



Molecular structure and intramolecular hydrogen bonding of Heptane-3,5-dione. A DFT study

Z. Hajian^a, A-R. Nekoei^{a,b}, M. Vakili^c, A. Kanaani^d

^a Islamic Azad University, Marvdasht Branch, Department of Chemistry, Marvdasht, Iran

^b Department of Chemistry, Shiraz University of Technology, Shiraz, 71555-313, Iran

^c Department of Chemistry, Ferdowsi University of Mashhad, Mashhad 91774-1436, Iran

^d School of Chemistry, Damghan University of Basic Sciences, Iran

Keywords: Heptane-3,5-dione; β -dicarbonyl; Intramolecular hydrogen bond; Density Functional Theory

Introduction

It is straightforward to show that a β -dicarbonyl, with at least one α -hydrogen, can transform bidirectionally into two enol forms by keto-enol tautomerism as illustrated in Fig. 1. Involved hydroxyl, carbonyl, and alkene functional groups of both enol forms contain six atoms that can contribute in a π -electronic resonance conjugation to induce a six-membered ring like structure referred to as a chelated ring. The noteworthy aim in ongoing research is to crosscheck the effects of different β -substitutions on the stabilities and IHB strengths of the two mentioned enol forms. Successive substitution of the CH_3 groups of acetylacetone (AA, $\text{R}_1=\text{R}_3=\text{CH}_3$, see Fig. 1) by $-\text{C}(\text{CH}_3)_3$ groups increase the enol content of β -dicarbonyl, that confirmed by $^1\text{H-NMR}$ spectroscopy studies [1]. These studies indicate that 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD, $\text{R}_1=\text{R}_3=\text{C}(\text{CH}_3)_3$) in the liquid phase is completely in the enol form, whereas the enol contents for 5,5-dimethyl-2,4-hexanedione (DMHD, $\text{R}_1=\text{CH}_3$, $\text{R}_3=\text{C}(\text{CH}_3)_3$) and AA are 94% and 79% [2], respectively. The NMR chemical shifts of the enolated protons in these compounds have indicated that substitution of the CH_3 groups of AA by t-But groups increase the IHB strength.

Heptane-3,5-dione (hereafter HPD) has two ethyl groups substituted for methyl groups in the β -positions of AA. This paper predicts the conformational stabilities, geometrical parameters and IHB strength of HPD molecule. Then, the calculated stable conformations, geometrical parameters, the IHB energies and $^1\text{H-NMR}$ shifts for HPD will be compared with AA, DMHD and TMHD results [3]. These comparisons give a clear understanding for the effects



of the substitution of the methyl groups of AA, and the t-But groups of DMHD and TMHD, by the ethyl groups on the structure and hydrogen bond strength of HPD.

Method of Analysis

All possible keto and enol conformers of HPD were fully optimized at the B3LYP level of Density functional theory (DFT) with 6-31G** basis set, using Gaussian 03W software package. The properties of stable cis-enol conformations are also computed at B3LYP level with the basis sets of 6-311G** and 6-311++G**.

Results and Discussion

For HPD, among several cis-enol conformers that are engaged in a six-membered ring intramolecular hydrogen bonded system, there are only four E1-E4 stable forms (other forms turns to these stable forms). The structures of these conformers, atom numbering of the system and their relative stabilities (in kcal/mol) are shown in Fig 2. The relative energies clearly suggest that the chelated cis-enol E1 and E2 forms are so stable that the presence of other conformers in significant amounts is unlikely. The selected of fully optimized geometrical parameters of E1 and E2 conformers of HPD, besides the averaged geometrical parameters for HPD, AA, DMHD and TMHD, calculated at the B3LYP/6-311++G** level of theory, are given in Table 1. According to the summarized results, especially by comparisons of O...O and O...H bond distances, O-H bond lengths and OHO bond angles, the following trend in hydrogen bond strength is concluded $TMHD > DMHD > AA > HPD$. These calculated data clearly suggest that ethyl substitutions for t-But and even for CH₃ groups at β -position of a β -dicarbonyl decrease the intramolecular hydrogen bond strength. This result is in excellent agreement with the experimental NMR chemical shifts of enolated proton summarized in Table 2. The averaged IHB energy (E_{IHB}) for HPD calculated at B3LYP/6-311++G** level of theory is 15.73 kcal/mol, compared to 15.34, 15.58 and 16.27 kcal/mol for AA, DMHD and TMHD, respectively. This comparison, also confirm the mentioned theoretical and experimental results for the effect of ethyl substitution in β -position on IHB strength of β -dicarbonyls.

