Journal of Molecular Structure 1176 (2019) 825–837

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Physicochemical studies on proton transfer reaction between methyl [5-(propylthio)-1H-benzoimidazole-2-yl]carbamate (albendazole, ABZ) with 2,4,6- trinitrophenol (picric acid, PA) in chloroform

Reem M. Alghanmi [a], Maram T. Basha [a], Moustafa M. Habeeb [a, b, *], Ohoud H. Al-mohmady [a]

[a] Chemistry Department, Faculty of Science, University of Jeddah, P.O .Box 80327, Jeddah 21589, Saudi Arabia
[b] Department of Chemistry, Faculty of Education, Alexandria University, Alexandria, Egypt

ARTICLE INFO

Article history:
Received 22 June 2018
Received in revised form
23 August 2018
Accepted 25 August 2018
Available online 14 September 2018

Keywords:
Albendazole
Hydrogen bond
Proton transfer
Spectroscopy
DFT
TD-DFT

ABSTRACT

In this study, a new proton transfer complex between albendazole drug (ABZ), methyl [5-(propylthio)-1H-benzoimidazole-2-yl]carbamate and picric acid (PA) has been synthesized and characterized in chloroform and solid state by different physicochemical methods. In chloroform, the proton transfer complex exhibited an absorption maxima at 409 nm. In addition, the complex was formed in a 1:1 molecular composition. The formation constant, spectroscopic physical parameters and enthalpy of formation confirmed that, the formed complex has high stability. The solid-state complex was also found in a 1:1 stoichiometric ratio from elemental analysis and was isolated as yellow crystals. Changes in vibrational mode wavenumbers and chemical shifts in infrared and ^{1}H NMR spectra were found in comparison with the reactants, confirming the complex formation. Furthermore, TG/DTA analysis provided information about changes in material properties as a function of temperature. Density functional theory (DFT) at B3LYP/6-31G (d,p) level of the theory was employed to support the experimental results. The optimized structures of reactants and the new complex, their geometrical parameters, reactivity parameters, molecular electrostatic potential maps (MEP) and natural atomic charges from natural bond orbital (NBO) analysis were calculated. It has been concluded from the investigated computational analysis that the presence of many hydrogen bonds in the formed complex beside charge transfer interaction are certainly responsible for its high stability. Time-dependent functional theory (TD-DFT) at the same was applied to explain the origin of the recorded electronic transition in chloroform. A good consistency was found between experimental and theoretical results.

1. Introduction

Albendazole (ABZ; methyl [5-(propylthio)-1H-benzoimidazole-2-yl]carbamate) is a benzimidazole derivative with an oral broad spectrum of activity against human and animal helminthes parasites [1]. Also, it is used to dominate flukes in different animals, including cattle, sheep, goats, swine, camels, dogs, cats, elephants, and poultry. ABZ therapy is often applied to ruminant live stock [2].

The proton donor–proton acceptor interaction is one of the most important phenomena in the biological systems [3]. Donor–acceptor complexation and structural recognition are major elements to enzyme catalysis, drug action, and ion transfer through lipophilic membranes [4,5].

Proton transfer interactions are especially important in macromolecular and biological structures, such as proteins, and nucleic acids, where they are responsible for the structure of DNA molecules [6]. Recently, Zhao et al. confirmed that the hydrogen-bonding dynamics in electronically excited states play a leading role in various phenomena, such as photoinduced electron transfer and fluorescence [7–11].

Quantum chemistry techniques, such as density functional theory (DFT) provides an acceptable information about the relationship between structures and spectral properties of molecules [12,13]. Also, the time-dependent density functional theory (TD-DFT) can calculate the electronic absorption spectra of the PT complexes [14–16]. In recent years, significant advances in spectroscopic techniques and quantum chemistry calculations helped scientists in understanding the H-bonding dynamics of H-bonded complexes.

---

* Corresponding author. Chemistry Department, Faculty of Science, University of Jeddah, P.O .Box 80327, Jeddah 21589, Saudi Arabia.
E-mail address: mostafh2002@yahoo.com (M.M. Habeeb).

https://doi.org/10.1016/j.molstruc.2018.08.083
0022-2860/© 2018 Elsevier B.V. All rights reserved.

In the present work, the proton transfer complexation of ABZ, as the H-acceptor with picric acid (PA) as the H-donor in chloroform was investigated experimentally and theoretically. The electronic spectra were recorded. The determination of the reaction stoichiometry, formation constant (K_{PT}), molecular extinction coefficient (ε) and thermodynamic parameters were estimated and evaluated. Selected spectroscopic physical parameters, including oscillator strength (f), transition dipole moment (μ), ionization potential (I_D), and resonance energy (R_N) were also calculated and analyzed. ˋThe synthesis, spectroscopic characterization, and thermal degradation analysis of the solid [ABZ-PA] PT complex (Fig. 1) will be aimed in this work. DFT computations will be applied to implement the experimental results. Optimized structures, geometrical parameters, MEP maps, reactivity parameters, and natural atomic charges will be computed at the B3LYP/6-31G (d,p) level of the theory. Furthermore, the origin of the observed electronic spectra and the contributing molecular orbitals are presented and analyzed using TD-DFT at same level of the theory.

