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Meta Substitution Effect on Energetic Property and Aromatization of Some Acetophenone Derivatives: A DFT study

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The energetic properties and relative aromaticity of some derivatives of acetophenone structures were investigated in which the acetophenone was substituted by $-NO_2$, -CN, -Cl, -H, $-CH_3$ and $-OCH_3$ groups in *meta* position. For this purpose, density functional theory (DFT) calculations were applied using B3LYP/6-31+G(d,p) method. The results indicated that the aromaticity of the derivatives changed in the order of $-NO_2$ > -CN > -Cl > $-OCH_3$ > -H > $-CH_3$ for *meta* position. In addition, the results were directly related to the electron withdrawing and electron releasing strength and steric hindrance of substituents. The electrophilicity (ω), HOMA, HOMED, aromatic stabilization energy, nucleic independent chemical shifts (NICS)(0) and NICS(1) indices of all derivatives were calculated and the results showed these descriptors have a nice correlation with Hammett constant.

Key Words: *Ab initio*, Aromatic stabilization energy, HOMA, HOMED, Nucleic independent chemical shifts.

INTRODUCTION

1-Phenylethanone or acetophenone (APH) structure is derived of benzene with the chemical formula $C_6H_5(CO)CH_3$. Acetophenone structure can be obtained by several methods. In industry, acetophenone is recovered as a by-product of the oxidation of ethylbenzene, which mainly gives ethylbenzene hydroperoxide for using in the production of propylene oxide. This compound is synthesized in laboratory and is made naturally in various foods like beef, banana, apple, apricot and cheese. However, acetophenone structure is used to pharmaceutical and related areas. Different drugs such as acetaminophen are derived from acetophenone structure[1-10] (Fig. 1).

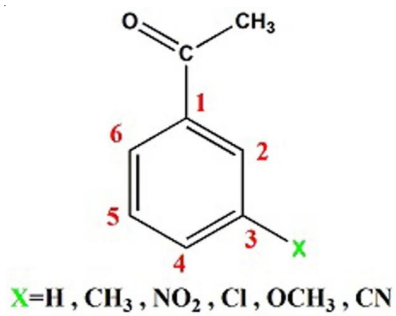

Fig. 1. Acetophenone structure with different substitutions including atom numbering

Before 19th, the aromatic compounds had been limited to benzene, naphthalene, anthracene, phenanthrene and five-membered heterocyclic compounds (*e.g.*, thiophene and pyrrole)[11,12]. It is not possible to determine the aromaticity experimentally[13]. Generally, the aromaticity is associated with the cyclic arrays of delocalized electrons with favourable symmetries. In contrast, antiaromatic systems have a localized electronic structure. Aromatic structures are cyclic conjugated systems which obey the Huckel rule[14] and have (4n + 2) of π electrons. This rule is true for many molecules. According to Huckel rule, by considering the energy levels of molecular orbitals which are calculated for cyclic conjugated molecules, there is always a molecular orbital with the lowest energy level and other molecular orbitals are located above it as degenerate pairs of same energy. When electrons are in the different molecular orbitals, two electrons are needed for occupying the lowest energy orbital while four electrons are required to fill each of energy levels, n[14].

More aromaticity in a structure leads to less reactivity and more stability. In these compounds, cyclic conjugated structure is maintained and there are no additional products. Hence, the aromaticity is a criterion of stabilization of molecules which directly has influences on chemical reactivity in kinetic and thermodynamic reactions[13-22].

Aromatic stabilization energy (ASE) is the first factor for calculation relative aromaticity in different structure. For this purpose we calculate the energy level of different state using

Fig. 2 (aromatic and non-aromatic) and calculation relative ASE and aromaticity.

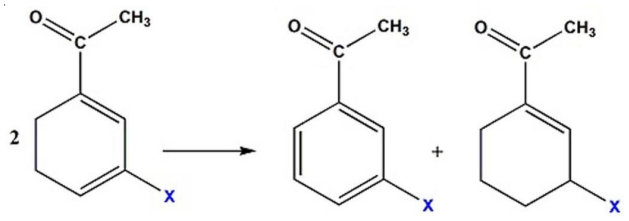

Fig. 2. One isodesmic formal equations for the estimation of the aromatic stabilization energies (ASE) of acetophenones

Enhanced resonance energies (REs) and the aromatic stabilization energies (ASEs) have long been recognized to be the cornerstone of aromaticity. The aromatic stabilization energy (ASE) reveals higher stability of compounds[17-22].

