



Theoretical Study Intramolecular Hydrogen Bond in Acetylacetone 3-substituted Derivatives: NMR, NBO analysis and Thermo-chemical Investigation

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ABSTRACT

The strength of the O–H...O hydrogen bridge in acetylacetone (AA) and acetylacetone derivatives is depending on the nature and size of the substitute groups and on the substitution position. We investigated the effect of electron-pull and electron-donor substitute on the formation of intramolecular hydrogen bonding at 3-substituted acetylacetone derivatives such as nitroacetylacetone (NAA) and methylacetylacetone (MAA). In this research NAA and MAA structures were fully optimized with B3LYP/6-31G*, 6-31G** and 6-311G**. From the electronic data we found that intramolecular hydrogen bonding in NAA is stronger than MAA.

Key words: Intramolecular hydrogen bond; Acetylacetone; Electronic data parameters.

INTRODUCTION

Hydrogen bonding is one of the most important phenomena in chemistry because it is crucial to understand many different interactions both in the gas phase and in condensed media^{1,2}. In a particular arrangement, which is represented by the intramolecular hydrogen bonds, two ends of the same molecule interact, resulting in a ring like structure. The properties of intramolecular hydrogen bond very often differ from those of intermolecular

hydrogen bond and a number of regularities and relationships resulting from a general theory of hydrogen bond cannot be fulfilled in the case of intramolecular hydrogen bond. Intramolecular hydrogen bonding has a large impact on the reactivity of molecules.

One of the more significant structures capable of bearing hydrogen bonds is the O–H...O unit, which is the most widely studied and documented in this respect³⁻⁶. Acetylacetone

(pentane-2,4-dione, here labelled AA) is one of the simplest members of β -diketones, which has been extensively studied both experimentally and theoretically⁷⁻¹⁰. AA is postulated to have unusually strong H-bonds (O–H...O type) in their cyclic, conjugated enolic forms (Figure 1). The strength of the O–H...O hydrogen bridge in acetylacetone and acetylacetone derivatives is depending on the nature and size of the substitute groups and on the substitution position^{5,6,11}. Several experimental data suggest that the strength of such a bridge is enhanced when the H atom in position 3 is substituted by electron-withdrawing groups¹²⁻¹³, and it increases strongly when very cumbersome substituents are involved because steric interactions push the two oxygen atoms closer to each other¹⁴⁻¹⁸.

The *ab initio* calculations using the Møller–Plesset approach indicate that strengthening of the hydrogen bridge, on passing from the parent (AA) to the 3-substituted derivatives, is not so relevant as expected on the ground of literature data, the maximum increase being about 21 kJ mol⁻¹ (in 3-*t*-butyl-acetylacetone)¹⁹.

MATERIAL AND METHODS

Ab initio calculations were carried out for nitroacetylacetone (NAA) and methylacetylacetone (MAA) using the Gaussian 98 program (Figure 2). We optimized the geometries of NAA and MAA to calculate ground state properties Becke's three parameter hybrid method (Becke, 1988) with the Lee *et al.* (1988)²⁰ correlation functional methods (B3LYP) and the following 6-31G*, 6-31G** and 6-311G** basis set. The Gaussian program does semi-empirical and *ab initio* calculations.

We chose B3LYP as according to Monajjemi *et al.*²¹⁻²² this method is appropriate for calculating NMR properties

Important information that can be gleaned from these calculations is the Hartree-Fock energy ("E), Atomic charge and Dipole moment (Debye). We used Gaussian98 at the NMR shift calculation using the B3LYP and 6-31G*, 6-31G** and 6-311G** basis set, as these calculations provide valuable information for exploring the experimental NMR

chemical shifts. The chemical shielding refers to the phenomenon which associated with the secondary magnetic field created by the induced motions of the electrons that surrounding the nuclei when in the presence of an applied magnetic field for chemical shielding (CS) tensors, which describes how the size of shielding varies with molecular orientation. The two values of the shielding tensor are frequently expressed as the isotropic value (σ_{iso}), the anisotropy shielding (σ_{aniso}) and the other parameters²³⁻²⁴.

