

Conventional and Unconventional Intramolecular Hydrogen Bonding in some Beta-diketones

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This study presents our view of unconventional and conventional intramolecular hydrogen bonds (HBs) for some beta-diketones theoretically and experimentally. According to our results, the groups such as phenyl and *t*-but in beta positions increase and CF₃ group decrease IHB strength, respectively. For better understanding of the substitution effects, the compounds with similar and different substitutions compared to each other experimentally and theoretically. Comparison between theoretical and experimental results, E_{HB} and δOH , shows that these parameters change by adding one substitution. These changes are almost doubled by adding another similar substitution. This conclusion achieved for DMPD with phenyl and *t*-But groups in beta positions. Whereas, TFBA, with phenyl and CF₃ groups, and TFDMD with CF₃ and *t*-But groups in beta positions do not follow this achievement. The ¹H NMR chemical shifts for the stable *cis*-enol forms of the mentioned compounds have been calculated at different levels with various basis sets in CHCl₃ as solvent using PCM method. For the most beta-diketones, the 6-311G** and 6-311++G** basis sets, in all our calculated levels, are in better agreement with the experimental results. According to AIM results, unconventional hydrogen bonding is created in some beta-diketones containing Ph group. The strength of this hydrogen bonding is the same for all these compounds and is about 2 kcal mol⁻¹.

Keywords: β -diketones, DFT, Conventional and unconventional intramolecular hydrogen bond, Atoms In Molecules Theory

INTRODUCTION

One of the strongest and the most common types of noncovalent bond is the hydrogen bond which plays an important role in chemistry, physics, and biology [1-3]. Large numbers of theoretical and experimental studies have been conducted to investigate the properties of intramolecular and intermolecular hydrogen bonding [4-7]. In an intramolecular hydrogen bond (IHB) system, both proton donor and proton acceptor groups, which may be of various kinds of functional groups, are located in the same molecule. Interaction of these functional groups leads to a ring like structure that is often introduced as chelated ring. Formation of IHB in *cis*-enol forms of β -diketone, β -aminoenone, and β -enaminoimine molecules leads to an enhancement of resonance conjugation in the π -electron system. This kind of hydrogen bond (IHB) was named by

Gilli *et al.* [8] as resonance assisted hydrogen bond (RAHB).

β -diketones are a well-known class of tautomeric compounds that are widely used in organic and inorganic chemistry. The *cis*-enol form of β -diketones is characterized by a strong intramolecular hydrogen bond. The nature of intramolecular O-H...O hydrogen bond in the enol form of symmetric and asymmetric β -diketones have been the subjects of intensive studies [9-11]. The NMR and vibrational spectroscopy techniques have been intensively used to study the hydrogen bond strength and also keto-enol equilibrium in these compounds [12]. On the other hand, it has been also shown that modern *ab initio* and density functional quantum chemical calculations can predict the strength and nature of the intramolecular hydrogen bond in β -dicarbonyl compounds extremely well [13-14]. The substitution in the α or β positions drastically changes the hydrogen bond strength and the equilibrium between enol and keto tautomers [15]. For example, the electron-

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withdrawing groups, such as trifluoromethyl (CF₃), and the electron supplying groups such as phenyl (C₆H₅) in beta position make IHB weaker and stronger, respectively [16-19]. The understanding of hydrogen bonding has changed in last years [20-22], since new types of H bonds have been introduced. Such interactions known as unconventional hydrogen bonds may be generalized in four ways: 1- The H bonds with C-H bonds as unconventional donors [23-26], 2- those with unconventional acceptors (π electrons within aromatic systems or the other π -electronic moieties or simple C-atoms) [27], 3-hydrogen bonds with unconventional donors and unconventional acceptors such as C-H...C (or C-H... π) systems, and the last dihydrogen bonds [28-29].

Experimental and theoretical investigations have been done to understand the nature of these unconventional hydrogen bonds [30-36]. Some structural and energetic similarities have been observed between the conventional hydrogen bond and the dihydrogen bond. The H...H distance in X-H...H-Y systems typically ranges from 1.7-2.4 Å. The interaction energy also lies within the range of typical hydrogen bonds, 3-10 kcal mol⁻¹. Being linearity in normal hydrogen bonds is preserved in unconventional hydrogen bonds. The H...H-X angles usually lie within 160-180°. However, the Y-H...H angles are found to be powerfully bent, falling in the range of 95-130° [37].

The aim of the present paper is investigating and comparing the simple conventional and unconventional H bonds in terms of their parameters related to hydrogen bonding of some beta-diketones “acetylacetone (AA), benzoylacetone (BA), dibenzoylmethane (DBM), 5,5-dimethyl hexane-2,4-dione (DMHD), 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD), 1,1-trifluoro-pentane-2,4-dione (TFAA), hexafluoro-acetylacetone (HFAA), 4,4,4-trifluoro-1-phenyl-1,3-butanedione (TFBA), 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (TFDMHD), and 4,4-dimethyl-1-phenylpentane-1,3-dione (DMPD)”, such as bond length and bond angles, chemical shift (δ), vibrational frequency (ν_{OH} and γ_{OH}), intramolecular hydrogen bond energy, E_{HB} , hyperconjugative interaction energy of $lp(O) \rightarrow \sigma^*(O-H)$, natural charges of bridged hydrogen, total electronic density, and Laplacian of total electronic density in critical points, by using DFT, NMR, NBO, and AIM calculations.