Existence of delocalized electrons in a compound refers to aromaticity of its structure. In a cyclic conjugated structure like acetophenone, there are various ways to evaluate the aromaticity. The first approach is to calculate the nucleic independent chemical shifts (NICS). Magnetic shielding presents information about aromaticity and delocalized electrons that we know it as NICS value. In fact, NICS is defined as the negative value of calculated absolute magnetic shielding in the center of ring and is calculated by considering visual atoms in different parts of the molecules. Usually, better results are obtained by calculating NICS at near the centre of ring. Negative values of NICS present the cyclic diastrophic current or aromaticity into the cycle, whereas positive values show the cyclic *para* tropic current or anti-aromaticity[17-19]. More negative NICS value in a compound leads to more aromaticity. For example, NICS values of benzene and naphthalene are -11.50 and -11.40, respectively while this value for cyclobutadiene is 28.8 as a non-aromatic structure. Therefore, using the NICS, it is possible to anticipate and calculate the resonance energy, magnetic susceptibilities and aromaticity values of the cyclic conjugated systems[19-21]. To obtain a measure of the aromaticity in acetophenone, NICS values were calculated at two points, at the centre and 1 Å above the ring, as illustrated in Fig. 3.

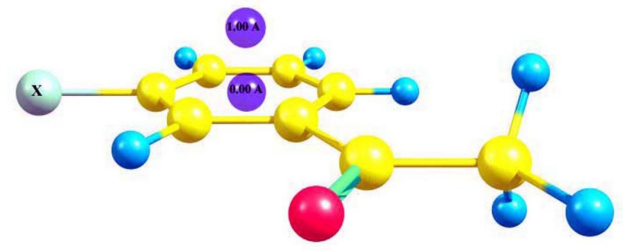

Fig. 3. Definition of points at which the NICS values were calculated

The other method to evaluate the aromaticity of rings is to calculate the harmonic oscillator model of aromaticity (HOMA)[21-28] which is calculated using eqn. 1 in which the obtained results vary between 0 and 1 for different systems. HOMA value of an aromatic compound is closed to 1 whereas that of non-aromatic structures is near to 0.

In eqn. 1, n is the number of single or double carbon-carbon bonds which HOMA index is calculated for[21-24] and α is the normal constant which is obtained by eqn. 2. R_o is the optimal bond length (R_o =1.388 A)[25-30] defined as the C-C bond for which the energy of the compression to the length of a double bond and expansion to the length of a single bond, R_s is single bond length[29], R_d is double bond length, α is 257.7 at the normal position[29] and R_i is obtained from calculation.

It must be mentioned that eqn. 1 is applicable for compounds that overly have a conjugated structure[26-30].

$$HOMA = \frac{1-\alpha}{n}\Sigma(R_o - R_i)^2 \quad (1)$$

$$\alpha = 2\{(R_0 - R_s)^2 + (R_o - R_d)^2\}^{-1} \quad (2)$$

Third way for the calculation of aromaticity is to measure the harmonic oscillator model of electron delocalization (HOMED). It must be noted that HOMA index is just applicable for conjugated systems[28-30] however, HOMED index can be calculated for both conjugated and non-conjugated structures. Similar to HOMA, obtained HOMED values vary between 0 (for non-aromatic systems) and 1 (for aromatic systems) which is calculated using eqn. 3 in which, (n) is the number of bonds that HOMED is calculated for it. The normal constant, α, is obtained by eqns. 4 or 5. R_o is optimal bond length (R_o = 1.394 A)[29], R_s is single bond length (R_s = 1.530 A)[29], R_d is double bond length (R_d = 1.328 A)[29], R_i is the experimental or computed bond length and (i) is applied when a compound do not have similar single or double bonds.

Eqn. 1 cannot be applied for systems with odd number (2i + 1) of bonds[29]; for such systems, α constant can be calculated from eqns. 4 or 5. Eqn. 4 corresponds to systems that have (i) double bonds while eqn. 5 refers to systems with (i) single bond and (i + 1) double bonds. While calculating HOMED for conjugated compounds, values of R_o = 1.394 A and α = 88.09 are used as reference[28-30].

