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Synthesis, molecular structure, conformational, and intramolecular hydrogen bond strength of ethyl 3-amino-2-butenoate and its N-Me, N-Ph, and N-Bn analogs; an experimental and theoretical study

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Abstract

Amino derivatives of ethyl acetoacetate like ethyl (Z)- 3-(amino)but-2-enoate (EAB), ethyl (Z)- 3-(methylamino)but-2-enoate (Me-EAB), ethyl (Z)- 3-(phenylamino)but-2-enoate (Ph-EAB), and ethyl (Z)- 3-(benzylamino)but-2-enoate (Bn-EAB) were synthesized. Their structures, conformations, and intramolecular hydrogen bonding (IHB) is characterized using computational analysis (density functional theory, DFT, methods) at the B3LYP/6-311++G(d,p) level and spectroscopic techniques (IR, UV, and NMR). All the mentioned theoretical and experimental

results were compared to those of (Z)-methyl 3-aminobut-2-enoate (MAB). The vibrational spectra of EAB are fully assigned. Vibrational spectroscopy results confirmed the existence of two conformers of title molecules. DFT calculations at the B3LYP/6-311++G(d,p) level show the calculated N-H bond lengths in EAB, Me-EAB, Ph-EAB, Bn-EAB, and MAB are 1.015, 1.017, 1.022, 1.018, and 1.014 Å, respectively. Also, according to the natural bond orbital (NBO) results, the σ N-H10 \leftrightarrow LP(2)O7 interactions for EAB, Me-EAB, Ph-EAB, and MAB are 5.21, 6.77, 8.65, 7.18, and 5.11 kcal/mol, respectively. So, the trend in IHB strength is: Ph-EAB > Bn-EAB ~ Me-EAB > EAB ~ MAB, which also agrees with the mentioned experimental results. The mentioned trend also is confirmed by the LP(O7) $\leftrightarrow \sigma$ N-H steric exchange interaction.

Keywords: Ethyl (Z)- 3-(amino)but-2-enoate; Intramolecular hydrogen bond; NMR; Vibrational spectroscopy; DFT.

1. Introduction

 β -enamino esters, with N–C=C–C=O skeleton, are used to prepare bio-active heterocyclic compounds such as pyridinone, tetronic acids, pyrazoles, quinolines, and oxazoles [1-4]. They have been used to prepare antitumor agents [5], anticonvulsant [6], anti-inflammatory [7], and antibacterial [8]. They are also important precursors for the synthesis of indolizidine alkaloids [9], azo compounds [10], 3-amino sugar derivatives [11], hexahydro azulenes [12], and β -amino ketones [13]. Theoretically, β -enamino esters can form three different tautomers including iminoenol, iminoketone, and aminoketone forms (see Fig. 1). The present study will elucidate the possible existence of all three. Examples of enaminones are many, but the resemblance between those and enaminoesters is slight due to the difficulty of esters to exist as enol forms. Nevertheless, a product in the iminoenol form has been postulated [14] (see Discussion).

<Fig. 1>

One of the most simple members of the β -enamino esters is MAB, which is used as a reference in this work. MAB's vibrational spectra, structure, and hydrogen bond strength have been studied experimentally and theoretically [15]. Recently, Singh et al. [16] synthesized EAB and a

few of its N-substituted derivatives to make 5-hydroxyindoles via scaffolds based on a Nenitzescu reaction, but the structure, conformation, and full interpretation of the vibrational bands in EAB and N-methyl, phenyl, and benzyl substitutions have not been reported. The above substitutions can affect the strength of the hydrogen bond by steric and electronic effects. Comparing the strength of the hydrogen bond with experimental and theoretical methods, such as NMR, UV-Vis, IR, Raman spectra, optimized geometric parameters, NBO, and atoms in molecules (AIM) [17] analysis, of the investigated molecules with MAB [15], can increase our insight into the effects of these substitutions on the strength of IHB.

2. Experimental

2.1. Materials and measurements

Unless stated otherwise, all chemicals were purchased from Sigma-Aldrich and used without further purification. Solvents used were HPLC grade and dried over molecular sieves (4 Å) before use. Analytical thin-layer chromatography was done on Merck Alufoils SiO₂ 60 F254 0.2 mm thick precoated TLC plates. Column chromatography was performed using SiO₂ from VWR 40–63 μm. ¹H and ¹³CNMR spectra were also recorded at 500 and 126 MHz, respectively, on a Bruker Avance 3 spectrometer with a BBFO probe. All chemical shifts (δ) are quoted in ppm, and all coupling constants (J) are in Hertz (Hz). The following abbreviations are used for diversity for NMR resonances: s=singlet, bs=broad singlet, d=doublet, t=triplet, q=quartet, and m=multiplet. HRMS LC/MS were recorded on a Dionex Acclaim RSLC 120 C18 2.2 lm 120 Å 2.150 mm column maintained at 40 °C carried out on a Bruker Micro TOF-QII system with ESI system.

The mid-IR spectra were obtained using KBr pellets or CCl₄ solution with a spectral resolution of 2 cm⁻¹ by averaging the results of 20 scans with a Bomem MB-154 Fourier transform spectrophotometer.

The FT-Raman spectrum of EAB was recorded on a Teksan, Takram P50C0R10 Raman spectrophotometer with 532 nm wavelength incident laser light.

The Far-IR spectra in the region 600-200 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 with the use of polyethylene disks. The spectrum was collected using CsI pellets with a resolution of 2 cm⁻¹ by signal averaging 32 scans.

The deuterated analog of EAB, D_3 -EAB, was prepared according to the literature [18]. According to the IR spectra, the hydrogen atoms of the amino group and α -position were replaced by deuterium.

The ultraviolet absorption spectra were examined in the 200–400 nm range using Perkin-Elmer LAMBDA 25 spectrophotometer equipped with a 10 mm quartz cell at 298 K. Ethanol was used as a solvent in the UV study.

2.2. Synthesis

The synthesis of ethyl (Z)-3-(methylamino)but-2-enoate, Me-EAB, and ethyl (Z)- 3-(phenylamino)but-2-enoate, Ph-EAB, was recently reported [19]. Ethyl (Z)- 3-(amino)but-2-enoate (EAB) and ethyl (Z)- 3-(benzylamino)but-2-enoate (Bn-EAB) were synthesized using the following protocols.

(Z)- 3-(amino)but-2-enoate, EAB:

In 100 ml, RBF was charged with ethyl acetoacetate (2.08 g, 16.0 mmol) and ammonium acetate (6.13 g, 80.0 mmol) in methanol (25 ml). The flask was stoppered, and the mixture was stirred at room temperature for 48 h. Then more ammonium acetate (2.03 g, 26.4 mmol) was added, and the mixture was stirred at room temperature for another 24 h. After the solvent was evaporated under reduced pressure, the residue was diluted with chloroform (60 ml). The resulting solid was filtered off and washed with chloroform (2 × 30 ml). The combined filtrate was washed with water, 1 M KH₂PO₄ solution, brine, and dried with anhydrous sodium sulfate. Evaporation of the solvent gave a white solid purified by flash column chromatography on silica gel, using n-hexane-ethyl acetate (3:2) as eluent to give the pure compound as a light amber oil which solidified on standing (1.58 g, 76%). ¹H NMR (500 MHz, CDCl₃): δ 7.88 (bs, -NH, 1H), 4.50 (s, 2H), 4.08 (q, 2H, *J*= 7.1 Hz), 1.88 (s, -CH₃, 3H), 1.23 (t, *J*= 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ 170.36, 159.77, 84.24, 56.61, 22.42, 14.68. HRMS-ESP (m/z): [M + H]⁺ calcd. For C₆H₁₂NO₂: 130.08680, found: 130.0874.

(Z)- 3-(benzylamino)but-2-enoate, Bn-EAB:

In 25 ml, RBF was charged with ethyl acetoacetate (1.30 g, 10.0 mmol), benzyl amine (1.07 g, 10.0 mmol), and glacial acetic acid (0.06 g, 1.0 mmol). The flask was stoppered and shaken in an ultrasound bath at 25 °C for 1.0 h. The reaction was monitored by TLC and showed complete conversion. The acetic acid was removed under reduced pressure, the amber oil residue was dissolved in dichloromethane (75 ml), washed with water (3x75 ml), and the organic portion was dried over anhydrous sodium sulfate. Evaporation of solvent affords light brown viscous oil purified by flash column chromatography on silica gel, using n-hexane-ethyl acetate (5:1) as eluent to give the pure compound as a light amber oil which solidified on standing (1.49 g, 68%). ¹H NMR (500 MHz, CDCl₃): δ 8.95 (bs, 1H9), 7.34-7.31 (m, 2H), 7.26-7.23 (m, 3H), 4.53 (s, 1H), 4.41 (d, *J*= 6.4 Hz, 2H), 4.10 (q, *J*= 7.1 Hz, 2H), 1.90 (s, 3H), 1.25 (t, *J*= 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ 170.92, 162.14, 139.08, 129.10, 127.65, 127.03, 83.51, 58.72, 47.11, 19.70, 14.96, these results are in agreement with literature [16] report. HRMS-ESP (m/z): [M + H]⁺ calcd. For C₁₃H₁₇NO₂: 220.13314, found: 220.13323.

3. Calculations

The calculations for the EAB, Me-EAB, Ph-EAB, and Bn-EAB have been done using the B3LYP functional [20, 21] and the 6-311++G(d,p) basis set using the Gaussian 09W program package [22]. The vibrational assignments of the normal modes are carried out with the GaussView 5.0 software [23]. In addition, the structure's optimization and conformational analysis have also been done at the MP2/6-311++G(d,p) level of theory [24, 25].

The AIM computations were applied according to Bader's AIM theory [17] using the AIM 2000 program [26]. The second-order interaction energies (E^2) [27] and steric exchange energies [28] were calculated using the NBO 5.0 program [29] at MP2/6-311++G(d,p) level of theory. The excitation transitions for the title molecules were calculated by time-dependent density functional theory (TD-DFT), using the polarizable continuum model (PCM) in ethanol as solvent [30]. The GIAO (Gauge-Including Atomic Orbital) method [31, 32] was used to calculate NMR chemical shifts. All the mentioned results were obtained at B3LYP/6-311++G(d,p) level.

4. Results and Discussion

4.1. Molecular structure and intramolecular hydrogen bond strength

As mentioned in the introduction, the EAB and its N-Me, N-Ph, and N-Bn derivatives can, in principle, exist in three different forms called iminoenol (IE), aminoketone (AK), and iminoketone (IK) (see Fig. 1). According to the calculated results, the IE tautomer in EAB is unstable and is changed to AK forms upon optimization. Also, the IK forms, which have no intramolecular hydrogen bond are between 4.3-8.8 kcal/mol higher in energy than AK1. So, the calculated results agree with the experimental and theoretical reported works that showed that the iminoketone and iminoenol tautomers are not stable [15, 33-35]. Also, the recorded NMR and IR spectra confirmed the mentioned results (see continue). So, we consider only AK forms. Only four AK conformers (AK1-AK4) have the N-H…O intramolecular hydrogen bond. AK1-AK4 forms are obtained by varying the C-O-C-C and O=C-O-C dihedral angles (see Fig S1 for EAB, supplementary material). According to the calculations at the B3LYP and MP2 levels with a 6-311++G(d,p) basis set, the AK1 is the most stable conformer, and AK3 and AK4 are the least ones. It agrees for N-Me, N-Ph, and N-Bn derivatives, too. The optimized structures for EAB, AK1, and AK2, with numbering, are shown in Fig. 2. The conformations of the ethoxy group with respect to the chelate ring, Ak1-Ak4, were obtained according to the reported work by Tayyari et al. [33].

