



Normal coordinate analysis, hydrogen bonding, and conformation analysis of heptane-3,5-dione



Samira Soltani-Ghoshkhaneh ^a, Mohammad Vakili ^{b, **}, Sayyed Faramaraz Tayyari ^{b, *}, Ali Reza Berenji ^c

^a Department of Chemistry, Ferdowsi University of Mashhad, International Campus, Mashhad 91775-1436, Iran

^b Department of Chemistry, Ferdowsi University of Mashhad, Mashhad 91775-1436, Iran

^c Department of Food Processing, Food Science and Technology Research Institute, Iranian Academic Centre for Education, Culture, and Research: ACECR, Mashhad 91779, Iran

ARTICLE INFO

Article history:

Received 22 June 2015

Received in revised form

6 September 2015

Accepted 7 September 2015

Available online 14 September 2015

Keywords:

Heptane-3,5-dione

Density functional theory

Intramolecular hydrogen bond

Vibrational spectroscopy

Atoms in molecules theory

ABSTRACT

Fourier transform Raman and infrared spectral measurements have been made for the heptane-3,5-dione (HPD) and simultaneously compared with those of acetylacetone (AA) to give a clear understanding of substitution effect of ethyl groups (in β -positions) on the structure, electron delocalization, and intramolecular hydrogen bonding (IHB). Molecular structure, conformational stabilities, and intramolecular hydrogen bonding of different oxo-enol forms of HPD, have been investigated by MP2, BLYP, B2PLYP, TPSSh, and B3LYP methods, using various basis sets, and experimental results. The energy differences between four stable E1-E4 chelated forms are relatively negligible. The theoretical and experimental results obtained for stable oxo-enol forms of HPD have been compared with each other and also with those of AA. According to the theoretical calculations, HPD has a hydrogen bond strength of about 15.9 kcal/mol, calculated at the B3LYP/6-311++G** level, which is the same as AA, 15.9 kcal/mol. This similarity in the IHB strength is also consistent with the experimental results of the band frequency shifts for the OH/OD and O...O stretching and OH/OD out-of-plane bending frequencies and chemical shift of the O–H group. The molecular stability and the hydrogen bond strength also were investigated by applying the topological analysis, geometry calculations, and spectroscopic results. Potential energy distribution (PED) and normal coordinate analysis have also been performed. A complete assignment of the observed band frequencies has been suggested the presence of four HPD forms at comparable amounts in the sample.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Enormous theoretical and experimental studies about intramolecular hydrogen bond (IHB), tautomerism, structure, metal complexes, and many other physical and chemical properties of β -dicarbonyls have been emerged over the past several decades. In the case of having at least one hydrogen atom in the α -position, these compounds are capable of forming syn-oxo-enol forms which are stabilized with an intramolecular hydrogen bond. The dioxo-oxo-enol tautomerism in these compounds has been the subject

of several studies [1–4]. The O...O distance in the oxo-enol form of these compounds lies in the range of 2.39–2.60 Å [5,6]. This is in agreement with a proton chemical shift for the proton of OH group in the 13–18 ppm range [7–10]. The IHB in the oxo-enol forms of these compounds is assisted by the resonance in the chelated ring [11]. Therefore, it is called resonance assisted hydrogen bond (RAHB). This kind of the IHB has attracted special attention and was studied by several theoretical [12–14] and experimental techniques, such as vibrational [15–20] and ¹H NMR [1,2,21,22] spectroscopy, X-ray [5,23,24], neutron [23–25], and electron [6] diffraction methods. The strength of the IHB and the position of dioxo-oxo-enol equilibrium depends on several parameters, such as temperature [26], the nature of solvent [27,28], the state of system [29], and the nature of substituted groups in the α - and β -positions [8,10,14,17–20,29]. It is well known that the electron withdrawing groups weakens the IHB [7,17] and increases the oxo-

* Corresponding author.

** Corresponding author.

E-mail addresses: vakili-m@um.ac.ir (M. Vakili), tayyari@ferdowsi.um.ac.ir (S.F. Tayyari).

enol content of the system [2]. Existence of bulky groups in α -position increases the IHB strength and decreases the oxo-enol content of the system [30,31]. On the other hand, substitution of bulky groups in the β -position increases both the IHB strength and oxo-enol content in the sample [17,18].

To the best of our knowledge, the heptane-3,5-dione (HPD) structure, conformations, and vibrational spectra, theoretically or experimentally, have not been described earlier. Therefore the aim of the present paper is to predict the structure, IHB strength, conformational stabilities, vibrational assignments, and ^1H and ^{13}C NMR chemical shifts by means of density functional theory (DFT) calculations. The theoretical results are compared with the experimental data. The obtained theoretical and experimental results will be also compared with those of acetylacetone, AA, to obtain a clear understanding of the substitution effects of methyl groups of AA with ethyl groups on the structure, vibrational band frequencies, and hydrogen bond strength. Finally, the structure and the IHB strength of stable syn-oxo-enol forms of HPD will be compared with the corresponding stable forms of AA, using the Atoms-In-Molecules (AIM) analysis.

2. Experimental

HPD was purchased from Alfa Aesar chemical company and used without further purification. The partially deuterated compound, D2-HPD (the H atoms in OH group and α -position are replaced with D atoms) was prepared by mixing the HPD with D₂O and leaving overnight. The organic layer was separated and dried over anhydrous sodium sulfate.

The IR spectra were recorded on a Bomem B-154 Fourier Transform spectrophotometer by averaging 20 scans with a resolution of 2 cm⁻¹. The spectra were measured as neat liquid. Lorentzian function is utilized for deconvolution of the infrared spectra.

