

## Vibrational assignment and crystal structure of 3-amino-1-phenyl-2-buten-1-one

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### HIGHLIGHTS

- X-ray molecular structure of 3-amino-1-phenyl-2-buten-1-one is reported.
- Vibrational spectra of 3-amino-1-phenyl-2-buten-1-one is reported.
- Substitution of CH<sub>3</sub> group with C<sub>6</sub>H<sub>5</sub> increases the H-bond strength.
- The results obtained for this molecule compared with those for APO.

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### ABSTRACT

3-Amino-1-phenyl-2-buten-1-one (APBO) was synthesized by amination of benzoylacetone (BA) and its structure was studied by X-ray crystallographic method. The geometry of APBO was also optimized by means of density functional theory (DFT) and *ab initio* calculations and the results were compared with the X-ray crystallographic data. The vibrational fundamentals predicted within harmonic model, calculated at the B3LYP/6-311++G\*\*, and by anharmonic model, calculated at the B3LYP/6-31G\*\* level, display excellent agreement with the measured data. The proposed assignments are further confirmed by observing the deuterium isotopic shifts of different bands through predictions by the same theoretical method. The theoretical results obtained for APBO were compared with those of 4-amino-3-penten-2-one (APO).

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### 1. Introduction

β-Functionalized enamine derivatives have been extensively used as valuable precursors in organic synthesis [1–8]. They have been utilized for the synthesis of various pharmaceutical and bioactive heterocycles, such as dopamine auto-receptor agonists, acetylcholinesterase inhibitors, oxytocin antagonists, and anticonvulsants [9–11]. In particular, they have been employed as synthons of different important antibacterial [12], anticonvulsant, anti-inflammatory [13], and antitumor agents [14].

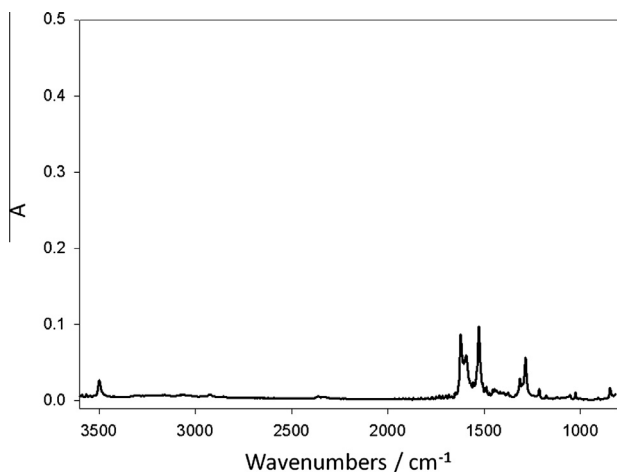
Among intramolecular hydrogen bridges involving nitrogen and oxygen atoms, the ketoenamine form is the most stable conformer [15–19]. Gilli et al. [20] reported that the N–H···O hydrogen bond formation leads to an enhancement of the resonance conjugation of the π-electrons. The strength (energy) of this hydrogen bond (EHB) is typically 30 kJ/mol [13,15]. In the analogous bridge of

enolimine, the EHB is in the 11.2–18.6 kJ/mol range [13,15]. Particularly, APBO is a ketoenamine with a strong N–H···O hydrogen bond. Comparing the geometrical parameters of APBO with those of APO will give us a clear understanding of substitution effects on the structure and hydrogen bond strength of this system.

In fact, Raissi et al. [19] already investigated the vibrational spectra of APBO a few years ago. However, in our study of ketoenamine compounds, after comparing our vibrational spectra with those reported previously [19], we identified many discrepancies in the frequencies of peak positions and in the physical properties such as insolubility in CCl<sub>4</sub>. In comparison, Raissi et al. reported their spectra in the CCl<sub>4</sub> solution with an absorbance of about 2.5 [19]! Such disagreement prompted us to carry out a thorough reassessment to resolve this issue. Although some of the observed geometrical parameters of the titled compound have been reported from the X-ray crystallographic data [21], to obtain more accurate and complete geometrical parameters of this molecule, its structure was also reinvestigated by X-ray crystallographic diffraction method.

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**Fig. 1.** The IR spectrum of saturated  $\text{CCl}_4$  solution of APBO with 0.2 mm path length in the 3600–850  $\text{cm}^{-1}$  range.

The aim of the present work is thus to study the structure of APBO by X-ray and computational chemistry calculations, and to obtain the full assignment of its vibrational spectra (including harmonic and anharmonic vibrational frequencies and relative intensities for Raman and IR spectra) with the aid of density functional theory (DFT) calculations.

