Tikrit Journal of Pure Science Vol. 31 (1) 2026

DOI:https://doi.org/10.25130/tjps.v31i1.1907

IRAQI
Academic Scientific Journals

Tikrit Journal of Pure Science
ISSN: 1813 – 1662 (Print) --- E-ISSN: 2415 – 1726 (Online)

Journal Homepage: https://tjpsj.org/

Tikrit Journal
of Pure Science

Theoretical Calculation of Hammett Constants for Benzoic Acid and Its Derivatives Using AM1-DFT Method

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Received: 13 Feb. 2025 **Received in revised forum:** 18 Apr. 2025 **Accepted:** 23 Apr. 2025
Final Proofreading: 7 Jul. 2025 **Available online:** 25 Feb. 2026

ABSTRACT

The Hammett equation constants were calculated theoretically by statistically correlating the practical Hammett equation constants for these compounds with several theoretically calculated structural properties. Two quantum-mechanical methods were used to calculate the structural properties. The experimental method (AM1) used the basic process (DFT), and the calculated structural variables were divided into two types. The first is the inductive, the energies of bond and charge distributions on atoms. In contrast, the second type includes the energy variables, which include the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), hardness (ŋ), and total energy (E). The single- and double-regression analyses were performed using the statistical analysis program (SPSS). The relationship between the theoretically calculated variables and the practical Hammett equation constants was evaluated through the correlation coefficients (R2). In a single regression analysis, several variables were found to strongly correlate with the practical Hammett equation constants, with the strongest being the charge on the oxygen atom at position 9 adjacent to the carbonyl group (C=O). By conducting the double regression analysis, we obtained the best correlation strength of the theoretically calculated variables with the values of the practical Hammett equation constants and the values of the correlation coefficients (R2) for the best two variables for each of the four methods gave the highest value of the correlation coefficient R2 = 1 through the variables (C6 + C7) because they are among the factors affecting the values of (σ).

Keywords: Computational Chemistry, Hammett Equation, Carboxylic Acid.

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Tikrit Journal of Pure Science Vol. 31 (1) 2026

DOI:https://doi.org/10.25130/tjps.v31i1.1907

الحساب النظري لثوابت هامت لحامض البنزويك ومشتقاته باستخدام طرق AM1-DFT

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الملخص

تم حساب ثوابت معادلة هاميت نظريًا من خلال ربط قيم ثوابت معادلة هاميت العملية لهذه المركبات إحصائيًا مع العديد من الخصائص البنيوية المحسوبة نظريًا. تم حساب الخصائص البنيوية بطريقتين ميكانيكيتين كميتين. تضمنت الطريقة التجريبية (AM1) العملية الأساسية (DFT)، حيث تضمنت المتغيرات البنيوية المحسوبة نوعين من المتغيرات. الأول هو المتغيرات الاستقرائية أو البنيوية، طاقات الروابط والشحنات على الذرات. في المقابل، يتضمن النوع الثاني متغيرات الطاقة، والتي تضمنت أعلى مدار جزيئي مشغول (HOMO) وأدنى مدار جزيئي غير مشغول (LUMO)، والصلابة (ŋ)، والطاقة الكلية (E). تم إجراء تحليلات الانحدار الأحادي والمزدوج بواسطة برنامج التحليل الإحصائي (SPSS). وتم تقييم العلاقة بين المتغيرات المحسوبة نظرياً وثوابت معادلة هاميت العملية من خلال معاملات الارتباط (R2). ومن خلال تحليل الانحدار الأحادي، وجد أن عدة متغيرات ترتبط بقوة بقيم ثوابت معادلة هاميت العملية، وكان أقوى هذه المتغيرات الشحنة على ذرة الأكسجين رقم 9 المجاورة لمجموعة الكاربونيل (C=O). ومن خلال إجراء تحليل الانحدار المزدوج، حصلنا على أفضل قوة ارتباط للمتغيرات المحسوبة نظرياً مع قيم ثوابت معادلة هاميت العملية وقيم معاملات الارتباط (R2) لأفضل متغيرين لكل من الطرق الأربع أعطت أعلى قيمة لمعامل الارتباط R2 = 1 من خلال المتغيرات (C6 + C7) لأنها من العوامل المؤثرة على قيم (σ).

INTRODUCTION

Hammett Equation

The Hammett Equation is one of the most important mathematical relationships used to study the effect of substituent groups on reaction rates. It links the chemical equilibrium constant (K) for the dissociation or ionisation of the substituent groups of benzoic acid in the meta and para positions to the reaction rate constant (k) for the reaction under study. (1, 2).

The following mathematical relationship gives Hammett's Equation:

$\log k/k_o = \rho\ \sigma$ -----(1)

k -: is the reaction rate constant for the substituted compound under study.

ko-: is the reaction rate constant for the unsubstituted compound under study.

ρ-: is a constant that can be practically calculated from the equation of the straight line when drawing between the values of log k/k_o versus the values of (σ) since the slope value (slope = ρ) and its value is a measure of the sensitivity of the reaction towards electronic changes, as the speed of reactions that are the value of ρ is positive when it is replaced by pulling groups, but if the value of ρ is negative, the speed of chemical reactions increases when the replacements are driving groups. The constant ρ also provides information about the nature of the reaction, its mechanism, and the specific step for the reaction rate.