COMPUTATIONAL DATA

Geometry optimizations and all the computations for the titled beta-diketones, in the present study, were performed at different levels using Gaussian 09 software package and AIM 2000 software [38-39]. The Atom in Molecule was applied to obtain electron density at hydrogen bond critical points according to Bader's atoms in molecules (AIM) theory [40] at the B3LYP/6-311++G** level. The NMR calculations, at B3LYP/6-311++G** level, were applied using gauge-independent atomic orbital (GIAO) method [41,42] at the different levels of theory in CHCl₃ solvent by PCM method. The predicted ¹H chemical shifts are derived from equation $\delta = \sigma_0 - \sigma$, where δ is the chemical shift, σ is the absolute shielding, and σ_0 is the absolute shielding of TMS. Eventually, correlations between some calculated and observed parameters related to IHBs with experimental enolic proton chemical shifts were investigated. Graphs were drawn and regression analyses were carried out using Microsoft Office Excel, 2010 software.

The second order interaction energies [43], and the natural charge [44] were calculated using NBO 5.0 program [45], which applied the wave function information file generated by earlier version of NBO 3.0.

RESULTS

The main goal of this work is investigating the variation in the conventional and unconventional parameters related to IHBs in some β -diketone compounds with adding one and two similar and different beta substitutions. Therefore, we classified the selected compounds in four categories. In the first three categories, AA participates with BA and DBM with one and two phenyl group instead of methyl group in AA (first arrangement), and in the other ones, TFAA and HFAA (second arrangement), DMHD and TMHD (third arrangement) with one and two CF₃, and *t*-But groups were substituted by methyl group of AA, respectively. The last class investigated includes 3 molecules with different β substitutions; named: DMPD (with Ph and *t*-But groups), TFBA (with CF₃ and phenyl groups), and TFDMHD (with CF₃ and *t*-But groups).

According to the pervious publications [46-53], some substitutions such as phenyl ring and *t*-But groups make the

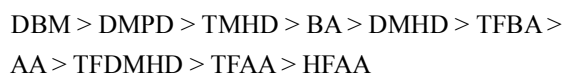
Table 1. The Calculated and Experimental Spectroscopic, Geometrical and Topological Parameters Related to the IHB Strength, Conventional and Unconventional HB Strength of DMPD, BA, TFBA, DBM, AA, DMHD, TMHD, TFAA, HFAA and TFDMDH^a

	DMPD				BA			TFBA			DBM	AA	DMHD	TMHD	TFAA	HFAA	TFDMDH
	E1	E2	E3	Avg ^d	2	4	Avg ^d	2	4	Avg ^d			Avg ^d	Avg ^d	Avg ^d		
δ OH ^b	16.8	16.3	17.3	16.8	16.8	16.3	16.6	16.1	15.8	16.0	17.1	15.7	16.0	16.3	14.6	13.7	15.4
				(16.6)			(16.2)			(15.1)	(16.8)	(15.4)	(16.0)	(16.8)	(14.2)	(13.0)	(14.9)
ν OH ^b	2948	2968	2849	2922	3006	2960	2983	3037	3051	3044	2914	3066	3007	2964	3166	3280	3073
				(2630)			(2650)			(2870)	(2620)	(2750)	(2660)	(2634)	(2900)	(3000)	(2785)
γ OH ^b	1000	991	1020	1004	994	992	993	837	959	898	1002	794	998	824	818	839	951
				(969)			(957)			(890)	(965)	(952)	(960)	(964)	(892)	(-)	(900)
ρ_{BCP}^c	0.066	0.065	0.070	0.067	0.062	0.063	0.062	0.059	0.057	0.058	0.066	0.057	0.061	0.065	0.052	0.041	0.058
$\nabla^2 \rho_{\text{BCP}}^c$	-0.0392	-0.0388	-0.0395	-0.0392	-0.0379	-0.0378	-0.0379	-0.0371	-0.0369	-0.0370	-0.0388	-0.0364	-0.0381	-0.0386	-0.0352	-0.0314	-0.0370
E_{HB}^c	16.1	17.3	16.9	16.8	20.0	20.5	20.3	18.9	17.9	18.4	22.1	18.1	19.7	21.4	15.9	11.6	18.4
R O...O ^c	2.506	2.515	2.492	2.504	2.52	2.513	2.517	2.525	2.540	2.523	2.502	2.544	2.525	2.508	2.558	2.593	2.539
$\angle \text{OHO}^c$	150.1	150.0	150.8	150.3	148.9	150.5	149.7	147	148.8	147.9	150.4	148.5	149.2	150.3	146.6	143.83	147.2
$\rho_{(\text{RCP})}^c$	0.0225	0.0219	0.0220	0.0221	0.0215	0.0218	0.0216	0.0214	0.0215	0.0214	0.0221	0.0210	0.0215	0.0219	0.0205	0.0190	0.0214
R H...H ^c	2.047	2.118	2.100	2.088	2.044	2.122	2.083	2.037	2.093	2.065	2.051	-	-	-	-	-	-
R C-H _a ^c	1.076	1.078	1.076	1.077	1.078	1.079	1.079	1.077	1.076	1.077	1.077	1.081	1.079	1.077	1.080	1.079	1.077
R C-H	1.0824	1.0828	1.0826	1.0826	1.0824	1.0828	1.0826	1.0822	1.0825	1.0824	1.0826	-	-	-	-	-	-
(of ph ring) ^c											(1.0828)						
$\rho_{\text{BCP un}}^c$	0.011	0.011	0.012	0.011	0.011	0.011	0.011	0.012	0.011	0.011	0.011	-	-	-	-	-	-
$\nabla^2 \rho_{\text{BCP un}}^c$	-0.0416	-0.0411	-0.0437	0.0421	-0.0431	-0.0411	-0.0421	-0.0440	-0.0428	-0.0434	-0.0418	-	-	-	-	-	-
E_{unHB}^c	2.0	1.9	2.1	2.0	2.1	1.9	2.0	2.1	2.0	2.1	2.0	-	-	-	-	-	-
$\rho_{\text{RCP un}}^c$	0.011	0.010	0.011	0.011	0.011	0.010	0.011	0.011	0.011	0.011	0.0101	-	-	-	-	-	-
lp(O)→σ*(O-H)	33.9	32.7	37.7	34.8	30.8	32.5	31.7	28.6	27.8	28.2	35.1	28.1	29.98	35.00	33.42	30.06	27.01