The calculations also provide valuable information for exploring the thermodynamic parameters. Geometry optimization in NAA and AA was performed at the B3LYP method and using and 6-31G*, 6-31G** and 6-311G** basis set. We obtained the energy (ΔE), enthalpies (ΔH), Gibbs free energy (ΔG), entropies (ΔS) of NAA and MAA²⁵⁻²⁶.

We also studied electronic structures of NAA and MAA using Natural Bond Orbital (NBO) analysis at the same levels that were mentioned above in gas phase. A full NBO analysis is obtained in Gaussian 98²⁷⁻²⁹. The main listing of NBOs, displaying the form and occupancy of the complete set of NBOs that span the input AO space and for each orbital gives the type of orbital and the occupancy²⁹⁻³¹.

RESULTS AND DISCUSSION

NMR parameters

In this section we report and analyze NMR shielding tensors of ¹H, ¹³C, ¹⁷O-NMR such as isotropic shielding (σ_{iso}) and anisotropic shielding (σ_{aniso}) of MAA and its NAA, which obtain at B3LYP level using 6-31G*, 6-31G** and 6-311G** basis set in gas phase. The NMR technique is based on the sensitivity of magnetic properties. The calculation of NMR parameters using *ab initio* methods has important role in the molecular structure investigation. The quantitative knowledge of chemical shielding anisotropy (CSA) tensors is important in the context of bimolecular applications of nuclear magnetic resonance (NMR). In our current research, we have presented the results of our studies the intramolecular hydrogen bonding effects on the ¹H, ¹³C, ¹⁵N-NMR shielding tensors of

MAA and NAA. According to our theoretical data, it is apparent that the intramolecular hydrogen bonding effects seem quite significant. The ^1H , ^{13}C , ^{17}O -NMR parameters of MAA and NAA are given in Table 1. According to Table 1, at three levels are shown the isotropic shielding value (σ_{iso}) and anisotropic shielding value (σ_{aniso}) for C_2 , C_3 , C_4 , O_7 ,

O_a and the hydrogen atom that in the intramolecular hydrogen bond formation is involved (H_{17} in NAA and H_{18} in MAA). The calculated results in Table 1 showed that isotropic shielding value (σ_{iso}) for H_{17} atom of NAA is smaller than H_{18} atom of MAA, while anisotropic shielding value (σ_{aniso}) for H_{17} atom of NAA is greater than H_{18} atom of MAA. In fact, H_{17} in

Table 1: NMR parameters, atomic charge and dipole moment (μ) for NAA and MAA with three levels

		B3LYP/6-31G*				B3LYP/6-31G**				B3LYP/6-311G**			
		σ_{iso} (ppm)	σ_{aniso} (ppm)	Atomic charge	μ	σ_{iso} (ppm)	σ_{aniso} (ppm)	Atomic charge	μ	σ_{iso} (ppm)	σ_{aniso} (ppm)	Atomic charge	μ
NAA	C_2	-2.866	117.592	0.466	1.479	-2.681	117.713	0.440	1.462	-23.672	125.896	0.270	1.416
	C_3	16.573	57.621	0.098		16.412	57.596	0.093		-4.042	66.972	-0.061	
	C_4	37.942	116.302	0.404		38.115	116.346	0.396		17.029	126.694	0.238	
	O_7	215.491	81.694	-0.565		219.306	82.815	-0.498		207.217	80.735	-0.290	
	O_a	-259.85	796.669	-0.546		-259.61	796.163	-0.543		-323.55	858.484	-0.386	
	H_{17}	26.060	14.508	0.464		25.030	15.432	0.394		25.252	14.907	0.277	
MAA	C_2	-15.178	145.538	0.415	3.195	-14.935	145.213	0.395	3.216	-36.144	156.314	0.249	3.261
	C_3	61.143	75.100	0.016		61.242	75.307	-0.016		43.765	82.358	-0.288	
	C_4	43.940	97.228	0.346		44.084	97.163	0.340		22.792	107.138	0.222	
	O_7	206.316	92.266	-0.598		210.177	94.675	-0.525		196.070	97.894	-0.326	
	O_a	-285.21	874.020	-0.556		-284.93	873.502	-0.559		-350.53	939.402	-0.409	
	H_{18}	26.073	13.069	0.450		25.098	13.988	0.374		25.319	13.496	0.269	

