Vibrational spectra, conformation and molecular transport of 5-amino-2,2,6,6-tetramethyl-4-hepten-3-one

Bazrafshan, Mahmood; Vakili, Mohammad; Tayyari , Sayyed Faramarz ; Kamounah, Fadhil S.; Hansen, Poul Erik; Housaindokht, Mohammad Reza

Published in:
Journal of Molecular Structure

DOI:
10.1016/j.molstruc.2022.134178

Publication date:
2023

Document Version
Peer reviewed version

Citation for published version (APA):
Bazrafshan, M., Vakili, M., Tayyari , S. F., Kamounah, F. S., Hansen, P. E., & Housaindokht, M. R. (2023). Vibrational spectra, conformation and molecular transport of 5-amino-2,2,6,6-tetramethyl-4-hepten-3-one. *Journal of Molecular Structure*, *1272*, Article 134178. https://doi.org/10.1016/j.molstruc.2022.134178

Vibrational spectra, conformation and molecular transport of 5-amino-2,2,6,6-tetramethyl-4-hepten-3-one

Mahmoud Bazrafshan [a], Mohammad Vakili [a], Sayyed Faramarz Tayyari *[a], Fadhil S. Kamounah [b], Poul Erik Hansen [c], Mohammad Reza Housaindokht [a]

[a] *Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran*

[b] *Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100, Copenhagen Ø, Denmark*

[c] *Department of Science and Environment, Roskilde University, Universitetsvej 1, P.O. Box 260, DK-4000, Roskilde, Denmark*

Abstract

In this research, the molecular structure and intramolecular hydrogen bonding (*IHB*) of 5-amino-2,2,6,6-tetramethyl-4-hepten-3-one (AMTMH) were studied using spectroscopic techniques (IR, Raman, UV, and NMR) and computational analysis (density functional theory (DFT) and the second-order Møller–Plesset (MP2) methods). The results of this study compared with those of 4-amino-3-penten-2-one (APO) and 3-methyl-4-amino-3-penten-2-one (3-MeAPO). The averaged calculated geometrical parameters of AMTMH (obtained by considering the populations of all conformers) agree with the averaged geometrical parameters obtained by X-ray crystallography of two conformations found in the crystal. Comparison of different parameters related to the *IHB* strength, such as NH stretching, experimental proton chemical shift, and deuterium isotope effects on ^{13}C chemical shifts of AMTMH with those of APO and 3-MeAPO, suggests the following trend for the IHB strength: 3-MeAPO > AMTMH > APO. All normal modes of AMTMH were successfully assigned and compared to the corresponding band frequencies of APO. The appearance of more than one band for several vibrational normal modes is related to the coexistence of different conformers in the sample. The molecular transport results show that the conductivity of the enol form (*on*-state) to keto form (*off*-state) changes, which suggests that this system has the potential to function as a molecular switch.
In addition, the experimental fluorescence and the calculated TD-DFT results confirmed both aminoketone and iminoenol forms are in the excited state.

Keywords: 5-amino-2,2,6,6-tetramethyl-4-hepten-3-one; Intramolecular hydrogen bond; Vibrational spectroscopy; NMR; DFT-NEGF.

[*]Corresponding author: tayyari@um.ac.ir (SF Tayyari)
Tel: +989153103538

1. Introduction

β-Ketoenamines can exist in three different tautomers: aminoketone, AK, iminoketone, IK, and iminoenol, IE, forms (Fig. 1). The XH bond (X=N or O) of the aminoketone and iminoenol tautomers are involved in the chelated ring of the intramolecular hydrogen bond, *IHB*, system [1-3].

As stated in the literature, aminoketones in the ground state are the predominant form of β-enaminones [2-5]. The *IHB* in this system is of the resonance-assisted type [6]. Due to wide diversity and potential use in the industrial, pharmaceutical, and biological contexts, the study on β-ketoenamines is rapidly increasing [7-12]. In addition, because of the non-linear optical properties of β-aminoketones, these compounds are used in many molecular electronic devices [13, 14].

The difference between 5-amino-2,2,6,6-tetramethyl-4-hepten-3-one (AMTMH) and 4-amino-3-penten-2-one (APO) (the simplest member of the β-enaminones) is the replacement of the methyl groups (-CH_3) by two bulky t-butyl groups (-$C(CH_3)_3$) in the β-positions of APO [2]. Comparing the spectroscopic, electronic, and structural properties of AMTMH with those for 3-MeAPO makes it possible to understand the difference between the steric effects of the t-butyl groups and the interwoven two methyl groups of 3-MeAPO. The d*ensity-functional theory* (*DFT*) is a computational *quantum mechanical* modelling *method used* in *physics and chemistry* to investigate to calculate the electronic structure of atoms, atomic charges, molecular geometry, thermodynamic functions, dipole moments, vibrational frequencies, and many more [15-17].

The present work aims to study the effects of the t-butyl group substituted in the β-position on the structure, conformations, *IHB* strength, spectroscopic behaviours, and conductivity of AMTMH. To obtain a clear understanding of these effects, the molecular structure and IHB strength of APO [2,18] and 3-MeAPO) [19] are compared with AMTMH. The calculated molecular structure and conformations of AMTMH compared with its X-ray diffraction results [20, 21]. The calculated current-voltage characteristics of enol and keto forms of the title molecule are also studied. Also, the structure of the excited state for the title compound is investigated by the calculations (TD-DFT) and fluorescence spectroscopy results.

2. Experimental

2,2,6,6-Tetramethyl-3,5-heptanedione and analytical grade reagents and solvents purchased from Sigma-Aldrich Chemical Co. Fluka silica gel, TLC-cards 60778 with fluorescence indicator 254 nm, were used for TLC chromatography. Merck silica gel 60 (0.040-0.063 mm) was used for flash chromatography purification of the products. ^{1}H NMR and ^{13}C NMR spectra were recorded at 500 MHz and 126 MHz on a Bruker Ultrashield Plus 500 spectrometer using $CDCl_3$ as solvent and TMS as internal standard. HRMS-ESI spectra were carried out on a Bruker MicrOTOF-QII-system with ESI-source with nebulizer 1.2 bar, dry gas 8.0 l/min, dry temperature 200 °C, capillary 4500 V endplate offset -500 V.