^aAll parameters are calculated at the B3LYP/6-311++G** level. The experimental values in the CDCl₃ solution are in parentheses, obtained from Ref. [46-53], “un” means unconventional. ^b δ , proton chemical shift in ppm; ν and γ are stretching and out-of-plane bending modes frequencies, respectively, in cm⁻¹. ^cR is bond length in Å, $\angle$ is the bond angle in degrees, E_{HB} and E_{unHB} is the conventional and unconventional IHB energy in kcal mol⁻¹, ρ_{BCP} is the density of critical point and $\rho_{(\text{RCP})}$ is the density of ring critical point, all calculated at B3LYP/6-311++G**. ^dThe average geometrical parameters for the stable forms.

IHB stronger due to the resonance effect and steric effect, respectively, while the CF₃ substitutions decrease the IHB strength, because of electron withdrawing effect. The parameters related to IHB strength, include optimized geometrical parameters, topological parameters, theoretical and experimental spectroscopic data consist of IR frequencies and NMR chemical shifts, and the natural bond orbital analysis (NBO), for each stable form and their averages are collected in Table 1. Comparison the geometrical parameters, reported in Table 1, such as the O...O, and O...H bond lengths, and also OHO bond angle and AIM results, including density and Laplacian of critical points, confirms the above conclusion. The O...O and O...H bond lengths decrease and increase by increasing and decreasing the IHB strength, respectively. Also, the density and Laplacian of critical points increase, when IHB strength increases.

Moreover, the following trend in the IHB strength for the mentioned molecules is obtained from Table 1:



According to the published works [46-53], the symmetrical β -diketones such as AA, DBM and HFAA have one stable *cis*-enol form, while in unsymmetrical ones, depending on the conformation, more than one form have been reported. The TMHD, TFAA, BA, DMHD, DMPD, TFBA, and TFDMHD molecules have 2, 2, 2, 3, 3, 2 and 3 stable *cis*-enol forms, respectively, which are shown in Fig. 1. In the case of molecules containing phenyl group in beta position, two possible isomers characterized by the position of the phenyl group, attached at C2 (*i.e.*, adjacent to C=O bond) or at C4, are conceivable. They are labeled as 2 and 4, respectively.

The average full optimized geometrical parameters of 2 and 4 *cis*-enol forms of the mentioned compounds show that the O...O distance in 4 tautomer is less than that in 2 tautomer, indicating stronger hydrogen bonding in 4 tautomers. For the molecules with phenyl substitutions, this is due to the replacement of phenyl group in C-OH side in 4 tautomers, which increases the C=C and C=O bond lengths,

while the C-C bond length decreases. These changes in the bond lengths indicate that the π -electron delocalization in the enol ring slightly increases by phenyl substitution in the hydroxyl side. Substitution of phenyl group in the carbonyl side only increases the C=O bond length and changes in the other bond lengths are negligible. This result suggests that in 2 tautomer, the phenyl group is conjugated only with the C=O group.

In the molecules with CF₃ group, the electron withdrawing effect of CF₃ is adjacent to the C-OH group, which by removing the electron charge from O atom increases the acidity of the OH group, therefore, increases the hydrogen bond strength. On the other hand, in 2 tautomer, the CF₃ group is adjacent to the C=O group and withdrawing electron from the carbonyl group makes the oxygen more positive, therefore, reduces the strength of the intramolecular hydrogen bond [6,49-50].