$$HOMED = \frac{1-\alpha}{n}\cdot\Sigma(R_0 - R_i)^2 \quad (3)$$

$$\alpha = (2i+1).\{(i+1).(R_o - R_s)^2 + i(R_o - R_d)^2\}^{-1} \quad (4)$$

$$Ga = (2i+1)\{i(R_o - R_s)^2 + (i+1)(R_o - R_d)^2\}^{-1} \quad (5)$$

Fourth way to characterize the stability is to calculate the electrophilicity (ω) index which has been successfully applied to describe the reactivity in different organic systems[31]. The electrophilicity index, which measures the stabilization in energy when the system acquires an additional electronic charge, ΔN, from the environment is given by eqn. 6 and is presented in terms of the electronic chemical potential, μ (the negative of electronegativity, χ) and the chemical hardness, η[31]. Both quantities may be approximated in terms of the energies of frontier molecular orbitals (ε_{HOMO} and ε_{LUMO}) as $\mu = (\varepsilon_H + \varepsilon_L)/2$ and $\eta = \varepsilon_L - \varepsilon_H$ (eqns. 7 and 8). Electrophilicity can also be approximated in terms of the ionization potential (I) and electron affinity (A) (eqns. 6 and 7)[30-38].

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \quad (6)$$

$$\chi = -\mu = -\left(\frac{\delta_E}{\delta_N}\right)_{v(r)} \approx \frac{(I+A)}{2} \approx -\frac{1}{2(\varepsilon_{HOMO} + \varepsilon_{LUMO})} \quad (7)$$

$$\eta = \left(\frac{\delta_{2E}}{\delta_{N2}}\right)_{v(r)} = (1 - A) \approx (\varepsilon_{LUMO} - \varepsilon_{HOMO}) \quad (8)$$

High values of μ and low values of η, characterize a good electrophonic species. The maximum amount of electronic charge, ΔN_{max}, that the electrophonic system may accept is given by eqn. 9 as[32].

$$\Delta N_{max} = -\frac{\mu}{\eta} \quad (9)$$

Thus, while the quantity of ω describes the propensity of the system to acquire additional electronic charge from the environment, the quantity of ΔN_{max} describes the charge capacity of the molecule[32-41].

COMPUTATIONAL METHOD

Density functional theory (DFT) calculations of acetophenone with different *meta* substitutions were conducted in which geometries, energies, electrophilicity index, aromatic stabilization energy, HOMA and HOMED values were obtained at the B3LYP/6-31+G(d,p) level. Calculations of the independent chemical shifts (NICS) for *meta* substituted acetophenone structures were carried out using the gauge invariant atomic orbital (GIAO) approach[42,43] in which NICS values were calculated at the centre (NICS(0)) and also at 1 Å above the ring (NICS (1)) using GIAO-B3LYP/6-31+G(d,p) method[42,43]. All calculations were conducted using GAUSSIAN 03W program package[44].

RESULTS AND DISCUSSION

Based on the group (-$COCH_3$) is a *meta* director, we expect *meta*-only products with high percentage and more efficiently to be formed. Therefore, the calculations were limited to *meta* group and we investigated change of aromaticity based on it.

Energies and stabilities: The value of energy of organic and inorganic compounds is a criterion of stability of the system. On the other hand, the chemical potential and chemical hardness that affect the electrophilicity are criteria of reactivity of a structure in different reactions.

Energetic properties: The energy descriptors and dipole moments of substituted acetophenone structures are filled in Table1. The energy of most stable substituted acetophenone has been considered as zero and energies of other derivatives have been calculated relatively. For *meta* substituted compounds, energy increases, kinetic and thermodynamic stabilities decreases in the order of -Cl > -NO_2 > -CN > -OCH_3 > -CH_3 > -H (Fig. 4).

These orders are dependent on EW or ER strengths, bond vibrations and steric hindrance of substituted groups. It is seen that the highest stability in both *meta* is obtained when chlorine is substituted. Furthermore, placing EW groups enhances the stability while substituting ER groups weakens it. According to the Table-1 results, it is seen that placing EW groups at *meta* position leads to more stability, because EW groups at *meta* position leads to more reaction yield in comparison to substituting at *ortho* and *para* position. Presence of an activating group (-$COCH_3$) leads to negative formal charges on *meta* positions and hence, easier substitution, due to the resonance and mesomery.