<Fig. 2>

The iminoenol form of Bn-EAB has been introduced in the work of Harrad et al. [14]. The proton transfer barrier from AK1 to corresponding IE has been calculated to investigate this further. The relative energy profile for the proton transfer process from the N atom to the O atom (aminoketone form change to iminoenol form) for EAB, calculated at the B3LYP/6-311++G(d,p) level, is shown in Fig. 3a. The activation energy required for the proton transfer process is 15.61 kcal/mol in the gas phase. In Fig. 3b, a similar profile is calculated for Bn-EAB. These two plots demonstrate no transition barrier between the iminoenol and aminoketone forms, indicating that the iminoenol form can not exist. Furthermore, the NMR data in Ref. [14] do not correspond to the iminoenol form.

<Fig. 3>

The most stable conformers of EAB, Me-EAB, Ph-EAB, and Bn-EAB (AK1 and AK2) are shown in Figs. 2 and S2 (see supplementary material). The conformation of OC_2H_5 in Me-EAB, Ph-EAB, and Bn-EAB in the mentioned stable forms is similar to that in the parent molecule (EAB). The selected optimized geometrical parameters for both stable conformers of EAB and their average for Me-EAB, Ph-EAB, and Bn-EAB at B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels are collected in Tables 1 and S1 (see supplementary material). The geometrical parameters of the mentioned molecules are also compared to the reported results for MAB [15]. EAB's chelated ring bond lengths (C2=C3, C2-N, C3-C4, and C4=O7) are similar to MAB's.

As previously reported, the N-Me and N-Ph groups in aminoketone molecules have more steric effect than the H atom [34]. Table 1 shows the calculated N…O distance (B3LYP/6-311++G(d,p)) in EAB, Me-EAB, Ph-EAB, Bn-EAB, and MAB, are 2.725, 2.721, 2.709, 2.722, and 2.728 Å, respectively. In addition, the calculated N-H and O…H distances in EAB, Me-EAB, Ph-EAB, Bn-EAB, and MAB are 1.014, 1.017, 1.022, 1.018, 1.014 Å, and 1.973, 1.912, 1.868, 1.909, 1.978 Å, respectively. The mentioned values indicate that the trend of the IHB strength of the mentioned molecules is:

 $Ph-EAB > Bn-EAB \sim Me-EAB > EAB \sim MAB$ (1)

Also, by comparing the structural parameters of EAB with the other substations, it can be concluded that the replacement of hydrogen atoms by Me, Ph, or Bn groups would reduce the C3-C2-N angle. At the same time, it increases the NHO, C2-C3-C4, and C3-C4-O8 bond angles.

The main effect of the ethoxy group ($-OC_2H_5$) or methoxy group ($-OCH_3$) on the C4 atom is to increase the N···O distance and decrease the N–H bond length, compared to the corresponding values of (Z)-4-aminopent-3-en-2-one (APO) [15]. The N···O distance and N–H bond length of APO at B3LYP/6-311++G(d,p) are 2.666 and 1.885 Å, respectively [15]. Soltani et al. [35] obtained an excellent correlation between the IHB strength and the N–H+H···O distances. The calculated N–H+H···O distances at B3LYP/6-311++G(d,p) in EAB, Me-EAB, Ph-EAB, Bn-EAB, and MAB are 2.988, 2.930, 2.891, 2.927, and 2.992 Å, respectively. These values also confirmed the trend of the IHB strength (1). The higher hydrogen bond strength in Ph-EAB is not related to the resonance of the phenyl with the chelated rings, as the dihedral angle between these two rings is 139.9°. It is due to the steric effect of the phenyl ring.

Table 2 shows some theoretical and experimental parameters related to the hydrogen bond strength (including the optimized geometrical parameters, AIM and NBO, and the results of different spectroscopic properties) for EAB, Me-EAB, Ph-EAB, Bn-EAB, and MAB [15, 36]. Some of these parameters, such as AIM, NBO, and spectroscopic results, are mentioned in the following sections, but since these parameters are related to the strength of the hydrogen bond, we have included them in this section.

In addition to geometric parameters such as the calculated N-H bond length, O···H, N···O, and N-H···O distances, and NHO bond angle in mentioned molecules, higher electron density (ρ_{BCP}) and minimum of Laplacian of the electron density ($\nabla^2 \rho_{BCP}$) of the bond critical points (BCP) at O7···H10 corresponds to a stronger intramolecular hydrogen bond strength too. The E_{HB} values, in the gas phase, according to Espinosa et al. [37], are 8.27, 7.51, 7.41, 6.05, and 6.20 kcal/mol in Ph-EAB, Bn-EAB, Me-EAB, EAB, and MAB, respectively. Also, the LP(2)O7 $\rightarrow \sigma^*$ N-H10 interaction values confirm the trend (1) for IHB strength. In addition, based on spectroscopic results, the order of hydrogen bond strength agrees with the previous theoretical results (geometrical, NBO, and AIM results).

4.2. Second-order perturbation and pairwise steric exchange analyses

Table 3 shows some selected second-order perturbation ($E^{(2)}$) and pairwise steric exchange energies (ΔE (i, j)), related to IHB strength. The interactions such as LP(1)N9 $\rightarrow \pi^*C2-C3$, $\pi C2-C3 \rightarrow \pi^*C4-O7$, and LP(2)O7 $\rightarrow \sigma^*C3-C4$ show that the π -delocalization in the chelated rings of Me-EAB, Ph-EAB, and Bn-EAB is higher than in EAB. Furthermore, the values for the Ph-EAB is larger than those for Me-EAB and Bn-EAB so its IHB strength is the highest. Also, the LP(2)O7 $\rightarrow \sigma^*$ N9-H10 interaction and summation of interactions in this table, which are related to IHB strength, confirmed the trend (1).

Besides the LP(O7) $\leftrightarrow \sigma$ N9-H10 steric exchange interaction energies, ΔE (i,j), for EAB, Me-EAB, Bn-EAB, Ph-EAB and MAB are: 7.62, 9.92, 9.73, 11.89 and 7.59 kcal/mol, respectively. These values again support trend (1) for hydrogen bond strength. In addition, the steric effect of methyl, benzyl and phenyl moieties in that order increase the resonance in the chelate ring and the IHB strength. This agrees with the reported work on the 3-MeAPO (3-methyl-4-amino-3-penten-2-one) and its N-Me and N-Ph substitutions [34].

< Table 3 >

4.3. NMR spectroscopy

The ¹HNMR and ¹³CNMR spectra of EAB and derivatives are shown in Fig. S3 (see supplementary materials). The measured chemical shifts (δ) and isotropic nuclear shielding (δ _{iso}) are listed in Table 4. The chemical changes agree with the previously reported results [38-40].

< Table 4 >

The experimental ¹H and ¹³C chemical shifts (δ_{exp} .) and the GIAO nuclear shielding ($\sigma_{calc.}$) calculated by DFT at the B3LYP/6-311++G(d,p) level is usually linear and described by the following equation: $\delta_{exp}=a(\sigma_{calc.})+b$. The equation for ¹H-NMR EAB is: 1.0165X+0.0328 (X is σ_{calc}) R²=0.9943 and for ¹³C-NMR including all four compounds is: 1.0429 X +1.605(X is σ_{calc}) R² = 0.9982 (see Fig. S4, see supplementary materials). The calculated and experimental δ NH's (in CDCl₃) of all molecules confirm the trend (1) in IHB strength. The broad NH resonances seen in the ¹H spectrum of EAB are due to the intermediate rotation of the NH₂ group because of the relatively weak intramolecular hydrogen bond.

4.4. UV-Vis spectra

In the β -ketoenamine, β -diketone, and β -ketoester compounds, the broad band in the region of about 300 nm can be due to chelated ring and IHB strength, too [34, 41]. The shifting of this band to higher wavelengths (red shifts) shows the increase in IHB strength. The UV spectra of EAB, Me-EAB, Ph-EAB, and Bn-EAB were recorded in ethanol (see Fig. S5, supplementary materials). Broad band at 274, 283, 300, and 277 nm were found for EAB, Me-EAB, Ph-EAB, and Bn-EAB, respectively. This band in the UV spectrum of MAB was reported at 272 nm [42]. The calculated UV wavelengths for EAB, Me-EAB, Ph-EAB, Bn-EAB, and MAB are 250, 264, 293, 265, and 250 nm, respectively, which are assigned to the HOMO \rightarrow LUMO gap. These calculated and experimental values confirmed the trend (1) for IHB strength too. The calculated energy gaps between HOMO and LUMO, ΔE_{H-L} , in titled molecules with their orbital composition distribution were shown in Fig. S6 (see supplementary materials). The calculated ΔE_{H-L} in EAB, Me-EAB, Ph-EAB, and Bn-EAB are 5.34, 5.17, 4.62, and 5.11 eV, respectively.

4.5. Vibrational assignment

The IR spectra of EAB and its deuterated analog, D_3 -EAB, in the CCl₄ solution are compared in Fig. 4a-b. In addition, Fig. 5 shows the Far-IR spectra of EAB and its deuterated analog in CCl₄. The deconvoluted IR spectrum of EAB in the CCl₄ solution and its IR spectrum in neat indicated is shown in Fig. S7 (see supplementary material). Also, the Raman spectrum of EAB in the liquid phase was given in Fig. 6. The computed scaled frequencies of vibrational harmonic bands and their approximate assignment, along with the experimental results of infrared frequencies for the stable aminoketone forms of EAB and its corresponding deuterated forms are presented in Tables 5 and 6, respectively. The assignment was compared to those reported for APO [43] and MAB [15] to support the assignments. The IR spectra of EAB in the liquid phase and MAB in the solid phase in the 3600–500 cm⁻¹ region are compared (see Fig. S8).

The proper scaling factor, 0.9609 for upper 2000 cm⁻¹ and 0.9859 for below 2000 cm⁻¹ regions, are used for theoretical numbers [44]. Most frequencies of AK1 and AK2 conformers of EAB and D₃-EAB analog are near each other. However, Tables 5 and 6 indicate a few wavenumbers which occur in different places for two forms, which confirms the existence of both conformers in the sample.

The IR spectra of Me-EAB and Ph-EAB and their deuterated isotopomers, D₂Me-EAB and D₂Ph-EAB, in the CCl₄ solution are shown in Figs. S9-S10 (see supplementary material). Also, the IR spectrum of Bn-EAB in the CCl₄ solution is shown in Figs. S11 (see supplementary material). Fundamental band assignments for Ph-EAB and Bn-EAB are reported in Tables S2-S3 (see supplementary material). These tables show several bands in different regions confirming the presence of both conformers AK1 and AK2 in these compounds that agree with the reported work by Hansen *et al.* [19].