One of the main aims in this work is investigating the effect of replacing one or two substitutions by CH₃ in the values of the δOH , νOH , γOH and E_{HB} parameters, experimentally and theoretically, at B3LYP/6-311++G** level. Comparison between BA and DBM with AA shows that by replacing one phenyl the experimental chemical shift and E_{HB} increase about 0.8 and 1.5 kcal mol⁻¹, respectively. By substituting *t*-But groups instead of methyl group in AA, δOH increases 0.5 ppm and E_{HB} changes 1.4 kcal mol⁻¹ in DMHD, respectively. While substituting of CF₃ group instead of methyl group in AA leads to a decrease in experimental chemical shifts about 1.2 ppm in TFAA. Also, the corresponding theoretical chemical shift variations are in agreement with that conclusion. By replacing the second ph and *t*-But groups, experimentally and theoretically, these values were considerably doubled, except for experimental chemical shift in HFAA and TFAA molecules (see Table 1). It is expectable for DMPD molecule, with phenyl and *t*-But groups substituents in beta position, δOH and E_{HB} change to 1.3 ppm and 3.0 kcal mol⁻¹ more than that in AA. The results of Table 1 confirm this conclusion. For TFBA, with CF₃ and phenyl groups in its β position, and TFDMHD, with CF₃ and *t*-But groups, the decrease of about 0.4 ppm (1.2-0.8) and 0.7 ppm (1.2-0.5) in δOH is predictable. While the experimental and theoretical δOH and E_{HB} of the TFBA

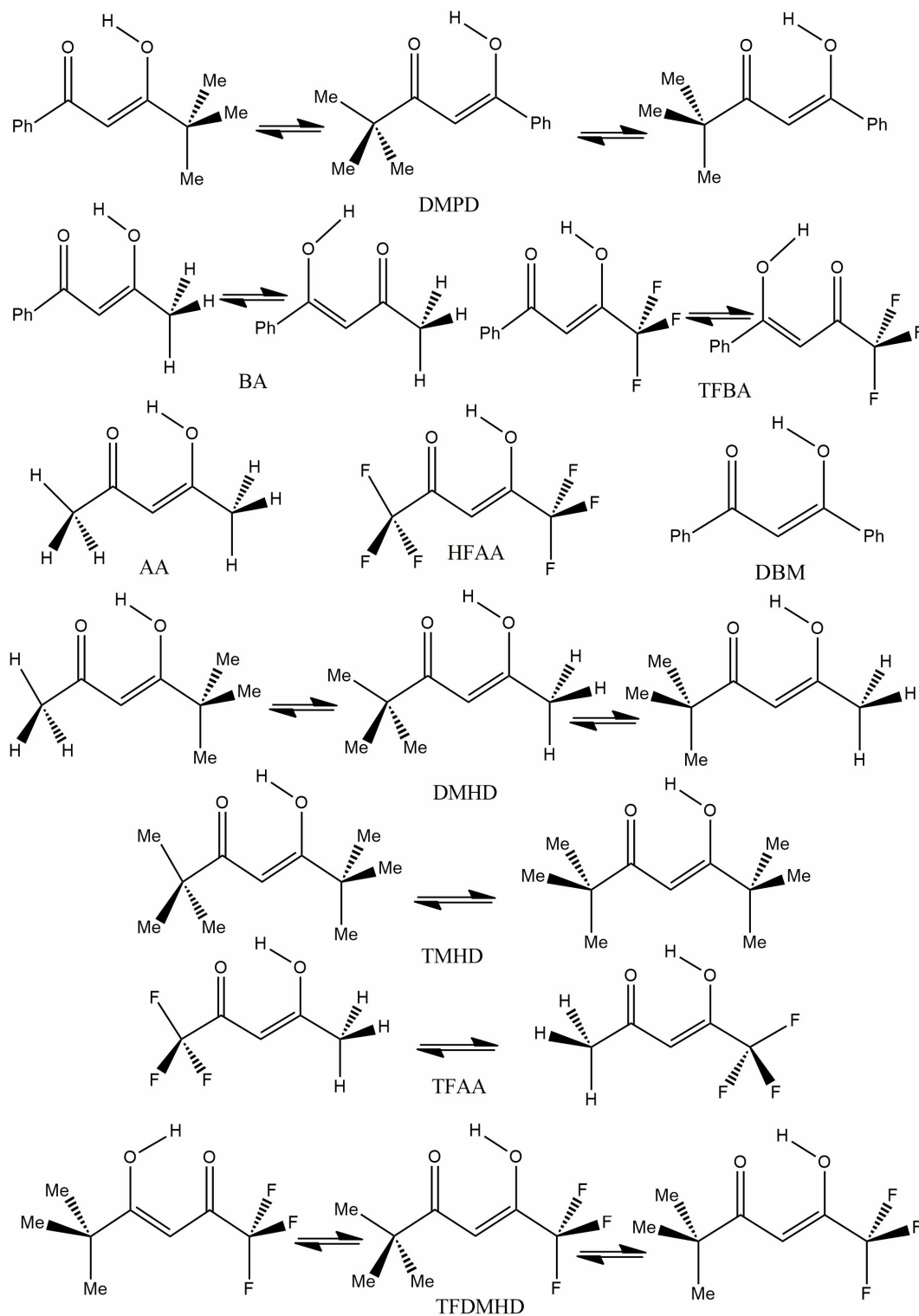


Fig. 1. The stable cis-enol forms of DMPD, BA, TFBA, AA, HFAA, DBM, DMHD, TMHD, TFAA and TFDMHD.