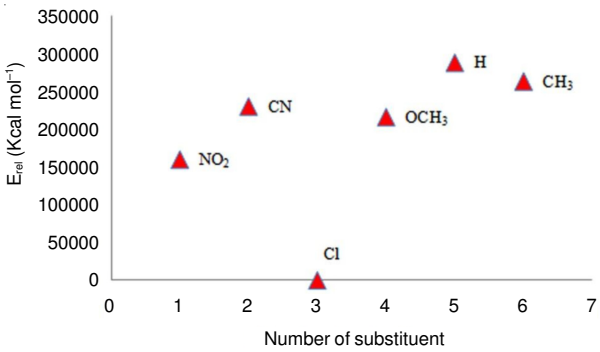

Fig. 4. Comparison of relative energies for *meta* derivatives of acetophenone

TABLE-1
VALUES OF ELECTRONIC ENERGIES, E(Kcal/mol), RELATIVE ELECTRONIC ENERGIES, E_{rel} (Kcal/mol), ZERO POINT VIBRATIONAL ENERGIES, ZPVE (kcal/mol) AND DIPOLE MOMENTS (DEBYE) OF *META* DERIVATIVES OF ACETOPHENONE CALCULATED AT THE B3LYP/6-31+G(d,p) LEVEL

X Substituent	E	E_{rel}	ZPVE	Dipole moment
-NO_2	-369860.9130	160067.0552	88.06923	6.6064
-CN	-299415.1837	230512.7845	85.65862	6.4649
-Cl	-529927.9682	0.0000	80.55256	4.1582
-OCH_3	-313397.2900	216530.6782	107.06945	4.4240
-H	-241532.2510	288395.7172	86.69691	3.3011
-CH_3	-266204.7395	263723.2287	103.92492	3.2533

Dipole moment: Study of dipole moment as a molecular descriptor showed this index is independent to EW or ER strength. For instance, -NO_2 and -CN groups as two EW groups in *meta* positions, have large amounts of dipole moment (Table-1).

Electrophilicity index: Let us consider the electrophilicity (ω) values amongst *meta* substitutions which are tabulated in Table-2. According to Table-2 results, for *meta* substituted species, electrophilicity declines in the order of -NO_2 > -CN > -Cl > -H > -CH_3 > -OCH_3.

Aromaticity indices: In continuation, descriptors including NICS, HOMA and HOMED indices were considered to evaluate the aromaticity of acetophenone derivatives. More aromaticity of a compound leads to more stability and less reactivity.

Harmonic oscillator model of aromaticity (HOMA) and harmonic oscillator model of electron delocalization (HOMED) indices: At *meta* position, aromaticity decreases in the order of -NO_2 > -CN > -Cl > -OCH_3 > -H > -CH_3. From (Table-3) results, it is seen that EW substituent like -NO_2 and -CN strengthen the aromaticity of acetophenone however, ER groups like -CH_3 weaken this property. At *meta* position, placing -NO_2 leads to the highest amount of aromaticity due to increasing the EW strength. On the other hand, -H and -CH_3 groups have the various behaviour while this group in *meta* position behave like an ER substituent.

Aromatic stabilization energies indices: Second method for detection of aromaticity is aromatic stabilization energies (ASE). Many approaches have been used to estimate the ASE. One example is homomolecular homodesmotic reactions. By this method aromaticity decreases in the order of -NO_2 > -CN > -Cl > -OCH_3 > -H > -CH_3 (Table-3). Placing -NO_2, -CN and -Cl leads to the highest amount of aromaticity due to increasing the EW strength.

TABLE-2
VALUES OF ENERGIES OF THE FRONTIER MOLECULAR ORBITALS (ε_{HOMO} AND ε_{LUMO}, eV),ELECTRONIC CHEMICAL POTENTIAL, μ (eV),CHEMICAL HARDNESS, η (eV),ELECTROPHILICITY, ω (eV) AND MAXIMUM AMOUNT OF ELECTRONIC CHARGE TRANSFER FOR ACETOPHENONE DERIVATIVES CALCULATED AT THE B3LYP/6-31+G(d,p) LEVEL

X Substituent	ε_{HOMO}	ε_{LUMO}	μ	η	ω	ΔN_{max}
NO_2	-0.28003	-0.11357	-0.19680	0.16646	0.003224	1.182266
CN	-0.27820	-0.09204	-0.18512	0.18616	0.003190	0.994413
Cl	-0.26665	-0.07984	-0.17324	0.18681	0.002803	0.927386
OCH_3	-0.23842	-0.06616	-0.15229	0.17226	0.001998	0.884071
H	-0.26035	-0.06957	-0.16496	0.19078	0.002596	0.864661
CH_3	-0.25798	-0.06751	-0.16274	0.19047	0.002522	0.854439

TABLE-3
NICS(0), NICS(1), ASE , HOMA AND HOMED VALUES OF ACETOPHENONE DERIVATIVES CALCULATED AT THE B3LYP/6-31+G(d,p) LEVEL INCLUDED WITH THE HAMMETT CONSTANT