The sign (ρa, ρb) means that the reaction centre has a positive charge or that the speed of that reaction increases in the presence of driving groups, i.e., the compound is activated by the presence of driving groups in the two positions (meta, para). The sign (ρc, ρd) means that the reaction centre has a negative charge and is accelerated by pulling groups. The value of (ρa, ρd) means that the sensitivity of these reactions is very high towards electronic changes Fig. 1.

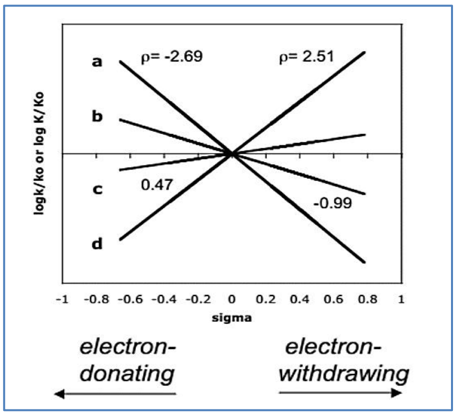


Fig. 1: The constant value (Rho) and its relationship to the sensitivity of the reaction center

The constant σ (sigma) is known as the substituted group constant. It is calculated from the dissociation constant of unsubstituted benzoic acid (K_o) and the dissociation constant of substituted benzoic acid (K) through the equation

$\log k/ko = \rho\sigma$ ------(2)

K= substituted benzoic acid dissociation constant

K_o= unsubstituted benzoic acid dissociation constant

The value of sigma (σ) is usually from (+1) to (-1) as this value depends on the ability of the substitutes to withdraw electrons from the reaction centre or push them to it compared to hydrogen in unsubstituted benzoic acid, and as is known, increasing the stability of the negative ion resulting from the dissociation of the acid increases its acidity. Hence, the presence of groups the puller in the two positions (meta and para) makes the negative ion resulting from the decomposition of benzoic acid more stable and thus more acidic, while the pushing groups in the two positions (meta and para) reduce the stability of the ion resulting from the decomposition of benzoic acid and thus reduce the acidity of the acid compared to the unsubstituted benzoic acid. On this basis, the dissociation constant for benzoic acid substituted with pulling groups is higher than the dissociation constant for unsubstituted benzoic acid. Thus, the value of Sigma (σ) is greater than zero for the pulling substituents. For the same reason, it is negative for pushing substituents. According to the following equation (3-8).

Computational chemistry is an important branch of physical chemistry and quantum chemistry (theory), including quantum mechanics and molecular mechanics. It is used to determine the most important properties of compounds by measuring selected variables and comparing the results with those from practical methods. To analyze, diagnose and support experiments of practical applications and basic chemistry research(9).

AM1 Method

Austin's method (AM1) is a unique semi-empirical method due to its widespread use among chemists. Also, it provides highly accurate results and is widely used in most quantum-chemical procedures. The (AM1) method is an extension of the (MINDO) method. (10).

The German scientist Miguel Dewar was the first to develop Austin's method in 1985. It is a method for quickly calculating the energy and formation of organic compounds (11).

Density Function Theory (DFT)

It is a function in which the solution of a function produces another function, and is considered one of the modern methods in quantum chemistry. (12, 13).

This theory was developed by the researchers (Hohenberge-Kohn) in 1964, and it was widely used and later became one of the basic theories for analytical methods. (14).

It is often used in theoretical calculations and computer-aided programs. (14).

Carboxylic acids are among the strongest organic acids. They contain the carboxyl group (OH) and the carbonyl linked together. The carboxyl group has three polar bonds: the double bond (C=O), the single bond (C-O), and the single bond (O-H).

They are called aromatic acids because their group is linked to an aromatic ring, as in benzoic acid and its derivatives. These acids are classified according to the hydroxyl group (OH) (15, 16).

A- Monocarboxylic acids
B- Dicarboxylic acids
C- Tricarboxylic acids

The carboxyl group may also be linked to a successive system, which pulls the electronic density away from the carboxyl group (COOH) and, in turn, increases the stability of the molecule and thus increases its acidity (pKa) (17).

MATERIALS AND METHODS

Practical part

Theoretical calculations:

Through theoretical calculations using quantum mechanics (Chem. Office). and the program (Gaussian program Gauss View (5.0.8), Gaussian 09), which contains a huge amount of important information, and through which important calculations can be made to obtain better results (18).

Among the conditions for working in these programs' fields are: - The personal and available calculator must have high specifications, as these programs require advanced computers to complete the work quickly and bypass determinants such as the size of the molecule, the number of atoms, and others.

To find the best and closest values for the constants of the Hammet equation for benzoic acid and its substitutes, the following methods were used (DFT, AM1) to find the best value close to its practical value.

The basic group can be defined as a set of functions used to describe atomic orbitals, as the linear combination of these angular functions and the basic group forms molecular orbitals. Molecular orbitals are classified using advanced mathematical equations derived from the solution of the famous Schrödinger equation, which explains the atomic orbitals of the hydrogen atom.

The orbitals derived from mathematical equations are known as Gaussian orbitals, and they are used to accurately describe the wave function in theoretical calculations that reveal the shapes of molecular orbitals.

The basic Pople group is one of the most widely used groups in molecular orbital theory to describe the state of an electron. This type of basic group is symbolized by the symbol (6-31G). The number 6 indicates the electrons in the inner orbitals; their properties are calculated and studied by (6) packages of the main orbital equations (GTO). In contrast, the number (31) is specific to the electrons of the outer orbital, as it is calculated and described by two packages: the first is from three packages of (GTO) specific to describing the principal quantum number (n), while the second package of (GTO) is only one and is specific to the angular quantum number (L). There are other Popple groups represented by the (6-311G) basis set that can calculate the magnetic quantum number (m) of the outer-shell electrons. With more than one type of basic group, it is widely used in theoretical studies of chemical molecules. Other groups are (4-22G,6-21G,6-311G,7-41G,4-31G,3-21G).