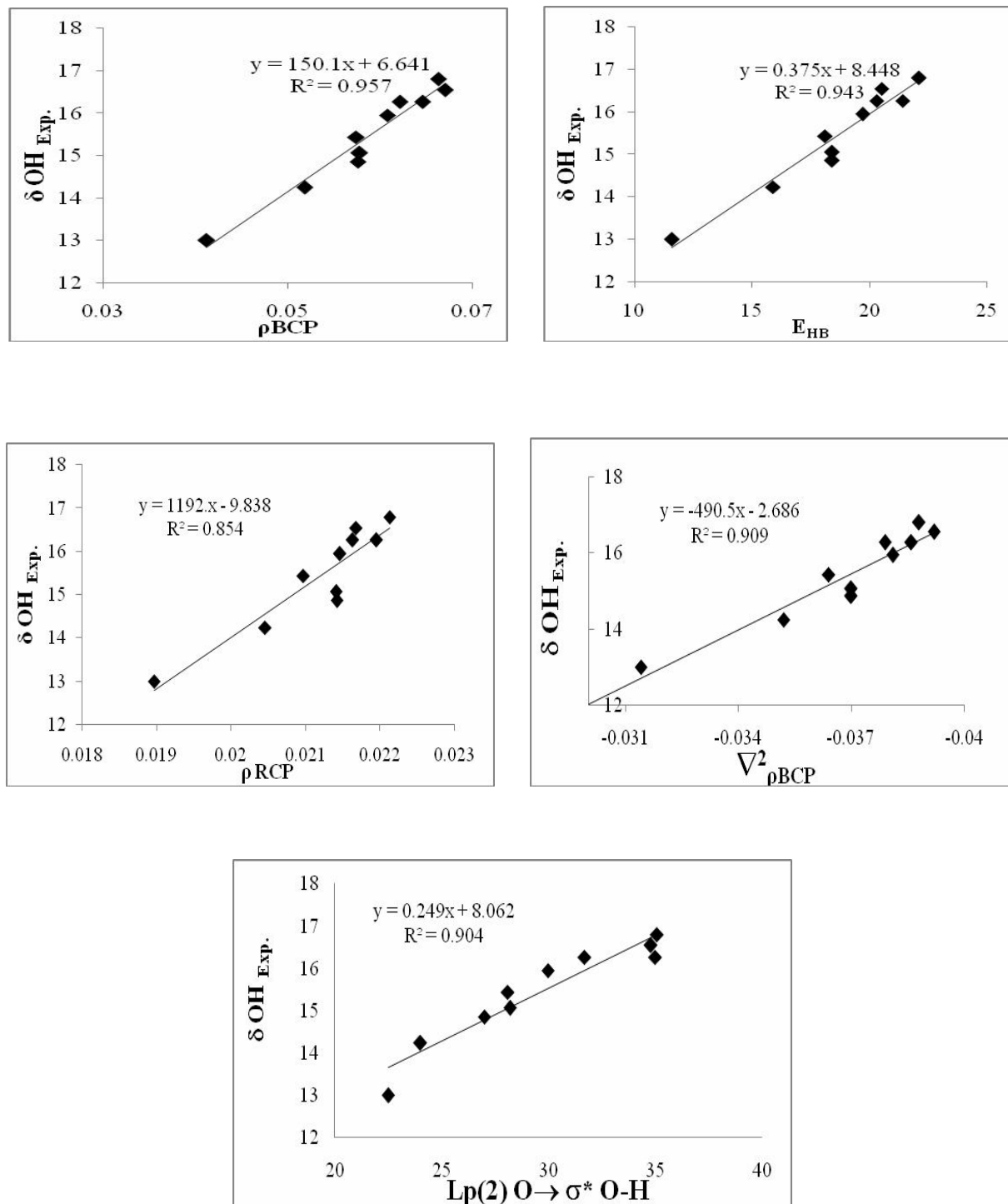


Fig. 2. The correlations between experimental chemical shifts of enolic proton with topological and NBO parameters related to the IHB strength.