AMTMH was prepared by a modification of a literature method [22]. A 25 ml single-neck flask, equipped with a condenser and stirring magnet, was charged with 2,2,6,6-Tetramethyl-3,5-heptanedione (1.0 g, 5.4 mmol) and formamidinium acetate (1.0 g, 9.6 mmol) in dry mesitylene (10 ml). The resulted suspension was heated to reflux at 200 °C for 15 h under a nitrogen atmosphere. The mesitylene was removed at room temperature by nitrogen bubbling into the reaction mixture to obtain a solid residue. The solid residue was dissolved in dichloromethane (15 ml) and chromatographed on silica gel. At first, dichloromethane was used as the eluent to remove the traces of mesitylene and unreacted 2,2,6,6-tetramethyl-3,5-heptanedione, then dichloromethane /ethyl acetate (95:5) was used to obtain the pure product as a colourless polycrystalline substance 0.61 g (61%) [22]. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.40 (bs, 1H NHin), 5.36 (s, 1H =CH), 5.12 (s, 1H NHout), 1.20 (s, 9H; $(CH_3)_3$-C-C-N), 1.15 (s, 9H; $(CH_3)_3$-C-C=O). 13C NMR (CDCl3, 126 MHz) δ 205.77 (C2); 173.79 (C4); 86.89 (C3); 42.24 (C1); 36.22 (C5); 28.97 (C22, C26, C30); 28.06 (C10, C14, C18) (For the atom numbering see Fig. 2). HRMS-ESI (*m/e*): $[M+H]^+$ calculated for $C_{11}H_{22}NO$ 184.1701, found 184.1695 (Fig. S1, supplementary materials).

The deuterated analogue, D_3-AMTMH, (including hydrogens in H34 (Hα) and NH_2) was prepared according to the literature [19].

The mid-IR spectra were recorded on a Bomem MB-154 Fourier transform spectrophotometer, using KBr pellets and CCl_4 solution with a spectral resolution of 2 cm^{-1} by averaging the results of 20 scans.

The Far-IR spectra, in the region 600-250 cm^{-1}, were recorded on a Thermo Nicolet NEXUS 870 FT-IR spectrometer, equipped with a DTGS/polyethylene detector and a solid-substrate beam splitter, using polyethylene disks. The spectra were collected with a resolution of 2 cm^{-1} by signal averaging 32 scans.

The FT-Raman spectrum of AMTMH was recorded on a Teksan Takram P50C0R10 Raman spectrophotometer using a 532 nm laser.

The ultraviolet absorption spectrum was measured from 200 to 400 nm in an ethanol solution using Perkin-Elmer LAMBDA 25 spectrophotometer equipped with a 10 mm quartz cell at 298 K.

The fluorescence spectrum was scanned on FluoroLog 3–22 (HORIBA) spectrofluorometer with a resolution of 2 nm in the 250–400 nm region with tuning 225 nm as excitation wavelength.

3. Computational details

The hybrid functional B3LYP [23, 24], using the 6-311++G(d,p) basis set, was adopted to calculate the properties of the titled molecule. Quantum chemical calculations were performed using the Gaussian 09W program package [25]. Each vibrational mode was assigned utilizing visual inspection using the GaussView 5.0 software [26]. Atoms in Molecules (AIM) analysis was achieved according to the Bader theory[27] using the AIM2000 program [28]. The second-order interaction energies, $E^{(2)}$, [29] were calculated using the NBO 5.0 program [30]. The geometry optimization and conformational analysis for AMTMH have also been done at the MP2 level [31, 32], using the 6-311++G(d,p) basis set.

The vertical and relaxation excitation transitions for AMTMH were calculated by the time-dependent density functional theory, TD-DFT, [33], using the polarizable continuum model, PCM, in ethanol as solvent [34]. The excitation energies, wavelengths, oscillator strength (*f*), the contributions to the frontier molecular orbitals (HOMO and LUMO), and density of the states (DOS) were calculated using the GaussSum 2.2 Software [35].

The ^{1}H and ^{13}C chemical shifts were calculated using the GIAO (Gauge-Including Atomic Orbital) method [36, 37].

The current through the device was calculated using the Landauer–Büttiker formula in the TranSIESTA package [38]. In the lateral dimension a 6×6 supercell was used, large enough to remove interactions between periodic images. Following the experimental results [39], the two hydrogen atoms which have to be connected to the metal surface were replaced with sulphur atoms, and The remaining part of the molecule was placed between two parallel *Y*(111) planes with a face-centered cubic (Fig. S2, supplementary materials) [40, 41]. The Au–S, Pt–S, and Ag–S distances for the hollow sites are set to 2.42, 2.41, and 2.46 Å, respectively [42-44]. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional is adopted for the generalized gradient approximation (GGA) [45]. We use a ξ plus single polarization (SZP) and double-ξ plus single polarization (DZP) basis sets for the electrons of the electrode and organic atoms in the transport calculations, respectively. We used a k-grid sampling of 6×6×100 with a mesh cutoff energy of 150 Ry. The transport calculations have been carried out in the bias voltage range valued from 0.0 to 2.0 V at 300 K.

4. Results and Discussion

4.1. Molecular structure

Theoretically, AMTMH can exist in three distinct forms: aminoketone, iminoenol, and iminoketone (Fig. 1). According to our calculations (performed at the B3LYP/6-311++G(d,p) level), the energy of the aminoketone (AK) tautomers is 6.25 kcal/mol lower than that of iminoenol (IE) and 12.65 kcal/mol less than that of iminoketone (IK) species (Fig. S3, supplementary materials). The calculated relative energies suggest that this molecule exists as an aminoketone, consistent with the experimental results. It seems that other β-aminoketones also show similar behaviour [2, 3, 19].

Rotation of t-butyl groups in AMTMH creates four stable aminoketone conformers, AK1, AK2, AK3, and AK4 (Fig. 2a). The X-ray analysis shows only two conformers in the unit cell [21], AK1 and AK2. AK1 is the only conformer obtained by the calculations using the MP2/6-311++G(d,p) level. Fig. 3 shows the topological map of an optimized dimer structure, based on its CIF crystallography, obtained by the AIM calculations. Fig. 3 also indicates two weak long-range contact intermolecular unconventional hydrogen bonds, the C-H…O and C-H…H-C interactions with the strength of 1.50 and 0.50 kcal/mol, respectively, but not detected in the corresponding single-crystal structure [21], which may be due to their weakness.

Table 1 lists the selected geometrical parameters, calculated at the B3LYP/6-311++G(d,p) level, along with the corresponding X-ray data for AMTMH, 3-MeAPO, and APO [19, 21]. Table 1 also includes the geometrical parameters calculated at the MP2/6-311++G(d,p) level for AMTMH. Two correlations in Fig. S4 (supplementary materials) compare the computational levels and the corresponding X-ray data. The regression coefficients (R^2) show that the data calculated at the B3LYP level better correlate with the experimental bond lengths and angles than those obtained by the MP2 level of theory. The calculations hereafter, thus, were performed only at the B3LYP level. As Table 1 shows, the averaged C2=O6 and C4-N7 bond lengths of the N-H…O forms of AMTMH are about 1.245 and 1.350 Å, respectively. The averaged bond angles of O6–C2–C3 and C3–C4–N7 are about 122.6º and 120.8º, respectively, consistent with the *sp2* hybrid character of C2 and C4 atoms [46-48]. According to this table, the averaged geometrical parameters, obtained by superposition of different conformers, are in excellent agreement with the results of the experimental data.

