzylamine as ligand have been synthesis by researchers[6,7]. The instrumentals ^{1}HNMR, IR and UV-Vis spectroscopy have been applied to identify the ligand complexes[8,9]. Benzyl-amine used as a reagent to prepare compounds like Pyrrolidino. The voltammetric instrumental (cyclic voltammetry) was been used to measure and characterized the reactions[10].

Also, the transfer of proton in the substituted of benzyl-amine was proposed in the protic solvents[11]. The equipment of HPLC was utilized the basicity of benzyl-amine which generated from ortho-substituted of aromatic groups[12]. Te theoretical calculations were useful and applied in many kinds of research to evaluate the relationship between the physic-chemical parameters[13-16]. The Structure-activity relationships (SAR) and quantitative structure-activity relationships (QSAR) were used for the benzyl-amine derivatives to evaluate the correlation between the electronic effect[17,18].

Imines or Shiff bases complexes were produced by the oxidation coupling of benzyl-amine using the Co-catalyzed[19] or self-coupling[20]. B3PW91/6-31+G(d) method was used to calculate the physical parameters of the (2-benzyl-amino-1,4-naphthalene-dione) compound. Inter and intramolecular hydrogen bonding have been characterized[21]. Benzyl-amine was used to synthesize of compounds[22,23] which applied clinically to development of the anti-bacterial drugs[24-26]. Zero-order kinetic was noticed in the hydrogenolysis of benzyl-amine which lead to adsorption of this compound at the surface[27].

Semi-empirical determination MNDO-PM3 was used to predict the different amines like benzyl-amine depending on the charges of some atoms[28]. Spectroscopic and theoretical calculations methods have been applied to the determination of the rate constant for the addition of benzyl-amine depends on the Michael addition[29].

2 Computational Methods:

The theoretical of the calculations methods AM1, PM3 and HF/STO-3G have been carried out by Chembio office 13 package. First, the model was minimized by MM2 to reach the best configuration depending on the less steric energy and more stable. Later, the model was determined by the other methods AM1, PM3 and HF/STO-3G. So, the physical properties of the substituted are calculated and tabulated to compare with the others.

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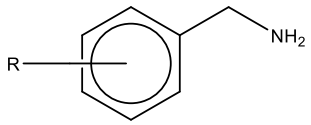
SPSS program was applied as a statistical method to compute and calculate the parameters. Single and multiple linear regression were used to determine the correlation between the practical values as dependent with calculated parameters as an independent.

3 Results and Discussion:

Figure (1) represents the structure of the derivative of benzyl-amine compounds. While table (1) listed the practical results of logK and Hammett standard values for benzyl-amine groups**[30]**.



Benzylamine

Figure 1. Benzyl-amine structure

Table1. Segma and rate constant values for derivatives benzyl-amine at temperature 303K

Substituent	Segma	Log 303K
H	0	1.279
m-CF3	0.43	0.262
m-CH3	-0.07	1.412
m-F	0.34	0.610
m-I	0.35	0.679
m-NH2	-0.16	1.599
m-OCH3	0.12	1.217
p-Br	0.23	1.000
p-CF3	0.54	0.107
p-Cl	0.23	1.124

Tables (2-4) were presented the physical properties of the substituted of the benzyl-amine which the AM1, PM3 and HF/STO-3G have been applied.

Table 2. Physico-chemical parameters for benzyl-amine substituted using AM1 method

Benzyl amine	log 303K	H.F	HOMO	Dipole	LUMO	Chemical potential	Hard-ness	Soft-ness	Electro-philicity
H	1.279	19.68	-9.351	1.466	0.414	-4.469	4.883	-3.883	2.045
m-CF3	0.262	-137.29	-9.985	2.798	-0.269	-5.127	4.858	-3.858	2.705
m-CH3	1.412	11.69	-9.291	1.103	0.459	-4.416	4.875	-3.875	2.000
m-F	0.610	-25.54	-9.489	1.442	0.102	-4.693	4.795	-3.795	2.297
m-I	0.679	35.81	-9.559	1.289	0.033	-4.763	4.796	-3.796	2.365
m-NH2	1.599	18.25	-8.564	1.700	0.500	-4.032	4.532	-3.532	1.794
m-OCH3	1.217	-20.87	-9.106	2.620	0.284	-4.411	4.695	-3.695	2.072
p-Br	1.000	24.46	-9.416	2.141	-0.039	-4.727	4.688	-3.688	2.383
p-CF3	0.107	-137.17	-10.035	4.080	-0.352	-5.194	4.842	-3.842	2.786
p-Cl	1.124	12.50	-9.370	2.007	0.049	-4.661	4.710	-3.710	2.306

