Atoms in Molecules, An Other Method For Analyzing Dibenzoylmethane

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Abstract—Proton transfer and hydrogen bonding are two aspects of the chemistry of hydrogen that respectively govern the behaviour and structure of many molecules, both simple and complex. All the theoretical enol and keto conformations of 1,3-diphenyl-1,3-propandion known as dibenzoylmethane (DBM), have been investigated by means of atoms in molecules (AIM) theory. It was found that the most stable conformers are those stabilized by hydrogen bridges.The aim of the present paper is a thorough conformational analysis of DBM (with special attention on chelated cis-enol conformers) in order to obtain detailed information on the geometrical parameters, relative stabilities and rotational motion of the phenyl groups. It is also important to estimate the barrier height for ptoton transfer and hydrogen bond strength, which are the main factors governing conformational stability.

Keywords—Acetylacetone, Atoms in molecules, Dibenzoylmethane, Intramolecular hydrogen bond, Resonance conjugation

I. INTRODUCTION

OVER many years, β-diketones [1]-[3] (β-dicarbonyl compounds) have been considerable interest to organic, inorganic and physical chemistry. A large group of applications of β-diketones concerns their role as an important organic reagent. Some of these compounds, for instance, are currently used in the perfume and cosmetic industries [4],[5]. On the other hand, β-diketones were found to be useful chelating ligands. This feature opens new possibilities for using substances of our interest. Special attention has been paid to the keto-enol tautomerism of β-diketones, the structural properties of both keto and enol forms and the nature of the strong intramolecular O-H…O hydrogen bond in the enol form. These properties were subject of intensive studies by different methods, including IR, Raman, microwave, NMR spectroscopy, X-ray and neutron diffraction, as well as quantum chemical calculations and some other techniques.

One of the most significant structures capable of bearing hydrogen bonds is the O-H··O unit, which is the most widely studied and documented in this respect [6]-[9]. Acetylacetone (AA) is one of the simplest members of β-diketones, which has been extensively studied both experimentally and theoretically [10],[11]. AA is postulated to have unusually strong H-bonds (O-H…O type) in their cyclic, conjugated enolic forms. The strength of the O-H…O hydrogen bridge in acetylacetone and acetylacetone derivatives is depending on the nature and dimension of the substitute groups and on the substitution position [8],[9],[12].

Dibenzoylmethane(1,3-diphenyl-1,3-propandion, hereafter DBM)(fig-1) is unique among the β-substitued acetylacetone derivatives so for investiyated. It is white crystals, melts at 74-77 °C and is soluble in most common organic solvents. It has a symmetric structure, at ambient temperature. It is solid and completely exists in the enol form, even in CDCl$_3$ solution, whereas in this media acetylacetone exhibits 17% keto tautomers and 3-methyl acetylacetone has 64% keto tautomers [7]. These characteristic of DBM causes this compound to be of potential interest.

The atoms in molecules theory (AIM) make a bridge between the quantum mechanics methods and traditional chemical concept and the natural bond orbitals described a molecule by a N-electron wave function ψ(1,2,…,N) in terms of localized orbitals which are closely related to the chemical bonding concept. These methods have been successfully applied to analyze the hydrogen bonded conformers in terms of bond critical point properties and orbital interactions.

The hydrogen bond formation, which stabilizes the chelated enol forms of β-diketones, leads to an enhancement of the π-electron resonance conjugation that causes a marked tendency for the bond order equalization of the valence bonds [13] in the resulting six-membered chelated ring. The implantation of different substituents in α- or β- position drastically changes the hydrogen bond strength and the equilibrium between the enol and keto tautomers [14]-[16].
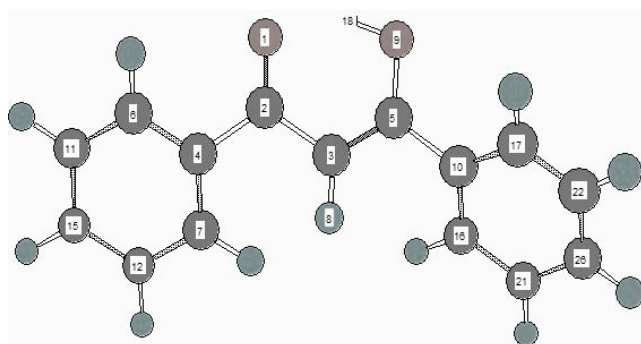

Fig. 1 View of DBM showing the atomic numbering scheme used in the paper

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II. METHOD OF ANALYSIS

The nature of the strong intramolecular hydrogen bond in the chelated ring of DBM and AA has been studied by using atoms in molecules theory of bader by means of AIM2000 [17] software, calculated at the B3LYP/6-31G** level. These wave functions obtained from the geometries at the same level. In AIM analysis we have located the bond critical points and acquired detailed information on the relative strength of the hydrogen bond which could be obtained in terms of electron density (ρ), and Laplacian ($\nabla^2\rho$).

