

Vibrational assignment, structure and intramolecular hydrogen bond study of 3-amino-1-phenyl-2-buten-1-one

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Abstract

Fourier transform infrared and Fourier transform Raman spectra of 3-amino-1-phenyl-2-buten-1-one and its deuterated analogue were recorded in the regions 400–4000 and 150–4000 cm^{-1} , respectively. Furthermore, the molecular structure and vibrational frequencies of title compound were investigated by a series of density functional theoretical, DFT, and ab initio calculations at the post-Hartree–Fock (MP2) level. Although, the calculated frequencies are generally in agreement with the observed spectra but the DFT results are in much better quantitative agreement with the observed spectra than the MP2 results. The observed wavenumbers were analyzed and assigned to different normal modes of vibration of the molecule. The calculated geometrical parameters show a strong intramolecular hydrogen bond with a N \cdots O distance of 2.621–2.668 Å. This bond length is shorter than that of its parent, 4-amino-3-penten-2-one (with two methyl groups in the β -position), which is in agreement with spectroscopic results. The topological properties of the electron density contributions for intramolecular hydrogen bond in 3-amino-1-phenyl-2-buten-1-one and 4-amino-3-penten-2-one have been analyzed in term of the Bader theory of atoms in molecules (AIM). These results also support the stronger hydrogen bond in the title compound with respect to the parent molecule.

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1. Introduction

Homo and heteronuclear hydrogen bonds systems involving oxygen and/or nitrogen atoms are well documented because they are present in numerous biological molecules and can give rise to very strong intramolecular hydrogen bridges when assisted by resonance. Their importance in chemistry and biology are mainly due to the vital role they are playing in determining the equilibrium conformation of all biological macromolecules such as proteins, polysaccharides, barbiturates, etc. [1,2]. Among the intramolecular bridges, the O–H \cdots O system has been widely studied experimentally as well as theoretically [3–7].

α,β -Unsaturated- β -ketoenamines are capable of forming tautomeric equilibria between ketoamine, enolimine and ketoimine forms. It is well known that the ketoamine form

of these compounds is generally more stable than the other tautomeric forms [8–10]. These compounds are engaged in an N–H \cdots O asymmetric hydrogen bonding system. The heteronuclear N–H \cdots O is even more important than the homonuclear O–H \cdots O bond because of its great importance in proteins folding and DNA pairing and its ever-growing application in molecular recognition and crystal engineering problems [11], however, no systematic investigation of strong N–H \cdots O bonds is available. Gilli et al. [12] have examined several molecular systems with N–H \cdots O inter or intramolecular hydrogen bonding. They concluded that this hydrogen bond formation leads to an enhancement of the resonance conjugation of the π -electrons. This fact was confirmed by recent experimental results and ab initio calculations [8,9]. Therefore, it seems that any parameter that affects the electron density of the chelated ring will change the hydrogen bond strength. Also, substitution in the α - or β -position drastically changes the hydrogen bond strength, similar to β -diketones [3,13,14]. In the case of β -diketones, several experimental

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data suggest that the strength of such a bridge is enhanced when bulky groups replace the CH₃ group in the β -position [15–21]. However, the effect of substitution in β -position of ketoamines neither has been investigated experimentally nor theoretically as extensively as β -diketones.

By analyzing the substitution effect of simple substitutes such as phenyl group, an electron withdrawing moiety with the steric effect on the structure, it is possible to study the mesomeric effect for this kind of substitution. These aspects of substituted phenyl group caused that the 3-amino-1-phenyl-2-buten-1-one (here after APBO) are of potential interest.

The aim of the present paper is to predict the structure and vibrational spectra (harmonic wavenumbers and relative intensities for Raman and IR spectra) of APBO by means of the ab initio calculation and density functional theory (DFT). Comparison of APBO and 4-amino-3-penten-2-one (here after APO) geometrical parameters gives a clear understanding of substitution effects of CH₃ group with phenyl group in the β -position on structure and hydrogen bond strength of the system. The calculated harmonic force constants of APBO were used for predicting the Raman and IR spectra of deuterated species. The calculated vibrational frequencies were compared with the experimental results.