As earlier reported for similar compounds, the $C(CH_3)_3$ group has more steric effect than a CH_3 group [49, 50]. Comparing the structural parameters of AMTMH with APO indicates that the bond lengths in the chelated ring (C3=C4, C3-C2, O6-C2, and C4-N7 bonds) are almost the same, while the N7…O6, O6…H9, and N7-H9 distances significantly different. Comparing the structures of these two molecules shows that replacing the methyl groups with the t-butyl groups reduces the O6-C2-C3 and C3-C4-N7 bond angles and increases the C2-C3-C4, C3-C4-C5, and N7-H9-O6 bond angles.

The calculated N…O and O…H distances in AMTMH (the averag of AK1-4), 3-MeAPO, and APO are 2.637, 2.597, 2.669 Ǻ, and 1.831, 1.802, 1.890 Ǻ, respectively. These results suggest the following trend in the strength of their *IHB*s:

$$3\text{-MeAPO} > \text{AMTMH} > \text{APO} \qquad (1)$$

A comparison between the IHB of AMTMH and 4-phenylamino-pent-3-en-2-one, APO-NPh, [3] indicates that the IHB of AMTMH is weaker than that of APO-NPh, based on N…O bond distances, NH stretching frequencies, UV, and NH chemical shift [3].

Fig. 4 shows the relative energy profile of proton transfer from the N atom to the O atom. As this figure shows, in the gas phase, the energy of aminoketone, AK3, is 6.05 kcal/mole lower than that of the iminoenol and the barrier height for this proton transfer is 6.94 kcal/mole.

Table 2 shows some parameters related to the hydrogen bond strength (including the optimized geometrical parameters, X-ray values, spectroscopic properties, AIM, and NBO results) for AMTMH, APO, and 3-MeAPO [19]. The higher total electron density, ρBCP, and its Laplacian, ∇^2ρBCP, as an absolute value, at the bond critical point (BCP) of O6…H9 corresponds to a stronger IHB. Table 2 shows that 3-MeAPO has the maximum ρBCP and the minimum ∇^2ρBCP.

The *EHB* values, estimated by the Espinosa *et al.* [51] method, are 7.67, 9.87, and 10.85 kcal/mol for APO, AMTMH (averaged over four conformers), and 3-MeAPO, respectively, are also listed in Table 2.

According to all parameters given in Table 2, except for the NMR proton chemical shifts, the IHB strength in AMTMH is slightly weaker than that in 3-MeAPO. A tiny difference in the values of proton chemical shift of AMTMH (10.40 ppm) and 3-MeAPO (10.32 ppm) can be due to the conditions of measurements, such as different temperatures or concentrations of solutions.

In the LP(2)O to σ*N7-H9 orbital interaction, the LP(2) and σ* are molecular orbitals, and the contribution of atomic orbitals (s and p orbitals) are 1% s and 99% p for LP(2)O and 31% s and 69% p for σ*N7-H9. The contribution of s orbital shows that the overlapping of the orbitals is also head-to-head (like Sigma orbitals) in addition to side-to-side (like p orbitals). Therefore, the hydrogen bond of the NHO system in this molecule is non-linear.

4.2. NMR spectroscopy

Fig. 5a-b shows the NMR spectra of AMTMH, while the chemical shifts and nuclear shielding, along with the previously reported results [21], are listed in Table S1 (supplementary materials). An excellent agreement exists between the experimental results and predicted data (Table S1). The correlations between the experimental ^{1}H and ^{13}C chemical shifts (σexp.) and the GIAO nuclear shielding (σcalc.) calculated by DFT at the B3LYP/6-311++G(d,p) level are usually linear and described by the following equation: σexp= a (σcalc.)+ b. For the ^{13}C chemical shifts of AMTMH in Table S1 (supplementary materials), the calculated regression coefficients (R^2) are 0.9991, 0.9992, 0.9910, and 0.9990 for the rotamers AK1-4. These results show that none of the four tautomers could be excluded based on the NMR data, which agrees with the theoretical calculations.

Deuterium isotope effects on ^{13}C chemical shifts

Partial deuteration of the NH proton leads to the following deuterium isotope effects on ^{13}C chemical shifts: C-4 0.06, 0.33, and 0.39 ppm. The first is due to deuteration at the non-hydrogen bonded NH, the second is due to the hydrogen-bonded NH and the third is when both NH are deuterated. 0.33 ppm can be compared to 0.29 ppm in 3-MeAPO and 0.21 in APO [19]. These results suggest a slightly stronger hydrogen bond in AMTHMD as compared to 3-MeAPO. Other isotope effects are: C=O carbon, 0.03 ppm, C-3 0.06, 0.06 and 0.12 ppm; C-5, 0.03 and ~0.03 ppm; C-1, unresolved shoulder.

The fact that the separate isotope effects can be observed shows that the NH_2 group has no internal rotation. Furthermore, despite the presence of water, the isotope effects can be observed. This indicates either strong hydrogen bonding (NH hydrogen bonded to C=O) and/or shielding from solvent.

4.3. Electronic properties, UV and Fluorescence spectra

The broadband at about 300 nm in the UV spectra of the β-ketoenamine compounds is related to the $\pi \rightarrow \pi^*$ transition of the chelated ring [3, 19, 52, 53]. A stronger hydrogen bond leads to a longer wavelength for this transition. The UV spectrum of AMTMH shows one broadband at 301 nm, Fig. S5 (supplementary materials). The corresponding band in the UV spectra of APO [54] and 3-MeAPO [19] occurs at 299 and 319 nm in the ethanol solution, respectively.

Figs. S6a and S6b (supplementary materials) show the density of the states (DOS) of AMTMH and APO. DOS graphs of AMTMH and APO confirm similar band gaps and display the population distribution over orbitals. In the DOS plots, the HOMO weight is positioned on the chelated ring while the LUMO weight is localized on the C=O, C-N, and t-But bonds.

The wavelength (λ), oscillator strength (*f*), and the significant contributions of transitions of AMTMH computed at the TD- B3LYP/6-311++G(d,p) level, are listed in Table S2 (supplementary materials). Since there is no difference between the absorbed theoretical wavelengths of AK1-AK4, so only the TD-DFT results of the AK2 form are listed. The calculated transition band for AK2 is predicted at 267 nm (in the ethanol solution) and the oscillator strength, *f*, is 0.4305, with a high contribution of H→L (97%). The corresponding wavelength in the gas phase is about 260 nm which correlated with its electronic band gap in the gas phase. The calculated bands for APO and 3-MeAPO are reported at 263 and 276 nm [3, 19], respectively. These values show that the IHB strength of APO is the lowest.