<Fig. 4> <Fig. 5> <Fig. 6> <Table 5> <Table 6>

The NH and CH stretching

In the aminoketone compounds, the symmetrical and asymmetrical NH stretching vibrations can be perturbed by intermolecular and intramolecular hydrogen bonds [45]. For example, in the CCl₄ solution, the symmetrical and asymmetrical stretching bands (v_s NH and v_a NH) of MAB and APO are reported at 3335, 3184, and 3447, 3375 cm⁻¹, respectively [15, 43]. This perturbation has been affected by the strength of the hydrogen bond.

the IR spectrum of EAB in CCl₄ solution shows two bands at 3449 and 3334 cm⁻¹. Upon deuteration of the NH₂ protons (hydrogen atoms with numbering of 10 and 12). These bands disappear and shift to 2587 and 2441 cm⁻¹ (see Fig. 4 and Tables 5-6). This assigns the bands 3449 and 3334 cm⁻¹ to the v_aNH_2 and v_sNH_2 , respectively. These bands in a neat phase of EAB were observed at 3446 and 3335 cm⁻¹, respectively. This shows that EAB's intramolecular hydrogen bond strength is similar to MAB's. The IR band in the CCl₄ solution at 3512 cm⁻¹ was assigned to NH₂ free, which was observed at 2625 cm⁻¹ in the deuterated molecule. The corresponding Raman bands of v_aNH_2 and v_sNH_2 are observed at 3427 and 3320 cm⁻¹, respectively. The NH stretching of their N-Me, N-Ph, and N-Bn substitutions was observed at 3295, 3254, 3289 cm⁻¹, respectively [19]. The mentioned values agree with trend (1) for IHB strength.

The IR spectrum of EAB in the CCl₄ solution shows a weak band at 3230 cm⁻¹. We believe this band is an overtone of IR at 1616 cm⁻¹. This band was observed in 3-MeAPO at 3200 cm⁻¹ [34].

The fragile intensity IR band of CCl₄ solution at 3088 cm⁻¹, which disappeared upon deuteration of H α , is assigned to the olefinic CH α stretching mode and agrees with the theoretical calculations. The corresponding band in MAB/D₃-MAB [15] occurs at 3080/2297 cm⁻¹. This movement appeared at 2301 cm⁻¹ in deuterated molecules.

The CH bond's stretching of the CH₃ groups generally appears in the 2900-3000 cm⁻¹ region [46, 47]. The IR spectrum of EAB in the CCl₄ solution indicates six bands with relatively medium to weak intensity at 2984, 2955, 2935, 2902, 2872, and 2845 cm⁻¹, which are assigned to the CH stretching modes of the CH₃ and CH₂ groups. The corresponding Raman bands were observed at 2986, 2938, 2911, and 2877 cm⁻¹.

1700-1000 cm⁻¹ region.

Besides the ρ (in-plane rocking) and δ (in-plane bending) modes of NH₂ and CH₃, other bands are expected to be observed in this region related to the vibrations of C-CH₃ and the chelated ring stretching, which arise from the C=C, C-C, C=O, and C-N stretching modes.

The IR spectrum of EAB in the CCl₄ solution shows three intense bands at 1670, 1616, and 1565 cm⁻¹ (see Fig. S7). The corresponding Raman bands of EAB were observed at 1660, 1610, and 1555 cm⁻¹ (see Fig. 6). According to the theoretical results, the band at 1670 cm⁻¹ is assigned to $v_aO=C-C=C$ coupled to δNH_2 and $v_sN-C=C-C$. We assign the IR band at 1616 cm⁻¹ to the δNH_2 coupled to $v_sO=C-C=C$, $v_sN-C=C-C$. For APO and MAB, the corresponding bands in CCl₄ solution occurs at 1630, 1599 cm⁻¹ and 1675, 1614 cm⁻¹, respectively [15, 43]. The mentioned values show that EAB's intramolecular hydrogen bond strength is almost equal to MAB and significantly lower than APO. In N-Me and N-Ph substitutions, the mentioned bands have shown a red shift and appeared at 1650 (1656) and 1615 (1620). These values in parenthesis are due to N-Ph substitution. These bands in N-Bn are 1660 and 1613 cm⁻¹ too. The small difference between the mentioned values of N-Me, N-Ph, and N-Bn substitutions is attributed to different coupling and different of intramolecular hydrogen bond strength.

The band at 1565 cm⁻¹ of EAB, is assigned to the NH₂ bending coupled with $v_sO=C-C=C$. Upon deuteration, this band disappears, and the new band appears at about 1135 cm⁻¹, while the bands at 1670 and 1616 cm⁻¹ shifted to 1663 and 1583 cm⁻¹, respectively.

The medium to weak intensity IR bands at 1480-1363 cm⁻¹ region, that deuteration has not much effect on their wavenumbers, are assigned to δ CH₃ and scissoring and wagging of CH₂, which were coupled to some other motions. According to theoretical results, the medium IR bands at 1305 cm⁻¹ were assigned to ω CH₂ for AK2. This band in N-Me substitution also appeared at 1301 cm⁻¹ for AK2 [19]. The existence of this band approved the presence of AK1 and AK2 in the sample.

The relatively sharp IR band at 1166 cm⁻¹ and its shoulder at 1174 cm⁻¹ are assigned to the δ CH α coupled to v_a C-O-C, ρ NH₂ for both stable conformers. According to calculated results and compared to MAB [15], two weak intensity IR bands at 1117 and 1097 cm⁻¹ are assigned to the rocking of NH₂ and ρ NH₂, coupled with other movements for AK1 and AK2. In addition, according to calculated results, three IR bands at 1095,

1088, and 1065 cm⁻¹ in the deuterated form of EAB are also due to the existence of both stable conformers. At low temperatures, two rotamers were also observed in the comparable compound 2-aminobenzoate [48].

Also, the presence of the bands at 1095, 975, 960, and 982, 977, 935 cm⁻¹ in the IR spectra confirm the existence of both conformers of AK1 and AK2 in Ph-EAB, and Bn-EAB, respectively (see Tables S2-S3, see supplementary materials).

Below 1000 cm⁻¹ region.

Two IR bands at about 977 and 960 cm⁻¹ of EAB and D₃EAB, assigned to v_sC3 -C4-O8, $\rhoC1H_3$ of AK1 and AK2 too. The medium IR band at 786 cm⁻¹ was assigned to out-of-plane bending of CH α , γ CH α . In deuterated form, it appeared at 560 cm⁻¹. In MAB γ CH/ γ CD were reported at 786/560 cm⁻¹ [15]. According to calculated results and compared to MAB [15], the broad IR band at 675 cm⁻¹ is assigned to γ NH₂, that in deuterated form appeared at 450 cm⁻¹. According to theoretical results, the IR bands at 444 and 425 cm⁻¹ are assigned to in-plane bending of the chelated ring Δ , which was coupled with other motions. The IR bands at 330 and 275 cm⁻¹ are assigned to N...O stretching and γ NH, respectively. The different values of N...O stretching in MAB and EAB are due to different coupling.

5. Conclusion

Ethyl 3-amino-2-butenoates were synthesized and characterized by FT-IR, UV, ¹H, and ¹³C NMR. The theoretical and experimental results showed that the keto-enamine tautomers are the most stable. Among all of the keto-enamine tautomers with NH...O hydrogen bonds, two conformers (AK1 and AK2) are present. Also, the existence of these conformers of EAB, Ph-EAB, and Bn-EAB are confirmed by vibrational spectroscopy. An excellent agreement was achieved between experimental results (δ NH, ν NH, γ NH, UV) and theoretical results (geometrical parameters, AIM, NBO, vibrational) with the E_{HB}. All theoretical and experimental results show that the following trend in IHB strength is obtained:

 $Ph-EAB > Bn-EAB \sim Me-EAB > EAB \sim MAB$

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Supplementary Information

Additional supporting information can be found in Tables S1-3 and Figures S1-11 in supplementary materials

Author contributions

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Declarations

Consent to participate

All authors agreed to participate in this research.

Competing interests

The authors declare that they have no conflict of interest.

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		EA	AB		Me-E	Me-EAB		AB	Bn-E	AB	MAB ^a	
-	B3LYP MP2			B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3I VP	MP2	
-	AK1 AK2 Avg. Avg.		Avg.	Avg. Avg. Avg. Avg.		Avg.	Avg. Avg.		DJLII	1011 2		
Bond length (Å)												
C1-C2	1.505	1.510	1.508	1.504	1.505	1.505	1.506	1.506	1.505	1.504	1.505	1.504
C2=C3	1.369	1.371	1.370	1.367	1.376	1.375	1.374	1.374	1.375	1.372	1.369	1.367
C2-N	1.354	1.352	1.353	1.366	1.353	1.361	1.364	1.365	1.357	1.370	1.355	1.366
C3-C4	1.446	1.444	1.445	1.453	1.439	1.448	1.443	1.448	1.440	1.451	1.444	1.452
C4=O7	1.229	1.230	1.230	1.229	1.232	1.232	1.231	1.233	1.232	1.232	1.228	1.228

Table 1. Some selected parameters of EAB, Me-EAB, Ph-EAB, Bn-EAB, and MAB calculated at B3LYP and MP2 levels with 6-311++G(d,p) basis set.

C4-O8	1.359	1.361	1.360	1.358	1.361	1.360	1.357	1.358	1.360	1.357	1.360	1.358
O8-C5	1.443	1.444	1.444	1.440	1.443	1.439	1.444	1.441	1.443	1.441	1.434	1.433
C5-C6	1.516	1.521	1.518	1.517	1.519	1.517	1.519	1.517	1.519	1.517		
N-H10	1.014	1.015	1.015	1.015	1.017	1.018	1.022	1.022	1.018	1.019	1.014	1.015
N-H12(or C)	1.005	1.004	1.005	1.008	1.450	1.452	1.411	1.413	1.451	1.456	1.005	1.008
N····O7	2.722	2.717	2.720	2.741	2.720	2.730	2.710	2.697	2.722	2.737	2.728	2.742
H10… O7	1.971	1.962	1.967	1.985	1.912	1.917	1.869	1.878	1.909	1.908	1.978	1.987
<u>Bond angles (°)</u>												
C1C2C3	121.1	120.5	120.8	121.2	120.2	120.2	119.3	120.1	120.0	120.7	12 1.1	121.2
C1C2N	115.7	116.5	116.1	115.2	117.4	116.9	119.7	118.3	117.8	116.7	115.8	115.2
C2C3C4	122.3	122.4	122.4	122.2	122.7	122.4	123.4	122.4	122.9	122.5	122.4	122.2
C3C4O7	126.1	125.9	126.0	126.2	126.0	126.2	125.9	126.0	126.1	126.3	126.3	126.4
C3C2N	123.1	123.2	123.2	123.5	122.5	122.8	120.9	121.5	122.2	122.6		
C3C4O8	112.3	112.1	112.2	111.5	112.3	111.7	112.2	111.9	112.3	111.6	112.2	111.6
C4O8C5	116.5	117.3	116.9	115.2	116.9	115.2	117.4	115.3	117.0	115.3	116.0	114.4
HNH (or C)	120.8	121.0	120.9	118.0	119.6	118.0	116.8	119.2	119.3	116.1	120.5	117.9
C2C3H11	119.5	119.4	119.5	119.6	119.4	119.5	119.1	119.4	119.3	119.6	119.6	119.6
NHO	128.7	128.9	128.8	129.1	134.1	134.7	137.3	134.9	134.6	136.3	128.6	129.0

^a Data source: Ref. [15].

