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Application of Hammett equation to intramolecular hydrogen bond strength in para-substituted phenyl ring of trifluorobenzoylacetone and 1-aryl-1,3-diketone malonates

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ABSTRACT



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The stability of two stable *cis*-enol forms in two categories of β -diketones, including para-substituted of trifluorobenzoylacetone (X-TFBA) and 1-aryl-1,3-diketone malonates (X-ADM, X: H, NO₂, OCH₃, CH₃, OH, CF₃, F, Cl, and NH₂) has been obtained by different theoretical methods. According to our results, the energy difference between the mentioned stable chelated enol forms for the titled compounds is negligible. The theoretical equilibrium constants between the two stable *cis*-enol of the mentioned molecules are in excellent agreement with the reported experimental equilibrium constant. In addition, the effect of different substitutions on the intramolecular hydrogen bond strength has been evaluated. The correlation between Hammett para-substituent constants, σ_p , with the theoretical and experimental parameters related to the strength of hydrogen bond in p-X-TFBA and p-X-ADM molecules also investigated by means of density functional theory calculations. The electronic effects of para-substitutions on the intramolecular hydrogen bond strength were determined by NMR and IR data related to intramolecular hydrogen bond strength, geometry, natural bond orbital results, and topological parameters. These parameters were correlated with the Hammett para-substituent constants, σ_p . Good linear correlations between σ_p and the several parameters related to the hydrogen bond strength, in this study were obtained.

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1. Introduction

A hydrogen bond is an associative interaction between molecules containing a polar H-A bond and an electron donor B. A and B are atoms with greater electronegativity than hydrogen and if A and B belong to the same molecule intramolecular hydrogen bonding the intramolecular hydrogen bond (IHB) occurs if the spatial configuration is favorable. In 1919, the concept of hydrogen bond had been proposed by Huggins [1]. After that, the properties of intramolecular and intermolecular hydrogen bonded systems have been studied theoretically and experimentally by several workers [2-6]. The *cis*-enol forms of β -diketones are engaged in an intramolecular hydrogen bond, IHB, system [7,8], which, as resulted by Gilli *et al.* [9-12], the π -electron delocalization between the donor and acceptor atoms is responsible to increase the intramolecular HB strength in malonaldehyde, β -diketones and derivatives. Formation of IHB causes an obvious affinity for equalization of the valence bonds in the resulting

chelated ring. Thus, any parameter that affects the electron density of the chelating ring will change the IHB strength, E_{HB} .

Two stable *cis*-enol forms of 4,4,4-trifluoro-1-phenyl-1,3-butanedione, known as trifluorobenzoylacetone (TFBA), and 1-aryl-1,3-diketone malonates (ADM) as asymmetric β -diketones, were characterized by the position of the phenyl group, which can be attached at C2 or at C4 (i.e. adjacent to C=O and C-O bonds), respectively (Figure 1). These tautomers are labeled as X-TFBA-2, X-TFBA-4, X-ADM-2, and X-ADM-4, respectively. Replacing the hydrogen atom in the para position of phenyl ring with an electron-withdrawing group (EWG) or electron donating group (EDG) causes a charge redistribution in the π -electrons of the chelated ring. Therefore, the IHB of these molecules is affected by the substitution on the para position of the phenyl group [13-16].

Hammett quantified the effects of substituents by considering an empirical electronic substituent parameter (σ), which obtained from the acid dissociation constants, K_a 's of substituted benzoic acids [17,18].

Table 1. Calculated relative energies of X-TFBA-2 with respect to X-TFBA-4, as the most stable form, in gas phase and in solution (in kcal/mol), and theoretical and experimental equilibrium constants between X-TFBA-4 \rightleftharpoons X-TFBA-2 ^a.

Calculation level	TFBA-2	F-TFBA-2	CH ₃ -TFBA-2	OCH ₃ -TFBA-2	NH ₂ -TFBA-2	NO ₂ -TFBA-2	CF ₃ -TFBA-2	OH-TFBA-2
A/6-311++G**	0.99 (0.89)	0.79 (0.72)	1.01 (0.86)	0.80 (0.93)	1.03 (1.08)	0.79 (0.71)	0.78 (0.69)	0.72 (0.74)
A /6-311G**	0.63 (0.60)	0.45 (0.44)	0.67 (0.62)	0.74 (0.80)	0.76 (0.70)	0.46 (0.46)	0.48 (0.48)	0.47 (0.45)
A /6-31G**	0.55 (0.50)	0.39 (0.38)	0.60 (0.54)	0.66 (0.60)	0.66 (0.59)	0.39 (0.39)	0.43 (0.40)	0.38 (0.36)
B /6-31G**	0.08	0.09	0.22	0.98	0.35	0.04	0.16	0.75
C /6-311++G**	1.07	0.88	1.11	1.18	1.19	0.89	0.89	0.89
CCl ₄ ^b	1.23 (1.15)	1.06 (0.96)	1.21 (1.18)	1.15 (1.19)	1.39 (1.31)	1.01 (0.94)	1.01 (0.93)	1.07 (1.02)
CH ₃ CN ^b	1.49 (1.35)	1.39 (1.18)	1.58 (1.41)	1.58 (1.43)	2.27 (1.72)	1.28 (1.18)	1.31 (1.17)	1.50 (1.42)
C ₂ H ₅ OH ^b	1.48 (1.62)	1.37 (1.18)	1.50 (1.40)	1.56 (1.43)	1.82 (1.71)	1.27 (1.17)	1.30 (1.17)	1.48 (1.41)
K _{eq} (exp.) ^c	1.03 (1.02)	1.04 (-)	1.03 (-)	1.04 (-)	1.03 (-)	1.01 (0.99)	1.01 (-)	1.06 (-)

^a A, B, and C are the calculated relative energies in gas phase at B3LYP, MP2, and TPSSh levels, respectively, the values of ZPE are in parentheses.