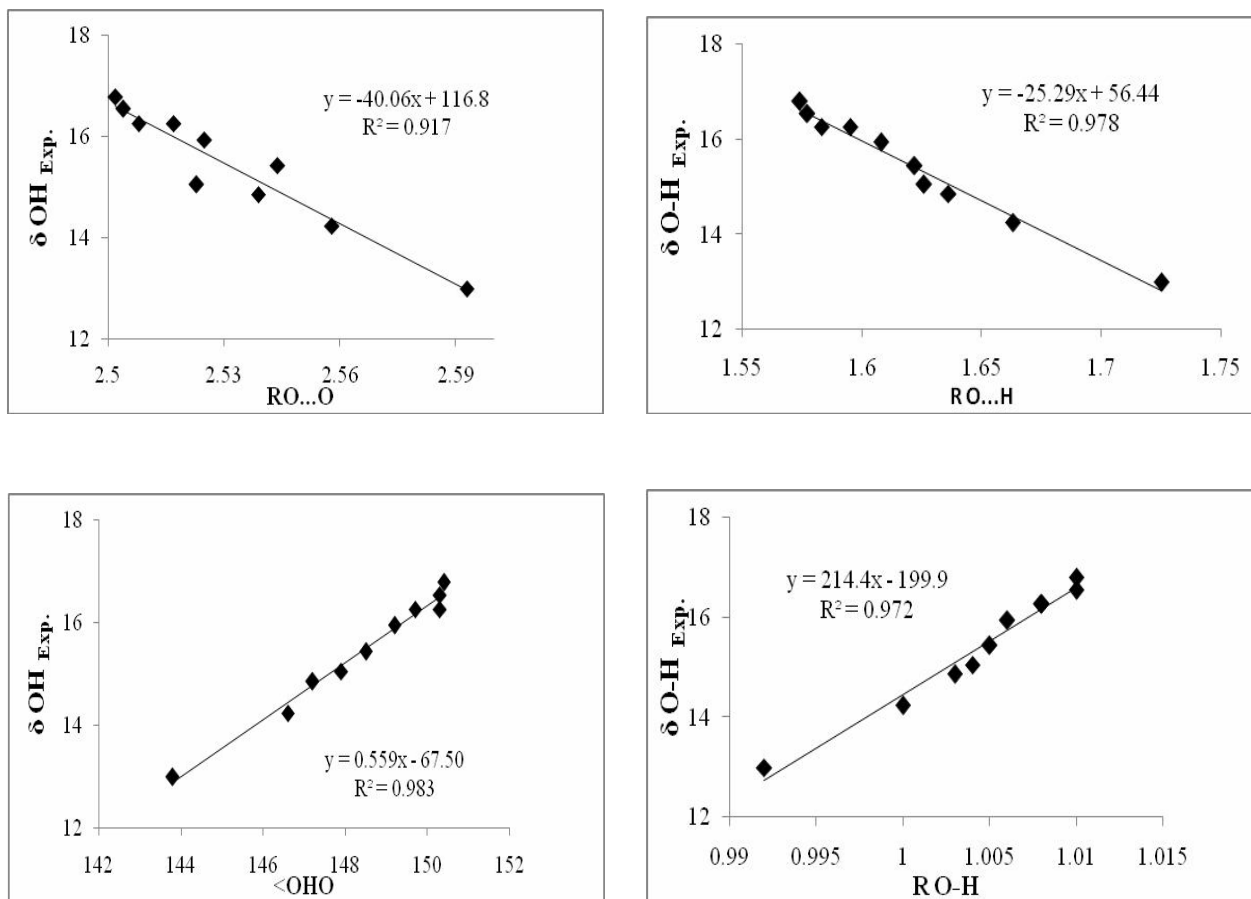


Fig. 3. The correlations between experimental chemical shifts of enolic proton with geometrical parameters.

and TFDMD molecules are more or less than those of the above expected values. Since, the experimental bands of νOH and γOH are very broad, we cannot find any relation in those frequencies of all mentioned compounds.

Figures 2-4 illustrate the linear correlation of the average parameters related to the hydrogen bond strength with the experimental δOH ($\delta\text{OH}_{\text{Exp.}}$). The coefficients are in the range of 0.823-0.983. More excellent correlations confirm our conclusions.

The ^1H NMR is one of the very significant tools in the analysis of hydrogen bonds. The electron density shifts occur when hydrogen bonding is present, resulting in perturbation of the proton shielding tensor [54]. The DFT calculations have been applied for analysis of hydrogen bonds within systems [55-56].

In order to find the key level for calculating the chemical shifts of OH, the B3LYP, TPSSH, BLYP, and X3LYP levels and 6-31G*, 6-31G**, 6-311G**, 6-311++G** basis sets were used in CHCl_3 solvent. According to Table 2, for the titled β -diketones, the values of δOH in the most levels are close to the experimental values, however, the 6-311G** and 6-311++G** basis sets in all levels are in better agreement with the experimental results.

As mentioned in introduction, the study of the unconventional hydrogen bond strength is one of the main goal in this study to analysis the new measures of the unconventional H-bond strength on a variety of hydrogen-bonded systems. Unconventional hydrogen bonding was created in some beta-diketones including Ph group. The