			5	
EAB	Me-EAB	Ph-EAB	Bn-EAB	MAB ^e
1.014	1.017	1.022	1.018	1.014
2.988	2.930	2.891	2.927	2.992
1.973	1.912	1.868	1.909	1.978
2.725	2.721	2.709	2.722	2.728
128.7	134.1	137.3	134.6	128.6
_				
0.0258	0.0299	0.0331	0.0303	0.0262^{f}
-0.0240	-0.0272	-0.0292	-0.0275	-0.0245 ^f
6.05	7.41	8.27	7.51	6.20 ^f
5.21	6.77	8.65	7.18	5.11 ^f
_				
8.12 (7.90)	8.62 (8.46)	10.88 (10.39)	9.53 (8.95)	8.44 ^f (7.83 ^g)
3703 (3334)	3469 (3294)	3388 (3255)	3463 (3290)	3506(3335)
250 (274)	262 (283)	293 (300)	265 (277)	250 ^f (272)
	EAB 1.014 2.988 1.973 2.725 128.7 0.0258 -0.0240 6.05 5.21 8.12 (7.90) 3703 (3334) 250 (274)	EAB Me-EAB 1.014 1.017 2.988 2.930 1.973 1.912 2.725 2.721 128.7 134.1 0.0258 0.0299 -0.0240 -0.0272 6.05 7.41 5.21 6.77 8.12 (7.90) 8.62 (8.46) 3703 (3334) 3469 (3294) 250 (274) 262 (283)	EAB Me-EAB Ph-EAB 1.014 1.017 1.022 2.988 2.930 2.891 1.973 1.912 1.868 2.725 2.721 2.709 128.7 134.1 137.3 0.0258 0.0299 0.0331 -0.0240 -0.0272 -0.0292 6.05 7.41 8.27 5.21 6.77 8.65 8.12 (7.90) 8.62 (8.46) 10.88 (10.39) 3703 (3334) 3469 (3294) 3388 (3255) 250 (274) 262 (283) 293 (300)	EABMe-EABPh-EABBn-EAB 1.014 1.017 1.022 1.018 2.988 2.930 2.891 2.927 1.973 1.912 1.868 1.909 2.725 2.721 2.709 2.722 128.7 134.1 137.3 134.6 0.0258 0.0299 0.0331 0.0303 -0.0240 -0.0272 -0.0292 -0.0275 6.05 7.41 8.27 7.51 5.21 6.77 8.65 7.18 8.12 (7.90) 8.62 (8.46) 10.88 (10.39) 9.53 (8.95) 3703 (3334) 3469 (3294) 3388 (3255) 3463 (3290) 250 (274) 262 (283) 293 (300) 265 (277)

Table 2. Comparing several properties related to the hydrogen bond strength for EAB, Me-EAB, Ph-EAB, Bn-EAB, and MAB calculated at B3LYP/6-311++G(d,p) level of theory.^a

^a All theoretical values are given the averages AK1-2 for EAB, Me-EAB, Ph-EAB, and Bn-EAB.

^b R is bond length in Å, θ is bond angle in degree.

^c The units of AIM results are: ρ_{BCP} (e au⁻³), $\nabla^2 \rho_{BCP}$ (e au⁻⁵), and H-bond energy E_{HB}; hydrogen bond energies (E_{HB}/kcal mol⁻¹=1/2*V*) [39] (kcalmol⁻¹).

 d^{d} v is stretching modes frequencies, in cm⁻¹. δ , proton chemical shift in ppm, and UV bands in nm. (Experimental values are given in parenthesis).

^e Data from Ref. [15].

^f Calculated this work.

^g Data from Ref. [44].

Table 3. Selected second order perturbation energies, $E^{(2)}$, in kcal/mol, of EAB, Me-EAB, Ph-EAB, Bn-EAB, and MAB.

Donor	Туре	Acceptor	Type	EAB	Me-EAB	Ph-EAB	Bn-EAB	MAB
Ν	LP(1)	C2-C3	π*	45.64	84.38	85.94	57.89	56.40
07	LP(2)	N-H10	σ^*	4.91	6.77	8.73	7.25	5.11
07	LP(2)	C3-C4	σ*	13.95	16.21	16.71	12.76	13.52
07	LP(1)	C4	RY*(1)	14.84	11.59	18.79	14.39	15.25
07	CR(1)	C4	RY*(1)	6.19	6.56	6.53	6.17	6.29
C2-C3	π	O7-C4	π^*	27.63	48.76	50.67	4.72	29.02

	EAB		Me-EAB		Ph-EAB		Bn-EAB		
Carbon-13	$\delta_{exp}(\delta_{cal})$	σiso	δexp(δcal)	σiso	δ _{exp} (δ _{cal})	σiso	δexp(δcal)	σiso	
Cl	22.42 (22.41)	160.11	19.28 (21.86)	162.66	20.36 (23.88)	160.64	19.44 (21.64)	30.98	
C2	159.77 (170.56)	13.96	162.91 (172.66)	11.86	158.96 (169.02)	15.50	161.89 (170.32)	179.55	
C3	84.24 (92.23)	92.29	81.99 (87.85)	96.67	86.13 (91.37)	93.15	83.25 (86.06)	57.32	
C4	170.36 (178.82)	5.70	170.79 (178.91)	5.61	170.44 (179.38)	5.14	170.66 (175.65)	99.94	
C5	58.61 (64.13)	120.39	58.38 (63.72)	120.80	58.80 (64.33)	120.19	58.46 (63.87)	60.85	
C6	14.68 (16.78)	167.74	14.76 (16.98)	167.54	14.66 (16.91)	167.61	14.71 (16.73)	25.67	
C12			29.67 (31.42)	153.10	139.42 (149.20)	35.32	46.85 (50.63)	38.06	
C13					124.95 (133.17 ^d)	51.35 ^d	138.82 (150.12)	190.13	
C14					129.10 (137.11 ^d)	47.42 ^d	126.77 (132.28 ^e)	179.36 ^e	
C15					124.45 (135.11)	49.41	126.77 (132.28°)	179.36 ^e	
C16					129.10 (137.11 ^d)	47.42 ^d	138.82 (135.74°)	186.25 ^e	
C17					124.95 (133.17 ^d)	51.35 ^d	138.82 (135.74 ^e)	186.25 ^e	
C18							127.40 (133.39)	183.89	
<u>Proton</u>									
H1(CH ₃ -C-N) ^b	1.88 (1.98)	30.00	1.90 (1.98)	29.99	1.99 (1.99)	29.98	1.90 (1.83)	6.77	
H3(C-CH-C) ^b	4.50 (4.95)	27.02	4.45 (4.78)	27.19	4.69 (5.04)	26.93	4.53 (4.79)	7.73	
H5(O-CH ₂ -C) ^b	4.08 (4.13)	27.84	4.07 (4.11)	27.86	4.15 (4.20)	27.77	4.09 (4.18)	5.75	
$H6(CH_3-C-O)^b$	1.23 (1.30)	30.67	1.23 (1.24)	30.72	1.28 (1.33)	30.42	1.25 (1.28)	8.21	
H10	7.90 (8.14)	23.83	8.46 (8.62)	23.35	10.39 (10.88)	21.09	8.95 (9.53)	16.46	
H12	4.4-4.9 (4.16)	27.81	2.89 (2.93)	29.04			4.42 (4.55)	6.35	
O-H ^c					7.08 (7.52)	24.46	7.26 (7.55)	8.60	
m-H ^c					7.31 (7.75)	24.23	7.33 (7.63)	5.47	
p-H°					7.14 (7.56)	24.41	7.26 (7.53)	4.59	

Table 4. Experimental, calculated, and estimated ¹³C and ¹H chemical shifts (δ) and isotropic nuclear shildings (σ_{iso}) for stable forms of EAB, Me-EAB, Ph-EAB, Bn-EAB.^a

^a δ_{exp} , experimental chemical shifts in CDCl₃, δ_{cal} , calculated chemical shifts by $\delta = \sigma_0 - \sigma$ equation. All chemical shifts in Chloroform are relative to TMS, which its ¹³C and proton magnetic shielding are 184.52 and 31.97 ppm, respectively. δ_{est} , estimated chemical shifts are obtained by using of the δ_{exp} vs. calculated nuclear shielding plot of EAB.

^b The numbering of hydrogen atoms on methyl groups are as same as the corresponding carbon atoms.

^c The ortho, meta, and para hydrogen atoms of Ph ring.

^d Averaged values for 13, 17 and 14, 15 atoms of Ph-EAB.

^e Averaged values for 14, 15 and 16, 17 atoms of Bn-EAB.

	EAB	Me-EAB	Ph-EAB	Bn-EAB	MAB
$E_{\rm HOMO}~({\rm eV})$	-6.300	-5.966	-5.989	-5.834	-6.074
$E_{\mathrm{HOMO-1}}~(\mathrm{eV})$	-7.762	-7.662	-7.289	-7.034	-7.424
$E_{\text{LUMO}} (eV)$	-0.944	-0.830	-1.227	-0.727	-0.730
$E_{\text{LUMO+1}} (eV)$	-0.250	-0.247	-0.751	-0.672	-0.432
<i>Е</i> номо-цимо gap (eV)	-5.356	-5.136	-4.762	-5.107	-5.344
chemical potential (μ)	3.622	3.398	3.608	3.281	3.402
Global hardness (η)	2.678	2.568	2.381	2.554	2.672
Global softness (S)	0.373	0.389	0.420	0.392	0.374
Elecronegativity (χ)	-3.622	-3.398	-3.608	-3.281	-3.402
Electrophilisity indices (ω)	2.449	2.248	2.734	2.107	2.166

Table 5. Calculated energy values of EAB, Me-EAB, Ph-EAB, Bn-EAB, and MAB at B3LYP/6-311++G(d,p) level of theory.