^b Calculated relative energies in various solvents at B3LYP/6-311++G** level of theory.

^c Calculated equilibrium constants are in gas phase at B3LYP/6-311++G** level of theory and experimental equilibrium constants are in parentheses from Ref. [40].

The Hammett equation have correlated some parameters, such as the equilibrium constants, rate constants, and different physical properties with Hammett constant to show the effect of electron donating/withdrawing ability of substituents on the mentioned properties. A few studies have been reported in connection with the Hammett equation [19,20].

p-X-ADM molecules were studied by Jimenez-Cruz *et al.* [21,22]. They reported the effects of para substitutions on the aromatic systems, by a correlation between ¹³C NMR chemical shifts and Hammett substituent constant (σ_p). Darugar *et al.* reported the correlation between theoretical and experimental parameters related to IHB strength with σ_p in para substituted benzoylacetones [23].

The aim of the present work is to predict the molecular structure, tautomeric stabilities, and IHB strength of the titled molecules by means of density functional theory (DFT), Atoms-In-Molecules (AIM) [24], and Natural Bond Orbital (NBO) analyses. Afterwards, the results related to IHB strength have been compared with the experimental enolic proton chemical shifts, δ_{OH} which shows the effect of different substitutions in para-positions of phenyl ring on the IHB strength of the title molecules. The parameters related to IHB, such as E_{HB} , ν_{OH} , γ_{OH} , δ_{OH} , geometrical and topological parameters would be correlated with the Hammett's para function, σ_p [25]. So, the electron donating/withdrawing substituent effects are discussed quantitatively by applying the Hammett equation.

2. Method of calculations

All calculations were performed using Gaussian 09 software package [26]. The *cis*-enol structure of all molecules has been optimized at the B3LYP [27-28], using 6-31G**, 6-311G**, and 6-311++G** basis sets, the second-order Møller-Plesset (MP2) [29,30], using 6-31G** basis set, and the TPSSh [31] levels, using 6-311++G** basis set. All of these levels and basis sets have been applied to confirm the relative stability of the *cis*-enol forms of the titled molecules. The zero-point vibrational energy, ZPE, corrections were obtained at the B3LYP level, without applying any scaling. The vibrational frequencies of the *cis*-enol forms were calculated at the B3LYP level of theory.

The SCRF-PCM method [32] at the B3LYP/6-311++G** level, was selected for calculations in solutions. Different polar and non-polar solvent such as, acetonitrile, carbon tetrachloride, and ethanol, were used to investigate the solvent dependence of tautomeric equilibrium.

The electronic charge density, $\rho(r)$, its corresponding Laplacian, $\nabla^2\rho(r)$, at the critical point of hydrogen bond, O...H, and E_{HB} were carried out by using the AIM2000 program [33,34]. The NBO 5.0 program [35] used to calculate the second-order interaction energies $E^{(2)}$, and natural charge of the bridged atom in the chelated ring (H). To obtain the

chemical shift of the enolic proton, δ_{OH} , NMR calculations were done by using gauge independent atomic orbital (GIAO) method [36, 37] at the B3LYP/6-311++G** level of theory in chloroform as solvent, by SCRF-PCM method. The predicted ¹H chemical shifts are derived from $\delta = \sigma_o - \sigma$. In this equation, δ and σ are the chemical shift and the absolute shielding of bridged hydrogen, respectively. The σ_o is the absolute shielding of hydrogen nuclei in TMS (Tetramethylsilane) as reference. To end, some theoretical and experimental parameters related to IHB strength were correlated with σ_p Hammett equation. Graphs were drawn and regression analyses were performed using Microsoft Office Excel, 2016 software.

3. Results and discussion

3.1. Tautomeric and IHB strength

Cis-enol forms of β -dicarbonyl compounds stabilized by an intramolecular hydrogen bond. In asymmetric β -diketones two different *cis*-enol forms are noticeable, such as titled molecules (Figure 1). According to this figure, in the X-ADM-4 and X-TFBA-4, the phenyl group and hydroxyl group are adjacent, were the phenyl group, C=C, and C=O creating a longer conjugate system is expected, while in X-TFBA-2 and X-ADM-2, which ph and C=O are neighbored, a conjugation between Ph and C=O can occur, as reported by Afzali *et al.* [38] and Tayyari *et al.* [39].

The relative stabilities of the mentioned stable forms of the titled molecules, along with the calculated and reported experimental equilibrium constants (K_{eq}) [21, 40], calculated at different levels of theory in the gas phase and solutions, are listed in Tables 1 and 2. According to these values, the *cis*-enol-4 and *cis*-enol-2 forms in the X-TFBA and X-ADM molecules are the most stable forms, respectively. The values show, the energy differences between the stable *cis*-enol forms of X-TFBA are in the range: 0.04-1.19, 1.01-1.39, 1.28-2.27, and 1.27-1.82, and for X-ADM are 0.16-0.64, 0.26-0.67, 0.10-0.50, and 0.10-0.42 kcal/mol both in the gas phase and in CCl₄, CH₃CN, C₂H₅OH solutions, respectively. Upon Zero-point energy (ZPE) corrections, these energy differences reduce to 0.36-1.08, 0.93-1.31, 1.17-1.72, and 1.17-1.71 for X-TFBA, and 0.02-0.48, 0.06-0.43, 0.03-0.21, and 0.03-0.18 kcal/mol for X-ADM, respectively. Therefore, coexisting of the these two-stable forms of X-TFBA and X-ADM in the samples are expected, which is in agreement with the reported experimental equilibrium constants. So, according to these values there is no significant difference between reported experimental and theoretical equilibrium constants, K_{eq} .

We obtained the calculated equilibrium constants by Equation (1),

$$\Delta G^\circ = -RT\ln(K_{eq}) \quad (1)$$

Table 2. Calculated relative energies of X-ADM-4 with respect to X-ADM-2, as the most stable form, in gas phase and in solution (in kcal/mol), and theoretical and experimental equilibrium constants between X-ADM-2 \rightleftharpoons X-ADM-4 ^a.

