



Spectroscopic investigation and computational analysis of charge transfer hydrogen bonded reaction between 3-aminoquinoline with chloranilic acid in 1:1 stoichiometric ratio



Khairia M. Al-Ahmary^a, Maha S. Alenezi^{a, b}, Moustafa M. Habeeb^{a, c, *}

^a Department of Chemistry, Faculty of Sciences – AL Faisaliah Campus, King Abdulaziz University, Jeddah, Saudi Arabia

^b Department of Chemistry, Faculty of Arts and Science, Northern Border University, Rafha, Saudi Arabia

^c Department of Chemistry, Faculty of Education, Alexandria University, Alexandria, Egypt

ARTICLE INFO

Article history:

Received 21 April 2015

Received in revised form

8 June 2015

Accepted 8 June 2015

Available online 12 June 2015

Keywords:

Charge transfer

Proton transfer

Spectroscopy

Molecular orbital calculations

ABSTRACT

Charge transfer hydrogen bonded reaction between the electron donor (proton acceptor) 3-aminoquinoline with the electron acceptor (proton donor) chloranilic acid (H₂CA) has been investigated experimentally and theoretically. The experimental work included the application of UV–vis spectroscopy to identify the charge transfer band of the formed complex, its molecular composition as well as estimating its formation constants in different solvent included acetonitrile (AN), methanol (MeOH), ethanol (EtOH) and chloroform (CHL). It has been recorded the presence of new absorption bands in the range 500–550 nm attributing to the formed complex. The molecular composition of the HBCT complex was found to be 1:1 (donor:acceptor) in all studied solvents based on continuous variation and photometric titration methods. In addition, the calculated formation constants from Benesi–Hildebrand equation recorded high values, especially in chloroform referring to the formation of stable HBCT complex. Infrared spectroscopy has been applied for the solid complex where formation of charge and proton transfer was proven in it. Moreover, ¹H and ¹³C NMR spectroscopies were used to characterize the formed complex where charge and proton transfers were reconfirmed. Computational analysis included the use of GAMESS computations as a package of ChemBio3D Ultra12 program were applied for energy minimization and estimation of the stabilization energy for the produced complex. Also, geometrical parameters (bond lengths and bond angles) of the formed HBCT complex were computed and analyzed. Furthermore, Mullikan atomic charges, molecular potential energy surface, HOMO and LUMO molecular orbitals as well as assignment of the electronic spectra of the formed complex were presented. A full agreement between experimental and computational analysis has been found especially in the existence of the charge and proton transfers and the assignment of HOMO and LUMO molecular orbitals in the formed complex as well as its high stability.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In the last decades the chemistry of quinolines has witnessed a profound progress in the field of synthetic organic chemistry. The quinoline system is a prevalent topic of research. Its presence, as key structural motifs, in a large number of bioactive drugs such as quinine, chloroquine, luotonine-A, and camptothecin has led to the design of numerous approaches towards the construction of this

skeleton [1–4]. Photophysics of various quinoline derivatives has been an area of intensive research in the past few decades because of their potential applications in the synthesis of various dyes and drugs [5]. These molecules also have the potential to serve as sensitive probes for measuring the polarity of microenvironment in chemical and biological systems and for the detection of water composition in binary aqueous solutions [6].

Proton or electron transfer complexes play an important role in the field of magnetic, electrical conductivity and optical properties [7,8]. A great number of charge transfer receptors have been reported under the basic construction strategy of employing hydrogen bonding [9]. Recent investigations have shown that

* Corresponding author. Department of Chemistry, Faculty of Sciences – AL Faisaliah Campus, King Abdulaziz University, Jeddah, Saudi Arabia.

E-mail address: mostafah2002@yahoo.com (M.M. Habeeb).

hydrogen bonds could work as efficient bridges to mediate electron transfer between bonded species and initiate the so-called proton coupled electron transfer [10,11]. Generally, CT-interaction between benzoquinones electron acceptors and electron donors containing nitrogen, oxygen or sulfur atoms has been reported over the last years. These types of interactions play an important role in the field of drug-receptors binding mechanism [12,13], surface chemistry [14], applications in solar energy storage [15], uses as organic superconductors [16], and in many biological fields as antibacterial and antifungal agents [17–19].

Computational chemical analysis based on molecular orbital calculations using ChemBio3D Ultra 12.0 [20] with GAMESS interface [21,22] have been applied for molecular modeling of both small and large molecules as 3D-protein–ligand complexes and DNA structures. GAMESS is a program for ab initio molecular quantum chemistry that can compute SCF wave functions ranging from RHF, ROHF, UHF, GVB and MCSCF. Correlation corrections to these SCF wave functions include configuration interaction, second order perturbation theory and coupled cluster approach as well as the density function approximation theory. Also, hydrogen bonding can be displayed as well as analyzed using GAMESS computations. Basic molecular modeling computations such as alignment, stochastic conformational sampling, dihedral driver and MM2 experiments can be effectively facilitated by using this software. Moreover, it can be used in prediction and visualization NMR, IR, Raman and UV spectra [23–28].