			The	oretical			Experimental			
Ν	1	AK1			AK2	2				
0	Fr	т	٨	Fr	т	٨		IR(nea	R(neat)	Assignment
	eq	1] D	A	eq	1] D	A		t)		
	•	R	R	•	R	R	14)			
							3512(1			vNHafree
							8)			vivii2nee
1	37	8	8	37	8	8	3449(6	3446(3427(4	v-NH2
1	03	6	3	03	6	2	,br)	25))	Var VII2
_	35	_	1	35	_	1	3334(1	3335(3320(1	
2	04	7	0	04	7	0	4)	25)	0)	$v_{s}NH_{2}$
		0	9		0	9	.,			
							3230(3233(0+1/1/
	22		(22		(w,br)	4,br)		2*1616
3	32	2	6 1	32	2	6	3088(v	3084(CIL
	21	2	1	22	2	2	W)	vw)	2007(1	νCHα
4	31 24	1 1	4	31 24	1	4	2984(1	2982(2986(1	$\nu_a C1H_3$
	54 21	1	2	54 21	1	ð	4) 2055(2	19)	4)	
5	31 10	4	2	25	2	8	2933(3	2933(v_aCH_2 , v_aC6H_3
	10 20	2	2	23	9	Q)	2) 2028(2028/2	
6	00	5 1	9 1	04	2	0 5	2935(4	2930(2938(2	$\nu_{a}CH_{2}, \nu_{a}C6H_{3}$
	77	1	4	04	2	1)	4)	2)	
7				30	3	0			2950	v C6H2 v CH2
'				93	0	7	2935	2938		vactilis, vactil
	30		8		U	/	2902(4	2902(2911(1	
	50 77	6	8)	6)	$\frac{2}{1} sh$	v_aC6H_3 , v_aCH_2
		U	1			1)	0)	2911	
8	30	1	0	30	1	0			2,11	$v_{2}C1H_{3}$
	73	2	8	74	3	7	2902	2902		· u = ===5
			-		-	1			2911	
				30	3	5				v _s CH ₂
				65	3	1	2902	2902		
	20		1						2877(s	
9	30 44	2	3				2872(2	2873(h)	vsCH2
	44	0	6)	2)	,	
1	20		1	20		1		ŕ	2877	
1	20 22	2	8	20 21	2	9				$\nu_s C6H_3$
0	55	3	8	51	3	9	2872	2873		
1	30		2	30		2				
1 1	25	2	7	25	2	7	2845(v	2845($\nu_s C1H_3$
1	23	8	4	23	9	3	w)	1)		
1	17	2		17	2	1	1670(7		1660	$v_0 O = C - C = C \delta NH_2 v_0 N -$
2	00	3	1	00	1	0	2)	1665((9)	C=C-C
-	00	9	0	00	9	0	2)	67)		
							1632(3			Combination
							6,sh)			

Table 6. Experimental (FT-IR wavenumbers (in cm^{-1})) and theoretical (scaled wavenumbers (in cm^{-1})) of EAB at B3LYP/6-311++G(d,p) level of theory. ^a

1 3	16 59	4 3 1	5 2	16 58	4 4 0	5 4	1616(5 3)	1623(81)	1610(1 0)	δNH ₂ , ν _s O=C-C=C, ν _s N- C=C-C
1 4	15 92	2 4 7	9 7	15 91	2 4 5	9 6	1565(4 9)	1566(38)	1555(9 9)	δNH_2 , $\nu_s O=C-C=C$
1 5	15 21	4	3	15 06	1 2	3	1480(4 ,sh)	1482(s h)		SciCH ₂ , δ_aC6H_3
1 6	14 98	4	1 1				1466(3 ,sh)	1465(s h)	1453(4)	$\delta_a C6H_3$, SciCH ₂
				14 93	3 2	3 0	1466	1465	1453	sciCH ₂ , δ_a C6H ₃ , δ_a C1H ₃
1 7	14 89	4 8	1 9				1445(1 1)	1447(8)	1440(4)	$\delta_a C1H_3, \delta NH_2$
				14 88	6	1 5	1445	1447	1440	$\delta_a C6H_3, \delta_a C1H_3, SciCH_2$
1 8	14 86	7	1 0				1445	1447	1440	$\delta_a C 6 H_3$
				14 86	2 8	7	1445	1447	1440	$\delta_aC6H_3, \delta_aC1H_3, SciCH_2$
1 9	14 83	1 0	8	14 82	9	8	1425(4 ,sh)	1422(s h)		$\delta_a C1H_3$
2 0	14 46	4	3	14 45	2	6	1425	1422		ν _a CH ₃ -C-N, δ _s C1H ₃ , δCHα, ωCH ₂
2 1	14 23	2	2	14 18	1 0	2	1390(4 ,sh)	1389(s h)		$\delta_sC6H_3,\omega CH_2,\delta_sC1H_3$
2 2	14 11	1 0	1 0	14 08	7	7	1377(1 0)	1377(12)	1380(6)	$\delta_s C1H_3, \delta_s C6H_3, \delta CH\alpha$
23	13 93	3	4	13 96	9	7	1363(1 0)	1360(17)	1355(7)	ωCH_2 , $\delta_s C6H_3$
2 4		4		13 34	3	7	1305(3 3)		10(0)	$\omega CH_2, \delta_s C6H_3$
2 5	13 14	4 3 3	1 2	13 14	3 4 7	1 0	1272(2 8)	1280(79)	1269(2 0)	v _a C3-C4-O8, ρNH ₂ , δCHα, vC2-C1, ωCH ₂
	12 94	1	1 0				,	,	1235(1 2)	$\tau CH_2, \delta_s C6H_3$
2 6		1		11 95	3 5 3	5	1174 (sh)	1173 (sh)		δCHα, v_a C-O-C, ρ NH ₂
	11 86	4 8 8	5				1166(1 00)	1165(100)		$\delta CH\alpha$, $\nu_a C$ -O-C, ρNH_2
2 7	11 76	3	1	11 81	9 4	2	1166	1165		ρCH ₂ , ρC6H ₃
2 8	11 35	4	1 6							πС6Н ₃ , δО8-С5-С6
				11 31	8 1	1 4	1117(1 1)	1114(8)	1110(1 0)	ρNH ₂ , ρC1H ₃ , νC5-O8

2 9	11 32	6 2	8				1117		1110	ρNH_2 , $\nu_a C=C-C-O$
-	02	-	0	11 13	1 7	2	1097(8	1095(17)	1090(3)	ρNH ₂ , νC5-C6, ρC6H ₃
3 0	10 61	1 3	1	10 61	2	1	1047(2 4)			$\pi C1H_3$
3 1	10 60	5 1	7	10 53	5 0	9	1047	1046	1040(5)	v_aC3 -C4-O8-C5, ρNH_2
3 2	10 30	1 7	2	10 26	2 2	2	1015(6	1014(11)		ρC1H ₃ ,v _a O8-C5-C6
3 3	99 3	1 9	3				978(3)	977(8)	983(12)	ν _s C3-C4-O8, νC5-C6, ρC1H ₃
				97 3	1 5	5	960(5)	960(9)	952(10)	ν _s C3-C4-O8, νC5-C6, ρC1H ₃
3 4	92 8	4	8	92 5	4	9	915(3)	916(8)	920(5)	ρNH ₂ , δC4C3C2, ρC6H ₃
3 5	87 2	4	5	86 3	3	5	856(4)	855(9)	860(12	0NH2 0C6H2 v.C4-O8-C5
3	81		1	81	2	1	s.o.	000()))	ρC6H ₃ , ρCH ₂
6 3 7	5 80 0	4 4 0	1	8 80 5	2 4 2	1	S.O.	786(3 6)	790(28)	γCHα, γC3C4O7, ρC6H ₃ , ρCH ₂
3 8	76 9	3	4				s.o.	752(8)		CO ₂ sci, pNH ₂ , vC2-CH ₃
3 9	76 8	1	0	77 2	1	0	s.o.	752		$\gamma NH_2, \gamma CH\alpha$
				72 8	7	9	s.o.	720(4)	725(1)	CO ₂ sci, pCH ₂
4 0	68 2	2	1	68 5	28	1	655(6) *	675(br	670(1)	γNH ₂ , Γ
4 1	57 1	1 9	2	57 2	2 0	2	565(20	567(1 4)	556(1)	γC2-C1H ₃
-	_	-	_		-		515(5, br)	508(1 4)	520(5)	Intermolecular, yNH12
4 2	50 3	0	5	51 6	1	5				δN-C-CH ₃
4 3				44 1	4	2	444(6)		450(4)	Δ , δ O-CH ₂ -CH ₃
	42 5	5	1				425(sh	430(5)	415(5)	Δ , δ O-CH ₂ -CH ₃
4 4	39 4	1 3	1	39 7	1 0	1	394(10	395(8)	380(11	νN…O, δC2-C1H ₃
4 5	32 6	2	5				,		330(4)	δC4-O8-C5, δC-C1H ₃
				34 8	1 7	0	330(7)	330(sh)		Δ, δC4-O8-C5, τC6H ₃
4 6				33 2	5	3	330(9)	330(sh		νN…O, δC2-C1H ₃
5	27 0	3 3	1	-	2	5	275(5)	, 26	275(4)	γNH ₁₂ ,τC6H3
								20		

4 7	26 5	5	1					νN…O, τC6H ₃
4	24	7	1	25	9			
8	7	1	4	0	7	4	275	$\gamma NH_{12}, \tau C6H_3$
				23 8	2	0		τC6H ₃
4 9	17 7	4 2	2					$\gamma NH_{12}, \Gamma, \tau C6H_3$
				17 1	6	0		τO-C ₂ H ₅
5 0	12 7	3	0					δC -O-C ₂ H ₅
				16 2	4 6	1		γNH12
5 1	12 1	1 6	1					Γ, τC1H ₃
				11 8	1 0	1		Γ, γC4O8
5	11			11				$\tau C1H_{2}$
2	5	1	0	2	0	0		
5 3	85	1 2	0	65	0	1		τO - C_2H_5
5 4	48	1	1	63	9	1		$\gamma O-C_2H_5$

^a Freq, vibrational wavenumber; I_{IR}, IR intensities in kM/mol; A_R, Raman scattering activities in A**4/AM; experimental relative intensities are given in parenthesis; br, broad; sh, shoulder; w, weak; v, very; s, symmetric; a, asymmetric v, stretching; δ , in-plane bending; γ , out-of-plane bending; ρ , rocking inplane; π , rocking out-of-plane; ω , wagging; Δ , in-plane chelated ring deformation; τ , torsion; sci, scissoring; Γ , out-of-plane ring deformation; s.o., solvent overlapped;*, below 600 cm⁻¹ obtained with different instrument.