Table 3. Physico-chemical parameters for the benzyl-amine substituted using PM3 method

Benzyl amine	log 303K	H.F	HOMO	Dipole	LUMO	Chemical potential	Hard-ness	Soft-ness	Electro-philicity
H	1.279	21.84	-9.361	1.253	0.296	-4.532	4.828	-3.828	2.127
m-CF3	0.262	-136.69	-9.700	2.654	-0.454	-5.077	4.623	-3.623	2.788
m-CH3	1.412	12.51	-9.310	1.024	0.306	-4.502	4.808	-3.808	2.108
m-F	0.610	-21.80	-9.540	1.316	-0.028	-4.784	4.756	-3.756	2.406
m-I	0.679	43.13	-9.041	0.964	-0.442	-4.742	4.300	-3.300	2.614
m-NH2	1.599	19.80	-8.616	1.533	0.334	-4.141	4.475	-3.475	1.916
m-OCH3	1.217	-16.07	-9.125	1.213	0.242	-4.441	4.683	-3.683	2.106
p-Br	1.000	29.46	-9.517	1.972	-0.040	-4.778	4.738	-3.738	2.409
p-CF3	0.107	-136.63	-9.731	3.868	-0.526	-5.128	4.602	-3.602	2.857
p-Cl	1.124	15.05	-9.284	1.772	-0.013	-4.648	4.635	-3.635	2.331

Table 4. Physico-chemical parameters for the benzyl-amine substituted using HF/STO-3G method

Benzyl amine	log 303K	H.F	HOMO	Dipole	LUMO	Chemical potential	Hard-ness	Soft-ness	Electro-philicity
H	1.279	-320.78	-0.271	1.496	0.270	0.000	0.271	0.729	7.39e-8
m-CF3	0.262	-651.75	-0.287	1.944	0.245	-0.021	0.266	0.734	8.47e-4
m-CH3	1.412	-359.37	-0.265	1.247	0.272	0.003	0.268	0.732	2.10e-5
m-F	0.610	-418.24	-0.263	1.429	0.261	-0.001	0.262	0.738	1.69e-6
m-I	0.679	-7170.90	-0.248	1.764	0.255	0.003	0.252	0.748	2.28e-5
m-NH2	1.599	-375.11	-0.237	2.417	0.271	0.017	0.254	0.746	6.01-4
m-OCH3	1.217	-433.20	-0.243	0.801	0.269	0.013	0.256	0.744	3.32e-4
p-Br	1.000	-2864.88	-0.256	2.733	0.254	-0.001	0.255	0.745	3.21e-6
p-CF3	0.107	-651.75	-0.288	3.118	0.242	-0.023	0.265	0.735	9.97e-4
p-Cl	1.124	-774.79	-0.280	3.748	0.244	-0.018	0.262	0.738	6.32e-4

Tables (5-7) were displayed the comparison between calculated physico-chemical parameters with experimental values in different methods of calculations.

Table 5. Bivariate correlation for the benzyl-amine substituted using AM1 method

AM1	Log 303K	Sigma	Dipole	HOMO	LUMO	Chem. Potential	Hard-ness	Soft-ness	Electro-philicity
log303K	1								
Sigma	-0.961	1							
Dipole	-0.625	0.608	1						
HOMO	0.909	-0.879	-0.532	1					
LUMO	0.924	-0.952	-0.716	0.863	1				
Chem. Potential	0.947	-0.941	-0.630	0.976	0.952	1			
Hardness	-0.486	0.392	0.053	-0.739	-0.297	-0.576	1		
Softness	0.486	-0.392	-0.053	0.739	0.297	0.576	-1.000	1	
Electro-philicity	-0.949	0.953	0.687	-0.937	-0.985	-0.990	0.457	-0.457	1

Table 6. Bivariate correlation for the benzyl-amine substituted using AM1 method

PM3	Log 303K	Sigma	Dipole	HOMO	LUMO	Chem. Potential	Hard-ness	Soft-ness	Electro-philicity
log303K	1								
Sigma	-0.961	1							
Dipole	-0.701	0.641	1						
HOMO	0.736	-0.708	-0.598	1					
LUMO	0.927	-0.927	-0.640	0.542	1				
Chem. Potential	0.947	-0.931	-0.705	0.877	0.879	1			
Hardness	0.202	-0.231	-0.046	-0.476	0.481	0.005	1		
Softness	-0.202	0.231	0.046	0.476	-0.481	-0.005	-1.000	1	
Electro-philicity	-0.966	0.954	0.697	-0.711	-0.976	-0.961	-0.279	0.279	1