Statistical analysis

The statistical analysis of the study was conducted using SPSS. Thus the analysis was carried out between the variables obtained from the theoretical calculations with the values of the Hamit equation constants for benzoic acid and its substitutes that we obtained from the literature, and by relying on the values of the correlation coefficient (R) as a measure for this purpose because it represents a measure of the strength of the relationship, as the variables were studied in general with the Hamit equation constants by deletion and insertion until the study to a specific number of variables because its correlation coefficient was acceptable to some extent, as the variables studied in the end included the variables of physical charge and the lengths of the bonds and energy.

(Homo, Lomo, w, n, μ, &, HF, Dip, SE, Dip2, ΔH, O9-H15, C7-O9, C7-C6, C7=O8, C1, C2, C3, C4, C5, C6, C7, O9, O10).

The most important steps that can be carried out during the application of the (SPSS) program for the variables with each other and with the constants of the Hamet equation for benzoic acid and its substitutes, in the four ways are as follows: -

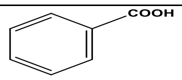
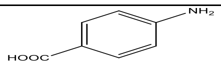
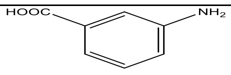
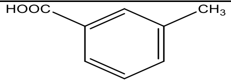
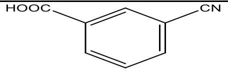
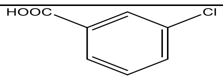
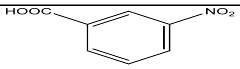
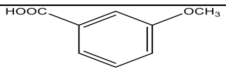
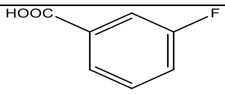
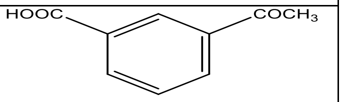
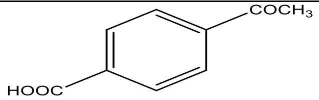
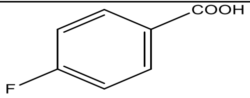
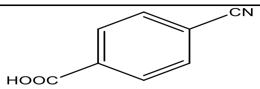
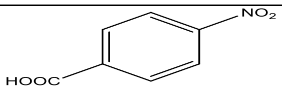
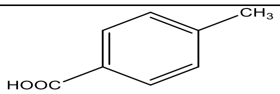
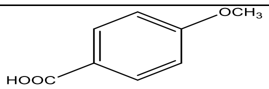
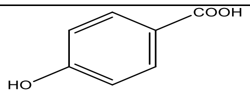
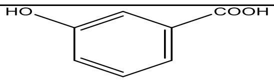
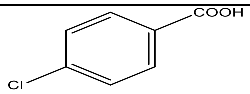
1- Entering the physical variables in succession, and they are considered non-dependent variables, while the constants of the Hamet equation are considered dependent.

2- Analyzing via SPSS (Linear + regression + analysis) for each variable, and from it we take (R) the correlation

3- After giving the commands, we get the value of the coefficient. The variable that can have an impact on the constants of the Hammett equation

4- After completing the simple regression analysis, we determine the values that have the most impact on the constants of the Hammett equation through the values of the correlation coefficient and then enter the functions into the equations to obtain the theoretical Hammett equation constants.

Table 1: Compounds under study

Comp. No.	Nome	Structure
1	benzoic acid	
2	4-aminobenzoic acid	
3	3-aminobenzoic acid	
4	3-methylbenzoic acid	
5	3-cyanobenzoic acid	
6	3-chlorobenzoic acid	
7	3-nitrobenzoic acid	
8	3-methoxybenzoic acid	
9	3-fluorobenzoic acid	
10	3-acetylbenzoic acid	
11	4-acetylbenzoic acid	
12	4-fluorobenzoic acid	
13	4-cyanobenzoic acid	
14	4-nitrobenzoic acid	
15	4-methylbenzoic acid	
16	4-methoxybenzoic acid	
17	4-hydroxybenzoic acid	
18	3-hydroxybenzoic acid	
19	4-chlorobenzoic acid	

RESULTS AND DISCUSSION

Theoretical calculations: Benzoic acid compounds are important in various fields, including medicine, industry, agriculture, and pharmacy. Given their importance, researchers have become more interested in studying the properties of these compounds to identify their behavior, stability, and effectiveness, and in developing software tools to support and enhance the practical results and experimental data reported in the literature. As for our theoretical

calculations, some physical variables of the compounds under study were calculated such as (HOMO, LUMO, atomic charges, hardness, electronic potential, bond length, spherical electrophilic index, electronic chemical potential), where the Hammet equation constants were calculated for all the compounds under study through the experiment and choosing the best relationship between all variables and the values of the Hammet equation constants, taking into account the effect of the compensating pushing and pulling groups on the ring in addition to the effect of each of induction, resonance and vacuum hindrance.

