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## Structural, thermal, morphological and biological studies of proton-transfer complexes formed from 4-aminoantipyrine with quinol and picric acid

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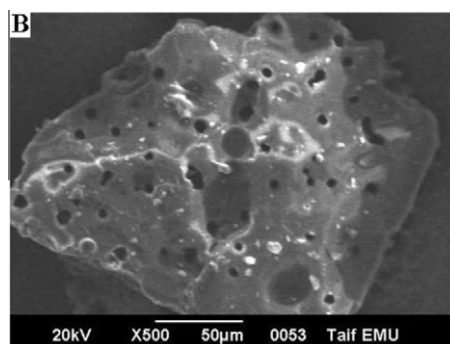
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## HIGHLIGHTS

- ▶ Two new CT complexes of 4-aminoantipyrine with QL and PA are obtained.
- ▶ Various spectroscopic and thermal analysis are used.
- ▶ The complex obtained with PA has a remarkable morphology and good thermal stability.

## GRAPHICAL ABSTRACT

Sponge-like morphology of [(4AAP)(PA)] complex.



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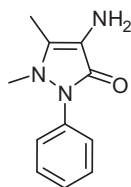
## ABSTRACT

4-Aminoantipyrine (4AAP) is widely used in the pharmaceutical industry, biochemical experiments and environmental monitoring. However, residual amounts of 4AAP in the environment may pose a threat to human health. To provide basic data that can be used to extract or eliminate 4AAP from the environment, the proton-transfer complexes of 4AAP with quinol (QL) and picric acid (PA) were synthesized and spectroscopically investigated. The interactions afforded two new proton-transfer salts named 1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-aminium-4-hydroxyphenolate and 1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-aminium-2,4,6-trinitrophenolate for QL and PA, respectively, via a 1:1 stoichiometry. Elemental analysis (CHN), electronic absorption, spectrophotometric titration, IR, Raman,  $^1\text{H}$  NMR and X-ray diffraction were used to characterize the new products. The thermal stability of the synthesized CT complexes was investigated using thermogravimetric (TG) analyses, and the morphology and particle size of these complexes were obtained from scanning electron microscopy (SEM). It was found that PA and 4AAP immediately formed a yellow precipitate with a remarkable sponge-like morphology and good thermal stability up to 180 °C. Finally, the biological activities of the newly synthesized CT complexes were tested for their antibacterial and antifungal activities. The results indicated that the [(4AAP)(QL)] complex exhibited strong antimicrobial activities against various bacterial and fungal strains compared with standard drugs.

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**Formula 1.** Molecular structure of 4-aminoantipyrine.

## Introduction

4-Aminoantipyrine (4AAP, **Formula 1**) is a metabolite of aminophenazone and is an aromatic substance with analgesic, antipyretic, antiphlogistic and anti-inflammatory properties [1–6]. Although today 4AAP is scarcely ever administered as an analgesic drug because of its side effects, it is still used as a precursor of 4AAP derivatives, which have better biological activities [7,8]. In addition, the compound is used as a reagent for biochemical reactions that produce peroxides or phenols [9,10] and can also be used to detect phenols in the environment [11]. Because 4AAP is widely used in pharmacological [12], clinical [13], biological, biochemical [14] and analytical applications [15], as well as in environmental monitoring, 4AAP has become an environmental pollutant [16]. The toxic effect of 4AAP on animals has been reported experimentally [17]. 4AAP can reduce blood flow [18] and form stable complexes with heme [19]; moreover, it has an obvious denaturing effect on bovine hemoglobin [20]. In recent years, 4AAP transition metal complexes and their derivatives have been extensively examined due to their wide biological, analytical and therapeutic applications. Furthermore, they have been investigated due to their diverse biological properties as antifungal, antibacterial, analgesic, sedative, antipyretic, anti-inflammatory and DNA-binding agents [21–24].

This paper aims to investigate the 4AAP charge-transfer complexes, which are readily prepared from the reaction of 4AAP with quinol (benzene-1,4-diol, QL) and picric acid (2,4,6-trinitrophenol, PA). The synthesized CT complexes were structurally characterized using elemental analysis; infrared (IR), Raman,  $^1\text{H}$  NMR and electronic absorption spectroscopy; powder X-ray diffraction; and scanning electron microscopy (SEM). The thermal behavior of the obtained complexes and the kinetic and thermodynamic parameters ( $E^*$ ,  $A$ ,  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$ ) were also investigated. Finally, the antimicrobial activity of the 4AAP complexes was determined against various bacterial and fungal strains.