					· • ·		•	
N			The	oretical			Experim ental	
IN	AK1				AK2			
0.	Fre		А	Fre		А	$\mathbf{IR}(\mathbf{CCL})$	Assignment
	q.	I_{IR}	R	q.	I_{IR}	R	IK(CCI4)	
1	313 4	11	50	313 4	11	51	2980(50)	$\nu_a C1H_3$
2	311 0	42	22	312 5	29	8	2957(23)	$\nu_a CH_2, \nu_a C6H_3$
3	309 9	31	94	310 4	12	85	2932(21)	v_aC6H_3 , v_aCH_2

Table 7. Experimental (FT-IR wavenumbers (in cm⁻¹)) and theoretical (scaled wavenumbers (in cm⁻¹)) of D3EAB at B3LYP/6-311++G(d,p) level of theory. ^a

4	307 7	6	88	309 3	30	10 7	2932	$\nu_a CH_2, \nu_a C6H_3$
5	307 3	12	10 8	307 4	13	10 7	2904(15)	v_aC1H_3
6	304 4	20	13 5	306	33	15 0	2872(8)	$\nu_s CH_2$
7	303 3	23	18 8	303 1	23	20 0	2801(4)	$\nu_s C6H_3$
8	302 5	29	27 7	302 5	29	27 5	2729(2)	$\nu_s C1H_3$
	U U		,	C C		C	2625(22)	vND ₂ free
9	273 7	64	32	273 7	64	32	2587(15)	$\nu_a ND_2$
10	253 8	49	58	253 9	48	58	2441(25)	$\nu_s ND_2$
11	238 0	1	23	238 0	1	24	2301(5)	νCDα
12	169 1	29 2	14	169 1	26 9	13	1663(44)	v _a O=C-C=C, v _a N-C-C- C
13	161 0	48 6	13 0	161 0	49 6	13 0	1583(45)	v _s O=C-C=C, v _s N-C-C- C
14	152 1	7	3				1480 (13)	SciCH ₂ , δ_aC6H_3
				150 6	16	3	1468(9,s h)	$\delta_a C6H_3$, SciCH ₂
15	149 9	4	11	149 2	28	34	1444(17)	$\delta_a C6H_3$, SciCH ₂
16	148 6	7	10	148 7	12	23	1432(18)	$\delta_a C 6 H_3$
17	148 5	51	47	148 4	36	27	1432	$\delta_a C1H_3$
18	148 2	9	8	148 2	10	8	1432	$\delta_a C1H_3$
19	145 2	63	5	145 0	55	3	1390(14)	νaCH3-C-N, δsC1H3, SciCH2
20	142 4	3	2	141 8	12	3	1375	$\delta_s C6H_3$, SciCH ₂
21	140 9	1	4	140 7	3	3	1375	$\delta_s C1H_3, \delta_s C6H_3$
22	139 4	5	1	139 7	11	2	1365(9)	$\omega CH_2, \delta_s C6H_3$
23	129 4	1	10				1295(7, sh)	τCH_2
				133 5	26	7	1274(90)	τCH_2
24	127 8	75 8	9	127 5	63 3	7	1256(90)	ν _a C3-C4-O8, ν _a CH ₃ -C- N, ωCH ₂
25	117 6	3	1				1161(64, sh)	ρC6H ₃ , ρCH ₂

				119 4	26	2	1175(45)	ρC6H ₃ , ρCH ₂
26	116 7	26	7	116 6	28	6	1135(10)	$\delta ND_2, \delta C = C - CH_3$
27	113 4	5	10					рС6H ₃ ,v _s C6-C5-O8
				111 6	11 9	3	1095(11)	ρC6H ₃ ,v _a C4-O8-C5
28	110 5	27 1	0				1088(13)	ν _a C5-O8-C4, ρC1H ₃ , ρND ₂
				109 5	15 1	2	1065(31)	ν _a C5-O8-C4, ρC1H ₃ , ρND ₂
29	105 9	1	1	105 9	2	1		ρC1H ₃
30	103 8	18	18	102 9	21	5	1023(6)	$v_aC6-C5-O8, \rho C1H_3$
31	992	25	4				975(6)	vsC3-C4-O8, vC5-C6, ρC1H3, δCDα
				976	26	5	965(5)	$v_{s}C3-C4-O8, vC5-C6,$
32	952	7	11	950	3	13	942(4)	δND12, δC2C3C4
33	885	0	6	883	1	3		$\delta CD\alpha$, ρND_2 , $\rho C6H_3$
34	877	3	4	867	2	6	865(20)	ρND ₂ , v _s C4-O8-C5, ρC6H ₃
35	822	0	3	823	0	3		ρND ₂ , δCDα, νC2-
36	815	1	1	812	2	1		ρC6H ₃ , ρCH ₂
37	791	23	0	794	23	0	670(5)	γC3C4O7, ρCH ₂ ,
51	171	25	Ū	151	25	Ū		$\rho C6H_3$
38	748	3	5					CO_2 sci, ρND_2 , $vC2$ - CH ₃
				713	7	9	630(1)	$CO_2sci, \rho CH_2$
39	589	2	3	592	2	4	587(1)	γC2-C1H ₃ , γCDα
40	571	4	1	574	4	0	560(2)	$\gamma CD\alpha, \gamma ND_2$
							536(2)	$270 \times 2 = 540 \text{ cm}^{-1}$
41				494	5	4	475(sh)	δN-C-CH ₃ , δC4-O8- C5
	480	17	2					γND10
42	468	11	3	478	21	0	450(5)	$\gamma ND_2, \gamma CD\alpha$
43				423	6	3	420(1)	Δ , δ O-CH ₂ -CH ₃
	408	4	2				410(1)	Δ , δ O-CH ₂ -CH ₃
44	390	13	1	392	11	1	390(br)	νN····O, δC-C1H ₃
45	322	2	4					δC4-O8-C5, δC-C1H ₃
				341	11	1		δC-C1H ₃ , τC6H ₃ , δC4-
				571	11	1		O8-C5
46	266	4	0			_		τC6H ₃
. –			_	320	6	2		vN····O
47	255	6	1		-	c		vN…O, δC-C6H ₃
				236	2	0		τC6H ₃

48	222	29	2	218	32	2	Γ
49	151	31	1				γND ₂ , δΟ-C2H ₅
				167	2	0	$\nu N \cdots O, \tau O - C_2 H_5$
50	125	3	0				νN…O, δC-C6H ₃
				137	40	1	$\Gamma, \gamma ND_2$
51	118	23	1	117	16	2	Γ
52	114	0	0	111	0	0	$\tau C1H_3$
53	83	14	0	64	1	1	$\tau O-C_2H_5$
54	47	1	1	62	9	1	$\gamma O-C_2H_5$
aC	C (4	CT 1	1 (

^a See footnote of Table 6.

Caption of the Figures:

Figure 1: The Tautomeric forms of β -Enaminones.

Figure 2: The optimized structures (the more stable aminoketone forms) of EAB at B3LYP/6-311++G(d,p) level, with the atom numbering.

Figure 3: Relative energy profile during the proton transfer process; a) EAB b) Bn-EAB (convert AK to IE).

Figure 4: The IR spectra of EAB (——) and its deuterated analogue (……) in CCl₄ solution: a) in the 1700–900 cm⁻¹ range. b) in the 3600–2300 cm⁻¹ range.

Figure 5: The IR spectra of EAB (——) and its deuterated analogue (……) in CCl₄ solution in the 700–250 cm⁻¹range.

Figure 6: The recorded Raman spectrum of EAB in liquid phase in the 1700–200 cm⁻¹ range.

Н Ĥ Η̈́

Iminoenol (IE)

EAB: R=H Me-EAB: R=Me Ph-EAB: R=Ph Be-EAB: R=CH₂-Ph

Figure 1.

Aminoketone (AK) (chelated)

Iminoketone (IK)







Figure 3.



Figure 4.



Figure 5.



Figure

Supplementary material:

Table S1. Some selected parameters for both stable conformers of Me-EAB, Ph-EAB, and Bn-EAB calculated at B3LYP and MP2 levels with a 6-311++G(d,p) basis set.

Table S2. Values of the Fukui function considering natural charges according with Eqs. (1)–(3) for EAB, Me-EAB, Ph-EAB, and Bn-EAB obtained by B3LYP level with the 6-311++G(d,p) basis set.

Table S3. Experimental (FT-IR wavenumbers (in cm⁻¹)) and theoretical (scaled wavenumbers (in cm⁻¹)) of Ph-EAB at B3LYP/6-311++G(d,p) level of theory.^a

Table S4. Experimental (FT-IR wavenumbers (in cm⁻¹)) and theoretical (scaled wavenumbers (in cm⁻¹)) of Bn-EAB at B3LYP/6-311++G(d,p) level of theory.^a

Fig. S1. The possible stable forms in aminoketone tautomer of EAB (The relative energies in kcal mol⁻¹, which were calculated at B3LYP/6-311++G(d,p)). The values in parentheses were calculated at MP2/6-311++G(d,p).

Fig. S2. The most stable conformers of Me-EAB, Ph-EAB, and Bn-EAB.

Fig. S3. NMR spectra of EAB, Me-EAB, Me-EAB, Ph-EAB, and Bn-EAB in CDCl₃.

Fig. S4. Plot of ¹³C chemical shifts vs. ¹³C nuclear shielding.

Fig. S5. UV absorption spectra of EAB, Me-EAB, Ph-EAB, and Bn-EAB in ethanol solvent at a concentration of 2×10^{-3} M with a 10 mm quartz cell.

Fig. S6. The calculated HOMO-LUMO energy gaps for the EAB, Me- EAB, Ph-EAB, and Bn-EAB.

Fig. S7. MEP (left) and the point charges, electric potential values (right) on atoms of EAB, Me-EAB, Ph-EAB, and Bn-EAB.

Fig. S8. The deconvoluted IR spectra of EAB in the CCl₄ solution: a) in the 1700–900 cm⁻¹ range. b) in the 3600–2800 cm⁻¹ range.

Fig. S9. The recorded infrared spectra of EAB in the liquid phase (———) as well as MAB in the solid phase (………) (in the 3600–500 cm⁻¹ range).

Fig. S10. The recorded infrared spectra of Me-EAB (_____) and its deuterated analog (.....) in CCl₄ solution: a) in the 1700–900 cm⁻¹ range. b) in the 3400–2200 cm⁻¹ range.

Fig. S11. The recorded infrared spectra of Ph-EAB (_____) and its deuterated analog (.....) in CCl₄ solution: a) in the 1700–900 cm⁻¹ range. b) in the 3400–2200 cm⁻¹ range.

Fig. S12. The recorded infrared spectra of Bn-EAB in CCl₄ solution (———) (in the 3500–800 cm⁻¹ range).

Table S1.

		Me-	EAB			Ph-	EAB		Bn-EAB			
	B3	LYP	M	P2	B3L	YP	M	P2	B3I	LYP	М	IP2
	AK1	AK2	AK1	AK2	AK1	AK2	AK1	AK2	AK1	AK2	AK1	AK2
Bond length (Å)												
C1-C2	1.505	1.505	1.505	1.505	1.506	1.506	1.506	1.506	1.505	1.505	1.504	1.504
C2=C3	1.376	1.376	1.375	1.375	1.374	1.374	1.374	1.375	1.375	1.375	1.371	1.372
C2-N	1.353	1.353	1.362	1.361	1.364	1.364	1.365	1.365	1.357	1.357	1.370	1.370
C3-C4	1.439	1.439	1.448	1.447	1.443	1.443	1.448	1.448	1.441	1.440	1.451	1.451
C4=O7	1.232	1.232	1.231	1.232	1.231	1.231	1.232	1.233	1.232	1.232	1.232	1.232
C4-O8	1.360	1.362	1.359	1.360	1.357	1.357	1.357	1.358	1.359	1.361	1.357	1.358
O8-C5	1.442	1.444	1.439	1.440	1.444	1.444	1.440	1.441	1.443	1.444	1.440	1.442
C5-C6	1.516	1.521	1.515	1.519	1.516	1.521	1.514	1.519	1.516	1.521	1.514	1.519
N-H10	1.017	1.017	1.018	1.018	1.022	1.022	1.022	1.021	1.018	1.018	1.019	1.019
N…O7	2.721	2.720	2.731	2.729	2.710	2.710	2.698	2.696	1.451	1.451	1.456	1.456
H10… O7	1.913	1.911	1.453	1.452	1.869	1.869	1.878	1.877	2.721	2.723	2.738	2.736
<u>Bond angles (°)</u>												
C1C2C3	120.2	120.1	120.2	120.2	119.3	119.3	120.2	120.1	120.1	120.0	120.7	120.7
C1C2N	117.4	117.4	116.9	116.9	119.7	119.7	118.3	118.3	117.7	117.8	116.7	116.7
C2C3C4	122.7	122.7	122.3	122.4	123.4	123.4	122.4	122.5	122.8	122.9	122.5	122.5
C3C4O7	126.1	126.0	122.7	122.8	126.0	126.0	121.5	121.5	126.1	126.0	126.4	126.2
C3C2N	122.4	122.5	126.3	126.2	120.9	120.9	126.1	125.9	122.1	122.2	122.6	122.6
C3C4O8	112.4	112.3	111.8	111.6	112.4	112.4	111.9	111.8	112.4	112.2	111.7	111.5
C4O8C5	116.6	117.3	114.9	115.5	116.6	116.6	115.0	115.6	116.6	117.4	115.0	115.6
HNH (or C)	119.6	119.5	118.0	118.1	116.6	116.6	119.2	119.2	119.3	119.3	116.1	116.1
C2C3H11	119.4	119.4	119.5	119.5	119.1	119.1	119.4	119.3	119.3	119.3	119.6	119.6
NHO	134.1	134.2	134.7	134.7	137.2	137.2	134.9	134.9	134.7	134.5	136.4	136.3