III. RESULTS AND DISCUSSIONS

The full optimized structural parameters of DBM calculated at B3LYP, G96LYP, BLYP, B3PW91 levels using 6-311++G**, 6-31G**, 6-31G* and D95** basis sets with the corresponding experimental X-ray [18],[19] results are summarized in Table I. For comparison the optimized geometry of AA at the same levels of calculations are also given in Table I.

Table I indicates that the calculated geometrical parameters are in good agreement with the observed results. The results of Table I show that the main effect of β substitution is shortening of the O…O and O…H distances and lengthening of the O-H bond length, compared with the corresponding values for the unsubstituted acetylacetone. The O…O distance in DBM is about 2.463 A^0 (calculated at B3LYP/D95**), shorter than that of AA (2.503 A^0 calculated at same level).

All the theoretical calculations agree with experimental data in predicting the two phenyl rings of DBM are not co-planar. To prevent a too close contact between the α-hydrogen and the ortho hydrogen of the phenyl rings, structure of DBM are not perfectly planar. In DBM, two phenyl groups are rotated by about 13^0 and 16^0 relative to the keto-enol fragment of the molecule.

Table I also shows that upon substitution on β-position both C=O and C=C bond lengths in the chelated ring are increased, whereas C-O and C-C bond lengths are decreased. Shortening of single bonds and lengthening of double bonds show that conjugation of the chelate ring is increased. The increase of conjugation in the chelate ring is induced by the steric hindrance of the substituent groups. The hydrogen bond energy (E_{HB}), evaluated as stability difference between the trans-enol and cis-enol conformations, is 18.04 kcal/mol (calculated at B3LYP/6-31G** level). The corresponding value for AA is 15.8 kcal/mol (at the same level of theory). Comparison between these values shows that the intramolecular hydrogen bond in DBM is stronger than the corresponding value of AA.

From a theoretical point of view, DBM has 11 conformers. All of conformations of phenyl groups with respect to the plane of the molecule and with respect to each other are shown in Fig 2.

Atoms in molecules theory was applied to detail analyzing of hydrogen bond in DBM. Formation of HB is associated with the appearance of a bond critical point (BCP)

between the hydrogen atom of donor group and acceptor atom. Poplier and Bader [20] proposed a set of criteria for the existence of hydrogen bonding within the AIM formalism. Two criteria are in connection with electron density, ρ_{BCP}, and Laplacian, $\nabla^2\rho_{BCP}$, of the electron density at BCP of two hydrogen boned atoms. The range of ρ_{BCP} and $\nabla^2\rho_{BCP}$ are 0.002-0.035 a.u. and 0.024-0.139 a.u., respectively, if hydrogen bond exists. The topological parameters (ρ_{BCP}, $\nabla^2\rho_{BCP}$) of various BCPs in chelated ring of DBM and AA were evaluated by means of the AIM approach at the B3LYP/6-31G** level and the results collected in Table II. It is evident from this table, the values of ρ_{BCP} and $\nabla^2\rho_{BCP}$ of critical points between the H atom of HB donor and O atom of HB acceptor (O…H), in AA and DBM, are (0.06431 a.u., 0.0400 a.u.), (0.0743 a.u. and 0.0417 a.u,) respectively. The electron densities at BCPs indicate the presence of intramolecular HB intraction. It can be also observed that the density and the Laplacian of charge density at the O…H bond critical point increases from AA to DBM. This augmentation is consistent with the contraction of the intramolecular O…O distance. Therefore, we can conclude that the hydrogen bond in DBM is stronger than the AA. This conclusion is strongly supported by hydrogen bond energies. Table II shows that for systems studied here the values of electron density are above mentioned range. It means that the intramolecular hydrogen bond in DBM and AA belong to the strong case. There is another factor, which will enhance the stability of DBM, which is associated with resonance assisted hydrogen bond (RAHB) theory [13]. The values of charge density at bond critical points (see Table II) reveal that the existence of intramolecular hydrogen bond in DBM favors a significant delocalization of charge with respect to AA.
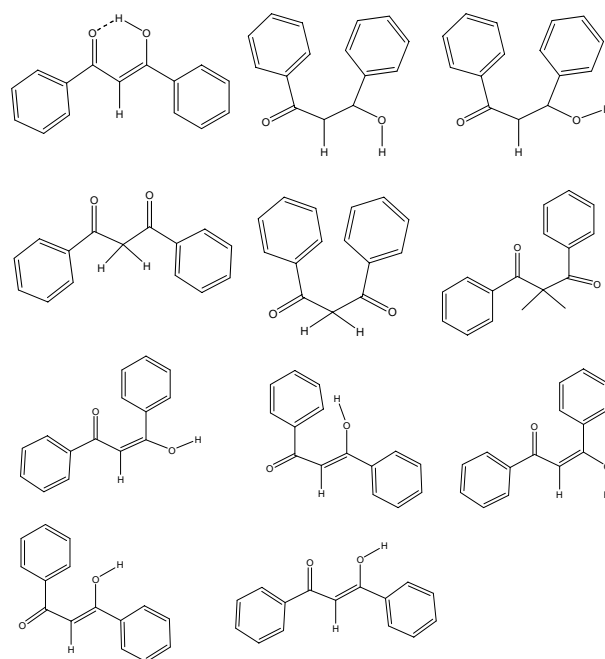