## Experimental

### Reagents

4-Aminoantipyrine (4AAP) ( $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}$ ) was obtained from Sigma–Aldrich Chemical Company, USA, with a stated purity of greater than 99% and was used without further purification. Quinol (benzene-1,4-diol, QL) and picric acid (2,4,6-trinitrophenol, PA) were purchased from Merck Chemical Co. and were also used as received.

### Synthetic procedure

The solid CT complexes of 4AAP with QL or PA were synthesized by mixing 1 mmol 4AAP with 1 mmol of each acceptor in methanol (10 ml). The mixtures were stirred at room temperature for 10 min, which resulted in the precipitation of the products. In the 4AAP/QL system, upon addition of QL to a solution of 4AAP, the color of the solution changed from light yellow to red to reddish-brown. A dark

reddish-brown precipitate was filtered off, washed several times with methanol and then dried under vacuum over anhydrous calcium chloride. In the case of the 4AAP/PA complex, upon addition of PA to 4AAP dissolved in methanol, a yellow precipitate formed immediately.

### Spectrophotometric titration measurements

Spectrophotometric titration measurements were performed for the reactions of 4AAP with QL or PA against methanol as a blank at wavelengths of 286 and 281 nm, respectively. A 0.25, 0.50, 0.75, 1.00, 1.50, 2.0, 2.50, 3.00, 3.50 or 4.00 ml aliquot of a standard solution ( $5.0 \times 10^{-4}$  M) of the appropriate acceptor in MeOH was added to 1.00 ml of  $5.0 \times 10^{-4}$  M 4AAP, which was also dissolved in MeOH. The total volume of the mixture was 5 ml. The concentration of 4AAP ( $C_d$ ) in the reaction mixture was maintained at  $5.0 \times 10^{-4}$  M, whereas the concentration of the acceptors ( $C_a$ ) changed over a wide range of concentrations ( $0.25 \times 10^{-4}$  M to  $4.00 \times 10^{-4}$  M) to produce solutions with an acceptor molar ratio that varied from 4:1 to 1:4. The stoichiometry of the molecular CT complexes was obtained from the determination of the conventional spectrophotometric molar ratio according to known methods [25] using a plot of the absorbance of each CT complex as a function of the  $C_d:C_a$  ratio. Modified Benesi–Hildebrand plots were constructed [26,27] to allow the calculation of the formation constant,  $K_{CT}$ , and the absorptivity,  $\epsilon_{CT}$ , values for each CT complex in this study.

### Instrumental analyses

#### Elemental analyses

The elemental analyses of the carbon, hydrogen and nitrogen contents were performed by the microanalysis facility at Cairo University, Egypt, using a Perkin–Elmer CHN 2400 (USA).

#### Electronic spectra

The electronic absorption spectra of methanolic solutions of the donor, acceptors and resulting CT complexes were recorded over a wavelength range of 200–800 nm using a Perkin–Elmer Lambda 25 UV/Vis double-beam spectrophotometer at Taif University, Saudi Arabia. The instrument was equipped with a quartz cell with a 1.0 cm path length.

#### Infrared and Raman spectra

The mid-infrared (IR) spectra (KBr discs) within the range of  $4000\text{--}400\text{ cm}^{-1}$  for the solid CT complexes were recorded on a Shimadzu FT-IR spectrophotometer with 30 scans at  $2\text{ cm}^{-1}$  resolution. The Raman laser spectra of the samples were measured on a Bruker FT-Raman spectrophotometer equipped with a 50 mW laser at Taif University, Saudi Arabia.

#### $^1\text{H}$ NMR spectra

$^1\text{H}$  NMR spectra were collected by the Analytical Center at King Abdul Aziz University, Saudi Arabia, on a Bruker DRX-250 spectrometer operating at 250.13 MHz with a dual 5 mm probe head. The measurements were performed at ambient temperature using DMSO- $d_6$  (dimethylsulfoxide,  $d_6$ ) as a solvent and TMS (tetramethylsilane) as an internal reference. The  $^1\text{H}$  NMR data are expressed in parts per million (ppm) and are internally referenced to the residual proton impurity in the DMSO solvent.

#### Thermal analysis

Thermogravimetric analysis (TGA) was performed under an air atmosphere between room temperature and  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  using a Shimadzu TGA-50H thermal analyzer at the Central Lab at Ain Shams University, Egypt.

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