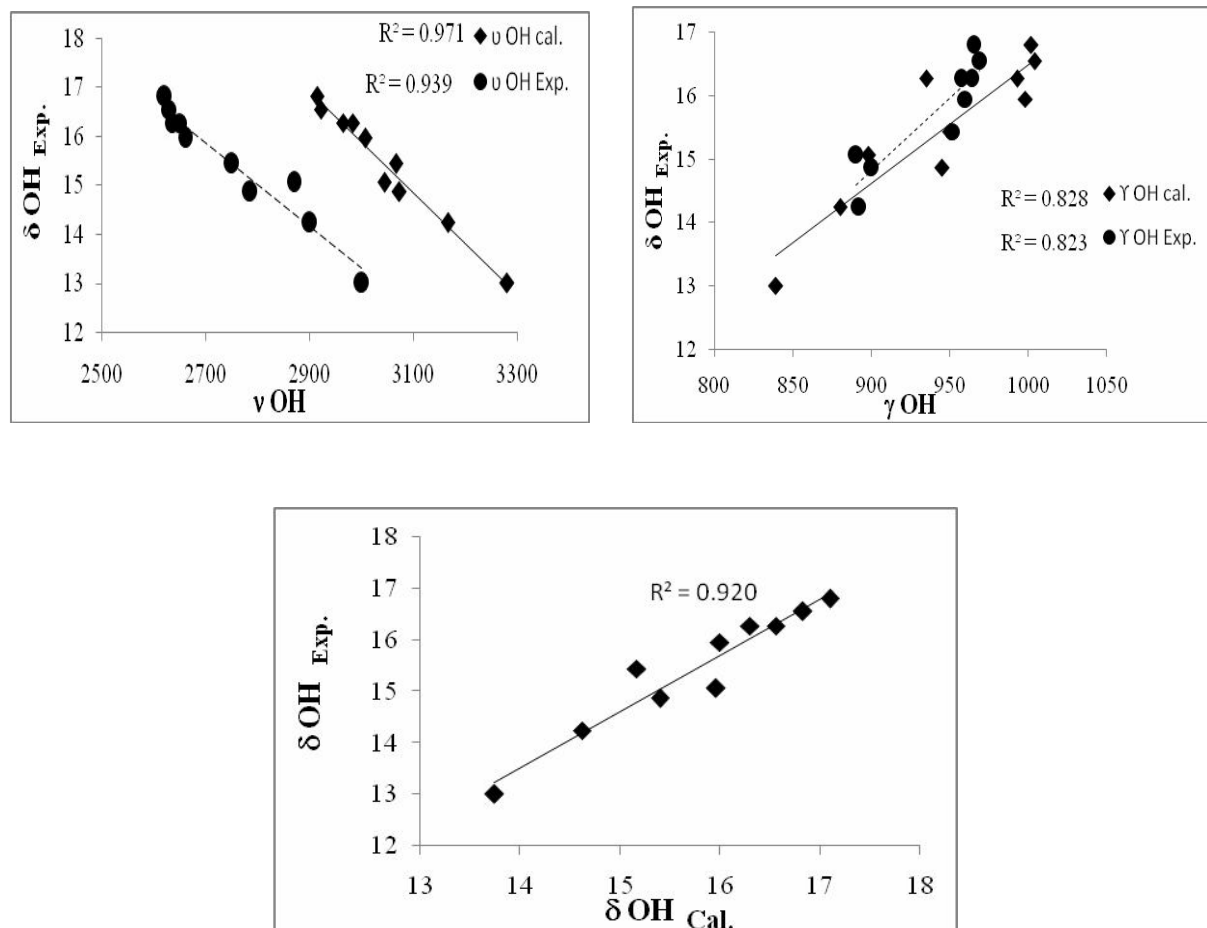
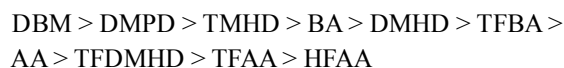


Fig. 4. The correlations between experimental chemical shifts of enolic proton with spectroscopic parameters related to IHBs.

system is unconventionally H bonded because of the unconventional donating H-H bond. These bonds occur between H_α and one of the hydrogens in phenyl ring in the neighboring of H_α . The parameters related to the mentioned hydrogen bond energy such as the H...H bond length, density of bond critical points (ρ_{BCP}) and ring critical points (ρ_{RCP}), Laplacian of these densities, and E_{unHB} show that there is no a significant difference in the strength of H...H bond in the target compounds. Meanwhile, CH_α and CH of the phenyl ring bond lengths, which form unconventional hydrogen bond, show no significant difference in above bond lengths of molecules including Ph ring (BA, DBM, DMPD and TFBA). The strength of the unconventional hydrogen bonds is about 2 kcal mol^{-1} in above molecules.

CONCLUSIONS

By comparing the theoretical and experimental parameters related to hydrogen bond strength, the following trend for IHB strength has been obtained:



Our calculations indicate that the 6-311G** and 6-311++G** basis sets in all levels are in better agreement with the experimental chemical shift of OH. By replacing one or two similar substitutions by CH_3 in the values of δOH in the mentioned compounds, the linear correlation has

Table 2. The ^1H NMR Chemical Shifts for Enolic Proton of Target Beta-diketones in Different Levels of Theory^a