Т	ิต	h	le	S2
	a	v.	IV.	04

		EAB				Me-EAE	3			Ph-EAF	3			Bn-EAF	3
Atoms	f_k^+	$f_{\overline{k}}$	f_k^0	Atoms	f_k^+	$f_{\overline{k}}$	f_k^0	Atoms	f_k^+	f_k^-	f_k^0	Atoms	f_k^+	$f_{\overline{k}}$	f_k^0
C1	0.001	-0.298	-0.148	C1	0.282	0.021	0.151	C1	0.001	-0.298	-0.148	C1	0.295	-0.296	0
C2	-0.067	0.106	0.019	C2	-0.155	0.004	-0.076	C2	-0.067	0.106	0.019	C2	-0.157	0.108	-0.024
C3	-0.047	0.383	0.168	C3	0.213	-0.340	-0.063	C3	-0.047	0.383	0.168	C3	0.218	-0.112	0.053
C4	-0.032	-0.119	-0.076	C4	-0.393	0.039	-0.177	C4	-0.032	-0.119	-0.076	C4	-0.391	0.383	-0.004
C5	-0.002	-0.013	-0.008	C5	-0.055	0.077	0.011	C5	-0.002	-0.013	-0.008	C5	0.011	-0.011	0
C6	-0.012	-0.291	-0.152	C6	0.279	0.007	0.143	C6	-0.012	-0.291	-0.152	C6	0.28	-0.291	-0.006
07	-0.042	-0.346	-0.194	07	1.032	-0.094	0.469	07	-0.042	-0.346	-0.194	07	0.336	-0.351	-0.008
08	-0.018	-0.286	-0.152	08	0.278	-0.067	0.106	08	-0.018	-0.286	-0.152	08	0.281	-0.289	-0.004
N9	0.004	-0.232	-0.114	N9	0.301	-0.241	0.030	N9	0.004	-0.232	-0.114	N9	0.308	-0.234	0.037
H10	-0.008	0.210	0.101	H10	-0.225	-0.019	-0.122	H10	-0.008	0.210	0.101	H10	-0.224	0.205	-0.01
H11	-0.016	0.091	0.037	H11	-0.121	-0.031	-0.076	H11	-0.016	0.091	0.037	H11	-0.12	0.089	-0.016
H12	-0.043	0.094	0.026	H12	0.144	0.037	0.091	C12	-0.043	0.094	0.026	C12	0.08	-0.087	-0.004
H13	-0.013	-0.093	-0.053	H13	-0.168	-0.024	-0.096	C13	-0.013	-0.093	-0.053	C13	0.021	0.007	0.014
H14	-0.035	-0.117	-0.076	H14	-0.207	-0.035	-0.121	C14	-0.035	-0.117	-0.076	C14	0.098	-0.099	0
H15	-0.072	-0.092	-0.082	H15	-0.222	-0.038	-0.130	C15	-0.072	-0.092	-0.082	C15	0.086	-0.107	-0.011
H16	-0.015	-0.117	-0.066	H16	-0.107	-0.021	-0.064	C16	-0.015	-0.117	-0.066	C16	0.085	-0.102	-0.009
H17	-0.039	-0.090	-0.065	H17	-0.112	-0.021	-0.066	C17	-0.039	-0.090	-0.065	C17	0.093	-0.112	-0.009
H18	-0.078	0.094	0.008	H18	-0.193	-0.024	-0.109	H18	-0.078	0.094	0.008	C18	0.078	-0.106	-0.014
H19	-0.017	0.099	0.041	H19	-0.138	-0.011	-0.074	H19	-0.017	0.099	0.041	H19	-0.172	0.09	-0.041
H20	-0.015	0.100	0.043	H20	-0.141	-0.011	-0.076	H20	-0.015	0.100	0.043	H20	-0.144	0.095	-0.024
				H21	-0.194	-0.037	-0.115	H21	-0.015	0.084	0.034	H21	-0.146	0.1	-0.023
				H22	-0.250	-0.042	-0.146	H22	-0.007	0.084	0.039	H22	-0.112	0.083	-0.015
				H23	-0.218	-0.063	-0.140	H23	-0.107	0.091	-0.008	H23	-0.106	0.083	-0.012
								H24	-0.035	0.097	0.031	H24	-0.183	0.09	-0.047

H25	-0.019	0.097	0.039	H25	-0.14	0.097	-0.022
H26	-0.029	0.097	0.034	H26	-0.136	0.096	-0.02
H27	-0.115	0.091	-0.012	H27	-0.138	0.096	-0.021
H28	-0.061	0.089	0.014	H28	-0.173	0.09	-0.042
H29	-0.031	0.091	0.030	H29	-0.119	0.114	-0.003
H30	-0.013	0.098	0.042	H30	-0.252	0.093	-0.079
				H31	-0.137	0.095	-0.021
				H32	-0.238	0.092	-0.073

Table S3

Ian	55					
	Theoretical Theoretical Experimental		Experimental			
No.	Ak	K1	AK2			
	Freq.	I _{IR}	Freq.	I _{IR}	IR(CCl ₄)	Assignment
1	3256	189	3257	187	3265(m,br)	vNH
2	3094	1	3095	1	3197(w)	$\nu CH(\alpha)$
3	3084	6	3086	6	3120(vw)	vCH(ph)
4	3067	18	3067	18	3097(vw)	vCH(ph)
5	3057	15	3057	15	3065(w)	vCH(ph)
6	3047	4	3047	4		vCH(ph)
7	3040	4	3040	4	3045(w)	vCH(ph)
8	3009	16	3010	15	2985(vw)	v _a C1H ₃
9			3004	30	2960(m)	v_aC6H_3 , v_aC5H_2
	299	41			2937(vw)	v_aC6H_3 , v_aC5H_2
10	2979	29	2984	11	~ /	v_aC6H_3 , v_aC5H_2

11			2977	8	2905(w)	v_aC6H_3
	2978	8				v_aC1H_3
12			2973	30	2877(w)	v_aC1H_3
	2959	5			2860(vw)	v_aC5H_2 , v_aC6H_3
13	2927	18	2946	36		$\nu_{s}C5H_{2}$
14			2923	11		$\nu_s C5H_2$
	2924	11				vsC1H3
15	2915	26	2913	25		vsC6H3
16	1660	236	1659	208	1656(s)	$v_aO=C-C=C, v_aN-C=C-C, \delta CH(\alpha)$
17	1643	592	1643	601	1620(s)	δ NH, ν_s O=C-C=C, ν_s N-C=C-C
18	1617	214	1616	212	1598(s)	v _a CC(ph)
19	1595	107	1595	114	1585(w,sh)	v _a CC(ph)
20	1521	64	1521	64	1505(m)	v_s N-C=C-C, δ CH11, δ NH, sciC5H ₂ ,
21	1502	45	1500	116	1490(m)	δ_a CH(ph), sciC5H ₂ , δ_a C6H ₃
22	1497	66			1490	$\delta_a CH(ph)$, sciC5H ₂ , $\delta_a C6H_2$
			1485	6		δ_a CH(ph), sciC5H ₂ , δ_a C6H ₃
23	1478	4	1472	12		sciC5H ₂ , δ_a C6H ₃
24	1472	17	1468	11		sciC5H ₂ , δ_a C1H ₃ , δ NH
25	1466	26	1465	13	1440(m)	sciC5H ₂ , δ_a C1H ₃ , δ cH(α)
26	1465	7	1465	24	1440	$\delta_a C 6 H_3$
27	1453	20	1452	16	1440	δ_a CH(ph), δ_a C1H ₃ , v_a N-C=C-C, δ CH(α),
28	1404	0				$\delta_s C1H_3$, $\delta_s C6H_3$, $\omega C5H_2$
			1401	112	1385(w)	$\delta_s C1H_3$, δNH
29	1402	121			1385	$\delta_s C1H_3$, $\delta_s C6H_3$, $\omega C5H_2$, δNH
			1397	9	1385	$\delta_s C6H_3, \omega C5H_2$
30	1383	90	1383	9	1385	δ_s C1H ₃ , δ NH, ν_s C-N-C, δ_s C6H ₃
31	1375	33	1375	97	1360(w)	$\delta_s C1H_3,\delta NH,\nu_s C\text{-}N\text{-}C,\delta_s C6H_3,\omega C5H_2$
32	1338	14	1337	16	1300(vw)	δ NH, v _s C3=C2-N, δ _s CH(ph), δ sC1H ₃