Table 2. Relative thermochemical parameters (energy ΔE kcal/mol, enthalpy ΔH kcal/mol, and Gibbs free energy ΔG kcal/mol, and entropy ΔS cal/(molK), of NAA and MAA obtained in gas phase using three level

	Level	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/molK)	C_v (cal/molK)
NAA	B3LYP/6-31G*	-345175.919	-345203.999	-345175.326	96.169	37.216
	B3LYP/6-31G**	-345184.691	-345212.762	-345184.098	96.141	37.182
	B3LYP/6-311G**	-345275.530	-345303.322	-345274.930	95.227	37.154
MAA	B3LYP/6-31G*	-241527.529	-241554.297	-241526.936	91.768	32.724
	B3LYP/6-31G**	-241538.973	-241565.844	-241538.380	92.112	32.695
	B3LYP/6-311G**	-241599.620	-241625.524	-241599.028	88.868	32.596

Table 3: Bond lengths (r , Å) for NAA and MAA

	NAA					MAA				
	C_2-C_3	C_3-O_a	C_2-C_4	C_4-O_7	O_7-H_{17}	C_2-C_3	C_3-O_a	C_2-C_4	C_4-O_7	O_7-H_{18}
B3LYP/6-31G*	1.468342	1.250883	1.40189	1.30820	1.028181	1.452308	1.258467	1.382302	1.327463	1.014881
B3LYP/6-31G**	1.458519	1.255806	1.406294	1.308652	1.044009	1.448367	1.256597	1.384689	1.329056	1.022718
B3LYP/6-311G**	1.460986	1.248778	1.398369	1.305425	1.025481	1.721367	1.218965	1.329665	1.434252	0.999064

NAA is more influenced by the magnetic field and is deshielder than H_{18} . Also listed in Table 1 show that dipole moment of MAA is more than that NAA.

According to Table 1, in both structures the atomic charge of O_7 atom is negative value whereas H_{17} and H_{18} atoms have positive values. Our obtained results from the analysis of the calculated values yielded strong evidence that existence of electron-pull and electron-donor substitute effect on the C_3 atom and intramolecular hydrogen bonding effect play very important role in determining the 1H , ^{13}C , ^{17}O -NMR chemical shielding tensors of NAA and MAA. With B3LYP/6-31G* level, atomic charge O_7 and H_{17} in NAA is -0.565 and 0.465 whereas atomic charge O_7 and H_{18} in MAA is -0.598 and 0.450, respectively. Electronic effects plays important role in determining the chemical shielding tensors. The electron-donor

substitutes increase electronic density and shielding value, while electron-pull substitutes decrease electronic density and shielding value. O_7 in NAA has low atomic charge rather than O_8 in MAA, there for H_{17} in NAA is free and contribute in formation of intramolecular hydrogen bonding. Also σ_{iso} value H_{17} is 26.060 ppm and H_{18} is 26.073 ppm. Our obtained results show good agreement was observed between atomic charges and NMR parameters.

Frequency calculations

The relative energy (ΔE), standard enthalpies (ΔH), entropies (ΔS), Gibbs free energy (ΔG) and constant volume molar heat capacity (C_v) values of NAA and MAA was obtained by theoretical methods using the 6-31G*, 6-31G** and 6-311G** basis set to obtain minima of the potential energy. In this paper according to values listed in Table 2,

Table 4: Second order perturbation theory analysis of Fock matrix in NBO basis threshold for printing: 0.50 kcal/mol for NAA and MAA