The geometrical optimization of AK1-4 and IE1-4 forms in the excited state shows that all of them convert to the AK2 and IE3 forms, respectively. Theoretically in the ethanol as solvent, the AK2 form shows emission at 292 nm with the oscillator strength of 0.4896 that is assigned to LUMO→ HOMO-1 transition. While the IE3 form displays singlet emission at 328 nm with the oscillator strength of 0.3034 that is assigned to the same transition (see Table S2 in supplementary materials). The experiment fluorescence spectrum of AMTMH in the ethanol solvent in the 250–400 nm region is presented in Fig. S5b, in supplementary materials. By applying the excitation wavelength of 225 nm in the fluorescence spectrum, two emission bands with very weak and very strong intensities are obtained at 280 and 345 nm that according to calculated results, confirmed the presence of both AK2 and IE3 in the excited state, respectively. The detecting aminoketone and iminoenol forms in the excited state also were reported for the NHO system by V. Latha et al. [55].

There is little difference between AK2's structure in the ground and excited states. The most important differences are the values of HN7H and C5C4N7H8 angles that in the ground state are 121.7° and 0.0° while in the excited changed112.3° and -41.1°, respectively. In IE3, the C5C4N7H8 angle in the excited state is 99.2°, in other words, the proton on the nitrogen atom is perpendicular to the chelated ring, see Fig. S5c-d in the supplementary materials.

4.4. Molecular electrostatic potential (MEP) surface

The MEP graphs for the AMTMH (AK1 form) and APO are given in Fig. S7 (supplementary materials). The red, green, and blue colours of MEP indicate the negative, neutral, and positive regions, respectively, that characterize the electrophilic and nucleophilic sites. The negative and positive places occurred around the O and H atoms. Also, the t-But groups are neutral sites. The maximum and minimum calculated negative electrostatic potential values for these electrophilic and nucleophilic sites in AMTMH and APO are about −22.41, −1.02, and −22.11, −1.02 a.u with point charges of −0.657, 0.436, and −0.654, 0.361 e, respectively.

The MEP surface demonstrates the weak positive area and the strong negative charge area over the H9 and O6 atoms in the intramolecular hydrogen bond (O…H–N) [56]. The MEP charges for O and H in AMTMH and APO are -0.6566, 0.4358 e, and -0.6537, 0.4313 e, respectively, which confirms that the IHB strength of APO is lower than that of AMTMH.

4.5 Vibrational analysis

Comparing the calculated vibrational spectra of all stable conformers of the titled compound with the corresponding experimental data may be used to confirm the structure, IHB strength, and the existence of different forms. Fig. 6 compares the IR spectra of APO and AMTMH in the CCl_4 solution and AMTMH in the solid phase in the 3550–2800 cm^{-1} region. Fig. 7 shows the IR spectra of AMTMH in the solid and CCl_4 solution. Figs. 8 and 9 show the Far-IR spectra of AMTMH and the Raman spectrum of AMTMH, respectively. The recorded infrared spectra of APO and AMTMH in CCl_4 are indicated in Fig. S8 (supplementary materials).

Table 3 lists the selected scaled calculated and observed vibrational frequencies and band assignments of AMTMH. Most vibrational bands of AK1, AK2, AK3, and AK4 conformers of AMTMH are near to each other. Also, the complete fundamental 3N-6 normal modes without scaling along to their IR intensities and Raman scattering activities of all conformers are listed in Table S3 (supplementary materials). Generally, the unscaled calculated wavenumbers are somewhat higher than the observed values, however, a good agreement between observed and scaled calculated wavenumbers exists. Several factors may be responsible for the discrepancies between the theoretical and experimental results, such as anharmonicity, media, and Fermi resonance. Hence, the proper scaling factors, 0.9609 for above 2000 cm^{-1} and 0.9859 for below 2000 cm^{-1} regions, are used for theoretical wavenumbers [57]. The calculated values are harmonic wavenumbers, while the measured values are anharmonic frequencies. The AMTMH molecule has a t-But group at its β-position. Therefore, comparing the vibrational spectra of the titled molecule with those of 2,2,6,6-tetramethyl-3,5-heptanedione, TMHD, and its copper complex, Cu(TMHD)$_2$, [49,50] could be helpful.

4.5.1. The NH and CH stretching vibrations

In the amins, the symmetric and asymmetric NH$_2$ stretching vibrations are observed in ranges 3420-3325 cm^{-1} and 3520-3420 cm^{-1} [58-60], respectively, which will be affected by hydrogen bonding formation [18]. For example, asymmetric and symmetric NH$_2$ stretching vibrations (νsNH and νaNH) of APO and 3-MeAPO (in the CCl$_4$ solution) are reported at 3184, 3135, and 3375, 3367 cm^{-1}, respectively [2,18,19,61].

The IR spectrum of AMTMH in the solid phase shows two bands at 3405 and 3346 cm^{-1}, which are assigned to the asymmetric and symmetric NH$_2$ stretching vibrational modes, respectively. The corresponding bands in the solid phase of APO occur at about 3353 and 3179 cm^{-1} [2]. In the solid phase, a Fermi resonance likely occurs between νsNH$_2$ and the overtone of the 1634 cm^{-1} band. These two bands, after perturbation, were observed at 3175 and 3346 cm^{-1}. In the solution, the intensity of the asymmetric NH$_2$ stretching band decreases and shifts significantly towards higher wavenumbers, 3421 cm^{-1} (see Fig. 7 and Table 3).

The two vibrational bands at 3145 and 3110 cm^{-1} in the IR spectrum of AMTMH are assigned to the CHα stretching vibration.

4.5.2 1700-1000 cm^{-1} region

The IR spectrum of AMTMH in the CCl_4 solution shows two strong bands at 1590 and 1520 cm^{-1} accompanied by two shoulders at 1610 and 1500 cm^{-1} (see Fig. 7). The corresponding Raman bands were observed at 1597, 1524, and 1503 cm^{-1}. The first three IR bands at 1610, 1590, and 1520 cm^{-1} are assigned to the symmetric and asymmetric stretching of CCCN and OCCC coupled to the bending modes of NH_2, CHα, and CH_3 groups.

The symmetric and asymmetric CH_3 deformations appear as weak-to-medium-intensity IR bands in the 1500-1360 cm^{-1} region. The CH_3 deformations are also somewhat coupled with the skeletal vibrations (Table 3). The strong intensity IR band at 1292 cm^{-1} was assigned to the symmetric C-C=C-N stretching, coupled to the νC-t-But and ρNH_2 vibrational modes.