The enol contents in pure liquid of AA, DMHD and TMHD have been reported to be 79% and 94% and 100% respectively [2]. A comparison between these values and the

corresponding value for pure liquid of HPD (76%) gives a clear understanding for the decreasing effect of substitutions of the methyl groups by the ethyl groups in AA (and also substitutions of the t-But groups by the ethyl groups in TMHD) on the enol content of the compounds.

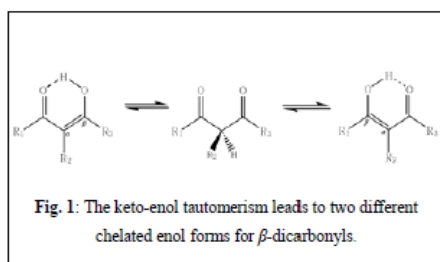
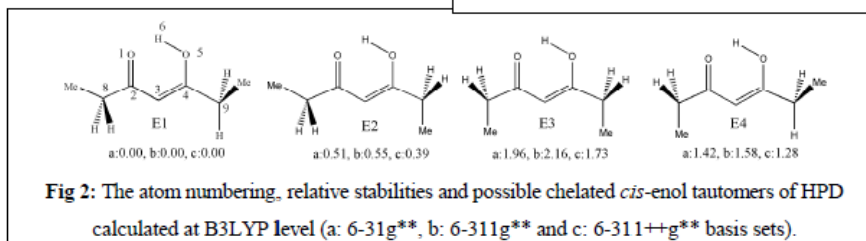


Table1: The geometrical parameters and IHB energies for *cis*-enol forms, all calculated at B3LYP/6-311++G** level, besides proton chemical shifts of HPD, AA, DMHD and TMHD.

distances(Å)	HPD			AA	DMHD	TMHD
	E1	E2	Avg	Avg	Avg	Avg
C2-O1	1.245	1.245	1.245	1.249	1.247	1.249
C2-C3	1.445	1.446	1.445	1.442	1.444	1.443
C3-C4	1.369	1.369	1.369	1.371	1.372	1.374
C4-O5	1.328	1.329	1.328	1.324	1.325	1.326
O5-H6	1.001	1.001	1.001	1.005	1.006	1.008
O1...H6	1.641	1.640	1.640	1.622	1.608	1.583
O1...O5	2.548	2.547	2.547	2.537	2.525	2.507
C2-C8	1.519	1.519	1.519	1.511	1.534	1.541
C4-C9	1.500	1.503	1.502	1.494	1.501	1.523
\angle O1H6O5	148.4	148.4	148.4	148.8	149.2	150.3
E_{HB} (kcal/mol)	15.83	15.63	15.73	15.87	16.57	17.90
δ OH(ppm)	15.04			15.34	15.58	16.27
Enol (%)	76			79	94	100



Conclusion

The comparisons of geometries, E_{HB} values, NMR proton chemical shifts and the enol contents of HPD with those of AA, DMHD and TMHD indicated a decreasing effect of substitutions of methyl and t-But groups by the ethyl groups on the enol content and hydrogen bond strength of β -dicarbonyls.

References

- [1] N.N. Shapetko, *Org. Mag. Res.* 5 (1973) 215.
- [2] G.K. Schweitzer, E.W. Benson, *J. Chem. Eng. Data* 13 (1968) 452.



- [3] M.Vakili, S.F.Tayyari, A.-R.Nekoei, H.Miremad, S.Salemi, R.E.Sammelson, *J. Mol. Struct.* 970 (2010) 160.