Journal of Molecular Structure 987 (2011) 241–254

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Conformational analysis, tautomerization, IR, Raman, and NMR studies of benzyl acetoacetate

Sayyed Faramarz Tayyari [a,*], Farnaz Naghavi [a], Sahar Pojhan [a], Ryan W. McClurg [b], Robert E. Sammelson [b]

[a] Department of Chemistry, Islamic Azad University, Shahrood Branch, Shahrood, Iran
[b] Department of Chemistry, Ball State University, Muncie IN 47306, USA

ARTICLE INFO

Article history:
Received 10 October 2010
Received in revised form 15 December 2010
Accepted 15 December 2010
Available online 22 December 2010

Keywords:
Vibrational spectra
Benzyl acetoacetate
Density functional theory
NMR
Conformational analysis
Tautomerism

ABSTRACT

A complete conformational analysis of the keto and enol forms of benzyl acetoacetate (BAA), a β-dicarbonyl compound, was carried out by *ab initio* calculations, at the density functional theory (DFT) level. By inspection of all possible conformers and tautomers, 22 stable cis-enol, 28 stable trans-enol, and five keto conformers were obtained.

Among all stable cis-enol forms only six of them are engaged in intramolecular hydrogen bond. The hydrogen bond strength of the most stable conformer of BAA is compared with that of acetylacetone (AA) and dimethyl oxaloacetate (DMOA). Harmonic vibrational frequencies of the most stable enol and keto forms and their deuterated analogues were also calculated and compared with the experimental data.

According to the theoretical calculations, the hydrogen bond strength of the most stable enol conformer of BAA is 56.7 kJ/mol (calculated at the B3LYP/6-311++G** level), about 10 kJ/mol less than that of AA. This weakening of hydrogen bond is consistent with the spectroscopic results. NMR studies indicate that BAA exists mainly as a keto tautomer in all considered solutions.

The Gibbs energies for keto/enol tautomerization were calculated at the B3LYP level, with several basis sets, in both gas phase and CH_3CN solution (using PCM model), for the most stable enol and keto conformers.

1. Introduction

In general β-dicarbonyl compounds may exist in several tautomeric forms (see Fig. 1). The position of the keto–enol equilibrium for this class of compounds strongly depends on electronic characteristics of the substituents, temperature, and the nature of solvent. The cis-enol forms of β-dicarbonyl compounds are stabilized by a strong intramolecular hydrogen bond with a double minimum character [1–4].

NMR and vibrational spectroscopy techniques have been intensively used to study the hydrogen bond strength and also keto–enol equilibrium in these compounds [5–15]. 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 [16–22].

The hydrogen bond formation leads to an enhancement of the resonance conjugation of the π-electrons, which causes a marked tendency for equalization of the bond order of the valence bonds in the resulting six-member chelated ring. Therefore, it seems that any parameter that affects the electron density of the chelated ring will affect the hydrogen bond strength. It is well known that substitution in the α or β-positions drastically changes the hydrogen bond strength and the equilibrium between enol and keto tautomers [12]. Experimental data from several research groups suggest that the strength of such a bridge decreases when an electron withdrawing group is present in the β position [16–20].

β-ketoesters are also members of β-dicarbonyl compounds, which are involved in the keto–enol tautomerism. β-ketoesters have been used in such reactions as the malonic ester synthesis [23], the Knoevenagel condensation [24], the Michael addition [25] and the reverse Claisen condensation [26]. Replacement of an alkyl group in a β-diketone by an alkoxy group depresses the enol content. For example, the enol contents of acetylacetone (AA) and ethyl acetoacetate (EAA), in the gas phase, are 97.6% and 53%, respectively [15]. On the other hand the intramolecular hydrogen bond in β-ketoesters is considerably weaker than in β-diketones. For instance the proton chemical shift of the enol proton in AA and methyl acetoacetate, both in the pure liquid phase, is 15.57 [14] and 11.96 [15] ppm, respectively.

Benzyl acetoacetate (BAA) is a β-ketoester, with different substitution effects such as electron withdrawing, steric and

---

[*] Corresponding author. Tel.: +98 9153103538.
E-mail address: sftayyari@hotmai.com (S.F. Tayyari).

0022-2860/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2010.12.034

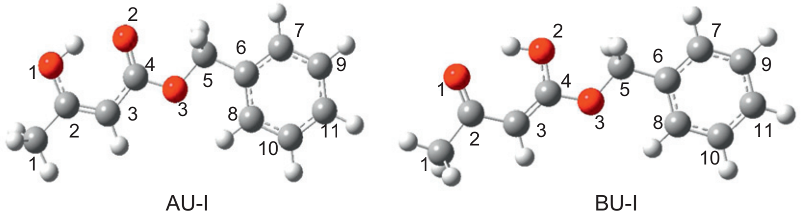

Fig. 1. Atom numbering system for "A" and "B" chelated cis-enol "U" conformers of BAA.

mesomeric effects and consequently, the study of these effects on H-bond strength is potentially interesting. Comparison of BAA with AA, which the methyl group is substituted by benzyloxy group, may give an understanding of the substitution effects that O-benzyl acts as an electron donating group and affects on structure and hydrogen bond strength of the system. In contrast to the regular asymmetric β-diketones, BAA seems to accept the enol proton solely on only one of its two oxygen atoms (i.e. posses an asymmetric single minimum potential).

2. Experimental

BAA was purchased from Sigma–Aldrich, Inc. and used as received. The partially deuterated BAA, d2-BAA, was prepared by adding D_2O to BAA and leaving overnight at room temperature. The organic layer was separated and then dried over anhydrous Na_2SO_4.