Table 7. Bivariate correlation for the benzyl-amine substituted using AM1 method

HF/STO	Log 303K	Sigma	Dipole	HOMO	LUMO	Chem. Potential	Hard-ness	Soft-ness	Electro-philicity
log303K	1								
Sigma	-0.961	1							
Dipole	-0.208	0.307	1						
HOMO	0.616	-0.571	-0.416	1					
LUMO	0.777	-0.852	-0.709	0.680	1				
Chem. Potential	0.742	-0.746	-0.578	0.946	0.881	1			
Hardness	-0.143	0.013	-0.078	-0.749	-0.025	-0.493	1		
Softness	0.143	-0.013	0.078	0.749	0.025	0.493	-1.000	1	
Electro-philicity	-0.433	0.381	0.543	-0.483	-0.596	-0.573	0.112	-0.112	1

The employed of the equations to calculate the logK theoretically depends on the calculated physical properties. The multiple linear regression method as the statistical method was used to evaluate and predicted the practical values. The equations showed different methods of the calculations AM1, PM3 and HF/STO-3G. For each theoretical method, two statistical methods (enter and stepwise) were applied to predicted the values.

AM1:
Enter Method:
logK=2.277–2.600 (segma) + 0.086 (dipole) – 18.879 (LUMO) + 9.366 (Hardness) – 19.087 (Electro-philicity)
R = 0.993 , St.error = 0.084 , F = 60.64

Stepwise Method:
logK = 1.352 – 2.107 (segma)
R = 0.961 , St. error = 0.145 , F = 97.13

PM3:
Enter Method:
logK = 3.949 – 1.742 (segma) + 0.015 (dipole) – 12.367 (Chempotential) – 6.643 (Hardness) – 12.546 (Electrophilicity)
R = 0.987 , St. error = 0.121 , F = 29.30

Stepwise Method:
logK = 4.558 – 1.534 (electrophilicity)
R = 0.966 , St. error = 0.135 , F = 111.90

HF/STO-3G:

Enter Method:
logK = -101.535 – 2.602 (segma) - 0.018 (dipole) – 124.587 (HOMO) – 42.353 (LUMO) +150.817 (Chemical potential) + 110.445 (Softness) – 251.18 (Electrophilicity)
R = 0.984 , St. error = 0.188 , F = 8.617

Stepwise Method:
logK = 1.352 – 2.107 (segma)
R = 0.961 , St. error = 0.145 , F = 97.13

Table (8) appeared the predicted values of the logK which calculated in different theoretical methods. Also, the correlation coefficient (R), the standard error and the fisher values have been determined.

Table 8. The predicted of logK for the benzyl-amine substituted using different methods of calculations

		AM1		PM3		HF/STO-3G	
	Practical	Enter	stepwise	Enter	stepwise	Enter	stepwise
H	1.279	1.288	1.352	1.256	1.295	1.252	1.352
m-CF3	0.262	0.339	0.446	0.341	0.281	0.386	0.446
m-CH3	1.412	1.372	1.499	1.379	1.325	1.446	1.499
m-F	0.610	0.666	0.636	0.759	0.867	0.626	0.636
m-I	0.679	0.631	0.615	0.629	0.547	0.803	0.615
m-NH2	1.599	1.612	1.689	1.697	1.619	1.684	1.689
m-OCH3	1.217	1.252	1.099	1.152	1.327	1.063	1.099
p-Br	1.000	1.020	0.867	0.967	0.862	1.088	0.867
p-CF3	0.107	0.047	0.214	0.068	0.175	0.098	0.214
p-Cl	1.124	1.021	0.867	1.028	0.983	0.989	0.867
R		0.993	0.961	0.987	0.966	0.980	0.961
St. error		0.060	0.145	0.085	0.135	0.104	0.145
Fisher value		605.85	97.04	296.59	112.00	194.62	97.04