Calculation level	ADM-4	Cl-ADM-4	F-ADM-4	CH ₃ -ADM-4	OCH ₃ -ADM-4	NH ₂ -ADM-4	NO ₂ -ADM-4	CF ₃ -ADM-4
A/6-311++G**	0.32(0.04)	0.47(0.08)	0.55(0.16)	0.35(0.20)	0.64(0.48)	0.38(0.17)	0.54(0.27)	0.51(0.34)
A /6-311G**	0.23(0.12)	0.39(0.02)	0.51(0.08)	0.25(0.21)	0.56(0.36)	0.33(0.15)	0.41(0.22)	0.46(0.23)
A /6-31G**	0.18(0.15)	0.33(0.02)	0.50(0.07)	0.21(0.11)	0.32(0.23)	0.25(0.11)	0.24(0.18)	0.27(0.14)
B /6-31G**	0.17	0.36	0.49	0.21	0.43	0.45	0.35	0.33
C /6-311++G**	0.18	0.36	0.45	0.17	0.20	0.23	0.16	0.19
CCl ₄	0.26(0.06)	0.40(0.30)	0.28(0.09)	0.67(0.43)	0.43(0.07)	0.29(0.21)	0.60(0.31)	0.30(0.29)
CH ₃ CN	0.10(0.04)	0.23(0.16)	0.11(0.10)	0.50(0.21)	0.32(0.03)	0.26(0.15)	0.43(0.20)	0.26(0.21)
C ₂ H ₅ OH	0.10(0.04)	0.17(0.10)	0.10(0.08)	0.38(0.14)	0.32(0.03)	0.18(0.13)	0.42(0.18)	0.17(0.12)
K _{eq} (exp.) ^b	2.90 (2.77)	3.10 (3.08)	2.25 (2.20)	2.76 (2.71)	2.49 (2.31)	2.45 (-)	3.01(-)	2.99 (2.95)

^a A, B, and C are the calculated relative energies in gas phase at B3LYP, MP2, and TPSSh levels, respectively, the values of ZPE are in parentheses.

^b Calculated equilibrium constants are in gas phase at B3LYP/6-311++G** level of theory and experimental equilibrium constants are in parentheses at 20 °C from Ref. [21].

Table 3. Some theoretical and experimental parameters related to the hydrogen bond strength for the TFBA-2/-4 and ADM-2/-4 molecules and the averaged values. ^a

Parameters	TFBA			ADM			X-ray ^e
	-2	-4	Avg.	-2	-4	Avg.	
δ OH ^b	15.32	15.04	15.18 (15.20)	15.67	15.20	15.44(16.09)	
ν OH ^b	3036	3083	3060	3000	3036	3018	
γ OH ^b	930	937	934	995	960	978	
R O...O ^c	2.523	2.542	2.533	2.519	2.531	2.525	2.488
R O-H ^c	1.006	1.001	1.004	1.007	1.004	1.006	0.963
R O...H ^c	1.619	1.632	1.626	1.602	1.613	1.608	1.654
<OHO ^c	147.1	148.7	147.9	148.9	149.6	149.3	142.4
E _{HB} ^d	19.0	18.1	18.5	20.1	19.4	19.8	
ρ_{BCP}	0.0592	0.0569	0.0581	0.0617	0.060	0.0609	
$\nabla^2\rho_{BCP}$	-0.1489	-0.1482	-0.1485	-0.1518	-0.1502	-0.1510	
Lp(1)O \rightarrow σ^* O-H	4.31	4.11	4.21	4.30	3.85	4.08	
Lp(2)O \rightarrow σ^* O-H	28.53	26.15	27.34	30.58	29.1	29.84	
Σ Lp(1,2)O \rightarrow σ^* O-H	32.84	30.26	31.55	34.88	32.95	33.92	

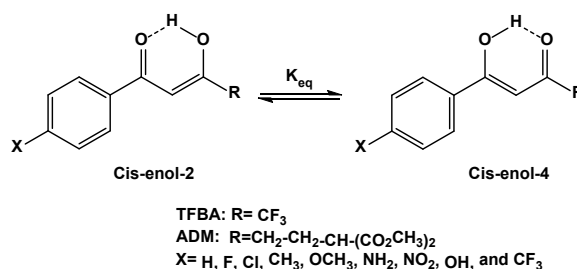
^a All calculated at the B3LYP/6-311++G** level of theory. The experimental values are in parentheses from Ref. [21,38].

^b δ , proton chemical shift in ppm; ν and γ are stretching and out-of-plane bending modes frequencies, respectively, in cm⁻¹.

^c R is bond length in Å, < is the bond angle in degrees.

^d E_{HB} is the IHB strength according to method of Espinosa et al. [40] in kcal/mol.

^e The experimental x-ray values from Ref. [22].

**Figure 1.** The cis-enol forms of two categories of β -diketones.

which for X-ADM the $\Delta G^{\circ}_{298} = (G^{\circ}_{\text{enol-2}} - G^{\circ}_{\text{enol-4}})$ and for X-TFBA the $\Delta G^{\circ}_{298} = (G^{\circ}_{\text{enol-4}} - G^{\circ}_{\text{enol-2}})$ all calculations are in 298 K. The Gibbs free energy values under standard conditions (G°), calculated at B3LYP/6-311++G** level within the harmonic approximation, (Tables 1 and 2).