2. Experimental

Benzoylacetone and all solvents were purchased from Fluka. Chloroform and deuterated chloroform were stored over 3 Å molecular sieves. The concentration of the sample for ¹H NMR and infrared measurements was 0.1 mol dm⁻³. APBO was synthesized by the modification of the method given for APO in Ref. [8].

The amount of 16.1 g (0.1 mol) of Benzoylacetone was dissolved in 60 cm³ ammonia solution 25%, refluxed for 2 h and then stirred continuously for 24 h at room temperature. The mixture was extracted (3 × 50 cm³) with chloroform. The organic layer was dried using anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was crystallized from CHCl₃. Yield was 10.5 g (65%) of colorless crystal; mp 60–62 °C, ¹H NMR (CDCl₃): δ 2.05 (s, 3H, CH₃), δ 5.26 (s, 1H, NH free); δ 5.76 (s, 1H, CH_α); δ 7.40 (m, 3H, CH); δ 7.85 (m, 2H, CH); δ 10.88 (s, 1H, NH bonded). The elemental analysis confirmed the results.

The solution of D₂APBO (deuteration done on amine protons) was prepared by shaking solution of APBO in CHCl₃ with D₂O for period of up to 24 h. However, the crystalline D₂APBO was prepared from CHCl₃ solution of D₂APBO which was dried over anhydrous Na₂SO₄ followed by removing the organic layer under reduce pressure.

The experimental IR spectra were obtained using a Nicolet Model 800 Fourier transform infrared (FT-IR) spectrometer, at a spectral resolution of 2 cm⁻¹, with 400 scans.

The experimental study of the Raman spectra was performed using a Nicolet Fourier transform spectrometer

(model 910). The excitation of the Raman spectrum in the Nicolet FT-Raman instrument was by the near-infrared line at 1.064 μ m (or 9398.5 cm⁻¹) from a 3 W cw Nd:YAG laser. About 2000 scans at a resolution of 2 cm⁻¹ were needed to ensure a high signal-to-noise ratio. The NMR spectra were obtained on a FT-NMR, Bruker Aspect 3000 spectrometer at 100 MHz frequency in CDCl₃ at 22 °C and TMS as internal standard.

3. Method of analysis

In the present study, the molecular equilibrium geometry, vibrational frequencies and infrared and Raman intensities were computed with the GAUSSIAN 98W software system [22] by using a selection of modern density functionals and the ab initio (MP2) method. The B [23] or B3 [24] or G96 [25] exchange functionals were combined with the PW91 [26] or LYP [27] correlation functionals, resulting in the four different functionals BLYP, G96LYP, B3PW91 and B3LYP. A series of calculations on APBO were performed with medium size 6-31G^{*} (202 basis functions, 380 primitive gaussians) and 6-31G^{**} (235 basis functions, 413 primitive gaussians) basis sets. Application of the B3LYP, BLYP and G96LYP density functional was repeated with the larger basis sets, 6-311+G^{*} (297 basis functions, 487 primitive gaussians) and 6-311++G^{**} (341 basis functions, 531 primitive gaussians). No scaling factors have been used in order to improve the agreement between the experimental and theoretical wavenumbers, because the DFT method is now considered to be a suitable theoretical level capable of reproducing satisfactorily the wavenumbers and intensities.

The nature of intramolecular hydrogen bond existing within APBO and APO has been studied by means of the Bader theory of atoms in molecules (AIM) [28] that is based on topological analysis of the electronic charge density, ρ . The optimized geometries were employed to obtain wave function files suitable for use with AIM 2000, which suits the programs [29] and were applied to perform the AIM calculations.

4. Results and discussions

4.1. Molecular geometry

The molecular equilibrium geometry predicted with the B3LYP, B3PW91, BLYP, G96LYP density functionals and the ab initio (MP2) method are given in Table 1. The geometry of APBO and the numbering of the atoms is given in Fig. 1. It is apparent that replacement of the LYP correlation functional with the PW91 functional leads to the prediction of a shorter O...H distance, corresponding to a more symmetrical H-bond. A somewhat similar trend was observed when B3 and B hybrid exchange functionals were replaced by the G96 functional. On the other hand, the main effect

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