Theoretical calculations for several physical properties of the compounds under study: Some of the physical and structural variables of benzoic acid compounds were measured using the following methods (AM1 and DFT). Among the variables that were calculated were the total energy, the bond lengths between the atoms, and the atomic charge of each atom (C1, C2, C3, C4, C5, C6, C7, O9, O10). The Mulliken Charge was used because it is present in all theories and is one of the most common charges used to calculate the constants of the theoretical Hamet equation, along with other variables such as HOMO, LUMO, hardness, electronic potential, and the spherical electrophilic index. The main goal of testing these variables in more than one way is to include them in comparison between the following methods, on the one hand, and to show the superiority and accuracy of the calculations of each method with the accepted scientific context, on the other hand, as choosing the method is important in such studies.

Table 2: Physical variables of the benzoic acid compounds under study calculated by the AM1 method

COM. NO.	Property compound	Charge (Coulomb)								
		C1	C2	C3	C4	C5	C6	C7	O9	O10
1	X=H	-0.0647	-0.1391	-0.0965	-0.1376	-0.1001	-0.1502	0.3396	-0.3031	-0.2854
2	p- CH3	-0.0605	-0.1413	-0.0315	-0.1425	-0.0946	-0.1581	-0.1885	-0.3051	-0.2864
3	m-CH_3	-0.0671	-0.075	-0.1005	-0.1333	-0.1062	-0.1461	-0.1831	-0.3038	-0.2861
4	p- Cl	-0.0566	-0.1350	-0.0328	-0.1342	-0.0913	-0.1512	0.0041	-0.2994	-0.2826
5	m- Cl	-0.0620	-0.0735	-0.0938	-0.1284	-0.1019	-0.1400	0.3393	-0.2967	-0.2823
6	p- OCH_3	-0.0593	-0.1902	-0.0364	-0.1675	0.1151	-0.2173	-0.0794	-0.3077	-0.2861
7	m- OCH_3	-0.1088	-0.1275	-0.1103	0.0370	-0.0789	-0.1392	-0.2250	-0.2994	-0.2844
8	p- F	-0.0401	-0.1767	0.1264	-0.1763	-0.0740	-0.1670	0.3416	-0.300	-0.2828
9	m- F	-0.1179	-0.1116	-0.1356	0.0861	-0.1046	-0.1228	0.3384	-0.2951	-0.2816
10	p- CN	-0.0711	-0.1012	0.0222	-0.1009	-0.1059	-0.1288	0.3368	-0.293	-0.2797
11	m- CN	-0.0466	-0.1424	-0.0601	-0.0164	-0.0644	-0.1537	0.3397	-0.2967	-0.2787
12	p- NH_2	-0.0112	-0.2331	0.1562	-0.2317	-0.0429	-0.2218	0.3493	-0.3174	-0.2911
13	m- NH_2	-0.1272	-0.0896	-0.1851	0.1190	-0.1963	-0.0979	0.3382	-0.3031	-0.2878
14	p- OH	-0.0327	-0.1682	0.1149	-0.2258	-0.0562	-0.1902	0.3445	-0.3063	-0.2857
15	m- OH	-0.0990	-0.1066	-0.1228	0.0754	-0.1888	-0.1125	-0.2454	-0.2980	-0.2840
16	p- NO_2	-0.0786	-0.0767	-0.1024	-0.0769	-0.1116	-0.1107	0.3342	-0.2857	-0.2737
17	m-NO2	-0.0296	-0.1462	-0.0383	-0.1398	-0.0432	-0.1580	0.3406	-0.3550	-0.3457
18	p- $COCH_3$	-0.0828	-0.0989	-0.1192	-0.0859	-0.1162	-0.1237	0.2646	-0.2970	-0.2815
19	m- $COCH_3$	-0.0405	-0.1533	-0.0599	-0.1626	-0.0484	-0.1633	0.3411	-0.3025	-0.2808

Table 3: Physical variables of the benzoic acid compounds under study calculated by the DFT method

COM. NO	Property compound	Charge (Coulomb)								
		C1	C2	C3	C4	C5	C6	C7	O9	O10
1	X=H	-0.0605	-0.0885	-0.0771	-0.0907	-0.0932	-0.1170	0.2302	-0.2119	-0.257660
2	p- CH3	-0.0587	-0.0960	-0.0002	-0.0969	-0.0908	-0.1248	-0.2558	-0.2152	-0.258996
3	m-CH$_3$	-0.0677	-0.0877	-0.0843	-0.0134	-0.0981	-0.1163	-0.2561	-0.2131	-0.257343
4	p- Cl	-0.0503	-0.0922	-0.0477	0.0947	-0.0826	-0.1172	0.2318	-0.2082	-0.253058
5	m- Cl	-0.0609	-0.0774	-0.0822	-0.0569	-0.0998	-0.1058	0.2326	-0.2055	-0.251898
6	p- OCH$_3$	-0.0526	-0.1222	0.1260	-0.1631	-0.0808	-0.1415	0.2295	-0.2595	-0.179455
7	m- OCH$_3$	-0.0699	-0.0844	-0.1112	0.1118	-0.1282	-0.1130	0.2307	-0.2572	-0.223108
8	p- F	-0.0487	-0.1367	0.1598	-0.1399	-0.0808	-0.1280	0.2315	-0.2122	-0.256053
9	m- F	-0.0717	-0.0765	-0.1266	0.1489	-0.1454	-0.1063	0.2324	-0.2075	-0.252978
10	p- CN	-0.0566	-0.0577	-0.0443	-0.0592	-0.0887	-0.1022	0.2315	-0.2028	-0.250643
11	m- CN	-0.0794	-0.0846	-0.0479	-0.0538	-0.0306	-0.1125	-0.0593	-0.2030	-0.249671
12	p- NH$_2$	-0.0480	-0.1461	0.0941	-0.1494	-0.0787	-0.1585	0.2284	-0.2285	-0.266232
13	m- NH$_2$	-0.1375	-0.0791	-0.1359	0.0839	-0.1208	-0.1054	0.2315	-0.2184	-0.259712
14	p- OH	-0.0488	-0.1248	0.1215	-0.1654	-0.0798	-0.1405	0.2299	-0.2176	-0.261353
15	m- OH	-0.1188	-0.0789	-0.1135	0.1112	-0.1388	-0.1055	0.2316	-0.2150	-0.255621
16	p- NO$_2$	-0.0543	-0.0747	0.0032	-0.0769	-0.0869	-0.0965	0.2319	-0.2353	-0.230798
17	m-NO2	-0.0732	-0.0816	-0.0662	-0.0063	-0.0470	-0.1110	0.2329	-0.2272	-0.237258
18	p- COCH$_3$	-0.0617	-0.0779	-0.0812	-0.0600	-0.0929	-0.1044	0.2305	-0.2078	-0.253556
19	m-COCH$_3$	-0.0468	-0.0891	-0.0664	-0.0930	-0.0655	-0.1158	0.2308	-0.2106	-0.253358