The parameters related to IHB strength, such as the optimized geometry parameters, the topological and NBO parameters, the theoretical and experimental spectroscopic data, include the IR frequencies and NMR chemical shifts, for both stable forms and their averages of X-TFBA and X-ADM molecules are collected in Tables 3-5. In addition, some reported structural parameters of H-ADM, CH₃-ADM, and NO₂-ADM are compared with the averaged calculated results of the mentioned molecules. As it is shown in these Tables, there is a fairly good agreement between the theoretical and experimental results. According to these Tables, the O...O distance in the -2 forms of title molecules are shorter than those in the -4 forms, therefore the IHB strength of 2 forms are stronger than those in 4 forms. These results are in agreement with the other parameters relate to IHB strength, such as theoretically and experimentally NMR proton chemical shifts (the experimental values of proton chemical shifts reported from references

[21,39-40]), and computed vibrational frequencies, which are shown in the mentioned Tables.

In Tables 3-5, the OHO angle cannot confirm the trend of the hydrogen bond strength between the 2 and 4 forms. This difference in angle is due to the very small difference in structure between the studied forms and the calculations cannot obtain the exact difference. At different computational levels, this upward trend exists for the values of OHO angle for 2 and 4 forms. However, their average values confirm the effect of the substitutions according to 1 and 2 trends. Also, given that the values of the OHO angles are related to the Hammett constants, it can be considered a criterion.

According to results of Tables 3-5, the substitutions with electron donating effect, such as NH₂, OCH₃, CH₃ and OH, increase the IHB strength, while electron-withdrawing substitutions such as CF₃, and NO₂ decrease the IHB strength of substituted molecules in comparison with TFBA, and ADM as the parent molecules. However, halogen substitutions, like F and Cl, have no significant effect on the IHB strength. So, the following trends in E_{HB} of titled molecules are concluded: NO₂-TFBA < CF₃-TFBA < TFBA ~ F-TFBA ~ CH₃-TFBA < OH-TFBA < OCH₃-TFBA < NH₂-TFBA (1) and NO₂-ADM ~ CF₃-ADM < ADM ~ Cl-ADM ~ F-ADM < CH₃-ADM < OCH₃-ADM < NH₂-ADM (2)

Table 4. Some theoretical and experimental parameters related to the intramolecular hydrogen bond strength for the X-TFBA-2/-4 molecules and the averaged values. ^a

Parameters	TFBA			F-TFBA		
	-2	-4	Avg.	-2	-4	Avg.
δ OH ^b	15.32	15.04	15.18 (15.20)	15.24	14.96	15.10(15.14)
ν OH ^b	3036	3083	3060	3046	3071	3059
γ OH ^b	930	937	934	928	936	932
R O...O ^c	2.523	2.542	2.533	2.525	2.539	2.532
R O-H ^c	1.006	1.001	1.004	1.005	1.002	1.004
R O...H ^c	1.619	1.632	1.626	1.622	1.629	1.626
<OHO ^c	147.1	148.7	147.9	147.0	148.8	147.9
$E_{\text{HIB}}^{\text{d}}$	19.0	18.1	18.5	18.8	18.4	18.6
ρ_{BCP}	0.0592	0.0569	0.0581	0.0587	0.0577	0.0582
