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Spectral and solvation effect studies on charge transfer complex of 2, 6-diaminopyridine with chloranilic acid

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ABSTRACT

Charge transfer complex formation between 2,6-diaminopyridine (2,6-DAP) as the electron donor, proton acceptor, with chloranilic acid (CLA) as the π-electron acceptor, proton donor, has been investigated spectrophotometrically in ethanol (EtOH), acetonitrile (AN) and binary mixture composed of 50% ethanol + 50% acetonitrile (v/v), (ANET). The stoichiometry of the complex has been identified by Job's, photometric and conductometric titration methods to be 1:1. Benesi–Hildebrand equation has been applied to estimate the formation constant (K_{CT}) and molecular extinction coefficient (ε), they recorded high values confirming high stability of the produced complex. Oscillator strength (f), transition dipole moment (μ), ionization potential (I_P) and dissociation energy (W) of the formed CT-complex were also determined and evaluated, they showed solvent dependency. Based on the simple composition and fast production of the CT-complex in solution, a rapid, simple and accurate spectrophotometric method for donor determination is suggested. The solid CT-complex between 2,6-DAP and CLA has been isolated and characterized using elemental analysis, FTIR and ^{1}H NMR measurements, it has been found that its molecular composition is 3:2 (electron donor: electron acceptor). Also, molecular modeling utilizing MM2 method including in ChemBio3D Ultra 12.0 software confirmed this molecular composition. Moreover, the present work showed the existence of proton transfer beside charge transfer in the obtained complex.

1. Introduction

Studies of charge-transfer (CT) interaction between benzoquinones electron acceptors and various electron donors have been reported over the last years [1–6]. CT-complexes are being regarded as important materials for use as organic superconductors [7], they play an important role in biological systems where they act as intermediates in a wide variety of biological reactions [8,9].

Aminopyridines constitute important groups of electron donors or proton acceptors, they have various medical and pharmacological applications in addition to their use in analytical chemistry [10,11]. In particular 2, 6-DAP exhibits many applications where it is used in a hair dye and energetic compound productions [12]. It is also used as a medium production-volume chemical, which is used in many pharmaceutical applications [13]. In recent years, synthesis and spectrophotometric studies of proton and electron transfer complexes of 2, 6-DAP with different electron acceptors have been reported due to their interesting properties [14–18].

In connection with our interest in studying charge transfer and proton transfer complexes and due to the importance and biological applications of diaminopyridines, we wish to report in the present article our findings about the electronic absorption spectra of the CT-complex formation between 2, 6-diaminopyridine and chloranilic acid in different polar solvents including ethanol, acetonitrile and binary mixture of ethanol and acetonitrile in 1:1 ratio (v/v). The aim of the present article is to determine the reaction stiochiometry, formation constants (K_{CT}), molecular extinction coefficient (ε), oscillator strength (*f*), transition dipole moment (μ), dissociation energy (W) and ionization potential of the formed CT-complex. Furthermore, the development and validation of a spectroscopic analytical method for 2,6-DAP determination is an important target of this work. Moreover, the isolation and characterization of the solid CT-complex between 2, 6-DAP and CLA is aimed.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical grade. 2, 6-diaminopyridine was supplied by Acros organics, chloranilic acid was supplied by Aldrich. Acetonitrile was purchased from PAL-ACS (UV-IR-HPLC isocratic) and ethanol was purchased from Panreac.

2.2. Physical measurements

The electronic absorption spectra were recorded in the region (700 to 250) nm using double beams ultraviolet–visible spectrophotometer

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(Shimadzu UV-160, Japan) with matched 1-cm quartz cells and personal spectroscopy software version 3.7, connected to Shimadzu TCC-ZUOA temperature controller unit (Japan). For conductometric titrations a 25 mL aliquot of a 5×10^{-4} M of 2,6-DAP solution in the different solvents was transferred to the conductivity cell (cell constant $K=0.96\ cm^{-1}$) and titrated with 5×10^{-3} M CLA solution at 25 ± 1.0 °C. The conductance value was recorded after each addition (2 min intervals) and plotted versus the volume of chloranilic acid. The infrared spectra were recorded as KBr disks on Bruker FTIR Tensor 37 Fourier transform infrared spectrophotometer (USA), evacuated to avoid water and CO_2 absorption. ^1H NMR (600 MHz) spectra were measured on a Bruker DPX spectrometer using DMSO-d_6 as solvent and TMS as an internal standard; chemical shifts are expressed as δ ppm. C, H and N contents were determined with the micro analyzer Perkin Elmer 2400 (USA).

