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New insights into the conformal stability, influence of hydrogen bonding and vibrational analysis of 2,6- and 3,5-Dihydroxyacetophenone – A comparative study

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ABSTRACT

The conformal stability of 2,6-Dihydroxyacetophenone (DHAP I) and 3,5-Dihydroxyacetophenone (DHAP II) were investigated using Potential Energy Surface scan studies and B3LYP/6-31G** level Density Functional Theory(DFT) calculations. The experimental (FT-IR and FT-Raman) spectra were recorded in the condensed phase in order to perform detailed vibrational analysis. The optimized geometry and vibrational wavenumbers were determined by using B3LYP/6-31G** level Density Functional Theory calculations. The effect of scaling on the calculated wavenumbers was analyzed by employing unscaled, uniform scaling and selective scaling procedures. A detailed comparative analysis on the effect of hydrogen bonding on the geometry, structural parameters and vibrational wavenumbers has been carried out using the results obtained from PES scan and DFT level calculations. The results from the above studies reveals that, the presence of strong intramolecular hydrogen bond in DHAP I has significantly altered the geometrical parameters and hence the vibrational wavenumbers. The hydrogen bonding in DHAP I is strong enough to make it more stable compared to that of DHAP II.

1. Introduction

This study is based on the increasing demand and interest on the biological importance and implications of the simplest aromatic ketone – Acetophenone. It is typically used in food, pharmaceuticals, agrochemical and fragrance industries. The wide presence of acetophenone was naturally observed in foods like apple, banana, apricot, cauliflower and cheese. Hypone, a derivative of acetophenone possess hypnotic and anticonvulsant properties [1–4]. Several attempts have been made to develop non-toxic and cheaper iron catalysts for the purpose of hydrogenation of carbonyl compounds to alcohols in the perfume, fine chemical and pharmaceutical industries [5–14]. Besides these applications, acetophenones was used to form resins, plasticizer and to create fragnences that resembles cherry, strawberry, jasmine, almond and honeysuckle. Dihydroxyacetophenones possess antimicrobial and anti-melanogenie nature and finds extensive application in the treatment of pathologic pregnancies with chronic defective utero-placental circulation [15–18]. Density Functional Theory (DFT) based conformational analysis and vibrational studies have been carried out on 2,4-dihydroxy-4-methyl-acetophenone and 2,4-dihydroxy-3-acetyl-6-methyl-acetophenone by Saiket K.Seth et al. [19].

In the present study, we report the complete vibrational characterization and conformational stability of the title compounds 2,6-Dihydroxyacetophenone (DHAP I) and 3,5-Dihydroxyacetophenone (DHAP II) with the aid of FT-IR, FT-Raman, UV–Vis spectra and calculations at the density functional theory (DFT) level. The main objective of taking this work is to investigate the impact of hydrogen bonding on acetophenone derivatives. The two different environments of acetophenone derivatives have been thoroughly investigated in the present study. From the study we observed that, the presence of strong intra molecular hydrogen bond between one of the hydroxyl group and its adjacent carbonyl group of DHAP I has significantly altered the geometrical parameters and vibrational wavenumbers when compared to the non-hydrogen bonded DHAP II. Various possible conformers were predicted and their corresponding harmonic force fields were calculated. From the results obtained using DFT level optimization and PES scan analysis, the most stable conformers of

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the two titled compounds were identified. A complete vibrational analysis of the titled compounds were made by combining the experimentally observed spectra and theoretically computed information using DFT based scaled quantum mechanical (SQM) approach on the most stable conformers. The effect of hydrogen bonding on the structural & vibrational parameters of the title compounds was investigated.

2. Methods

2.1. Experimental section

The fine polycrystalline samples of 2,6- Dihydroxyacetophenone (DHAP I) and 3,5- Dihydroxyacetophenone (DHAP II) were obtained from M/S. Sigma Aldrich chemicals company USA and used as such for spectral measurements. The room temperature FT-IR spectra were obtained for KBr disks prepared using standard sample preparation procedures in the region 4000–400 cm^{-1} at a resolution of +1 cm^{-1} using Perkin- Elmer spectrum R1 spectrophotometer equipped with He–Ne laser source, KBr beam splitter and LiTaO3 detector. FT- Raman measurements for the samples made using the Nicolet model 950 FT-Raman spectrometer using the 1064 nm line of a Nd:YAG laser for excitation at a 200 mw output power in the range 4000–50 cm^{-1}. Typically 1000 scans were collected with a resolution of 4 cm^{-1} with time duration of 6 h. The Ultraviolet–visible (UV–Vis) absorption spectrum of the title compounds was recorded in the range 800–200 cm^{-1} using Analytik Jena specord plus 200 UV/Vis spectrophotometer.