$\nabla^2\rho_{\text{BCP}}$	-0.1488	-0.1482	-0.1485	-0.1485	-0.1487	-0.1486
Lp(1)O $\rightarrow \sigma^* \text{O-H}$	4.31	4.11	4.21	4.26	4.17	4.22
Lp(2)O $\rightarrow \sigma^* \text{O-H}$	28.53	26.15	27.34	28.03	26.57	27.30
$\Sigma \text{Lp}(1,2)\text{O} \rightarrow \sigma^* \text{O-H}$	32.84	30.26	31.55	32.29	30.74	31.52
$\Delta E(\text{HOMO-LUMO})^{\text{e}}$	4.68	4.25	4.47	4.63	4.22	4.43
	CH ₃ -TFBA			OCH ₃ -TFBA		
	-2	-4	Avg.	-2	-4	Avg.
δ OH ^b	15.37	14.97	15.17(15.24)	15.27	15.14	15.21(15.41)
ν OH ^b	3024	3080	3052	3004	3056	3030
γ OH ^b	933	918	926	938	923	931
R O...O ^c	2.522	2.542	2.532	2.519	2.537	2.528
R O-H ^c	1.006	1.001	1.004	1.007	1.003	1.005
R O...H ^c	1.615	1.631	1.623	1.609	1.622	1.616
<OHO ^c	147.3	148.9	148.1	147.6	149.3	148.5
$E_{\text{HIB}}^{\text{d}}$	19.2	18.1	18.7	19.6	18.7	19.2
ρ_{BCP}	0.0598	0.0570	0.0584	0.0607	0.0580	0.0595
$\nabla^2\rho_{\text{BCP}}$	-0.1490	-0.1482	-0.1486	-0.1497	-0.1492	-0.1494
Lp(1)O $\rightarrow \sigma^* \text{O-H}$	4.33	4.10	4.22	4.35	4.20	4.28
Lp(2)O $\rightarrow \sigma^* \text{O-H}$	29.03	26.32	27.68	29.62	27.38	28.50
$\Sigma \text{Lp}(1,2)\text{O} \rightarrow \sigma^* \text{O-H}$	33.36	30.42	31.89	33.97	31.58	32.78
$\Delta E(\text{HOMO-LUMO})^{\text{e}}$	4.56	4.15	4.36	4.23	3.97	4.10
	NH ₂ -TFBA			NO ₂ -TFBA		
	-2	-4	Avg.	-2	-4	Avg.
δ OH ^b	15.43	14.99	15.21 (-)	15.16	14.53	14.85 (14.70)
ν OH ^b	2985	3044	3015	3085	3153	3119
γ OH ^b	944	926	935	919	913	916
R O...O ^c	2.516	2.536	2.526	2.533	2.557	2.545
R O-H ^c	1.009	1.003	1.006	1.003	0.998	1.001
R O...H ^c	1.604	1.620	1.612	1.636	1.658	1.647
<OHO ^c	147.9	149.6	148.8	146.3	147.6	147.0
$E_{\text{HIB}}^{\text{d}}$	20.0	18.8	19.4	18.0	16.6	17.3
ρ_{BCP}	0.0615	0.0587	0.0601	0.0567	0.0533	0.0550
$\nabla^2\rho_{\text{BCP}}$	-0.1499	-0.1492	-0.1496	-0.1471	-0.1446	-0.1459
Lp(1)O $\rightarrow \sigma^* \text{O-H}$	4.43	4.22	4.33	4.10	3.83	3.97
Lp(2)O $\rightarrow \sigma^* \text{O-H}$	30.73	27.83	29.28	26.19	23.21	24.7
$\Sigma \text{Lp}(1,2)\text{O} \rightarrow \sigma^* \text{O-H}$	35.16	32.05	33.61	30.29	27.04	28.67
$\Delta E(\text{HOMO-LUMO})^{\text{e}}$	3.97	3.77	3.87	3.87	3.98	3.93
	CF ₃ -TFBA			OH-TFBA		
	-2	-4	Avg.	-2	-4	Avg.
δ OH ^b	15.30	14.70	15.00 (14.85)	15.34	15.07	15.21 (-)
ν OH ^b	3071	3132	3102	3017	3055	3036
γ OH ^b	922	918	920	936	924	930
R O...O ^c	2.530	2.553	2.542	2.521	2.537	2.529
R O-H ^c	1.004	0.999	1.002	1.007	1.003	1.005
R O...H ^c	1.631	1.650	1.641	1.613	1.623	1.618
<OHO ^c	146.6	147.9	147.3	147.5	149.2	148.4
$E_{\text{HIB}}^{\text{d}}$	18.3	17.0	17.7	19.4	18.6	19.0
ρ_{BCP}	0.0575	0.0544	0.0559	0.0601	0.0582	0.0591
$\nabla^2\rho_{\text{BCP}}$	-0.1477	-0.1458	-0.1468	-0.1493	-0.1489	-0.1491
Lp(1)O $\rightarrow \sigma^* \text{O-H}$	4.19	3.91	4.05	4.34	4.21	4.28
Lp(2)O $\rightarrow \sigma^* \text{O-H}$	26.9	24.11	25.51	29.36	27.31	28.34
$\Sigma \text{Lp}(1,2)\text{O} \rightarrow \sigma^* \text{O-H}$	31.09	28.02	29.56	33.70	31.52	32.61
$\Delta E(\text{HOMO-LUMO})^{\text{e}}$	3.99	4.10	4.45	4.34	4.03	4.19