While table (9) was showed the percent error of the parameters compare with the practical values. This (%error) values were calculated depends on the following equation :

$$Percent = \frac{theoretical - experimental}{theoretical} x100$$

Table(9): Percent error for predicted benzyl-amine derivatives

	AM1 (%error)		PM3 (%error)		HF/STO-3G (%error)	
	Enter	stepwise	Enter	stepwise	Enter	stepwise
H	0.68	5.42	-1.79	1.24	-2.13	5.42
m-CF3	22.64	41.15	22.97	6.74	31.92	41.15
m-CH3	-2.92	5.86	-2.34	-6.56	2.36	5.86
m-F	8.52	4.09	19.74	29.71	2.64	4.09
m-I	-7.62	-10.56	-7.99	-24.13	15.37	-10.56
m-NH2	0.84	5.35	5.80	1.24	5.07	5.35
m-OCH3	2.77	-10.76	-5.70	8.28	-14.51	-10.76
p-Br	1.94	-15.29	-3.39	-16.01	8.05	-15.29
p-CF3	-127.85	49.95	-56.88	38.71	-9.50	49.95
p-Cl	-10.08	-29.57	-9.37	-14.37	-13.67	-29.57
Average	-11.11	4.56	-3.90	2.49	2.56	4.56

Figures (2) showed the fisher values of the benzyl-amine derivatives which determination at different methods of the calculations and different statistical methods. While figure (3) was presented the average of the percent error (%error) for all methods and at different statistical methods.

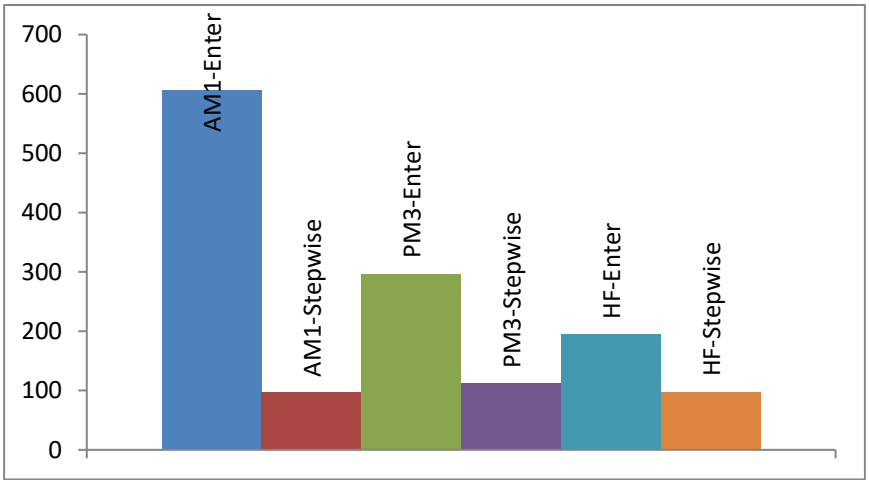


Fig 2. Fisher values calculated at different methods

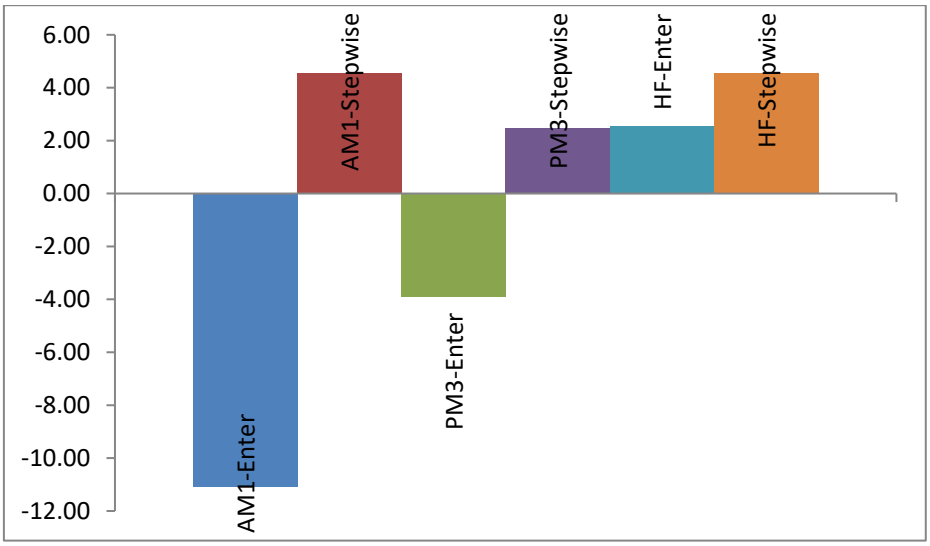


Fig 3. Average parameters at various methods of calculation

4 Conclusions:

Different variations of the substituted of benzyl-amine compounds were determined theoretically using different methods. The correlation between the predicted values and the practical showed excellent correlations. The equations for each method AM1, PM3 and HF/STO-3G were given a model to predicted the (logK) data. Finally, the fisher values or the (%error) data were an indicated parameter to calculated or predicted the practical data depends on the model or on the used methods.

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