## 2. Experimental

APBO was synthesized according to the literature [22] and after recrystallization from hexane/ethylacetate (1:1), the white shining crystals were yielded. Analytic Found: C, 74.11%; H, 7.13%; N, 8.79%; Calculation for  $\text{C}_{10}\text{H}_{11}\text{ON}$ : C, 74.53%; H, 6.83%; N, 8.70%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 100 MHz, reference: solvent residual peak,  $\delta$  7.24 ppm):  $\delta$  5.8 ppm (s, H,  $\text{CH}_\alpha$ ),  $\delta$  5.3 ppm (b, H, free NH),  $\delta$  10.3 ppm (b, H, NH involved in an intramolecular hydrogen bond),  $\delta$  7.46 ppm (m, 5H, Ph),  $\delta$  2.05 ppm (s, 3H,  $\text{CH}_3$ ).

Any effort for direct deuteration of APBO by simple mixing of APBO solutions with  $\text{D}_2\text{O}$ , as suggested by Raissi et al. [19], was unsuccessful. However, deuteration was simply done by adding a few drop of trimethylamine to the mixture of  $\text{CH}_2\text{Cl}_2$  solution of

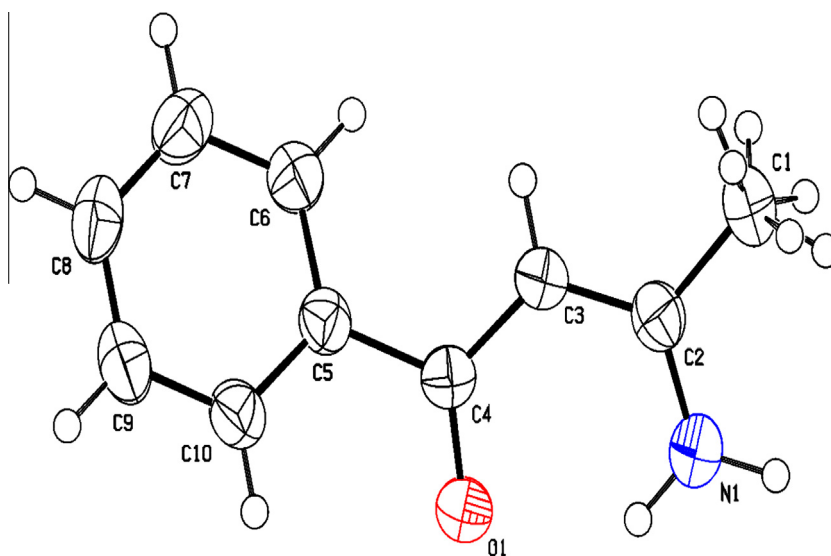
APBO and  $\text{D}_2\text{O}$ . Then, the organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  followed by removing the organic layer under reduced pressure.

The mid-IR spectra of APBO and  $\text{D}_2\text{APBO}$  were recorded by using Bomem MB-154 Fourier Transform Spectrophotometer in the region 500–4000  $\text{cm}^{-1}$  in KBr pellet and in  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  solution. The spectra were collected with a resolution of 2  $\text{cm}^{-1}$  by coadding the results of 16 scans.

Raissi et al. claimed that they took the IR spectra of APBO and its deuterated analog in  $\text{CCl}_4$  solutions [19]. However, we found that APBO and  $\text{D}_2\text{APBO}$  are both *hardly* soluble in  $\text{CCl}_4$ . Fig. 1 shows the IR spectrum of saturated APBO in  $\text{CCl}_4$  with 0.2 mm path

**Table 1**  
Crystallographic data for 3-amino-1-phenyl-2-buten-1-one.

Empirical formula	$\text{C}_{10}\text{H}_{11}\text{NO}$
Formula weight	161.20
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pbca
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	9.8785(5)
<i>b</i> (Å)	8.7512(4)
<i>c</i> (Å)	19.8710(10)
$\alpha$ (°)	90.00
$\beta$ (°)	90.00
$\gamma$ (°)	90.00
<i>V</i> (Å <sup>3</sup> )	1717.82(15)
Calculated density ( $\text{g cm}^{-3}$ )	1.247
Absorption coefficient, $\mu$ ( $\text{mm}^{-1}$ )	0.081
<i>F</i> (000)	688
Crystal size (mm)	0.40 × 0.36 × 0.12
$\theta$ range for data collection (°)	2.91–26.220
Limiting indices	$-12 \leq h \leq 12$ ; $-10 \leq k \leq 10$ ; $-18 \leq l \leq 23$
Reflections collected/unique [ <i>R</i> (int)]	1689/1137 [0.0412]
Completeness to $\theta$ (%)	97.7
Absorption correction	Multi-scan
Max. and min. transmission	0.896–0.990
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	1689/0/118
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.013
Final <i>R</i> indices	$R_1 = 0.0489$ , $wR_2 = 0.0921$
<i>R</i> indices (all data)	$R_1 = 0.1038$ , $wR_2 = 0.1069$
Largest diff. peak and hole ( $\text{e Å}^{-3}$ )	0.17 and $-0.15$



**Fig. 2.** ORTEP structure and atom numbering of APBO. Displacement ellipsoids are drawn at the 50% probability level.

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