^a All calculated at the B3LYP/6-311++G** level of theory. The experimental values are in parentheses from Ref. [36,37,43-44].^b δ , proton chemical shift in ppm; ν and γ are stretching and out-of-plane bending modes frequencies, respectively, in cm⁻¹.^c R is bond length in Å, α is the bond angle in degrees.^d E_{HIB} is the IHB strength according to method of Espinosa *et al.* [42] in kcal/mol.^e The energy difference between HOMO and LUMO orbitals in eV.

3.2. The correlations of some calculated and observed parameters with the IHB strength and para Hammett substituent constant, σ_p

The Hammett equation, as a linear free energy relationship, is written in terms of equilibrium constants as Equation (2) [18],

$$\log_{10} K = \rho\sigma - \log_{10} K_0 \quad (2)$$

The IHB strength of O...H-O systems is one of the most surprising examples of intramolecular hydrogen bond. In this work, we correlated the calculated and experimental parameters related to the IHB strength with electrophilic substituent constants, σ_p , for some para-substitutions of target molecules.

Table 5. Some theoretical and experimental parameters related to the intramolecular hydrogen bond strength for the X-ADM-2/-4 molecules and the averaged values. ^a

Parameters	H-ADM			X-ray ^c	Cl-ADM		
	-2	-4	Avg.		-2	-4	Avg.
δ OH ^b	15.67	15.20	15.44(16.09)		15.49	15.34	15.42(15.96)
ν OH	3000	3036	3018		3014	3026	3020
γ OH	995	960	978		991	958	975
R O...O	2.519	2.531	2.525	2.488	2.520	2.528	2.524
R O-H	1.007	1.005	1.006	0.963	1.006	1.005	1.006
R O...H	1.602	1.613	1.608	1.654	1.606	1.610	1.608
<OHO	148.9	149.6	149.3	142.4	148.7	149.6	149.2
E _{HB}	20.1	19.4	19.8		20.0	19.7	19.9
ρ BCP	0.0617	0.0600	0.0609		0.0615	0.0600	0.0608
$\nabla^2\rho$ BCP	-0.1518	-0.1502	-0.1510		-0.1515	-0.1500	-0.1508
Lp(1)O $\rightarrow\sigma^*$ O-H	4.30	3.85	4.08		4.25	3.80	4.03
Lp(2)O $\rightarrow\sigma^*$ O-H	30.58	29.10	29.84		30.50	29.00	29.75
Σ Lp(1,2)O $\rightarrow\sigma^*$ O-H	34.88	32.95	33.92		34.75	32.80	33.78
ΔE (HOMO-LUMO)	4.61	4.37	4.49		4.53	4.27	4.40
CH ₃ -ADM				OCH ₃ -ADM			
	-2	-4	Avg.	X-ray ^c	-2	-4	Avg.
δ OH ^b	15.59	15.18	15.39(16.10)		15.64	15.21	15.43(16.11)
ν OH	2988	3020	3004		2986	3015	3001
γ OH	997	965	981		998	970	984
R O...O	2.517	2.529	2.523	2.511	2.516	2.521	2.519
R O-H	1.007	1.005	1.006	0.904	1.008	1.006	1.007
R O...H	1.599	1.609	1.604	1.731	1.597	1.609	1.600
<OHO	149.0	149.9	149.5	143.0	149.1	149.9	149.5
E _{HB}	20.3	20.0	20.2		20.5	21.0	20.8
ρ BCP	0.0622	0.0606	0.0614		0.0625	0.0610	0.0618
$\nabla^2\rho$ BCP	-0.1522	-0.1507	-0.1515		-0.1524	-0.1510	-0.1517
Lp(1)O $\rightarrow\sigma^*$ O-H	4.35	3.95	4.15		4.40	4.00	4.20
Lp(2)O $\rightarrow\sigma^*$ O-H	31.00	30.00	30.50		31.33	31.50	31.42
Σ Lp(1,2)O $\rightarrow\sigma^*$ O-H	35.35	33.95	34.65		35.73	33.50	35.62
ΔE (HOMO-LUMO)	4.61	4.38	4.50		4.48	4.29	4.39
F-ADM				NH ₂ -ADM			
	-2	-4	Avg.	X-ray ^c	-2	-4	Avg.
δ OH ^b	15.52	15.28	15.40(16.09)		15.94	15.60	15.77(16.12)
ν OH	3011	3022	3017		2967	3005	2986
γ OH	992	962	977		1002	975	989
R O...O	2.520	2.528	2.524		2.514	2.506	2.510
R O-H	1.006	1.005	1.006		1.009	1.008	1.009
R O...H	1.605	1.609	1.607		1.592	1.595	1.594
<OHO	148.8	149.7	149.3		149.4	151.2	150.3
E _{HB}	20.1	19.6	19.9		20.8	22.0	21.4
ρ BCP	0.0610	0.0607	0.0609		0.0633	0.0620	0.0627
$\nabla^2\rho$ BCP	-0.1516	-0.1505	-0.1510		-0.1527	-0.1520	-0.1523
Lp(1)O $\rightarrow\sigma^*$ O-H	4.31	3.91	4.11		4.43	4.20	4.32
Lp(2)O $\rightarrow\sigma^*$ O-H	30.14	29.98	30.06		32.09	35.12	33.61
Σ Lp(1,2)O $\rightarrow\sigma^*$ O-H	34.45	33.89	34.17		36.52	39.32	37.92
ΔE (HOMO-LUMO)	4.65	4.44	4.55		4.24	4.01	4.13
NO ₂ -ADM				CF ₃ -ADM			
	-2	-4	Avg.	X-ray ^c	-2	-4	Avg.
δ OH ^b	15.47	14.99	15.23(15.70)		15.49	15.02	15.26(15.85)
ν OH	3040	3055	3048		3028	3042	3035
γ OH	986	945	971		989	953	966
R O...O	2.527	2.545	2.536	2.567	2.524	2.543	2.534
R O-H	1.005	1.003	1.004	0.865	1.005	1.004	1.005
R O...H	1.616	1.634	1.625	1.758	1.611	1.631	1.621
<OHO	148.4	148.8	148.6	155.0	148.5	148.7	148.7
E _{HB} ^d	19.2	18.7	19.0		19.5	18.5	19.0
ρ BCP	0.0596	0.0584	0.0590		0.0603	0.0590	0.0597
$\nabla^2\rho$ BCP	-0.1506	-0.1487	-0.1497		-0.1511	-0.1490	-0.1501
Lp(1)O $\rightarrow\sigma^*$ O-H	4.15	3.69	3.92		4.21	3.71	3.96
Lp(2)O $\rightarrow\sigma^*$ O-H	28.63	27.76	28.26		29.23	27.28	28.26
Σ Lp(1,2)O $\rightarrow\sigma^*$ O-H	32.78	31.45	32.12		33.44	30.99	32.22
ΔE (HOMO-LUMO)	3.98	3.66	3.82		4.20	3.90	4.05

^a All calculated at the B3LYP/6-311++G** level of theory. The experimental values are in parentheses from Ref. [36,37,43-44].

^b The experimental values are in parentheses from Ref. [21].

^c The experimental x-ray values from Ref. [22].

The regression coefficients of Hammett correlations of enol-2, enol-4, and their average in target molecules are shown in Tables 6-8. These tables show good linear correlations between some the mentioned parameters with σ_p , as Equation (3),

$$\text{Parameter} = \rho\sigma_p + \text{const.} \quad (3)$$

In addition, according to our results, the correlations of the reported and theoretical equilibrium constants (K_{eq}) between two stable *cis*-enol forms and σ_p have no fairly good regression coefficients. The r^2 values for $\log K_{eq}$ are 0.5284 (0.3487), 0.4301 (0.3719), for X-TFBA, X-ADM, respectively. The values in the parentheses are the experimental equilibrium constants.

Table 6. The R square values for theoretical and experimental correlations of δ_{OH} , ν_{OH} , and γ_{OH} vs σ_{p} .

Parameters	X-TFBA			X-ADM		
	2	4	Avg. ^a	2	4	Avg. ^a
δ_{OH} (Calc.)	0.7348	0.6989	0.8127 (0.9826)	0.7285	0.6693	0.7893 (0.8143)
ν_{OH} (Calc.)	0.9650	0.9351	0.9787	0.9821	0.8823	0.9845
γ_{OH} (Calc.)	0.9629	0.1520	0.7213	0.9719	0.9876	0.9725

^a The R square values for the experimental values are in parenthesis.

Table 7. The R square values between geometrical parameters related to IHB strength vs. σ_{p} .