Fig. 2 All conformers of DBM

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TABLE I
COMPARISON OF THEORETICAL AND EXPERIMENTAL GEOMETRIC PARAMETERS OF
DBM AND AA

Bond lenghts	DBM																AA			
	B3LYP[b]	G96LYP[c]	BLYP[d]	B3LYP[e]	B3PW91[b]	G96LYP[b]	BLYP[b]	BLYP[c]	BLYP[a]	B3LYP[d]	B3PW91[a]	G96LYP[a]	G96PW91[b]	G96PW91[a]	B3LYP[a]	Exp.[f]	B3LYP[b]	B3LYP[e]	B3LYP[c]	Exp.[g]
O1-C2	1.262	1.273	1.254	1.267	1.262	1.283	1.283	1.275	1.279	1.254	1.258	1.278	1.284	1.277	1.259	1.279	1.252	1.258	1.246	1.238
C2-C3	1.437	1.442	1.44	1.44	1.432	1.439	1.441	1.444	1.445	1.44	1.436	1.443	1.43	1.436	1.441	1.425	1.442	1.446	1.444	1.412
C3-C5	1.383	1.392	1.378	1.389	1.383	1.399	1.398	1.393	1.396	1.378	1.38	1.395	1.4	1.395	1.38	1.394	1.374	1.381	1.37	1.338
C5-O9	1.324	1.335	1.326	1.326	1.316	1.332	1.336	1.339	1.341	1.326	1.322	1.338	1.319	1.327	1.329	1.318	1.325	1.327	1.326	1.331
O9-H18	1.023	1.038	1.008	1.03	1.033	1.061	1.054	1.034	1.041	1.008	1.021	1.044	1.089	1.057	1.015	1.163	1.013	1.021	1.003	1.03
C3-H8	1.079	1.083	1.078	1.079	1.08	1.085	1.086	1.084	1.087	1.078	1.08	1.086	1.085	1.086	1.079	1.072	1.083	1.083	1.081	---
C2-C4	1.494	1.502	1.495	1.498	1.49	1.5	1.502	1.504	1.504	1.495	1.491	1.502	1.492	1.495	1.496	1.477	1.513	1.515	1.511	1.478
C5-C10	1.479	1.484	1.477	1.482	1.475	1.485	1.486	1.485	1.486	1.477	1.475	1.484	1.482	1.48	1.478	1.477	1.497	1.500	1.494	1.554
O1...O9	2.477	2.490	2.506	2.463	2.447	2.457	2.474	2.506	2.518	2.506	2.496	2.506	2.414	2.469	2.519	2.463	2.519	2.503	2.544	2.535
O1...H18	1.524	1.516	1.582	1.498	1.477	1.452	1.480	1.571	1.547	1.582	1.549	1.530	1.373	1.471	1.585	-	1.586	1.538	1.634	-
Bond angles																				
O1C2C3	120.8	120.5	120.8	120.6	120.8	120.4	120.6	120.5	120.8	120.8	121.1	120.7	120.2	120.7	121.1	120.1	121.6	121.4	121.5	120.5
C2C3C5	119.9	120.4	120.7	119.7	119.3	119.6	119.8	120.7	120.6	120.7	120.1	120.4	118.8	119.7	120.6	120.4	120.0	119.6	120.8	122.2
C3C5O9	120.9	120.4	121.1	120.5	120.7	120.2	120.4	120.5	120.8	121.1	121.2	120.7	120	120.5	121.3	120.3	121.9	121.5	121.9	122.8
O1C2C4	118.2	118.3	118.5	118.3	118.1	117.9	118	118.4	118	118.5	118.2	118.1	117.8	118	118.2	117.6	119.4	119.6	119.9	---
C10C5O9	114.8	115.0	114.4	115.0	115.1	115.3	115.1	114.8	114.6	114.4	114.6	114.8	115.9	115.2	114.3	115.7	114.0	114.3	113.8	---
H8C3C5	119.5	119.2	119.1	119.7	119.8	119.7	119.6	119.1	119.1	119.1	119.3	119.2	120.2	119.6	119.1	118.9	119.8	120.0	119.3	---
H8C3C2	120.5	120.3	120.2	120.6	120.8	120.6	120.5	120.2	120.3	120.2	120.5	120.3	120.9	120.6	120.2	120.7	120.2	120.6	119.9	---
C10C5C3	124.4	124.6	124.5	124.5	124.2	124.5	124.5	124.6	124.6	124.5	124.2	124.5	124.2	124.3	124.3	124.0	124.17	124.16	124.2	---
C4C2C3	121.0	121.2	120.7	121.1	121.1	121.6	121.5	121.1	121.2	120.7	120.7	121.2	122	121.3	120.6	122.2	119.0	119.0	118.6	---
H18O9O1	16.5	16.0	18.4	15.7	15.4	14.3	14.9	16.7	16.4	18.4	17.1	16.0	12.7	14.7	18.0	….	18.0	16.7	19.6	---
O1H18O9	152.5	153.1	150.0	153.5	153.9	155.4	154.6	152.3	152.6	150.0	151.7	153.1	157.3	154.8	150.6	154.7	150.7	151.8	148.49	---