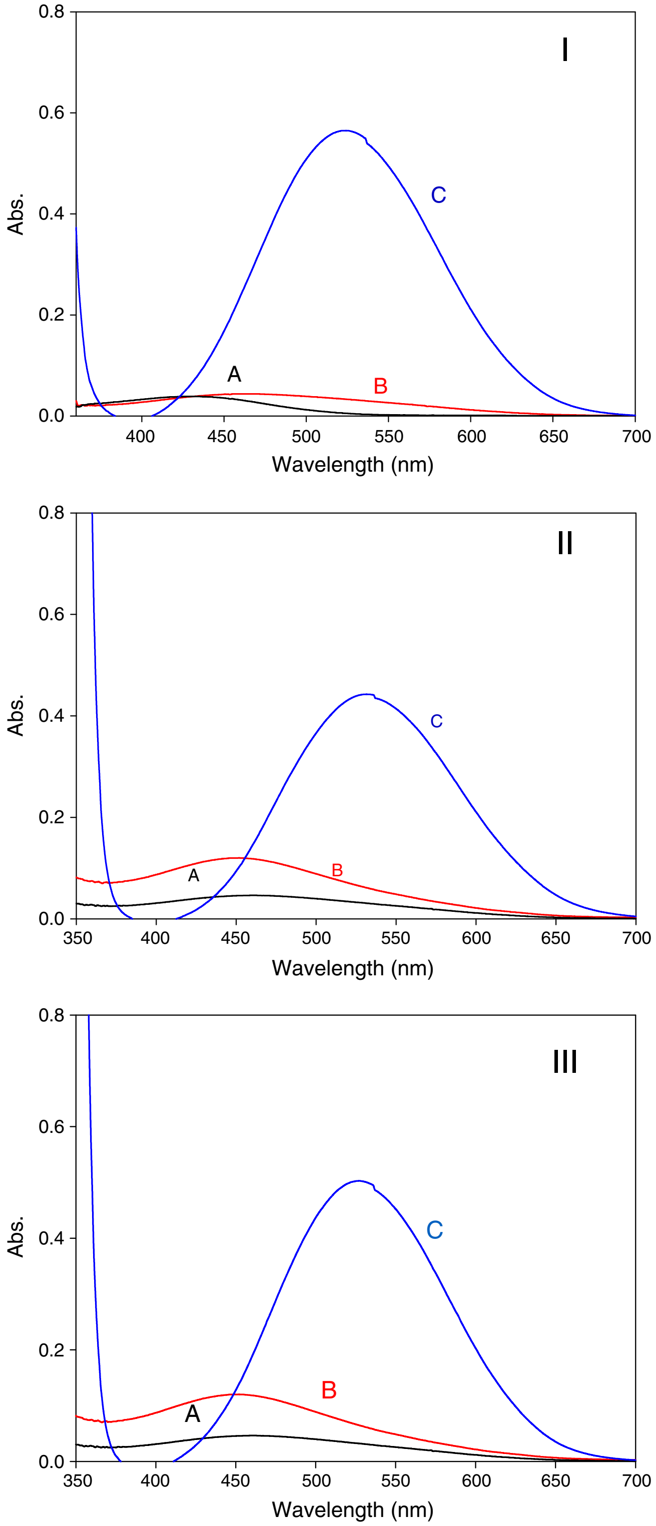


Fig. 1. Electronic spectra: (*A*) 5×10^{-4} mol·L^{-1} (2,6-DAP), (*B*) 5×10^{-4} mol·L^{-1} (CLA) and (*C*) [5×10^{-4} mol·L^{-1} (2,6-DAP) + 5×10^{-4} mol·L^{-1} (CLA)] in (I) AN, (II) EtOH and (III) ANET.

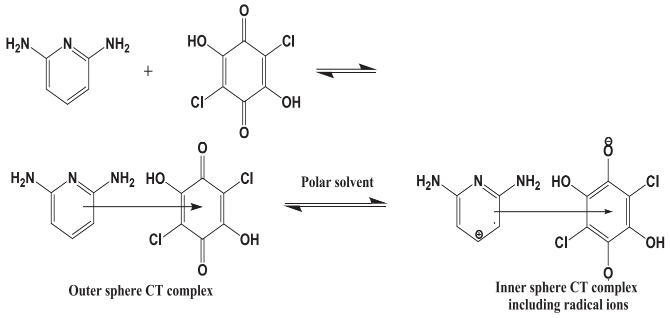
2.3. Synthesis of the solid CT-complex

The solid CT-complex between 2,6-DAP and CLA was prepared by mixing equimolar amounts of 2,6-DAP and CLA in acetonitrile. The resulting complex solution was allowed to evaporate slowly at room temperature where the complex was isolated as dark pink crystals. The isolated complex was filtered, washed well with acetonitrile and dried over calcium chloride for 24 h. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets protected with silica gel (Merck, Kieselgel 60F-254).Visualization was accomplished by UV light. Both the analytical and spectroscopic data confirmed ≥95% purity of the prepared compound. Anal. Calc. for [(2,6-DAP)$_3$(CLA)$_2$] $C_{27}H_{25}N_9Cl_4O_8$ Complex: C, 43.48%; H, 3.36%; N, 16.91%. Found: C, 43.28%; H, 3.62%; N, 16.98%. MP > 380 ^{O}C.

3. Results and discussion

3.1. Electronic spectra

Fig. 1 shows the electronic absorption spectra of the charge transfer complex of 2, 6-DAP with CLA in AN, EtOH and ANET solutions, respectively. Although neither of the reactant spectra displays any measurable absorption in the region 450–650 nm, the absorption spectra of mixed donor–acceptor solutions are characterized by the appearance of new absorption bands. This new absorption bands are attributed to the π–π^* transition of the resulting pink color CT-complex and are centered at 522, 530 and 526 nm in AN, EtOH and ANET solutions, respectively. A shift of the position of the charge transfer band from 522 nm (in acetonitrile) to 530 nm (in ethanol) was observed reflecting the high sensitivity of the CT-reaction to the polarity of the used solvent. It is important to report that all spectra of mixtures containing the acceptor and donor were recorded against the corresponding acceptor as reference in order to eliminate a possible overlap that may arise between CT-complex and CLA bands. Moreover, it is worth mentioning that the resulting new long wavelength absorption bands are presumably attributed to the formation of CLA radical anion [4] resulting from the electron transfer from 2,6-DAP to CLA according to the following Scheme 1.



Scheme 1. Sequence of the CT reaction in polar solvents.