4.5.3 Below 1000 cm^{-1} region

According to our calculations, the IR bands in the 940-860 cm^{-1} region are related to the CH_3 rocking vibrational modes. The corresponding Raman bands occur at 931 and 920 cm^{-1}. The 775, 728, and 634 cm^{-1} IR bands are assigned to the NH_2 out-of-plane bending mode coupled with the CHα out-of-plane bending and ring deformation. The corresponding vibrational bands in APO and 3-MeAPO appear at 755 [2] and 645 [26] cm^{-1}, respectively. The presence of more than one band confirms the coexistence of more than one conformer for AMTMH.

The IR band at 403 cm^{-1} in AMTMH is assigned to the N…O stretching coupled with δCH_3-C-CH_3. This band in 3-MeAPO and APO was observed at about 404 and 360 cm^{-1}, respectively [2, 25, 26]. The wavenumber of νN…O vibration of AMTMH, 3-MeAPO, and APO also agrees with the trend (1) for the IHB strength.

The four vibrational bands observed at 360, 326, 310, and 284 cm^{-1}, according to the DFT calculations, are caused by torsional vibrations of the $C(CH_3)_3$ and CH_3 groups coupled with the N…O stretching mode.

4.6 Electronic transport

In a proof of concept paper, it has been reported that enamines can be utilized as a switching device in electronic transport [62]. However, judging from Fig. 4, the IE form is high in energy in the ground state. Fortunately, this state can be reached in an ESIPT process [55]. The previous works have shown that the hollow site is most likely, based on energy [63, 64], while the results for APO showed the top site to be better than the bridge and hollow sites [62]. Due to the similarity of AMTMH with APO, the top site was chosen for the titled compound.

The transmission spectra at zero-bias on Au (111) electrode with the top site verified the significant difference between the enol and the keto forms (Fig. 10). According to the Landauer–Büttiker formula, only electrons for which the energy is near the Fermi energy play a role in the current. Fig. 10 shows that the transmission coefficient of the keto form (AK) is lower than the enol form (IE).

The I-V characteristics for both enol and keto forms of AMTMH, AK and IE forms, with three different electrodes (Pt, Au, and Ag), are shown in Fig. 11a-c. As this figure shows, the current for the IE is higher than that for the AK using Pt and Au electrodes, while in the case of using the Ag electrode, both tautomers show the same behaviour. Upon replacing IE with AK, the conductivity changes from *on* to *off* state. Fig. 11d also indicates that the highest conductivity occurs in the IE with the Pt electrode at about 0.8 V. In the Pt electrode, by increasing the voltage, the current ratio initially increases and then decreases, whereas, in the Au electrode, the current ratio solely decreases.

5. Conclusion

5-amino-2,2,6,6-tetramethyl-4-hepten-3-one (AMTMH) was synthesized and characterized theoretically and experimentally. The results demonstrated that the keto-enamine tautomer is more stable than the imino-enol and keto-imine tautomers. The keto-enamine tautomer exists as four conformers, AK1-4 at B3LYP/6-311++G(d,p). While according to calculated results at MP2/6-311++G(d,p), the AK4 is unstable. All theoretical results (AIM and NBO) and experimental results suggest that the hydrogen bond strength in 3-MeAPO is stronger than that in AMTMH. The following trend for hydrogen bond strength is concluded: 3-MeAPO >AMTMH > APO. The stronger hydrogen bond in 3-MeAPO and AMTMH is caused by pushing the O and NH_2 groups towards each other by the terminal methyl groups (see Figs. 2a and 2b). Furthermore, by considering the intensity and wavenumbers of the vibrational band frequencies theoretically and experimentally, the presence of more than one conformer in the sample was concluded which is in agreement with the reported X-ray results. The transport results showed that the IK form's current is higher than that of the AK form. Comparing TD-DFT calculations with the experimental fluorescence results show that both aminoketone and iminoenol forms are possible in the excited state.

Acknowledgments

The authors are grateful to the Ferdowsi University of Mashhad for financial support.

The authors wish to thank Eva Marie Karlsen (Roskilde University) for scanning of IR and UV spectra of the AMTMH molecule.

Supplementary Information

Additional supporting information can be found in Tables S1-3 and Figures S1-8 in supplementary materials.

Author contributions

Mahmoud Bazrafshan: Methodology, Formal analysis and investigation, writing the original draft

Dr. Mohammad Vakili: Conceptualization, Supervision, Writing-review and editing

Prof. Sayyed Faramarz Tayyari*: Supervision, Writing-review, and editing

Dr. Fadhil S. Kamounah: preparation, Writing-review, and editing

Prof. Poul Erik Hansen, Writing-review and editing

Prof. Mohammad Reza Housaindokht, Writing-review, and editing

Funding

The authors did not receive support from any organization for the submitted work.

Declarations

Consent to participate

All authors agreed to participate in this research.

Competing interests

The authors declare that they have no conflict of interest.

References

[1] G. Türkoğlu, H. Berber, H. Dal, C. Öğretir, Synthesis, characterization, tautomerism and theoretical study of some new Schiff base derivatives, Spectrochim Acta. A 79 (2011) 1573-1583. https://doi.org/10.1016/j.saa.2011.04.089

[2] S. F. Tayyari, H. Raissi, F. Tayyari, Vibrational assignment of 4-amino-3-penten-2-one, Spectrochim Acta. A 58 (2002) 1681-1695. https://doi.org/10.1016/S1386-1425(01)00620-5

[3] V. Darugar, M. Vakili, S. F. Tayyari, P. E. Hansen, F. S. Kamounah, Molecular structure, intramolecular hydrogen bond strength, vibrational assignment, and spectroscopic insight of 4-phenylamino-3-penten-2-one and its derivatives: A theoretical and experimental study, Journal of Molecular Liquids 334 (2021) 116035. https://doi.org/10.1016/j.molliq.2021.116035

[4] H. Eshghi, S. M. Seyedi, E. Safaei, M. Vakili, A. Farhadipour, M. Bayat-Mokhtari, Silica supported $Fe(HSO_4)_3$ as an efficient, heterogeneous and recyclable catalyst for synthesis of β-enaminones and β-enamino esters, J. Mol. Catal. A Chem. 363 (2012) 430-436. https://doi.org/10.1016/j.molcata.2012.07.021

[5] P. E. Hansen, M. Vakili, F. S. Kamounah and J. Spanget-Larsen, NH Stretching Frequencies of Intramolecularly Hydrogen-Bonded Systems: An Experimental and Theoretical Study, Molecules 2021, 26, 7651. https://doi.org/10.3390/molecules26247651

[6] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, Intermolecular N–H···O hydrogen bonds assisted by resonance. Heteroconjugated systems as hydrogen bond strengthening functional groups, Acta. Crystallogr. B 51 (1995) 1004-1015. https://doi.org/10.1107/S0108768195004009

[7] G. A. Jeffrey, W. Saenger, Hydrogen bonding in biological structures, Springer Science & Business Media, 2012.