Parameters	X-TFBA			X-ADM		
	2	4	Avg.	2	4	Avg.
R O...O	0.9700	0.8857	0.9554	0.9709	0.8989	0.9449
R O-H	0.9640	0.9099	0.9699	0.9241	0.8962	0.9424
R O...H	0.9710	0.9246	0.9695	0.9887	0.9090	0.9642
R O...H+R O-H	0.9640	0.9310	0.9651	0.9846	0.8899	0.9519
<OHO	0.9700	0.9793	0.9847	0.9877	0.9189	0.9543
E_{HB}	0.9680	0.9010	0.9638	0.9828	0.8600	0.9273
ρ_{BCP}	0.9680	0.9113	0.9668	0.9523	0.9511	0.9856
$\nabla^2_{\rho_{\text{BCP}}}$	0.9560	0.8684	0.9250	0.9734	0.9816	0.9961

3.2.1. Correlation between the chemical shifts of enolic proton with σ_{p}

The experimental and calculated proton chemical shifts of enolated proton (δ_{OH}) play an important role in characterization of the nature of IHB strength [41]. The calculated δ_{OH} of both stable *cis*-enol forms and their average values of title molecules with their report chemical shifts are given in Tables 4 and 5. According to these values, the IHB strength of all molecules are in agreement with the increasing of δ_{OH} . Table 6 and Figure S1 (supplementary material), show a linear dependence with weak to very good regression coefficients, in the range of 0.6689-0.9826 between the theoretical and experimental δ_{OH} of 4- and 2-forms and their average with σ_{p} ,

$$\delta = \rho\sigma_{\text{p}} + \text{constant} \quad (4)$$

Table 6 shows which the best correlations are related to the experimental δ_{OH} values and σ_{p} .

3.2.2. Correlation between the positions of IR bands related to IHB strength with σ_{p}

The values of OH stretching (ν_{OH}) and out of plane bending of OH (γ_{OH}) in the IR have important roles in strength of the IHB [41-43]. The increasing of γ_{OH} and decreasing of ν_{OH} wavenumbers are in agreement with increasing of the IHB strength of the mentioned molecules. Table 6 and Figure S2 (supplementary material) show good linear correlations between the theoretical ν_{OH} and γ_{OH} frequencies of 2- and 4-tautomers and their average values with σ_{p} , except for γ_{OH} of X-TFBA-4 form, this correlation is not shown. This behavior could be easily explained, if we consider the calculation results. According to the calculation results, in some substitutions, the mentioned γ_{OH} is coupled with out of plane bending of $\text{CH}\alpha$ ($\gamma_{\text{CH}\alpha}$).

3.2.3. Correlation between σ_{p} and geometrical parameters related to IHB strength

Geometrical parameters of chelated ring are very important for explaining of IHB strength in the *cis*-enol forms of β -diketones, because the IHB strength in these molecules is explained by the resonance-assisted hydrogen bond [43-47]. Since the O...O, O...H, and O-H+O...H distances, the O-H bond length, and the O...H-O bond angle are very important indicators for the IHB strength, so we collected these geometrical parameters (all calculated at the B3LYP/6-311++G** level) in Table 7. By increasing the IHB strength, the calculated O...H and the O...O bond lengths decreases, while

the calculated OHO bond angle and the O-H bond length increase. Relatively excellent correlations exist between the aforementioned parameters and σ_{p} for enols-2, enols-4 and their average (see Table 7 and Figure S3 in supplementary material), the correlation figures for O...O, O-H+O...H distances, and OHO bond angle are not shown.

3.2.4. Correlation between σ_{p} and AIM results related to IHB strength

In the topological theory of AIM, a bond critical point (BCP) appears between two adjacent atoms. The nature of chemical bonds is described by the total electronic density, $\rho(r)$, and its corresponding Laplacian, $\nabla^2\rho(r)$, of the critical point. The hydrogen bond energies (E_{HB}), according to the Espinosa *et al.* suggestion [42], the calculated total electronic density and its corresponding Laplacian of O...H BCP of the stable *cis*-enol forms and their average values, calculated at the B3LYP/6-311++G** level, are given in Tables 3-5. According to these Tables, the IHB strength of the titled molecules are in agreement with our reported trends (see trends 1 and 2 in the section 3.1).

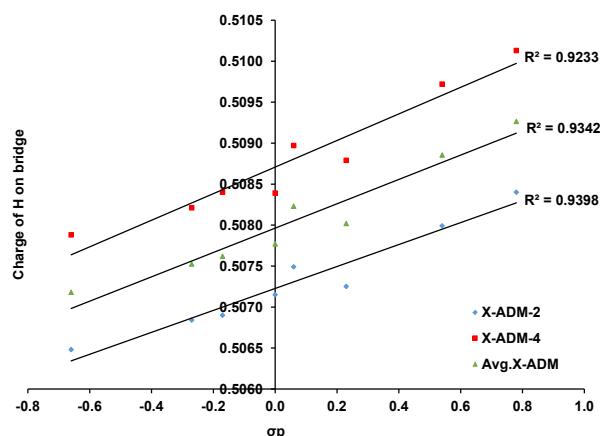
Table 7 and Figure S4 show fairly good linear correlations between the IHB strength, $\rho(r)$, and its corresponding Laplacian of O...H BCP, the correlation figures for Laplacian are not shown, at the O...H bond critical point of two *cis*-enol forms, their average and σ_{p} . According to these results, the correlation coefficients are in the range 0.8600-0.9961. It means that the topological parameters as well as the mentioned parameters described the relationship between the H-bond strength and σ_{p} .

3.2.5. Correlation between σ_{p} and NBO results related to IHBs

The natural bonding orbital (NBO) calculations were carried out by using the same method. The NBO analysis presents an effective method not only for studying the intra- and inter-molecular bonding, but also for investigating conjugative interaction in molecular systems by using second order perturbation theory. The second order Fock matrix was performed to assess the interactions between donor and acceptor in the NBO analysis. The larger $E^{(2)}$ values show the more intensive interaction between electron donors and electron acceptors, that is, more donating tendency from electron-donors to electron-acceptors and greater the extent of conjugation of the whole system. The NBO study, such as charge analysis, Wiberg bond orders, and hyperconjugative interactions, can be used as the other method for characterization of IHBs [48].

Table 8. The R square values between NBO results and difference energy HOMO and LUMO vs σ_p .