Level	NAA			MAA		
	Donor NBO (i)	Acceptor NBO (j)	$E^{(2)}$	Donor NBO (i)	Acceptor NBO (j)	$E^{(2)}$
B3LYP/6-31G*	BD(1) C_2-O_8	BD*(1)(O_7-H_{17})	2.33	BD(1) C_2-O_8	BD*(1)(O_7-H_{18})	1.72
	BD(1) C_4-C_5	BD*(1)(O_7-H_{17})	2.42	BD(1) C_4-C_5	BD*(1)(O_7-H_{18})	2.21
	BD(1) O_7-H_{17}	BD*(1)(C_4-C_5)	5.52	BD(1) O_7-H_{18}	BD*(1)(C_4-C_5)	5.63
	LP(2) O_8	BD*(1)(O_7-H_{17})	50.82	LP(2) O_8	BD*(1)(O_7-H_{18})	40.21
	CR(1) N_6	RY*(1)(C_3)	1.29	CR(1) C_4	RY*(2)(C_3)	1.33
	LP(2) O_7	RY*(1)(H_{17})	1.53	LP(2) O_7	RY*(1)(H_{18})	1.38
	CR(1) O_7	RY*(1)(H_{17})	0.87	CR(1) O_7	RY*(1)(H_{18})	0.82
B3LYP/6-31G**	BD(1) C_2-O_8	BD*(1)(O_7-H_{17})	0.95	BD(1) C_2-O_8	BD*(1)(O_7-H_{18})	2.38
	BD(1) C_4-C_5	BD*(1)(O_7-H_{17})	2.34	BD(1) C_4-C_5	BD*(1)(O_7-H_{18})	2.16
	BD(1) O_7-H_{17}	BD*(1)(C_4-C_5)	5.99	BD(1) O_7-H_{18}	BD*(1)(C_4-C_5)	5.95
	LP(2) O_8	BD*(1)(O_7-H_{17})	63.76	LP(2) O_8	BD*(1)(O_7-H_{18})	47.65
	CR(1) N_6	RY*(1)(C_3)	1.33	CR(1) C_4	RY*(2)(C_3)	1.35
	LP(2) O_7	RY*(1)(H_{17})	1.32	LP(2) O_7	RY*(1)(H_{18})	1.28
	CR(1) O_7	RY*(1)(H_{17})	0.86	CR(1) O_7	RY*(1)(H_{18})	0.86
B3LYP/6-311G**	BD(1) C_2-O_8	BD*(1)(O_7-H_{17})	0.95	BD(1) C_2-O_8	BD*(1)(O_7-H_{18})	2.26
	BD(1) C_4-C_5	BD*(1)(O_7-H_{17})	2.06	BD(1) C_4-C_5	BD*(1)(O_7-H_{18})	1.16
	BD(1) O_7-H_{17}	BD*(1)(C_4-C_5)	5.82	BD(1) O_7-H_{18}	BD*(1)(C_4-C_5)	4.38
	LP(2) O_8	BD*(1)(O_7-H_{17})	48.16	LP(2) O_8	BD*(1)(O_7-H_{18})	42.35
	CR(1) N_6	RY*(1)(C_3)	1.64	CR(1) C_4	RY*(3)(C_3)	0.58
	LP(2) O_7	RY*(1)(H_{17})	1.81	LP(2) O_7	RY*(1)(H_{18})	0.96
	CR(1) O_7	RY*(1)(H_{17})	1.26	CR(1) O_7	RY*(1)(H_{18})	0.50

we compared intramolecular hydrogen bonding effect on thermochemical parameters of the NAA and MAA.

The calculated results in Table 2 showed that the relative energy (ΔE) Gibbs free energy (ΔG) and standard enthalpies (ΔH) values of NAA in the three levels are negative values and entropy (ΔS) and constant volume molar heat capacity (C_v) values are positive. The thermochemical

parameters values in NAA are larger than MAA that shows NAA is more stable than MAA.