[8] H. El-Boraey, Structural and thermal studies of some aroylhydrazone Schiff's bases-transition metal complexes, J. Therm. Anal. Calorim. 81 (2005) 339-346. https://doi.org/10.1007/s10973-005-0789-0

[9] M. Kalita, T. Bhattacharjee, P. Gogoi, P. Barman, R. D. Kalita, B. Sarma, S. Karmakar, Synthesis, characterization, crystal structure and bioactivities of a new potential tridentate (ONS) Schiff base ligand n-[2-(benzylthio) phenyl] salicylaldimine and its Ni (II), Cu (II) and Co (II) complexes, Polyhedron. 60 (2013) 47-53. https://doi.org/10.1016/j.poly.2013.04.062

[10] M. S. Refat, M. Y. El-Sayed, A. M. A. Adam, Cu (II), Co (II) and Ni (II) complexes of new Schiff base ligand: Synthesis, thermal and spectroscopic characterizations, J. Mol. Struct.1038 (2013) 62-72. https://doi.org/10.1016/j.molstruc.2013.01.059

[11] N. Raman, V. Muthuraj, S. Ravichandran, A. Kulandaisamy, Synthesis, characterisation and electrochemical behaviour of Cu (II), Co (II), Ni (II) and Zn (II) complexes derived from acetylacetone and p-anisidine and their antimicrobial activity, J. Chem. Sci. 115 (2003) 161-167. https://doi.org/10.1007/BF02704255

[12] V. Kuz'min, A. Artemenko, R. Lozytska, A. Fedtchouk, V. Lozitsky, E. Muratov, A. Mescheriakov, Investigation of anticancer activity of macrocyclic Schiff bases by means of 4D-QSAR

based on simplex representation of molecular structure, SAR QSAR Environ. Res. 16 (2005) 219-230. https://doi.org/10.1080/10659360500037206

[13] P. Alivisatos, P. F. Barbara, A. W. Castleman, J. Chang, D. A. Dixon, M. L. Klein, G. L. McLendon, J. S. Miller, M. A. Ratner, P. J. Rossky, From molecules to materials: Current trends and future directions, Adv. Mater., 10 (1998) 1297-1336. https://doi.org/10.1002/(SICI)1521-4095(199811)10:16<1297::AID-ADMA1297>3.0.CO;2-7

[14] L. Dalton, Nonlinear optical polymeric materials: From chromophore design to commercial applications, Polymers for photonics applications, Springer, 2002, pp. 1-86. https://doi.org/10.1007/3-540-44608-7_1

[15] M. Vakili, S. Tayyari, A. Kanaani, A.-R. Nekoei, S. Salemi, H. Miremad, A. Berenji, R. Sammelson, Conformational stability, molecular structure, intramolecular hydrogen bonding, and vibrational spectra of 5, 5-dimethylhexane-2, 4-dione, J. Mol. Struct. 998 (2011) 99-109. https://doi.org/10.1016/j.molstruc.2011.04.045

[16] M. Vakili, A.-R. Nekoei, S. Tayyari, A. Kanaani, N. Sanati, Conformation, molecular structure, and intramolecular hydrogen bonding of 1, 1, 1-trifluoro-5, 5-dimethyl-2, 4-hexanedione, J. Mol. Struct. 1021 (2012) 102-111. https://doi.org/10.1016/j.molstruc.2012.04.009

[17] B. Koşar, Ç. Albayrak, C. C. Ersanlı, M. Odabaşoğlu, O. Büyükgüngör, Molecular structure, spectroscopic investigations, second-order nonlinear optical properties and intramolecular proton transfer of (e)-5-(diethylamino)-2-[(4-propylphenylimino) methyl] phenol: A combined experimental and theoretical study, Spectrochim Acta. A 93 (2012) 1-9. https://doi.org/10.1016/j.saa.2012.03.004

[18] S. F. Tayyari, M. Fazli, F. Milani-Nejad, Molecular conformation and intramolecular hydrogen bonding in 4-amino-3-penten-2-one, J. Mol. Struct. 541 (2001) 11-15. https://doi.org/10.1016/S0166-1280(00)00641-2

[19] S. Seyedkatouli, M. Vakili, S. F. Tayyari, P. E. Hansen, F. S. Kamounah, Molecular structure and intramolecular hydrogen bond strength of 3-methyl-4-amino-3-penten-2-one and its N-me and N-ph substitutions by experimental and theoretical methods, J. Mol. Struct. 1184 (2019) 233-245. https://doi.org/10.1016/j.molstruc.2019.02.007

[20] P. Stabnikov, G. Zharkova, I. Baidina, S. Tkachev, V. Krisyuk, I. K. Igumenov, Synthesis and properties of a new ketoiminate derivative of the 2, 2, 6, 6-tetramethylheptane-3, 5-dionate ligand

to prepare volatile CVD precursors, Polyhedron. 26 (2007) 4445-4450. https://doi.org/10.1016/j.poly.2007.05.046

[21] P. A. Stabnikov, S. I.Dorovskikh, N. V. Pervukhina, , L. G. Bulusheva, G. V. Romanenko, Crystal and molecular structures of bis (2, 2, 6, 6-tetramethyl-3-methylaminoheptan-5-onate) copper (II) and nickel (II), Journal of Structural Chemistry, *55*(3), (2014) 488-492. https://doi.org/10.1134/S0022476614030147

[22] K. Dietrich, K. Konig, G. Mattern, H. Musso, Organische Metallkomplexe, XX. Strukturen der Quecksilber (II)-Verbindungen von Stickstoff- und Schwefel-Analoga des 2,2,6,6-Tetramethyl-3,5-heptandions, Chem. Ber. 121 (7) (1988) 1277-1283. https://doi.org/10.1002/cber.19881210711

[23] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvatti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785. https://doi.org/10.1103/PhysRevB.37.785

[24] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Results obtained with the correlation energy density functionals of Becke, Lee, Yang and Parr, Chem. Phys. Lett. 157 (1989) 200-206. https://doi.org/10.1016/0009-2614(89)87234-3

[25] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Gaussian, Inc., Wallingford CT, 2009.

[26] R. D. Dennington, T. A. Keith, J. M. Millam, GaussView 5.0.8, Gaussian Inc., 2008.

[27] R. F. Bader, Atoms in molecules, Wiley Online Library, 1990.

[28] F. Biegler-König, J. Schönbohm, Update of the AIM2000 program for atoms in molecules. J. comp. chem., 23(15), (2002) 1489-1494.