2.2. Computational details

Quantum chemical calculations were performed on the title molecules by applying DFT method using the Gaussion 09 program suite [20] at the Becke-3-Lee-Yang-Par (B3LYP) level [21,22] combined with the standard 6-31G** basis set. During optimization procedure, all the parameters were allowed to relax in order to obtain the stable structure with minimum energy. The global minimum energy for various possible conformers was ascertained from the structure optimization procedure. A full normal coordinate analysis was performed on the titled compounds using the Molvib 7.0 Program written by sundius [25,26]. This includes the transformation of Cartesian force field to local symmetry coordinates followed by scaling the force field by selective scale factors as recommended by pulay et al. [23] and the subsequent normal coordinate analysis (NCA) including the least square fit refinement of the scale factors, calculation of potential energy distribution (PED) and prediction of IR and Raman intensities.

$$F_{ij}^{scaled} = (C_i C_j)^{\frac{1}{2}} F_{ij}^{B3LYP} \quad (1)$$

where C_i is the scale factor of coordinate i, F_{ij}^{B3LYP} is the B3LYP/6-31G** force constant in the local internal coordinates, and F_{ij}^{scaled} is the scaled force constant.

The Raman activities (s_i) calculated by the Gaussian 09 program were converted to Raman intensities (I_i) using the following relationship [27,28].

$$I_i = \frac{f(v_o - v_i)^4 S_i}{v_i \left[1 - \exp\left[\frac{-hcv_i}{kT}\right]\right]} \quad (2)$$

where v_0 is the exciting frequency (in cm^{-1} units), v_i is the vibrational wavenumber of the ith normal mode, h, c and k are the universal constants, and f is the suitably chosen common normalization factor for all the peak intensities. For the plot of spectra, digital version of the observed and simulated spectra of the title compound was used.

For simulation of Raman spectra, pure Lorentzian band shapes were used with a bandwidth (FWHM) of 10 cm^{-1}. The Natural bonding orbital (NBO) calculation was performed using NBO 5.1 program [29] as implemented in the Gaussian 09 package at DFT/B3LYP level. The hyperconjugation and the interaction energy within the molecule were deduced from the second order perturbation approach [30–32].

3. Results and discussion

3.1. Conformal stability through DFT analysis

To find the most optimized geometry, the energy calculations were performed for DHAP I and the DHAP II using the DFT (B3LYP/6-31G**) method for various possible conformers. The possible conformers of DHAP I and DHAP II, were shown in Figs. 1 and 2(A)–(D) respectively. The total energies obtained for these conformers were compared and listed in Table 1. It was clear that the conformer C of DHAP I (Fig. 1(C), Table 1) and conformer A of DHAP II (Fig. 2(A), Table 1) possessed minimum energy and hence they were found to be the most stable conformers.

3.2. Conformal stability through PES analysis

In order to confirm the choice of most stable conformer of the title compounds, a potential energy surface scan using DFT method at B3LYP/6-31G** level was carried out. Two different scans were performed on the optimized geometry by rotating the hydroxyl groups (O–H) independently from 0° to 360° with an increment of 10°. The scan plot for DHAP I was shown in Fig. 3(A) and (B) and that for DHAP II in Fig. 4(A) and (B). For DHAP I, the most stable conformer was obtained when dihedral angle for C2–C3–O14–H15 and C6–C5–O17–O18 was at 180°. The PES scans of DHAP II reveals that, the most stable conformer was obtained when dihedral angle for C2–C3–O14–H15 and C6–C5–C17–C18 was at 180°. This angle along with other geometrical parameters matches exactly with those of the conformers predicted by DFT optimization earlier.

Further, to standardize the results, the third PES scan was performed on the title compounds by rotating both the hydroxyl groups simultaneously. The scan plot for DHAP I was shown in Fig. 3(C) and (D) and that for DHAP II in Fig. 4(C) and (D). This scan reveals that the most stable conformers were obtained for both the molecules for a dihedral angle of 180° for both the hydroxyl groups. This further confirms the choice of optimized geometry.

3.3. Molecular geometry

The optimized molecular structure of DHAP I and DHAP II were shown in Fig. 1(C) and Fig. 2(A). The optimized geometrical parameters obtained for the title compounds from DFT optimization were presented in Table 2. In the most stable conformer structure of DHAP II (Fig. 2(A)), the two O–H groups were coplanar with the ring and are facing upwards. The energy obtained for this optimized structure was −12345.4364 kcal/mol.

For DHAP I, the optimized energy of −12345.7405 kcal/mol was obtained for the most stable conformer with the hydrogen atom H19 (Fig. 1(C)) of the hydroxyl group (O18–H19) turned towards the carbonyl group (C7=O8) and the other hydrogen atom H14 (Fig. 1(C)) of the hydroxyl group (O13–H14) facing downwards. This clearly shows that the strong influence of intramolecular hydrogen bonding over the formation of the optimized structure of the stable conformer of DHAP I. In a similar