Table 4: Physical variables of the benzoic acid compounds under study calculated by the AM1 method

COM. NO.	Property compound	Bond Length (Å) O_9-H_{15}	Bond Length (Å) C_7-O_9	Bond Length (Å) $C_7=O_8$	Bond Length (Å) C_6-C_7	ΔH Kcal\Mol	T.E Kcal\Mol	Dipole/Dipole Kcal\Mol
1	X=H	0.9683	1.3563	1.2142	1.3643	-61.9698	-37347.7529	5.0524
2	p- CH3	0.9647	1.3680	1.2342	1.4734	-69.8897	-40942.4185	4.9581
3	m-CH_3	0.9649	1.3677	1.2339	1.4750	-69.6667	-40942.194	4.9393
4	p- Cl	0.9685	1.3564	1.2143	1.3647	-68.4009	-45651.2762	5.5287
5	m- Cl	0.965	1.3672	1.2334	1.4765	-67.9829	-45650.8582	5.6417
6	p- OCH_3	0.9642	1.3680	1.2345	1.4723	-100.434	-48321.8688	5.2283
7	m-OCH_3	0.9647	1.3678	1.2336	1.4757	-97.4579	-48318.8927	5.1772
8	p- F	0.9655	1.3678	1.2337	1.4744	-106.692	-48218.2253	5.5472
9	m- F	0.9647	1.3665	1.2332	1.4772	-105.778	-48217.3111	5.6875
10	p- CN	0.9644	1.3663	1.2333	1.4770	-28.7876	-44737.1805	5.6553
11	m- CN	0.9649	1.3657	1.2337	1.4756	-29.0372	-44737.43	6.1222
12	p- NH_2	0.9647	1.3699	1.2352	1.4675	-64.8137	-42446.0828	5.2154
13	m- NH_2	0.9639	1.3674	1.2341	1.4769	-62.3175	-42443.5867	5.2388
14	p- OH	0.9646	1.3680	1.2343	1.4713	-106.629	-44741.3188	5.3313
15	m- OH	0.9644	1.3676	1.2336	1.4760	-105.227	-44739.9175	5.7565
16	p- NO_2	0.9651	1.3644	1.2329	1.4793	-55.3902	-56504.6647	6.2024
17	m-NO2	0.9654	1.3646	1.2333	1.4772	-56.1577	-56505.4322	6.3782
18	p-$COCH_3$	0.9654	1.3663	1.2334	1.4762	-96.2476	-51274.6161	5.0584
19	m-$COCH_3$	0.6004	1.3565	1.2144	1.3649	-98.5602	-51276.9287	4.7477

Table 5: Physical variables of the benzoic acid compounds under study calculated by the DFT method

COM. NO.	Property compound	Bond Length (Å) $O_9—H_{15}$	Bond Length (Å) $C_7—O_9$	Bond Length (Å) $C_7=O_8$	Bond Length (Å) $C_6—C_7$	ΔH Kcal\Mol	T.E Kcal\Mol	Dipole/Dipole Kcal\Mol
1	X=H	0.9907	1.3815	1.2245	1.4978	-418.2488	-262454.8862	4.8372
2	p- CH3	0.9911	1.3827	1.2253	1.4952	-457.3241	-286974.9999	5.3536
3	m-CH_3	0.9916	1.3818	1.2249	1.4981	-457.3235	-286974.6076	5.2194
4	p- Cl	0.9910	1.3792	1.2245	1.4990	-875.5793	-549433.913	3.1277
5	m- Cl	0.9917	1.3774	1.2237	1.5010	-875.5795	-549433.9774	2.8333
6	p- OCH_3	0.9909	1.3839	1.2260	1.4930	-532.0874	-333889.6293	6.5808
7	m- OCH_3	0.9907	1.3814	1.2243	1.4981	-532.0803	-333885.1692	5.0379
8	p- F	0.9904	1.3813	1.2249	1.4959	-516.9168	-324369.9468	3.7470
9	m- F	0.9901	1.3793	1.2245	1.5008	-516.9160	-324369.4592	3.4968
10	p- CN	0.9898	1.3782	1.2240	1.5010	-509.9326	-319987.2935	2.8332
11	m- CN	0.9905	1.3785	1.2239	1.5048	-509.9327	-319987.3601	6.2618
12	p- NH_2	0.9897	1.3877	1.2272	1.4853	-473.2729	-296982.7294	7.5559
13	m- NH_2	0.9901	1.3817	1.2251	1.4992	-473.2701	-296981.2559	5.0208
14	p- OH	0.9904	1.3849	1.2255	1.4912	-493.0182	-309373.3906	6.1219
15	m- OH	0.9914	1.3799	1.2249	1.4977	-493.0185	-309373.5805	3.3466
16	p- NO_2	0.9899	1.3766	1.2239	1.5029	-621.5028	-389998.5897	2.6182
17	m-NO2	0.9909	1.3776	1.2237	1.5020	-621.5026	-389998.4923	6.4045
18	p- $COCH_3$	0.9909	1.3792	1.2247	1.4991	-569.9702	-357661.295	2.4347
19	m- $COCH_3$	0.9912	1.3785	1.2246	1.4987	-569.9712	-357662.3632	5.2408