[29] A. E. Reed, L. A. Curtiss, F. Weinhold, Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint, Chem. Rev. 88 (1988) 899-926. https://doi.org/10.1021/cr00088a005

[30] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, NBO 5.0., 2001.

[31] M. J. Frisch, M. Head-Gordon, J. A. Pople, A direct MP2 gradient method, Chem. Phys. Lett. 166 (1990) 275. https://doi.org/10.1016/0009-2614(90)80029-D

[32] C. Muller, M. S. Plesset, Note on an Approximation Treatment for Many-Electron System, Phys. Rev. 46 (1934) 618–622. https://doi.org/10.1103/PhysRev.46.618

[33] N. Version, 3.Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold; b) A. E. Reed, L. A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.

[34] S. Miertuš, E. Scrocco, J. Tomasi, Electrostatic interaction of a solute with a continuum. A direct utilization of ab initio molecular potentials for the prevision of solvent effects, Chem. Phys. 55 (1981) 117-129. https://doi.org/10.1016/0301-0104(81)85090-2

[35] N.M. O′boyle, A.L. Tenderholt, K.M. Langner, J. Comput. Chem. 29(5), (2008) 839–845.

[36] K. Wolinski, J. F. Hinton, P. Pulay, Efficient implementation of the gauge-independent atomic orbital method for NMR chemical shift calculations, J. Am. Chem. Soc. 112 (1990) 8251-8260. https://doi.org/10.1021/ja00179a005

[37] K. Woliński, A. J. Sadlej, Self-consistent perturbation theory: Open-shell states in perturbation-dependent non-orthogonal basis sets this work was partly supported by the institute of low temperatures and structure research of the polish academy of sciences under contract no. MR-I. 9.4. 3/2, Mol. Phys. 41 (1980) 1419-1430. https://doi.org/10.1080/00268978000103631

[38] M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, K. Stokbro, Density-functional method for nonequilibrium electron transport, Phys. Rev. B 65 (2002) 165401-165419. https://doi.org/10.1103/PhysRevB.65.165401

[39] Y. Cao, Q. Ge, D.J. Dyer, L. Wang, Steric effects on the adsorption of alkylthiolate self-assembled monolayers on au (111), J. Phys. Chem. B 107 (2003) 3803-3807. https://doi.org/10.1021/jp021989+

[40] H. Kondo, J. Nara, H. Kino, T. Ohno, Transport properties of a biphenyl-based molecular junction system—the electrode metal dependence, J. Phys. Condens. Matter 21 (2009) 064220. https://doi.org/10.1088/0953-8984/21/6/064220

[41] W. Geng, J. Nara, T. Ohno, Adsorption of benzene thiolate on the (111) surface of m (m= Pt, Ag, Cu) and the conductance of m/benzene dithiolate/m molecular junctions: A first-principles study, Thin Solid Films 464 (2004) 379-383. https://doi.org/10.1016/j.tsf.2004.06.083

[42] J.A. Rodriguez, J. Hrbek, M. Kuhn, T. Jirsak, S. Chaturvedi, A. Maiti, Interaction of sulfur with pt (111) and sn/pt (111): Effects of coverage and metal-metal bonding on reactivity toward sulfur, J. Chem. Phys. 113 (2000) 11284-11292. https://doi.org/10.1063/1.1327249

[43] B. Martorell, A. Clotet, J. Fraxedas, A first principle study of the structural, vibrational and electronic properties of tetrathiafulvalene adsorbed on ag (110) and au (110) surfaces, J. Comput. Chem. 31 (2010) 1842-1852. https://doi.org/10.1002/jcc.21465

[44] H. Sellers, A. Ulman, Y. Shnidman, J.E. Eilers, Structure and binding of alkanethiolates on gold and silver surfaces: Implications for self-assembled monolayers, J. Am. Chem. Soc. 115 (1993) 9389-9401. https://doi.org/10.1021/ja00074a004

[45] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865-3868

[46] A. D. Khalaji, G. Grivani, M. Seyyedi, K. Fejfarova, M. Dusek, Zinc (II) and Mercury (II) complexes [Zn ((2, 6-Cl-ba) 2 en) 12] and [Hg ((2, 6-Cl-ba) 2en) Br2] with the bidentate Schiff base ligand (2, 6-cl-ba) 2 en: Synthesis, characterization and crystal structures, Polyhedron. 49 (2013) 19-23. https://doi.org/10.1016/j.poly.2012.09.054

[47] M. Morshedi, M. Amirnasr, A. M. Slawin, J. D. Woollins, A. D. Khalaji, Synthesis and coordination chemistry of new tetradentate N2S2 donor Schiff-base ligand ca(2)-dapte: Mononuclear and dinuclear Copper (I) complexes [Cu(ca(2)-dapte)] ClO4 and [{Cu (PPh 3)(x)}2 ca(2)-dapte)](x= I and Br), Polyhedron. 28 (2009) 167-171. https://doi.org/10.1016/j.poly.2008.10.018

[48] M. Morshedi, M. Amirnasr, S. Triki, A. D. Khalaji, New (NS) 2 Schiff base with a flexible spacer: Synthesis and structural characterization of its first coordination polymer $[Cu_2$ (μ-i$)_2$ (μ-(thio$)_2$dapte$)]_n$ (1), Inorg. Chim. Acta 362 (2009) 1637-1640. https://doi.org/10.1016/j.ica.2008.07.002

[49] M. Vakili, S.F. Tayyari, A.-R. Nekoei, H. Miremad, S. Salemi, R.E. Sammelson, Structure, intramolecular hydrogen bonding, and vibrational spectra of 2,2,6,6-tetramethyl-3,5-heptanedione, J. Mol. Struct. 970 (2010) 160–170. https://doi.org/10.1016/j.molstruc.2010.02.072

[50] M. Vakili, S. F. Tayyari, R. Afzali, Conformation, molecular structure, and vibrational assignment of bis (2, 2, 6, 6-tetramethylheptane-3, 5-dionato) copper (II), Spectrochim. Acta A. 136 (2015) 1827-1833. https://doi.org/10.1016/j.saa.2014.10.092

[51] E. Espinosa, E. Molins, C. Lecomte, Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities, Chem. Phys. Lett. 285 (1998) 170-173. https://doi.org/10.1016/S0009-2614(98)00036-0

[52] H. Houjou, T. Motoyama, S. Banno, I. Yoshikawa and K. Araki, Experimental and Theoretical Studies on Constitutional Isomers of 2,6-Dihydroxynaphthalene Carbaldehydes. Effects of Resonance-Assisted Hydrogen Bonding on the Electronic Absorption Spectra, J. Org. Chem. (2009), 74, 520–529. https://doi.org/10.1021/jo802345f