Calculation level	AA	BA	DBM	DMHD	TMHD	DMPD	TFAA	HFAA	TFBA	TFDMHD
Theo.										
B3LYP/6-31G*	14.2	14.8	15.3	15.7	14.9	15.2	12.8	12.0	14.2	14.0
B3LYP/6-31G**	15.8	16.6	17.1	16.1	16.6	17.0	14.1	13.2	15.8	15.6
B3LYP/6-311G**	15.7	16.5	17.1	16.0	16.3	16.8	14.0	13.1	15.7	15.4
B3LYP/6-311++G**	15.8	16.7	17.1	16.2	16.5	16.9	14.2	13.3	15.9	15.6
TPSSH/6-31G*	14.2	14.9	15.3	15.8	14.9	15.2	12.8	12.1	14.2	14.0
TPSSH/6-31G**	15.9	16.6	17.1	16.2	16.6	17.0	14.2	13.3	15.9	15.6
TPSSH/6-311G**	15.7	16.5	17.0	16.2	16.3	16.8	14.0	13.2	15.7	15.4
TPSSH/6-311++G**	15.8	16.7	17.1	16.2	16.5	16.9	14.2	13.4	15.8	15.6
BLYP/6-31G*	14.2	14.8	15.1	15.7	14.8	15.1	13.1	12.0	14.1	13.9
BLYP/6-31G**	15.9	16.6	17.0	16.1	16.6	16.9	14.6	13.3	15.8	15.6
BLYP/6-311G**	15.7	16.5	17.0	16.1	16.3	16.8	14.4	13.2	15.7	15.4
BLYP/6-311++G**	15.8	16.6	18.1	16.2	16.4	16.9	14.6	13.4	15.8	15.6
X3LYP/6-31G*	14.2	14.9	15.3	15.7	14.9	15.2	13.1	12.0	14.2	14.0
X3LYP/6-31G**	15.8	16.6	17.1	16.1	16.6	17.0	14.5	13.2	15.8	15.6
X3LYP/6-311G**	15.7	16.5	17.1	16.1	16.4	16.8	14.4	13.1	15.7	15.4
X3LYP/6-311++G**	15.9	16.7	17.2	16.2	16.5	17.0	14.6	13.3	15.9	15.6
Exp. ^b	15.4	16.2	16.8	16.0	16.8	16.6	14.2	13.0	15.1	14.9

^aAll chemical shifts are relative to TMS in ppm. ^bThe experimental values are in the CDCl_3 solution from Ref. [46-53].

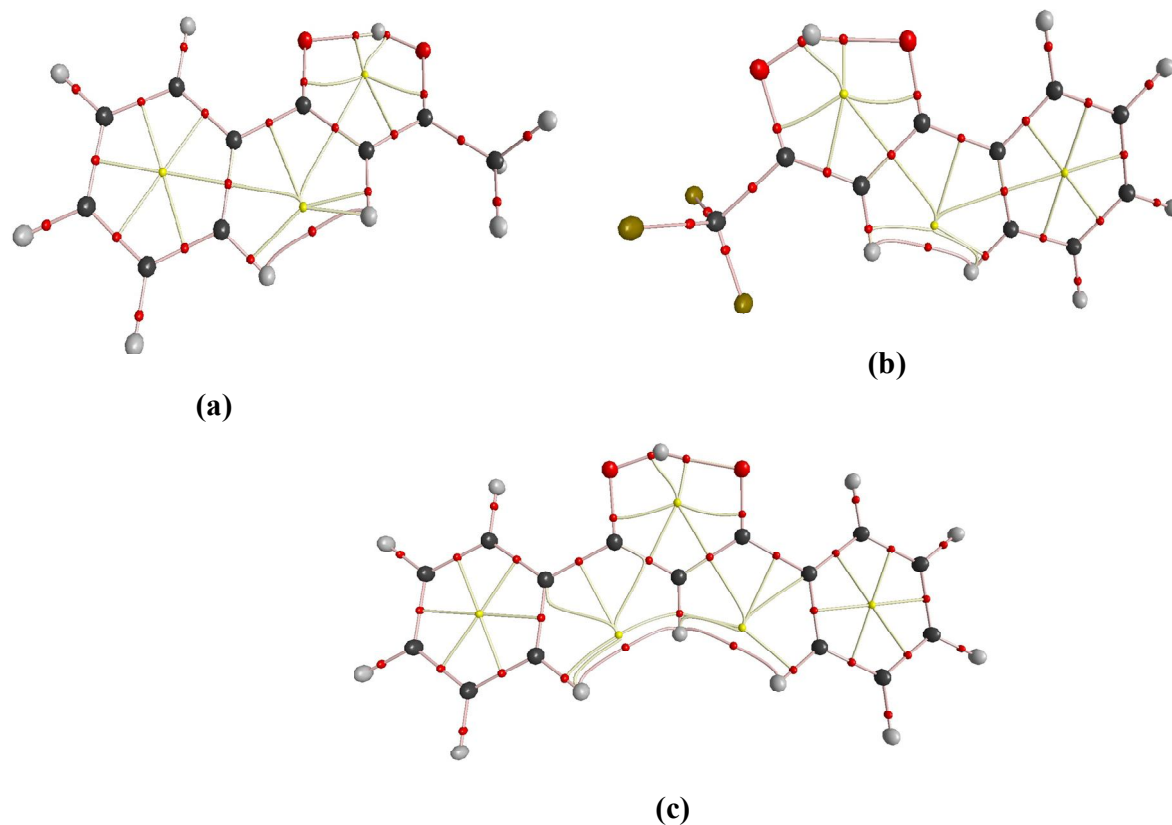


Fig. 5. The unconventional hydrogen bond in three compounds of β -diketones with phenyl ring, a) 2BA, b) 2TFBA and c) DBM.

been found for the titled β -diketones. The AIM results show that the unconventional hydrogen bonds occur in the beta-diketones including phenyl group. Our geometrical and AIM results indicate that the strength of unconventional hydrogen bond in the mentioned compounds is very weak and similar to each other.

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