33	1311	4	1314	39	1300	v _s C3=C2-N, δ _s CH(ph), δsC1H ₃ , ωC5H ₂
34	1284	704	1311	1	1270(s)	$\delta cH(\alpha), v_sC3=C2-N, \delta_sCH(ph), \delta_sC1H_3, \omega C5H_2$
35	1276	1	1285	595	1270	τC5H ₂ , πCH ₃
36	1237	220	1235	171	1235(s)	v _a C3-C4-O8, v _a C1-C2-N-C12, δCH(α)
37	1186	2	1185	3		τC5H ₂ , πCH ₃
38	1168	544	1177	90	1165(s)	v _a C3-C4-O8, v _a C1-C2-N-C12, δCH(α)
39	1165	10	1166	411	1165	δ _a CH(ph)
40	1159	3	1165	43	1165	ρC5H ₂ , ρC6H ₃
			1123	127		vN-CH ₂ , δ C=C-N, v _a C-O-CH ₂ , δ CH(α), δ _a CH(ph)
41	1118	5				δO-CH ₂ -CH ₃ , ρC6H ₃ , νCH ₂ -O
			1099	68	1095(vw)	$\rho C6H_3$, $\nu_a OCH_2$ -CH ₃
42	1090	8	1090	6		δ _a CH(ph)
43	1065	90	1058	58	1058(w)	ν _a OCH ₂ -CH ₃ , ν _a C-C-O-CH ₂ , ρC1H ₃
44	1043	4	1042	4		$\pi C1H_3$
45	1035	18	1035	15	1025(vw)	$\delta CCC(ph), \pi C1H_3$
46	1023	52	1017	58	1018(w)	ρC1H ₃ , ν _a O-CH ₂ -CH ₃
47	1001	0	1001	0		ρC1H ₃ , ν _a O-CH ₂ -CH ₃
48	982	1				γCH(ph), vC2-C1H ₃ , vC5-C6H ₃ , v _s C3-C4-O8
			981	0		γCH(ph), ρC1H ₃ , πC12H ₂
49	980	31			975(vw)	γCH(ph), ρC1H ₃ , δC2C3C4, νC5-C6H ₃ , ν _s C3-C4-O9
			964	0		γCH(ph)
50	966	0				γCH(ph)
			962	22	960(vw)	ρC1H ₃ , δC2C3C4, νC5-C6H ₃ , ν _s C3-C4-O9
51	953	2	933	7	940(w)	γ CH(ph), π C12H ₂
52	903	5	901	5	900(vw)	γCH(ph),
53	870	2	860	2	870(w)	$\nu_a OCH_2$ -CH ₃ , $\nu_a C$ -C-O-CH ₂
54	831	2	829	2		Δ, ρC6H ₃ , ν _s C1H ₃ -C2-N, νO8-C5
53	809	3	811	3		ρС6Н3, ρС5Н2, Γ

Table S4

	Theoretical Theoretical Experimental		Experimental			
No.	AK	K1	AK	.2		
	Freq.	I _{IR}	Freq.	I _{IR}	IR(CCl ₄)	Assignment
1	3326	124	3329	122	3450(vw)	vNH
2	3094	1	3096	1	3290(m,br.)	$\nu CH(\alpha)$
3	3065	14	3065	14	3207(w)	vCH(ph)
4	3058	19	3058	19	3115(vw)	vCH(ph)
5	3049	13	3049	13	3095(w)	vCH(ph)
6	3040	0	3040	0	3070(w)	vCH(ph)
7	3025	9	3025	9		vCH(ph)
8	3012	13	3012	12	3035(w)	$\nu_a C1H_3$
9			3003	31	2993(vw)	v_aC6H_3 , v_aC5H_2
	2988	41			2950(m)	v_aC6H_3 , v_aC5H_2
10	2978	31	2983	12	2930(vw)	v_aC6H_3 , v_aC5H_2
11			2971	29		$\nu_a C6H_3$
	2962	7			2910(w)	v_aC1H_3
12			2963	29		v_aC1H_3
	2957	6			2870(w)	v_aC1H_2 , v_aC6H_3
13	2945	14	2945	13	2885(vw)	$\nu_a C12H_2$
14			2944	35		$\nu_s C5H_2$
	2924	20				$\nu_s C5H_2$
15	2916	33	2915	37		v_sC1H_3 , v_sC12H_2

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16	2915	31	2912	26		$\nu_s C6H_3$
17	2912	6	2912	7	2840(w)	v_sC1H_3 , v_sC12H_2
18	1659	326	1660	292	1660(s)	$v_aO=C-C=C, v_aN-C=C-C, \delta CH(\alpha)$
19	1632	568	1634	585	1613(s)	δNH , $v_s O=C-C=C$, $v_s N-C=C-C$
20	1620	14	1620	14	1613	v _a CC(ph)
21	1601	4	1601	4	1588(sh)	v _a CC(ph)
22	1513	83	1512	97	1500(m)	v_s N-C=C-C, δ CH(α), δ NH, sciC5H ₂ , sciC12H ₂
23	1503	10	1503	12	1496(m)	$\delta_a CH(ph)$, sciC12H ₂
24	1498	10	1485	5	1496	sciC5H ₂ , δ_a C6H ₃
25	1476	29	1478	29	1460(m)	$\delta_a C1H_3$, sciC12H ₂ , δNH
26	1477	4	1470	11	1460	$sciC5H_2, \delta_aC1H_3, \delta NH$
27	1468	14	1467	7	1440(m)	$\delta_a C1H_3$, sciC12H ₂
28	1465	7	1465	9	1440	$\delta_a C6H_3$
29	1461	10	1461	12	1433(sh)	$\delta_a CH(ph), \delta_a C1H_3, \omega C12H_2$
30	1458	23	1458	19	1433	$\delta_a C1H_3$, sciC12H ₂
31	1404	6				$\delta_s C1H_3$, $\delta_s C6H_3$, $\omega C5H_2$
			1403	77	1387(m)	$\delta_{s}C1H_{3}, \delta NH$
32	1402	71			1387	δ_s C1H ₃ , δ_s C6H ₃ , ω C5H ₂ , δ NH
			1398	10	1370(vw)	$\delta_s C6H_3, \omega C5H_2$
33	1384	15	1386	15	1370	δ _s C1H ₃ , δNH, ωC12H ₂ , ν _s C-N-C
34	1375	2	1378	15	1360(w)	$\delta_s C6H_3, \omega C5H_2$
35	1359	83	1359	81	1340(vw)	ω C12H ₂ , δ NH, ν sC3=C2-N, δ sCH(ph), δ sC1H ₃
36	1333	3	1333	3	1350(w)	δ_{s} CH(ph), ω C12H ₂
37			1315	76	1310(sh)	$\omega C5H_2$
38	1312	151			1310	$\tau C12H_2$, $\omega C5H_2$, $\delta CH(\alpha)$, $\nu_a C-C(ph)$
			1312	75	1310	$\tau C12H_2$, $\tau C5H_2$, $\delta CH(\alpha)$, $\nu_a C$ -C(ph)
39	1290	133	1290	132	1280(m)	v_a C-C(ph), τ C12H ₂ , δ CH(α)
40	1276	0				τC5H ₂ , πCH ₃

			1289	132	1280	τC5H ₂ , ν _a C3-C4-O8, ν _a C1-C2-N-C12
41	1246	476	1243	386	1234(s)	τC12H ₂ , v _a C3-C4-O8, v _a C1-C2-N-C12, δCH(α)
42	1195	56	1195	41	1199(w)	ν _a C13-C12-N, ν _a C3-C4-O8, δCH7
43	1184	12	1185	8	1190(w)	$\delta_a CH(ph), \delta CH(\alpha)$
44			1178	116	1173(s)	ρC5H ₂ , ρC6H ₃
	1174	311			1173	$\delta CH(\alpha), v_s N-C12-C13, v_a C-O-CH_2$
45			1172	194	1173	δCH(α), v _s N-C12-C13, v _a C-O-CH ₂
	1164	0			1173	$\delta_a CH(ph)$
46			1165	0		$\delta_a CH(ph)$
	1159	3			1150(m)	ρC5H ₂ , ρC6H ₃
47	1125	90			1121(m)	vN-CH ₂ , δ C=C-N, ρ C6H ₃ , ν_a C-O-CH ₂ , δ CH(α), δ_a CH(ph)
			1123	127	1120	ν N-CH ₂ , δ C=C-N, ν _a C-O-CH ₂ , δ CH(α), δ _a CH(ph)
48	1116	36			1120	δO-CH ₂ -CH ₃ , ρC6H ₃ , νCH ₂ -N
	0		1099	58	1105(vw)	ρC6H ₃ , v _a OCH ₂ -CH ₃
49	1083	23	1084	17	1075(w)	$\delta_a CH(ph), \nu CH_2-N$
50	1065	75	1059	45	1060(w)	$\nu_a OCH_2$ -CH ₃ , $\nu_a C$ -C-O-CH ₂ , $\rho C1H_3$
51	1045	4	1046	3		$\pi C1H_3$
52	1033	13	1033	13	1030(vw)	δCCC(ph)
53	1027	50	1022	59	1015(w)	ρ C1H ₃ , ν _a O-CH ₂ -CH ₃ , π C12H ₂
54	1002	1	1002	1	1002(vw,sh)	δCCC(ph)
55	991	2	991	1		γ CH(ph), π C12H ₂
56	984	14			982(vw)	γCH(ph), vC2-C1H ₃ , vC5-C6H ₃ , v _s C3-C4-O8
			981	2		γCH(ph), ρC1H ₃ , πC12H ₂
57	976	12			977(vw)	γCH(ph), ρC1H ₃ , δC2C3C4, νC5-C6H ₃ , ν _s C3-C4-O9, πC12H ₂
			972	0		γCH(ph)
58	971	0				γCH(ph)
			961	21	935(m)	ρC1H ₃ , δC2C3C4, νC5-C6H ₃ , ν _s C3-C4-O9
59	904	2	904	2	900(vw)	γ CH(ph), π C12H ₂

60	885	1	877	0		γCH(ph), ρC6H ₃ , δC3C4O8, v _s C4-O8-C5, πC12H ₂
61	845	0	846	1		γCH(ph)
62	831	7	828	6		Δ, ρC6H ₃ , v _s C1H ₃ -C2-N, vO8-C5
63	803	3	806	2	845(w)	ρС6Н3, ρС5Н2, Г
64	792	3	793	3		δCCC(ph), vC12-C13, γNH

^a See footnote of Table 6.























Fig. S4.



Fig. S5.



Fig. S6.





-6.750e -2



	Charges (e)	Electric Potential (a.u)
C1	-0.6079	-14.760
C2	0.2722	-14.712
C3	-0.4437	-14.794
C4	0.7720	-14.665
C5	-0.0321	-14.726
C6	-0.5880	-14.783
07	-0.6784	-22.405
08	-0.5679	-22.346
N9	-0.7731	-18.375
H10	0.4319	-1.029
H11	0.2204	-1.115
H12	0.3802	-1.016

	Charges	Electric Potential
	(e)	(a.u)
C1	-0.6116	-14.762
C2	0.2905	-14.716
C3	-0.4483	-14.799
C4	0.7691	-14.670
C5	-0.0316	-14.728
C6	-0.5877	-14.785
07	-0.6873	-22.408
08	-0.5695	-22.350
N5	-0.6072	-18.372
H10	0.4331	-1.036
H11	0.2190	-1.120
C12	-0.3612	-14.730

	Charges (e)	Electric Potential (a.u)
C1	-0.6127	-14.761
C2	0.2910	-14.707
C3	-0.4310	-14.790
C4	0.7709	-14.661
C5	-0.0322	-14.723
C6	-0.5883	-14.781
07	-0.6892	-22.400
08	-0.5648	-22.342
N9	-0.5979	-18.361
H10	0.4385	-1.026
H11	0.2209	-1.112
C12	0.1554	-14.719

6.750e-2



	Charges (e)	Electric Potential (a.u)
C1	-0.6156	-14.764
C2	0.2938	-14.714
C3	-0.4450	-14.797
C4	0.7699	-14.667
C5	-0.0318	-14.726
C6	-0.5878	-14.783
07	-0.6854	-22.405
08	-0.5679	-22.348
N9	-0.6130	-18.372
H10	0.4341	-1.035
H11	0.2200	-1.118
C12	-0.1887	-14.720

Figure S7.



Fig. S8.



Fig. S9.



Fig. S10.



Fig. S11.



Fig. S12.