[53] V.Lazić, M.Jurković, T.Jednačak, T.Hrenar, J. P.Vuković, P. Novak, Intra-and intermolecular hydrogen bonding in acetylacetone and benzoylacetone derived enaminone derivatives. Journal of Molecular Structure, (2015),1079, 243-249. https://doi.org/10.1016/j.molstruc.2014.09.048

[54] J. Weinstein, G. Wyman, A study of β-amino-α, β-unsaturated ketones1, J. Org. Chem. 23 (1958) 1618-1622. https://doi.org/10.1021/jo01105a009

[55] V., Latha, B., Annaraj, M. A. Neelakantan, ESIPT inspired dual fluorescent probe (Z)-3-((4-(4-aminobenzyl) phenyl) amino)-1, 3-diphenylprop-2-en-1-one: Experimental and DFT based approach to photophysical properties. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, (2014), 133, 44-53. https://doi.org/10.1016/j.saa.2014.04.192

[56] P. Politzer, M. C. Concha, and Jane S. Murray "Density functional study of dimers of dimethylnitramine." International Journal of Quantum Chemistry. (2000), 80(2) 184-192. https://doi.org/10.1002/1097-461X(2000)80:2<184::AID-QUA12>3.0.CO;2-O

[57] S.F. Tayyari, T. Bakhshi, S.J. Mahdizadeh, S. Mehrani, R.E. Sammelson, Structure and vibrational assignment of magnesium acetylacetonate: A density functional theoretical study, J. Mol. Struct. 938 (2009) 76-81. https://doi.org/10.1016/j.molstruc.2009.09.006

[58] Y. P. Singh, P. Rupani, A. Singh, A. K. Rai, R. C. Mehrotra, R. D. Rogers, J.L. Atwood, Synthesis and IR, UV, NMR (^{1}H and ^{11}B), and mass spectral studies of new. Beta.-ketoamine complexes of

boron: Crystal an molecular structure of $OC_6H_4OBOC(R)CHC(R')$ NR" (R= p-ClC_6H_4, R'= C6H5, R"= CH_3), Inorg. Chem. 25 (1986) 3076-3081 .https://doi.org/10.1021/ic00237a030

[59] M. M. Borah, T. G. Devi, Vibrational studies of thyroxine hormone: Comparative study with quantum chemical calculations, J. Mol. Struct. 1148 (2017) 293-313. https://doi.org/10.1016/j.molstruc.2017.07.063

[60] N. Colthup, Introduction to infrared and Raman spectroscopy, Elsevier, 2012.

[61] A. R. Berenji, S. F. Tayyari, M. Rahimizadeh, H. Eshghi, M. Vakili, A. Shiri, Structure and vibrational analysis of methyl 3-amino-2-butenoate, Spectrochim Acta. A 102 (2013) 350-357. https://doi.org/10.1016/j.saa.2012.10.042

[62] J. Gottschalck, B. Hammer, A density functional theory study of the adsorption of sulfur, mercapto, and methylthiolate on au (111), J. Chem. Phys. 116 (2002) 784-790. https://doi.org/10.1063/1.1424292

[63] A.C. Van Duin, A. Strachan, S. Stewman, Q. Zhang, X. Xu, W.A. Goddard, Reaxffsio reactive force field for silicon and silicon oxide systems, J. Phys. Chem. A 107 (2003) 3803-3811. https://doi.org/10.1021/jp0276303

[64] S. Seyedkatouli, M. Vakili, Current-voltage characteristics of β-ketoenamines molecular switches induced by intramolecular hydrogen transfer, Indian J. Phys. 93 (2019) 1527-1535. https://doi.org/10.1007/s12648-019-01420-y

Caption of the Figures:

Fig. 1. Tautomerization equilibrium in APO.

Fig. 2. a) The atom numbering (the numbering is non-IUPAC in order to facilitate a comparison between AMTMH, 3-MeAPO, APO) and stable aminoketone conformers of AMTMH, the values are the relative energies and the calculated percentages at B3LYP and MP2 levels with 6-311++G(d,p) basis set in parenthesis, the US is unstable, and b) stable aminoketone conformers of 3-MeAPO from Ref. [19].

Fig. 3. Topological map for the dimer of AMTMH.

Fig. 4. Relative energy profile of intramolecular proton transfer in gas phase (convert IE1 to AK3).

Fig. 5. The NMR spectrum of AMTMH in $CDCl_3$ a) ^{1}HNMR and b) ^{13}CNMR.

Fig. 6. The recorded infrared spectra of APO and AMTMH (in CCl_4 solution), and AMTMH in solid phase (in the 3550–2800 cm^{-1} range).

Fig. 7. The IR spectra of AMTMH in the solid phase (——) and in CCl_4 solution (⊠).

Fig. 8. The recorded Far-IR spectrum of the AMTMH in solid phase (in the 670–220 cm^{-1} range).

Fig. 9. The recorded Raman spectrum of AMTMH, in solid phase (in the 1700–150 cm^{-1} and 3450-3090 cm^{-1} ranges).

Fig. 10. The transmission spectra of the molecular switch at zero bias with Au electrode.

Fig. 11. The calculated I–V characteristics of AMTMH with top site: (a) Pt, (b) Au, (c) Ag, and (d) current switching ratio as a function of applied bias with different electrodes.

Supporting information

Fig. S1. HRMS-ESI spectrum of AMTMH.

Fig. S2. Schematic molecular junctions used in our calculations.

Fig. S3. The possible stable forms in IE and IK tautomers of AMTMH. US; unstable, the relative energies in kcal mol^{-1} were calculated at B3LYP/6-311++G(d,p) level.

Fig. S4. The correlations of theoretical structure versus its experimental X-ray for the averaged of AK1-AK4 upon calculated populations.

Fig. S5. a) UV absorption spectra of AMTMH and 3-MeAPO in ethanol solvent at a concentration of 2×10^{-3}M with a 10 mm quartz cell, b) Fluorescence spectrum of AMTMH in ethanol, c) The excited structure of AK2 form, d) The excited structure of IE3 form.

Fig. S6a-b. a) DOS plot of AMTMH b) DOS plot of APO.

Fig. S7. Molecular electrostatic potential (MEP) of AMTMH and APO.

Fig. S8. The recorded infrared spectra of APO (………) and AMTMH (———) in CCl_4 (in the 1700–900 cm^{-1} range).

Table S1. The **e**xperimental ^{13}C and ^{1}H chemical shifts (δ) and theoretical isotropic nuclear shielding (σ_{iso}) values for the stable aminoketone forms (AK1-4) of AMTMH.

Table S2. Theoretical and experimental absorption wavelength, λ_{max}(nm), and oscillator strengths (*f*) of AMTMH using TD-DFT at B3LYP/6-311++G(d,p).

Table S3. Total fundamental band assignment of AMTMH (frequencies in cm^{-1}).