Geometry optimization

Analysis of the geometrical parameters and according to values listed in Table 3 indicates that the main effect of 3-substitution is a lengthening of $r(O_7-H_{18})$ in MAA shortening of $r(O_7-H_{17})$ in NAA, that showing an electron-donor group decrease length bond O-H and electron-pull group increase

Table 5: Calculated NHOs and the polarization coefficient for each hybrid in the corresponding NBO (in parentheses) for NAA and MAA

Bond	B3LYP/6-31G*		B3LYP/6-31G**		B3LYP/6-311G**	
	A	B	A	B	A	B
NAA						
C ₂ -C ₃	$s p^{1.84} [0.6922]$	$s p^{1.36} [0.7217]$	$s p^{1.89} [0.6992]$	$s p^{1.36} [0.7207]$	$s p^{1.82} [0.6914]$	$s p^{1.31} [0.7224]$
C ₂ -O ₈	$s p^{1.45} d^{0.01} [0.3830]$	$s p^{1.46} d^{0.01} [0.8125]$	$s p^{1.59} d^{0.01} [0.3826]$	$s p^{1.41} d^{0.01} [0.8127]$	$s p^{1.45} d^{0.01} [0.3814]$	$s p^{1.46} [0.8136]$
C ₃ -C ₆	$s p^{1.69} [0.7120]$	$s p^{1.36} [0.7022]$	$s p^{1.70} [0.7126]$	$s p^{1.40} [0.7016]$	$s p^{1.63} [0.7138]$	$s p^{1.31} [0.7008]$
C ₃ -O ₇	$s p^{1.85} d^{0.01} [0.5760]$	$s p^{1.86} d^{0.01} [0.8175]$	$s p^{1.85} d^{0.01} [0.5765]$	$s p^{1.86} d^{0.01} [0.8171]$	$s p^{1.83} d^{0.01} [0.5735]$	$s p^{1.81} [0.8192]$
C ₇ -N ₆	$s p^{1.14} [0.6176]$	$s p^{1.71} [0.7865]$	$s p^{1.71} [0.6180]$	$s p^{1.70} [0.7862]$	$s p^{1.19} [0.6160]$	$s p^{1.31} [0.7878]$
O ₇ -H ₁₇	$s p^{1.14} d^{0.01} [0.8991]$	$s [0.4377]$	$s p^{1.14} d^{0.01} [0.8902]$	$s [0.4250]$	$s p^{1.12} [0.8904]$	$s [0.4558]$
MAA						
C ₂ -C ₃	$s p^{1.81} [0.6938]$	$s p^{1.10} [0.7182]$	$s p^{1.86} [0.6963]$	$s p^{1.10} [0.7178]$	$s p^{1.11} [0.7029]$	$s p^{1.84} [0.7113]$
C ₂ -O ₈	$s p^{1.44} d^{0.01} [0.3837]$	$s p^{1.46} d^{0.01} [0.8120]$	$s p^{1.46} d^{0.01} [0.3835]$	$s p^{1.46} d^{0.01} [0.8121]$	$s p^{1.43} d^{0.01} [0.3695]$	$s p^{1.21} [0.8220]$
C ₃ -C ₆	$s p^{1.69} [0.7119]$	$s p^{1.44} [0.7023]$	$s p^{1.66} [0.7121]$	$s p^{1.41} [0.7020]$	$s p^{1.44} [0.7065]$	$s p^{1.40} [0.7077]$
C ₃ -O ₇	$s p^{1.85} d^{0.01} [0.5732]$	$s p^{1.88} d^{0.01} [0.8180]$	$s p^{1.86} d^{0.01} [0.5738]$	$s p^{1.88} d^{0.01} [0.8176]$	$s p^{1.83} d^{0.01} [0.5705]$	$s p^{1.31} [0.8213]$
C ₇ -C ₆	$s p^{1.04} [0.7122]$	$s p^{1.61} [0.7020]$	$s p^{1.03} [0.7118]$	$s p^{1.61} [0.7023]$	$s p^{1.06} [0.7066]$	$s p^{1.11} [0.7076]$
O ₇ -H ₁₈	$s p^{1.14} d^{0.01} [0.8942]$	$s [0.4477]$	$s p^{1.14} d^{0.01} [0.8990]$	$s [0.4379]$	$s p^{1.13} d^{0.01} [0.8660]$	$s [0.3001]$

Table 6: Occupancy and energy (kcal/mol) for NAA structure and MAA structure.