Theoretical energy functions calculated by the four methods In addition to calculating the physical variables, some energy variables were calculated, including the HOMO orbital energy and the LUMO orbital energy, which were used to calculate some variables that are related to the tendency or stability of molecules to interact, in addition to other variables: Total Energy, Hardness, Spherical Electrophile Index, and Chemical Potential. The previously mentioned energy variables were calculated by searching for each one separately and by the four theoretical methods, as in the following tables :

Table 6 shows the theoretical values of the energy variables calculated using the AM1 method for benzoic acid compounds.

Comp. NO	HOMO	LUMO	&	ω	Ƞ	μ
	(e.v)	(e.v)	(e.v)	(e.v)	(e.v)	(e.v)
1	-0.0025	0.0531	0.94565	7.30579E-05	0.05435	0.05185
2	-0.0097	0.0065	0.98865	1.54502E-08	0.01135	0.00165
3	-0.0108	0.0036	0.991	1.458E-08	0.009	-0.0018
4	-0.0002	0.0553	0.9446	8.4403E-05	0.0554	0.0552
5	-0.0234	0.0316	0.9567	8.57362E-06	0.0433	0.0199
6	-0.0118	0.0308	0.9633	1.13772E-05	0.0367	0.0249
7	-0.0011	0.0305	0.96895	1.3926E-05	0.03105	0.02995
8	-0.0067	0.0537	0.94295	7.23144E-05	0.05705	0.05035
9	-0.014	0.0421	0.9509	3.02458E-05	0.0491	0.0351
10	-0.0163	0.0273	0.96455	6.50016E-06	0.03545	0.01915
11	-0.0105	0.0201	0.97465	2.79512E-06	0.02535	0.01485
12	-0.014	0.0421	0.9509	3.02458E-05	0.0491	0.0351
13	-0.0189	0.0286	0.96195	6.9769E-06	0.03805	0.01915
14	-0.0058	0.0034	0.9937	7.875E-10	0.0063	0.0005
15	-0.0001	0.0532	0.94675	7.52136E-05	0.05325	0.05315
16	-0.0035	0.0536	0.94465	7.44021E-05	0.05535	0.05185
17	-0.0071	0.0513	0.94515	6.25307E-05	0.05485	0.04775
18	-0.0055	0.0409	0.95635	3.17646E-05	0.04365	0.03815
19	-0.0118	0.0308	0.9633	1.13772E-05	0.0367	0.0249

Table 7 shows the theoretical values of the energy variables calculated using the DFT method for benzoic acid compounds.

Comp.	HOMO	LUMO	&	ω	Ƞ	μ
	(e.v)	(e.v)	(e.v)	(e.v)	(e.v)	(e.v)
1	-0.0049	0.0587	0.93885	9.67412E-05	0.06115	0.05625
2	-0.0088	0.0074	0.9882	5.31E-08	0.0118	0.003
3	-0.0322	0.0321	0.9518	6.1696E-06	0.0482	0.016
4	-0.0027	0.0616	0.93705	0.000114256	0.06295	0.06025
5	-0.0526	0.0387	0.935	4.9972E-06	0.065	0.0124
6	-0.0197	0.0311	0.95905	9.24574E-06	0.04095	0.02125
7	-0.0087	0.0382	0.95745	2.43774E-05	0.04255	0.03385
8	-0.0037	0.0592	0.93895	0.000100397	0.06105	0.05735
9	-0.0064	0.0513	0.9455	6.30459E-05	0.0545	0.0481
10	-0.0494	0.0298	0.9455	7.08773E-07	0.0545	0.0051
11	-0.0158	0.0038	0.9883	9.83385E-08	0.0117	-0.0041
12	-0.0161	0.0512	0.94075	5.51595E-05	0.05925	0.04315
13	-0.029	0.0234	0.9621	1.50103E-06	0.0379	0.0089
14	-0.0379	0.0377	0.94335	9.95801E-06	0.05665	0.01875
15	-0.0024	0.0628	0.936	0.000121426	0.064	0.0616
16	-0.0029	0.0584	0.94015	9.70558E-05	0.05985	0.05695
17	-0.0072	0.0567	0.9397	8.50112E-05	0.0603	0.0531
18	-0.0476	0.0061	0.9701	4.68369E-06	0.0299	-0.0177
19	-0.0202	0.0234	0.9665	2.96291E-06	0.0335	0.0133

Statistical analysis using two variables

After the results obtained in the statistical analysis tables using one variable, the results were satisfactory and scientifically acceptable, which encouraged us to move forward and continue the theoretical study of benzoic acid compounds, where statistics were conducted for two variables based on the Hamet equation constant as a fixed variable with variable and other variables, as shown in the following tables.