a) Calculated with 6-31G* basis set.
b) Calculated with 6-31G** basis set.
c) Calculated with 6-311++G** basis set.
d) Calculated with 6-311+G* basis set (a p added on hydrogen bonded proton).
e) Calculated with D95** basis set.
f) Data from [8].
g) Data from [21].

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TABLE II
PROPERTIES OF THE ELECTRON DENSITY AT BOND CRITICAL POINTS FOR
DBM AND AA AT B3LYP/6-31G** LEVEL

	DBM		AA	
	ρ	$\nabla^2\rho$	ρ	$\nabla^2\rho$
$O_1\cdots H_{18}$	0.0746540	-0.0417123	0.064311	-0.0400110
C_2-O_1	0.3685075	0.0272126	0.3751782	0.0031651
C_2-C_3	0.2930123	0.1914477	0.2914318	0.1901913
C_3-C_5	0.3208706	0.2243441	0.3255604	0.2305344
C_5-O_9	0.3191011	0.0794490	0.318062	0.073377
O_9-H_{18}	0.3006946	0.3945854	0.0310656	0.422686
C_2-C_4	0.2680532	0.1673926	0.2590067	0.1585928
C_5-C_{10}	0.2752409	0.1773253	0.2655853	0.1678894
C_4-C_6	0.3084586	0.2076124	-	-
C_6-C_{11}	0.3147832	0.2163631	-	-
C_{11}-C_{15}	0.3119880	0.2133597	-	-
C_{15}-C_{12}	0.3124830	0.2138506	-	-
C_{12}-C_7	0.3133291	0.2141457	-	-
C_7-C_4	0.3077165	0.2060568	-	-
C_6-H	0.2885280	0.2669199	-	-
C_{11}-H	0.2847856	0.2559023	-	-
C_{15}-H	0.2849078	0.2563413	-	-
C_{12}-H	0.2846094	0.2552501	-	-
C_7-H	0.2858339	0.2567988	-	-
C_{10}-C_{17}	0.3075158	0.2060592	-	-
C_{17}-C_{22}	0.3142101	02156635	-	-
C_{22}-C_{26}	0.3125900	0.2140393	-	-
C_{26}-C_{21}	0.3119701	0.2132956	-	-
C_{21}-C_{16}	0.3143580	0.2154539	-	-
C_{16}-C_{10}	0.3070386	0.2055066	-	-
C_{17}-H	0.2886974	0.2664366	-	-
C_{22}-H	0.2849397	0.2563050	-	-
C_{26}-H	0.2850458	0.2566739	-	-
C_{21}-H	0.2848124	0.2558233	-	-
C_{16}-H	0.2858550	0.2571992	-	-

IV. CONCLUSIONS

Among 11 possible conformers of DBM, only 1 conformer has the chelated intramolecular hydrogen bond. The energy of this chelated enol tautomer, is lower than those of keto tautomers, due to the HB. The keto tautomers are considerably more stable than other non- chelated enol tautomers. The absence of intramolecular hydrogen bond and high steric hindrances , lead to the instability of the non-chelated enols. The theory of atoms in molecules enables us to take advantage of the single most important observation of chemistry, that of a functional group with a characteristic set of properties. Two criteria in this theory which could help to analyze the structure of DBM are electron density and its Laplacian at BCP of two hydrogen bonded atoms. These values in DBM are found higher than those in AA that refers to stronger hydrogen bond in DBM.

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