Parameters	X-TFBA			X-ADM		
	2	4	Avg.	2	4	Avg.
LP (1) O \rightarrow σ^* O-H	0.9780	0.8785	0.9564	0.9694	0.9398	0.9711
LP (2) O \rightarrow σ^* O-H	0.9810	0.9427	0.9854	0.9615	0.8345	0.9202
Σ LP (1), LP (2) O \rightarrow σ^* O-H	0.9820	0.9385	0.9844	0.9680	0.8432	0.9262
Bond order O...H	0.9800	0.9416	0.9847	0.9649	0.9089	0.9188
Bond order O-H	0.9778	0.8964	0.9774	0.9916	0.8514	0.9414
Charge of Hydrogen on the bridge	0.9585	0.9553	0.9583	0.9398	0.9233	0.9342
ΔE (HOMO-LUMO)	0.8937-0.9661	0.9243-0.9639	0.9035-0.9899	0.9376-0.9964	0.9185-0.9986	0.9318-0.9980

**Figure 2.** The linear correlation between charge of H on bridge hydrogen bond and σ_p .

One of the most important hyperconjugative interactions that is proportional to IHB strength, is $Lp(O) \rightarrow \sigma^*(O-H)$, which are shown in Tables 3-5. Table 8 and Figure S5 correlated these interactions and $\Sigma LP(1), LP(2)O \rightarrow \sigma^*O-H$ with σ_p for both stable *cis*-enol forms of the title molecules and their average, which indicates excellent agreement with σ_p . The correlation figure of $\Sigma LP(1), LP(2)O \rightarrow \sigma^*O-H$ with σ_p is not shown.

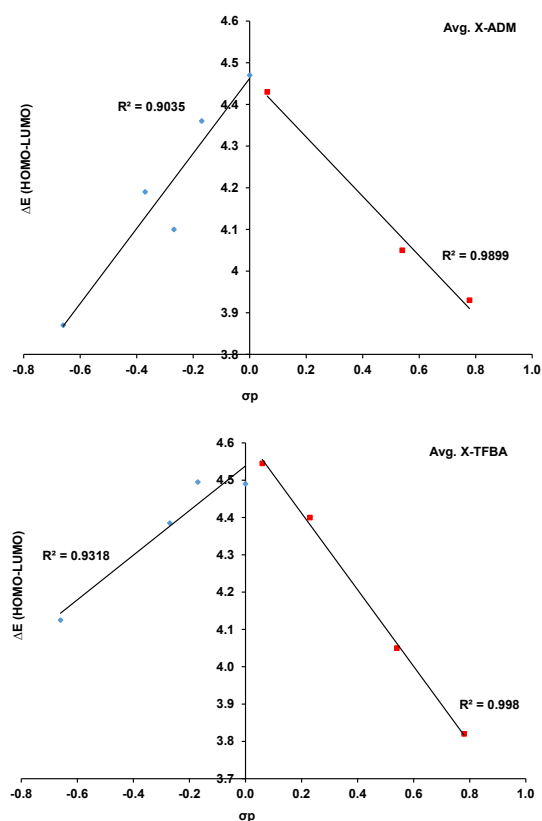
The calculated Wiberg bond orders [49] of O-H bond and O...H and O...O distances for two stable *cis* enols, and their average, for comparison, are considered. We correlate these bond orders with the σ_p . Excellent linear relationships between the O-H and O...H bond orders with σ_p were obtained (Table 8 and Figure S6). The correlation between O...O bond length with σ_p is not shown. Because of poor correlation between O...O bond length with σ_p , it is not shown here.

The natural charge on the bridged hydrogen, obtained by the NBO calculations for optimized geometries of *cis*-enol forms and their average, is well correlates with σ_p . The R square values between the proton charge and σ_p are presented in Table 8 and Figure 2 good linear relationship between them is obtained.

3.2.6. Correlation between σ_p and the energy difference between the orbitals of HOMO and LUMO

The HOMO and LUMO describe the ability to donate and obtain an electron, respectively, and the energy gap between the HOMO and LUMO reveals the chemical activity of the molecule [50,51]. The average energy difference between the HOMO and LUMO of the title molecules are in the 3.87-4.49 eV range (Tables 4 and 5). This energy gap indicates that the title molecules are very stable [52-55]. Our results show that there are good linear correlations between σ_p and the energy difference between HOMO and LUMO in the studied molecules, see Table 8 and Figure 3. This figure shows positive and negative slopes in the region of the negative and positive σ_p , respectively. Therefore, with increasing of EW and ED of

substitutions, the energy gap between the HOMO and LUMO decrease.

**Figure 3.** Correlation between σ_p and the average energy difference between the orbitals of HOMO and LUMO.

4. Conclusion

There are two stable *cis*-enol forms for the titled β -diketones. The theoretical equilibrium constant (K_{eq}) between the considered tautomers are in agreement with the reported experimental values.

The intramolecular hydrogen bond for the TFBA and ADM molecules and its substitutions in para position have been investigated using the B3LYP/6-311++G** level of theory. The results obtained from the calculations, such as the topological parameters, geometrical parameters, NBO method, theoretical and experimental IR and NMR spectroscopies, have been used to estimate the IHB strength. All these results show that electron donating substitutions at the para position, such as NH_2 , OCH_3 , CH_3 , and OH , increases the hydrogen bond strength, while electron-withdrawing substitutions, such as NO_2 and CF_3 decreases the IHB strength. The halogen substitutions have no significant effect on the IHB strength. According to various correlation graphs, correlation some of the geometrical and topological parameters for enol-4 and enol-2 forms and their average with σ_p show good linear dependence. It means that the above parameters and σ_p are good descriptor for the IHB strength.

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Supporting information

Supplementary material data related to this article can be found at journal webpage.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.

Author contributions: All authors contributed equally to this work.

Ethical approval: All ethical guidelines have been adhered.

Sample availability: Samples of the compounds are available from the author.

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