Table 8: Values of the correlation coefficient (R2) between the constant of the Hammett equation and two variables using the AM1 method.

Comp. No	S.E	R2	Variables
1	0.347	0.837	C6-C7+C6=O8
2	0.326	0.860	C6=O8+O9-H15
3	0.434	0.732	LUMO+HOMO
4	0	1	HOMO+&
5	0	1	HOMO+W
6	0	1	HOMO+n
7	0	1	&+n
8	0	1	&+W
9	0	1	LUMO+&
10	0	1	C6+C7
11	0	1	C3+C7
12	0	1	C2+C7
13	0	1	C7-O9+ C6-C7
14	0	1	C1+C7
15	0.234	0.941	C2+C3
16	0	1	LUMO+W
17	0	1	LUMO+n
18	0	1	O9-H15+C6-C7

Table 9: Values of the correlation coefficient (R2) between the constant of the Hammett equation and two variables using the DFT method.

Comp. No	S.E	R2	Variables
1	0	1	HOMO+&
2	0	1	HOMO+W
3	0	1	LUMO+&
4	0	1	LUMO+W
5	0	1	&+W
6	0.185	0.961	O9-H15+C7=O8
7	0.339	0.861	O9-H15+C6-C7
8	0.242	0.931	C7-O9+ C6-C7
9	0	1	C7-O9+ΔH
10	0.315	0.895	C7=O8+ C6-C7
11	0	1	C7=O8+ΔH
12	0	1	C6-C7+ΔH
13	0.332	0.885	C1+C3
14	0	1	C1+C7
15	0.182	0.962	C4+C6
16	0	1	C4+C7
17	0	1	C6+C7
18	0.147	0.971	C2+C5

Calculating the theoretical Hammett equation constants for the compounds under study using two variables

The statistical analysis was conducted using two variables between the value of the Hammett equation constant and the other calculated variables to calculate the value of the theoretical Hammett equation constant and find the difference between it and the value taken from the literature (practical) using the four methods, where the best value of the correlation coefficient in the (AM1) method was (1R2=) for the Hammett equation constant with the variables (C6+C7), so it is one of the most influential values on the Hammett equation constant in this method. The Hammett equation constant was calculated using the following equation. In the (PM3) method, the best value of the correlation coefficient was (R2=1) between the Hammett equation constant and the variables (C6+C7) as well, so it is the most influential variable on the ionization constant, and this constant was calculated according to the following equation.

σ =0.001 + (C6 * -1.995) + (-0.984 * C7).

Table 10: Calculation of Hammett equation constants for the compounds under study using two variables, using the AM1 method.

Constant	0.001		
C6	-1.995		
C7	-0.984		
Comp. No.	C6	C7	σ\Theo
1	-0.1502	0.3396	-0.033
2	-0.1581	-0.1885	-0.602
3	-0.1461	-0.1831	-0.147
4	-0.1512	0.0041	-0.076
5	-0.1400	0.3393	0.556
6	-0.2173	-0.0794	0.421
7	-0.1392	-0.2250	0.612
8	-0.1670	0.3416	0.191
9	-0.1228	0.3384	0.412
10	-0.1288	0.3368	0.438
11	-0.1537	0.3397	0.600
12	-0.2218	0.3493	0.099
13	-0.0979	0.3382	0.712
14	-0.1902	0.3445	0.732
15	-0.1125	-0.2454	-0.231
16	-0.1107	0.3342	-0.176
17	-0.1580	0.3406	-0.343
18	-0.1237	0.2646	0.154
19	-0.1633	0.3411	0.312

In the DFT method, the best correlation coefficient value was (R2=1) between the Hammett equation constant and the variables (C6+C7) as well. Thus, it is the most influential variable on the Hammett equation constant. The Hammett equation constant value was calculated according to the following equation: -

σ =-0.155 + (C6 * -4.089) + (-1.218 * C7)

Table 11: Calculating the constants of the Hammet equation for the compounds under study using two variables using the (DFT) method.

Constant	-0.155		
C6	-4.089		
C7	-1.218		
Comp. No.	C6	C7	σ\Theo
1	-0.1502	0.3396	0.045
2	-0.1581	-0.1885	-0.721
3	-0.1461	-0.1831	-0.166
4	-0.1512	0.0041	-0.058
5	-0.1400	0.3393	0.555
6	-0.2173	-0.0794	0.302
7	-0.1392	-0.2250	0.688
8	-0.1670	0.3416	0.111
9	-0.1228	0.3384	0.418
10	-0.1288	0.3368	0.385
11	-0.1537	0.3397	0.592
12	-0.2218	0.3493	0.051
13	-0.0979	0.3382	0.668
14	-0.1902	0.3445	0.698
15	-0.1125	-0.2454	-0.167
16	-0.1107	0.3342	-0.198
17	-0.1580	0.3406	-0.287
18	-0.1237	0.2646	0.028
19	-0.1633	0.3411	0.197

In the two methods used above, these factors (C6+C7) were chosen because they are among the factors affecting the values of σ according to the data of organic chemistry, which indicate that the location of the atom and the charges are among the most important factors affecting the inductive effect of the substituents on the values of (σ).

Table 12: The values of the Hammett equation constant (σ) calculated theoretically and practically, and the difference between them for the compounds under study using two variables.