2. Experiment

Powdered ABZ (purity ≥ 98%) was obtained from Across Organics; picric acid (purity ≥ 98%) was obtained from Sigma-Aldrich, and spectroscopic grade chloroform was used. Standard stock solutions of ABZ (5×10^{-3}molL^{-1}) and PA (1×10^{-3}molL^{-1}) were immediately prepared before each series of measurements by dissolving appropriate amount in 50 mL of chloroform. All solutions were stored in dark place for at least one week. The electronic absorption spectra of the ABZ, PA, and the formed PT complex were measured over the wavelength range of 300–600 nm using a Shimadzu UV-1800 spectrometer (Japan) connected to a Shimadzu TCC-ZUOA temperature controller unit. The infrared spectra (KBr disks) in the range of 4000 to 400 cm^{-1} for the solid PT complex was recorded on Perkin-Elmer model Frontier FT spectrometer (USA). ^{1}H NMR (600 MHz) spectra were recorded on a Bruker DPX spectrometer using 10 mg of the sample in DMSO-d6 and TMS as an internal standard. The elemental analysis (CHN)was carried out using a Perkin-Elmer 2400 micro Analyzer (USA). Thermogravimetric analysis (TGA) and differential thermogravimetricanalysis (DTG) were carried out on a Perkin-Elmer Pyris 6 TGA (USA) computerized thermal analysis system.

The solid [ABZ–PA] PT complex was synthesized by adding ABZ, (0.2 mmol–10 mL– chloroform solution) to PA (0.2 mmol–10 mL–chloroform solution). The mixed solution was allowed to evaporate at room temperature and the formed yellow crystals were collected, washed well with chloroform and dried over anhydrous calcium chloride in a desiccator. Analytical calculations for the [ABZ-PA]complex: molecular formula: $C_{18}H_{18}N_6O_9S$ (M/w: 494.43 g/mol), C, 43.48%; H, 3.64%; N, 16.98%. Found: C, 43.48%; H, 3.28%; N, 16.52%. MP: 201 °C.

3. Quantum chemical calculations

All DFT calculations were performed using the Gaussian 09 program [17]. Geometry optimization was carried out using DFT with Becke's three parameter exchange functional [18], the Lee–Yang–Parr correlation functional (B3LYP) and the split-valence double zeta basis set enlarged with two polarized basis functions (d and p) (6-31G (d,p)) [19]. The d-type orbital was added to all atoms except the hydrogen atom while the p-type orbital was added to all hydrogen atoms. The addition of these polarization functions was very important for improving the representation of the electron density of the molecule. During geometry optimizations, every bond length, bond angle and dihedral angle were allowed to relax free of constraints. TD-DFT calculations were carried out at the same level of theory (B3LYP/6-31G (d,p)), using the default polarizable continuum model for chloroform as absolvent to explain the origin of the observed electronic spectra for the produced complex. GaussView 5.1 and Chemcraft programs have been used to extract the calculation results, and visualize the optimized structures, the frontier molecular orbitals (FMOs) and molecular electrostatic potential (MEP) maps.

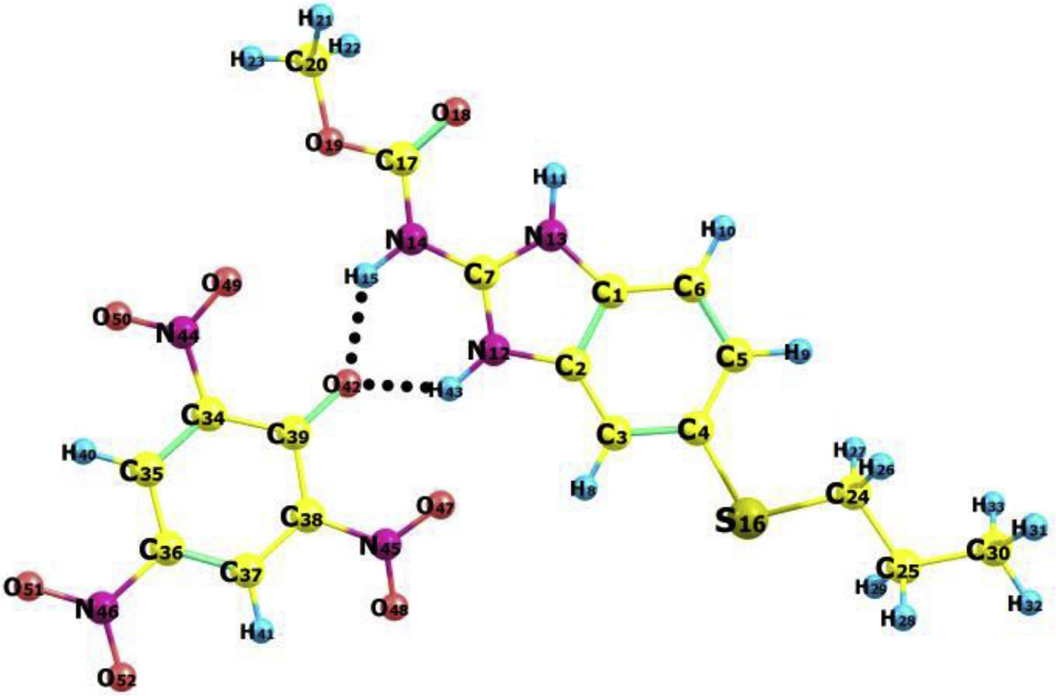

Fig. 1. Molecular structures of the ABZ-AP complex including atom labeling, numbering and hydrogen bonds in chloroform.