



Charge-transfer complexes formed in the reaction of 2-amino-4-ethylpyridine with π -electron acceptors

Siham Y. AlQaradawi ^{a,*}, Adel Mostafa ^b, A.A. Bengali ^b

^a Department of Chemistry and Earth Sciences, College of Arts and Sciences, Qatar University, P.O. Box 2713, Doha, Qatar

^b Department of Chemistry, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar

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ABSTRACT

Molecular charge-transfer complexes (CT) of electron donor 2-amino-4-ethylpyridine (2A4EPy) with π -acceptors tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD) have been studied spectrophotometrically in chloroform at 25 °C. These were investigated through electronic, infrared, mass spectra and thermal measurements as well as elemental analysis. All formed complexes exhibit well resolved charge-transfer bands in the regions where neither donor nor acceptors have any absorption. The obtained results show that the formed solid CT-complexes have the structures [(2A4EPy)(TCNE)₂], [(2A4EPy)₂(DDQ)] and [(2A4EPy)₂(TBCHD)] for 2-amino-4-ethylpyridine in full agreement with the known reaction stoichiometries in solution as well as the elemental measurements. The formation constant K_{CT} , molar extinction coefficient ϵ_{CT} , free energy change ΔG^0 , CT energy E_{CT} , ionization potential I_p and oscillator strength f have been calculated for these three CT-complexes.

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1. Introduction

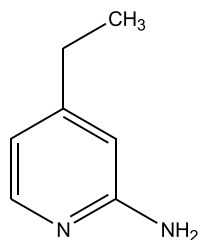
The study of charge-transfer complexes formed in the reaction of π -acceptors with many electron donors are of interest due to their interesting physical and chemical properties. Charge-transfer complexes are known to take part in many chemical reactions such as addition, substitution and condensation. The molecular interactions between electron donors and acceptors are generally identified by the intense color of these CT complexes which absorb radiation in the visible region [1–8]. The photometric methods used to study these interactions are usually simple and convenient because of the rapid formation of the complexes. The chemical and physical properties of charge-transfer (CT) complexes formed by the reactions of π - and σ -electron acceptors with different donors like amines, crown ethers, polysulfur bases and oxygen–nitrogen mixed bases have been the subject of many studies both in solution and in the solid state [9–13]. It was found that the reaction stoichiometries as

well as the structure of these CT-complexes depend strongly on the number of nitrogen donor atoms as well as on their terminal attached groups, hydrogen or donating groups like alkyl or withdrawing atoms like halogens. Electrons donating alkyl groups were found to enhance the acceptor: donor stoichiometry. Interestingly, most of the CT-complexes have many applications in chemical analysis like quantitative drug estimation and some complexes have interesting physical properties like electrical conductivities [14–17].

In this paper, we report the formation of three new CT-complexes formed by the reaction of 2-amino-4-ethylpyridine with different types of π -electron acceptors. The π -acceptors are tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD). All reactions were carried out in CHCl₃ as a solvent. The obtained results enabled us to investigate the stoichiometries and structure of these new CT-complexes.

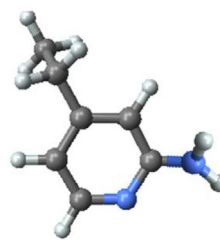
* Corresponding author.

E-mail addresses: siham@qu.edu.qa (S.Y. AlQaradawi), adel.saeid@qatar.tamu.edu (A. Mostafa).

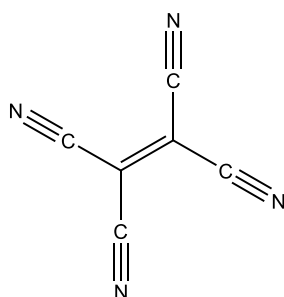


2-Amino-4-ethylpyridine

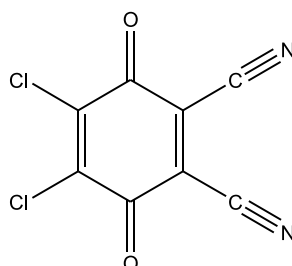
(2A4EPy)



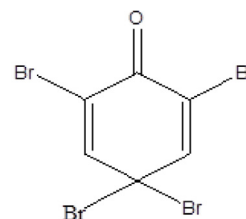
2A4EPy 3D structure

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TCNE



DDQ



TBCHD

2. Experimental

2.1. Materials

All chemicals used were of analytical grade and obtained from Sigma–Aldrich, USA, and used without further purification.

2.2. Instrumentation

The UV/Vis electronic absorption spectra of the CHCl_3 solutions of the solid CT-complexes formed in the reactions of the donor 2-amino-4-ethylpyridine and the acceptors tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD) as well as the reaction products were checked in the region 320–1500 nm using a lambda 950 Perkin Elmer UV–Vis–NIR spectrometer with quartz cell of 1.0 cm path length. Elemental analysis was done using a Perkin Elmer CHNSO Elemental Analyzer model 2400 series II. The obtained CT – complexes have been checked using Agilent Triple Quad LC MS/MS model 6420. The infrared spectra of the reactant, (2A4EPy), TCNE, DDQ, and TBCHD and the obtained CT-complexes (KBr pellets) were recorded on a Spectrum One Perkin Elmer FTIR spectrometer.

2.3. Photometric titration

Photometric titration measurements were performed for the reactions between the donor (2A4EPy) and each of the acceptors TCNE, DDQ, and TBCHD in CHCl_3 at 25 °C in order to determine the reaction stoichiometries according to a literature method [18]. The measurements were conducted under the conditions of fixed donor (2A4EPy) concentration while those of the acceptors TCNE, DDQ or TBCHD were changed over a wide range, to produce in each case reaction solutions where the molar ratio of donor: acceptor varies from 1:0.25 to 1:4. The peak absorbancies of the formed CT

complexes were measured for all solutions in each case and plotted as a function of the acceptor to donor molar ratio.

2.4. Preparation of the solid CT-complexes

The three solid CT-complexes formed in the reaction of 2A4EPy with each of TCNE, DDQ and TBCHD were prepared in CHCl_3 by the drop wise addition of a saturated solution (75 ml) of each of the donors to a saturated solution (95 ml) of each of the acceptors. In each case the mixing of reactants was associated with a strong change in color. The resulting precipitate in each case was filtered off, washed with minimum amounts of CHCl_3 and dried in vacuum over P_2O_5 . The complexes were characterized using spectroscopic techniques (FTIR and UV–vis) and by elemental analysis shown in Table 1.

3. Results and discussion

3.1. Electronic absorption spectra

Fig. 1 shows the electronic absorption spectra of the reactions of tetracyanoethylene (TCNE) with the donor 2A4EPy. While none of the reactants spectra display any measurable absorption in the region 400–650 nm, the resulting CT-complexes show strong absorptions centered on 397, 387 and 372 nm for 2A4EPy–TCNE reactions. These absorptions are associated with a strong change in color observed upon mixing of reactants (dark green from colorless solution) for 2A4EPy–TCNE, and reflect the electronic transitions in the formed CT-complexes.

Photometric titration measurements based on these absorptions were performed in order to determine the reactions stoichiometries in CHCl_3 (Fig. 2). The donor: TCNE molar ratio was found to be 1:2. This is in good agreement with the elemental analysis of the three solid CT-complexes (Table 1). On the basis of these experimental data, the complex obtained can be formulated as

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