AM1			DFT		
σ \Calcu.	σ \Theo.	Δ σ	σ \Calcu.	σ \Theo.	Δ σ
0	-0.033	0.033	0	0.045	-0.045
-0.660	-0.602	-0.058	-0.660	-0.721	0.061
-0.160	-0.147	-0.013	-0.160	-0.166	0.006
-0.070	-0.076	0.006	-0.070	-0.058	-0.012
0.560	0.556	0.004	0.560	0.555	0.005
0.370	0.421	-0.051	0.370	0.302	0.068
0.710	0.612	0.098	0.710	0.688	0.021
0.120	0.191	-0.071	0.120	0.111	0.008
0.340	0.412	-0.072	0.340	0.418	-0.078
0.380	0.438	-0.058	0.380	0.385	-0.005
0.500	0.600	-0.100	0.500	0.592	-0.092
0.060	0.099	-0.039	0.060	0.051	0.009
0.660	0.712	-0.052	0.660	0.668	-0.008
0.780	0.732	0.048	0.780	0.698	0.082
-0.170	-0.231	0.061	-0.170	-0.167	-0.003
-0.270	-0.176	-0.094	-0.270	-0.198	-0.072
-0.370	-0.343	-0.027	-0.370	-0.287	-0.083
0.120	0.154	-0.034	0.120	0.028	0.091
0.230	0.312	-0.082	0.230	0.197	0.033

The following graphic shows the strength of the relationship (R2) between the constants of the Hammett equation, calculated theoretically using two variables and practically using all four theoretical methods.

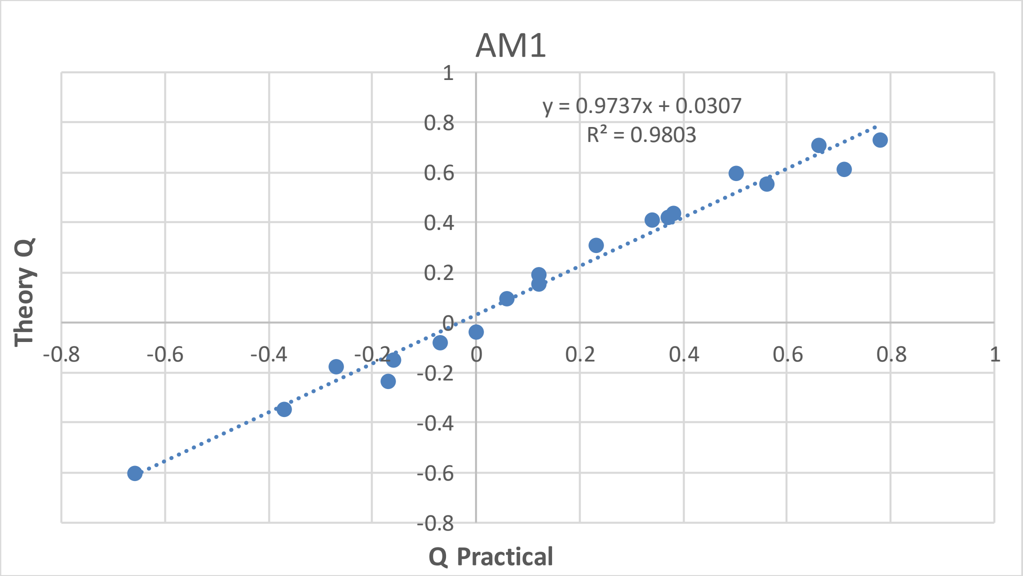


Fig. 1: The relationship between the practical and theoretical values of the Hammett equation constant using two variables, using the (AM1) method.

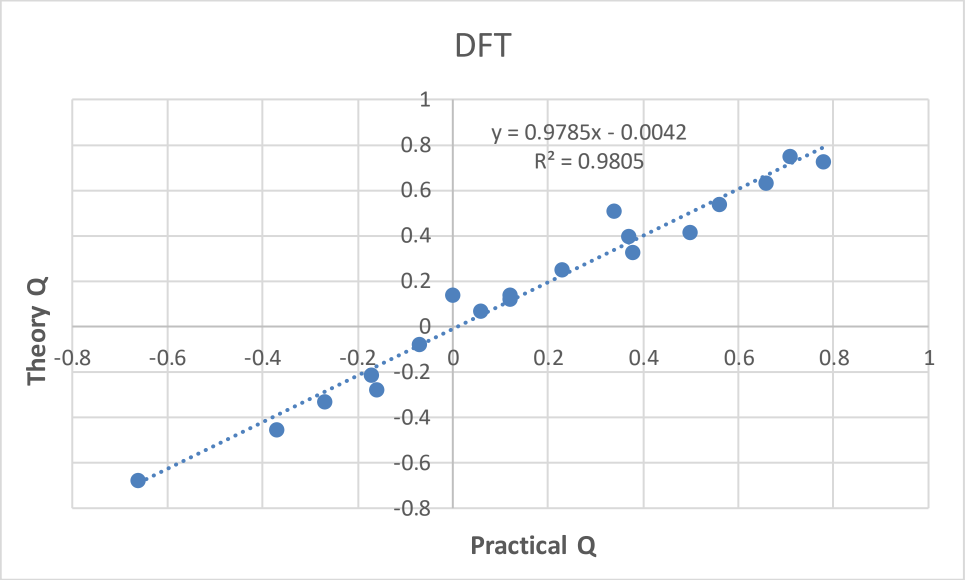


Fig. 2: The relationship between the practical and theoretical values of the Hammett equation constant using two variables, using the DFT method

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