Hence, the aim of the current work is the continuation of our work on charge and proton transfer complexes through studying the hydrogen bonded proton transfer complex between the electron donor 3AQ with the electron acceptor H₂CA, experimentally and theoretically. The experimental work will include the use of different spectroscopic techniques (UV–vis, infrared and ¹H, ¹³C NMR) spectroscopies to characterize the formed complex in different solvents included (AN), (MeOH), (EtOH) and (CHL). These characterizations included the identification of the complex stoichiometry, estimation of the formation constant, calculation of the some spectroscopic physical parameters as well as estimating the quantitative parameters of the formed complex. Computational analysis will include the use of GAMESS computations to energy minimize of the formed complex, calculating its stabilization energy and geometrical parameters. Also the molecular potential energy surface and HOMO and LUMO molecular orbitals will be presented and analyzed. The Consistency between spectroscopic and GAMESS computational data is a main target of this work.

2. Experimental

2.1. Materials and stock solutions

All chemical used were of analytical grade. 3AQ was supplied by Acros Organics (Geel, Belgium); H₂CA was supplied by Aldrich (Cambridge, UK). Spectroscopic grade solvents were used without further purification. Stock solutions of 3AQ and H₂CA at concentration of $5 \times 10^{-3} \text{ mol l}^{-1}$ were freshly prepared before each series of measurements by dissolving accurately weighted amounts in the appropriate volume of different solvents. The stock solutions of donor and acceptor were protected from light. Solutions for spectroscopic measurements were made by mixing appropriate volumes of donor and acceptor stock solutions with the solvent.

2.2. Instrumentation and physical measurements

The electronic absorption spectra were recorded in the region (700–250) nm using UV–vis Shimadzu UV-1601 with personal spectroscopy software version 3.7. The infrared spectra of the

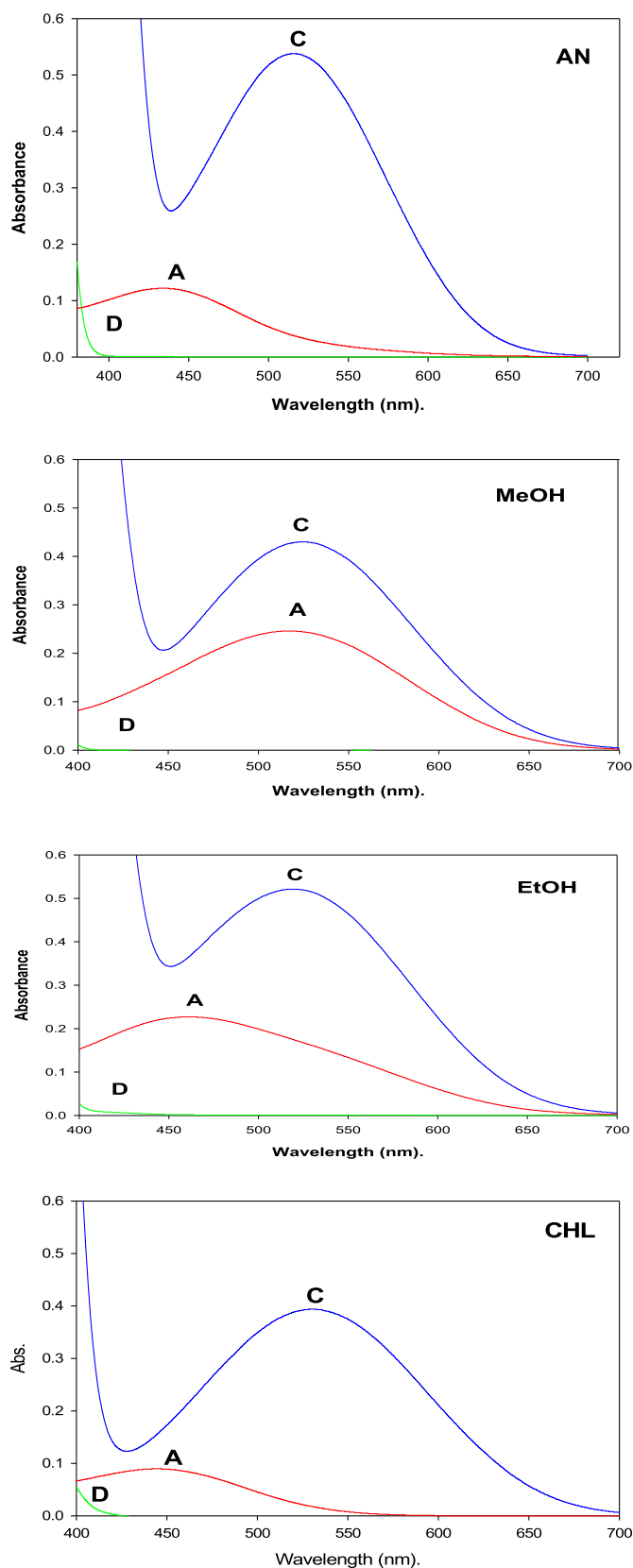


Fig. 1. Electronic absorption spectra of donor (D), acceptor (A) and complex (C) in different solvents.

Download English Version:

<https://daneshyari.com/en/article/1409231>

Download Persian Version:

<https://daneshyari.com/article/1409231>

[Daneshyari.com](https://daneshyari.com)