The mid-IR spectra of BAA and d2-BAA were recorded using a Bomem MB-154 Fourier transform spectrophotometer in the region 600–4000 cm^{-1}. The spectra of liquids were obtained as neat samples between KBr windows and the CCl_4 solution (~0.1 M) spectra were obtained between 0.2 mm path length KBr windows. The spectra were collected with a resolution of 2 cm^{-1} by averaging the results of 15 scans.

The Far-IR spectra in the region 600–100 cm^{-1} were obtained using a Thermo Nicolet NEXUS 870 FT-IR spectrometer equipped with a DTGS/polyethylene detector and a solid substrate beam splitter. The spectra were collected with a resolution of 2 cm^{-1} by averaging the results of 64 scans.

The FT-Raman spectra in the region 3200–50 cm^{-1} were recorded employing a 180° back-scattering geometry and a Bomem MB-154 Fourier transform Raman spectrometer operating at the 1064 nm excitation line of a Nd:YAG laser. It was equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Rayleigh filtration was afforded by two sets of two holographic technology filters. The spectra were accumulated for 1500 scans with a resolution of 2 cm^{-1}. The laser power at the sample was 600 mW. The spectra of the liquids were recorded from the sample sealed in a glass half-silvered bulb.

The ^1H and ^{13}C NMR spectra were recorded at 298 K on a JEOL Eclipse spectrometer operating at 400 and 100 MHz for proton and carbon-13, respectively. Samples of either 10 mg of BAA for proton or 100 mg of BAA for carbon-13 were dissolved in 0.70 mL of the deuterated solvent. The chemical shifts are reported in ppm relative to the TMS signal. Gradient HMQC and HMBC experiments were performed on BAA in each solvent to determine the atom assignments as shown in Table 1.

3. Method of analysis

The calculations of geometrical parameters were performed using the Gaussian 03 program package [27]. Numbering of the optimized molecules is given in Fig. 2.

In this work, we applied the DFT method including the hybrid gradient-corrected exchange functional proposed by Becke [28,29] with the gradient corrected correlation functional of Lee, Yang, and Parr [30], B3LYP, using the basis set 6-31G**. The chelated enol (I), the corresponding open structure (II), and all possible stable keto conformers of BAA are fully optimized at the B3LYP/6-31G** level. For the stable chelated enols and the most stable keto conformers, the calculations were also performed using 6-311++G** basis set.

Table 1
Selected geometrical parameters for stable cis-enol tautomers of BAA, AA, and DMOA.[a]

	C=O	C–C	C=C	C–O	O···O	O–H	C–C=O	C–C=C	C=C–O	C–O–H	q_1	q_2	Q	λ	E_{HB}
AU1	1.243	1.445	1.366	1.333	2.586	0.997	124.0	119.9	122.9	106.2	0.079	0.090	0.169	0.236	62.1
	1.235	1.446	1.363	1.334	2.607	0.990	124.2	120.4	123.0	107.1	0.083	0.099	0.182	0.216	56.7
AU2	1.241	1.446	1.366	1.333	2.585	0.998	124.3	119.7	122.9	106.2	0.080	0.092	0.172	0.231	62.8
	1.234	1.446	1.362	1.334	2.609	0.990	124.4	120.3	123.0	107.2	0.084	0.100	0.184	0.213	57.1
AU3	1.239	1.447	1.372	1.326	2.532	1.007	122.8	118.9	122.9	105.5	0.075	0.087	0.162	0.247	70.0
	1.232	1.448	1.368	1.327	2.554	0.998	122.7	119.6	123.0	106.5	0.080	0.095	0.175	0.227	NC
AU4	1.239	1.447	1.372	1.325	2.531	1.008	122.7	119.0	122.8	105.5	0.075	0.086	0.161	0.248	71.6
	1.232	1.449	1.369	1.325	2.555	0.999	122.7	119.6	122.9	106.5	0.080	0.086	0.173	0.230	NC
BU3	1.268	1.421	1.395	1.297	2.421	1.069	121.9	117.2	121.7	103.4	0.026	0.029	0.055	0.414	72.1
	1.257	1.427	1.388	1.302	2.466	1.035	122.0	118.2	122.0	104.6	0.039	0.045	0.084	0.369	NC
BU4	1.266	1.424	1.394	1.299	2.430	1.061	121.9	117.3	121.8	103.5	0.030	0.033	0.063	0.402	69.5
	1.256	1.428	1.389	1.303	2.474	1.031	122.0	118.4	122.0	104.7	0.039	0.047	0.086	0.366	NC
AA	1.252	1.442	1.374	1.325	2.520	1.013	121.7	120.0	121.9	105.2	0.068	0.073	0.141	0.280	72.8
	1.246	1.444	1.370	1.326	2.544	1.003	121.5	120.8	122.0	106.3	0.074	0.080	0.154	0.259	66.5
DMOA	1.238	1.451	1.361	1.329	2.600	0.966	124.0	119.0	124.9	105.7	0.090	0.091	0.181	0.217	38.1
	1.231	1.452	1.357	1.328	2.621	0.989	124.0	119.6	125.0	106.7	0.095	0.097	0.192	0.200	31.0

[a] E_{HB}, hydrogen bond energy (in kJ/mol), energy difference between trans- and cis-enol forms. Upper and lower figures are obtained by using 6-31G** and 6-311++G** basis sets, respectively. NC, not calculated.