Level	NAA			MAA		
	NBO	Occupancy	Energy	NBO	Occupancy	Energy
B3LYP/6-31G*	BD(1)C ₂ -O ₈	1.99436	-1.05683	BD(1)C ₂ -O ₈	1.99569	-1.02015
	BD*(1)O ₇ -H ₁₇	0.11331	0.35323	BD*(1)O ₇ -H ₁₈	0.09711	0.40110
	LP(1)O ₇	1.97050	-0.59702	LP(1)O ₇	1.97347	-0.56245
	LP(2)O ₈	1.83761	-0.37486	LP(2)O ₈	1.84767	-0.32322
B3LYP/6-31G**	BD(1)C ₂ -O ₈	1.99425	-1.05246	BD(1)C ₂ -O ₈	1.99562	-1.01602
	BD*(1)O ₇ -H ₁₇	0.13254	0.36449	BD*(1)O ₇ -H ₁₈	0.10983	0.41747
	LP(1)O ₇	1.96896	-0.59176	LP(1)O ₇	1.97226	-0.55719
	LP(2)O ₈	1.82400	-0.39603	LP(2)O ₈	1.83896	-0.33671
B3LYP/6-311G**	BD(1)C ₂ -O ₈	1.99321	-1.06806	BD(1)C ₂ -O ₈	1.99631	-1.10015
	BD*(1)O ₇ -H ₁₇	0.11330	0.32964	BD*(1)O ₇ -H ₁₈	0.01790	0.38667
	LP(1)O ₇	1.97057	-0.61398	LP(1)O ₇	1.98112	-0.58431
	LP(2)O ₈	1.83294	-0.37356	LP(2)O ₈	1.86616	-0.28420

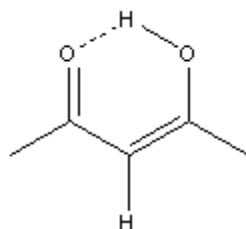


Fig. 1: Intramolecular hydrogen bond in enol form of Acetylacetone (AA)

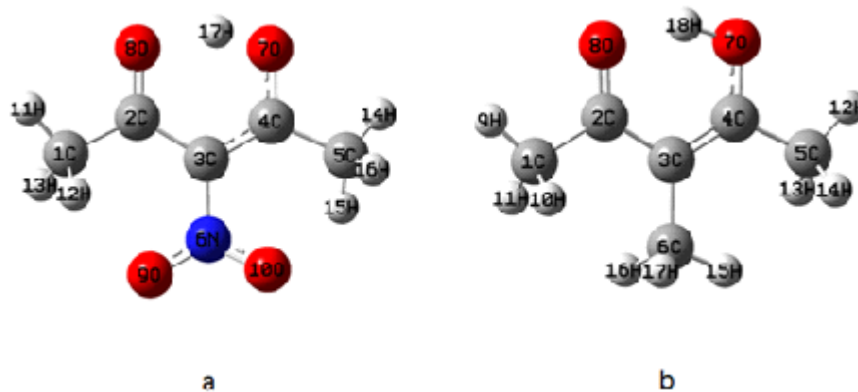


Fig. 2: Structure of a: nitroacetylacetone (NAA) and b: methylacetylacetone (MAA)

of interaction is a loss of occupancy from the concentration of electron NBO of the idealized Lewis structure into an empty non-Lewis orbital. A careful examination of all possible interactions between “filled” (donor) Lewis-type NBOs and “empty” (acceptor) non-Lewis NBOs, allows us to get an estimate of their energetic importance by second-order perturbation theory. For each donor (i) and acceptor (j), the stabilization energy $E^{(2)}$ associates with the delocalization $i \rightarrow j$. The strengths of these delocalization interactions, $E^{(2)}$, are estimated by second order perturbation theory. Some of significant donor–acceptor interactions and their second order perturbation stabilization energies $E^{(2)}$ which were NAA and MAA are given in Table 4. This section shows some of the donor–acceptor interactions and their second order perturbation energies ($E^{(2)}$) for NAA and MAA.