The Far-IR spectra in the 600–350 cm⁻¹ region were obtained using a Thermo Nicolet NEXUS 870 FT-IR spectrometer. The spectrum of neat liquid was collected with a resolution of 2 cm⁻¹ by averaging the results of 64 scans.

The FT-Raman spectra were recorded employing a 180° back-scattering geometry and a Bomem MB-154 Fourier Transform Raman spectrometer. The instrument was equipped with a Nd:YAG laser beam source, ZnSe beam splitter, and a TE cooled InGaAs detector. Rayleigh filtration was afforded by a set of two holographic technology filters. The spectra were accumulated for 3000 scans with a resolution of 2 cm⁻¹. The laser power at the sample was 600 mW.

The NMR spectra were obtained on Avance Bruker-400 MHz spectrometers. All chemical shifts on NMR experiments are reported as ppm, using 2 mol% solution in CDCl₃ at 22 °C, ^1H NMR (CDCl₃): δ 15.435 (b, 1H, OH, oxo-enol), 5.497 (s, H $_{\alpha}$, 74.4% oxo-enol), 3.570 (s, H $_{\alpha}$, 25.6% dioxo), 2.538 (q, CH₂ groups, J = 7.2 Hz, dioxo), 2.316 (q, CH₂ groups, J = 7.2 Hz, oxo-enol), 1.130 (t, CH₃ groups, J = 7.6 Hz, oxo-enol), 1.053 (t, CH₃ groups, J = 7.6 Hz, dioxo), and for ^{13}C NMR: δ 195.16 (C6), 97.65 (C5), 31.40 (CH₂ (8,9)), 9.63 (CH₃ (10,11)).

The observed ^{13}C chemical shifts at 204.85, 56.50, 37.05, and 7.44 ppm are attributed to the existence of dioxo form in the sample. The first two signals are assigned to the carbon atoms of the carbonyl and C $_{\alpha}$, respectively, the signal at 37.05 ppm is assigned to the CH₂ groups and the latter is attributed to the carbon atoms of the methyl groups.

3. Computational studies

Full geometry optimization for all possible syn-oxo-enol

conformations of HPD has been performed, using the B3LYP [32,33], the MP2 [34,35], with the extended 6-311++G**, 6-311G**, and 6-31G** basis sets, and BLYP [36,33], TPSSh [37], and B2PLYP [38] levels with the 6-311++G** and 6-31 + G** basis set. All optimizations have been done by extremely tight optimization convergence criteria. Subsequently, harmonic vibrational frequencies, infrared intensities, and Raman scattering activities were calculated at the B3LYP/6-311++G** level of theory. All computations were carried out with the Gaussian 09 program [39]. The GaussView [40] was used to illustrate the calculated atomic displacements associated with normal modes.

AIM 2000 software [41] was applied to obtain electron density at bond critical points (ρ_{BCP}) and the Laplacian of electron density at the bond critical points ($\nabla^2\rho_{\text{BCP}}$) parameters, for all O...H bonds of stable syn-oxo-enol forms, according to Bader's AIM theory [42].

The absolute shielding for HPD and tetramethylsilane (TMS) have been obtained using the gauge-including atomic orbital (GIAO) method [43,44] at the B3LYP/6-311++G**//B3LYP/6-311++G** level in chloroform, using the PCM model [45]. All chemical shifts are reported in δ units down field from TMS.

A normal coordinate analysis was carried out to provide a complete assignment of the fundamental vibrational wavenumbers for the four syn-oxo-enol forms of HPD, E1-E4. The displacement internal coordinates were obtained from Gaussian outputs, as described elsewhere [46]. The full sets of 79 standard internal coordinates containing 22 redundancies are defined as given in Table S3 (Supplementary material). From these internal coordinates, a non-redundant set of local symmetry coordinates was constructed by a suitable linear combination of internal coordinates (see Tables S3). Then, all these symmetry coordinate were normalized through all 57 normal coordinates. The normalized symmetry coordinates were used to calculate the potential energy distributions (PED) for each normal mode. The "HPModes" keyword was applied in Gaussian (using B3LYP/6-311++G** level) in order to obtain the high precision format (to five figures) for vibrational frequency eigenvectors (Cartesian displacement coordinates) in the frequency output of Gaussian program. All the normal coordinate analysis calculations were carried out using the Microsoft Excel 2013 program. The results of potential energy distribution (PED) in conjunction with the GaussView program illustrations and deuteration effects give the vibration assignments with a high degree of accuracy. The calculated harmonic frequencies were scaled by a factor of 0.9621 for CH/CD and OH/OD stretching vibrations and by 0.9802 for the remaining harmonic frequencies, as regression coefficient, R² = 0.9314 and 0.9986, respectively. Lorentzian function is utilized for deconvolution of the infrared and Raman spectra, using solver optimization tool in Microsoft Excel 2013 program.

4. Results and discussion

4.1. Conformational stability, molecular structure, and intramolecular hydrogen bond strength

All theoretically possible conformers of HPD, considered by rotation of the molecule about its bonds, were optimized using the mentioned methods. The results of full optimization were four syn-oxo-enol stable conformers, which are shown in Fig. 1 (which the O–H and C4=C5 bonds are in the syn arrangement, designated as I in Fig. 1). The stable forms at B3LYP with 6-311++G**, 6-311G**, and 6-31G** basis sets, BLYP, TPSSh with 6-311++G** basis set, and B2PLYP/6-31 + G(2d,p), were E1-E4 with C₁, C_s, C₁, and C_s symmetries, respectively, while in MP2 level with the same basis sets the stable conformers are E1-E2, and E4. According to the MP2 calculation E3 was unstable and upon full optimization turns to E1.

Download English Version:

<https://daneshyari.com/en/article/1409080>

Download Persian Version:

<https://daneshyari.com/article/1409080>

[Daneshyari.com](https://daneshyari.com)