X Substituent	NICS(0)	NICS(1)	HOMO	HOMED	ASE	σ_m Hammett
NO_2	-2.5647	-23.8887	0.9666	0.9964	32.0018	0.71
CN	-2.4198	-23.6710	0.9645	0.9962	31.8192	0.56
Cl	-2.2027	-23.2902	0.9628	0.9950	31.8006	0.37
OCH_3	-2.1288	-23.1609	0.9532	0.9945	30.0132	0.12
H	-1.9839	-23.0065	0.9484	0.9939	26.1455	0.00
CH_3	-1.9801	-22.9512	0.9429	0.9929	26.0234	-0.07

Nucleic independent chemical shifts (NICS) indices: After interpreting HOMA and HOMED indices, nucleic independent chemical shifts (NICS) of acetophenone derivatives were considered for determination of aromaticity in which two visual points were supposed at the center and 1A above the ring (Fig. 3). Data are filled in Table-3. According to NICS(0) values, the aromaticity of *meta* substituents change in the order of $-NO_2 > -CN > -Cl > -OCH_3 > -H > -CH_3$ and for NICS(1) and NICS(0) values[45]. It can be clearly seen that placing steric hindrance substituent at *meta* position strengthens the aromaticity of acetophenone structure (Table-3).

Relationships between energy and aromaticity descriptors of acetophenone derivatives: The correlations between different molecular descriptors including HOMA, HOMED, NICS(0), NICS(1), ASE and Hammett constant (σ_m) in Table-4 and electrophilicity (ω), chemical potential (μ), chemical hardness (η), maximum amount of transferred electronic charge (ΔN_{max}), relative energy (E_{rel}) and zero point vibration energy (ZPVE) for *meta* substituted structures were investigated which are illustrated in Table-5. The relationships with the regression coefficients of more than 0.900 can be considered as good correlations. For example, there are nice correlations between HOMED and HOMA in Table-4 or HOMO and LUMO in Table-5 for various derivatives. Other correlations can be easily seen in Tables 4 and 5.

Conclusion

Energetic property and aromaticity of some *meta* substituted derivatives of acetophenon structure were investigated at B3LYP/6-31+G(d,p) level of theory. It was seen that placing EW groups enhances the stability while substituting ER groups weakens the stability of acetophenone. Aromaticity indices of acetophenone derivatives including HOMA, HOMED, ASE, NICS(0) and NICS(1) methods were calculated in which the

TABLE-4
CORRELATIONS 1 BETWEEN DIFFERENT MOLECULAR DESCRIPTORS OF *meta* ACETOPHENONE DERIVATIVES. REGRESSION COEFFICIENTS (R^2) OF MORE THAN 0.900 ARE IN BOLD TYPE

Aromaticity indices	NICS(0)	NICS(1)	HOMA	HOMED	ASE	σ_m Hammett
NICS(0)	1.000	–	–	–	–	–
NICS(1)	0.994	1.000	–	–	–	–
HOMA	0.832	0.819	1.000	–	–	–
HOMED	0.913	0.917	0.930	1.000	–	–
ASE	0.727	0.681	0.911	0.803	1.000	–
Hammett constant	0.966	0.963	0.930	0.942	0.796	1.000

TABLE-5
CORRELATIONS 2 BETWEEN DIFFERENT MOLECULAR DESCRIPTORS OF *meta* ACETOPHENONE DERIVATIVES, REGRESSION COEFFICIENTS (R^2) OF MORE THAN 0.900 ARE IN BOLD TYPE

Energetic parameters	E_{rel}	ZPVE	HOMO	LUMO	μ	η	ω	ΔN_{max}
E_{rel}	1.000	–	–	–	–	–	–	–
ZPVE	0.245	1.000	–	–	–	–	–	–
JOMO	0.055	0.565	1.000	–	–	–	–	–
LUMO	0.085	0.258	0.693	1.000	–	–	–	–
μ	0.077	0.416	0.099	0.931	1.000	–	–	–
ω	0.031	0.041	0.000	0.319	0.108	1.000	–	–
ω	0.058	0.553	0.996	0.725	0.002	0.002	1.000	
ΔN_{max}	0.077	0.151	0.523	0.967	0.488	0.488	0.556	1.000

aromaticity results is similar and the aromaticity decreased in the order of -NO_2 > -CN > -Cl > -OCH_3 > -H > -CH_3 for *meta* position. Finally, it was included that placing EW substituent at *meta* position enhance the aromaticity (and hence the stability) while substituting acetophenone by ER groups, weakens the aromaticity (and stability).

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