It seems that in NBO analysis of hydrogen bond systems, the charge transfer between the lone pairs of proton acceptor and antibonds of proton donor is most significant. The results of the NBO

length bond O-H. Also $r(C_2-C_3)$ and $r(C_3-C_4)$ in NAA is longer than MAA, while $r(C_2-O_8)$ and $r(C_4-O_7)$ in NAA is shorter than MAA. With existence electron-pull group and formation of intramolecular hydrogen bonding increase length bond O-H but reduce length bond C-O.

NBO analysis

Natural bond orbital analysis provides the accurate possible natural Lewis structure. The result

analysis in Table 4 show that in NAA structure, $LP(2)O_8$ participates as donor and the $BD^*(O_7-H_{17})$ interactions as acceptor in intramolecular hydrogen bonding interaction and in MAA structure, $LP(2)O_8$ participates as donor and the $BD^*(O_7-H_{18})$ interactions as acceptor in intramolecular hydrogen bonding interaction. Electron density is transferred from one pair $LP(2)O_8$ to the anti-bonding $BD^*(O_7-H_{17})$ orbital's in NAA and $LP(2)O_8$ to the anti-bonding $BD^*(O_7-H_{18})$ orbital's in MAA. The resonance energy ($E^{(2)}$) indicates amount of Participation of electrons in the resonance.

According to the simple bond orbital picture, each bonding NBO is defined as an orbital formed from two directed valence hybrids (NHOs) h_A , h_B on atoms A and B, with corresponding polarization coefficients c_A , c_B . Table 5 show share of orbitals contribute in the bonds (BD for 2-center bond). According to Table 3, by using B3LYP/6-311G** for NAA, in the O_7-H_{17} bond, $BD = 0.9052sp^{2.71}d^{0.01} + 0.4250s$ reported. Polarization coefficients of the O_7-H_{17} bond $O_7 = 0.9052$ and $H_{17} =$

0.4250 reported, that sizes of these coefficients show the importance of the hybrid of O_7 in the formation of the bond, while for MAA in the O_7-H_{18} bond $BD = 0.8990sp^{2.73}d^{0.01} + 0.4379s$ reported. Polarization coefficients of the O_7-H_{18} bond $O_7 = 0.8990$ and $H_{18} = 0.4379$ reported, that sizes of these coefficients show the importance of the hybrid of O_7 in the formation of the bond. Also values of Polarization coefficients H_{17} and H_{18} show share of contribute H_{18} in bond O_7-H_{18} at MAA is greater than share of contribute H_{17} in bond O_7-H_{17} at NAA. There for H_{17} in NAA greater than H_{18} in

MAA contribute in formation of intramolecular hydrogen bonding

In the present study, we used a combination of theoretical tools to compare nitroacetylacetone (NAA) structure and methylacetylacetone (MAA) structure. The following conclusions are obtained from the current study:

1. The most stable structure, according to the optimization energy is NAA. It seems that intramolecular hydrogen bonding in NAA is stronger than MAA.
2. NBO analysis indicated the presence of donor-acceptor centers in the investigated structures. In both the structures the resonance energy ($E^{(2)}$) indicates amount of Participation of electrons in the resonance. The comparison between the NBO analysis

of two Compounds shows that values of $E^{(2)}$ for MAA are lower than NAA which means that in the MAA structure lesser electrons are involved in the resonance.

3. The s_{iso} value of H_{17} in the NAA structure is lower than s_{iso} value of H_{18} in MAA structure. This means that electron density around H_{17} is lower than H_{18} . There for participation of H_{17} at formation intramolecular hydrogen bonding is higher than that H_{18} in MAA.
4. The comparison of thermochemistry parameters of two structures that are expressed show that DG, DH, DE, DS and Cv values for NAA are more than those of MAA which again indicates the greater stability of NAA.
5. Analysis of the geometrical parameters and according to values listed showing an electron-donor group decrease length bond O-H and electron-pull group increase length bond O-H. With existence electron-pull group in NAA and formation of intramolecular hydrogen bonding increase length bond O-H but reduce length bond C-O.
6. Finally, our studies on the structures showed that intramolecular hydrogen bonding in NAA stronger than that MAA and NAA structure and NAA is more stable than MAA structure.

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