Journal of Molecular Structure 983 (2010) 153–161

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Charge-transfer complexes of 1-(2-aminoethyl) piperazine with σ- and π-acceptors

Adel Mostafa, Hassan S. Bazzi *

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

A R T I C L E I N F O

Article history:
Received 26 April 2010
Received in revised form 24 August 2010
Accepted 24 August 2010
Available online 31 August 2010

Keywords:
1-(2-Aminoethyl) piperazine
Iodine
DDQ
TCNQ
TBCHD
CHL

A B S T R A C T

The solid charge-transfer (CT) molecular complexes formed in the reaction of 1-(2-aminoethyl) piperazine (AEPIP) with the σ-acceptor iodine and π-acceptors 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 7,7,8,8-tetracyanoquinodi-methane (TCNQ), 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD) and 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL) were studied in chloroform at 25 °C. The products were investigated through electronic and infrared spectra as well as elemental analysis. The obtained results showed that the formed solid CT-complexes have the formulas $[(\mathrm{AEPIP})\ \mathrm{I}]^+\ \mathrm{I}_5^-$, $[(\mathrm{AEPIP})(\mathrm{DDQ})_2]$, $[(\mathrm{AEPIP})(\mathrm{TCNQ})_2]$, $[(\mathrm{AEPIP})_2(\mathrm{TBCHD})_3]$ and $[(\mathrm{AEPIP})(\mathrm{CHL})]$ which are in full agreement with the known reaction stoichiometries in solution as well as the elemental analysis measurements. The formation constant K_{CT}, molar extinction coefficient ε_{CT}, free energy change ΔG^0 and CT energy E_{CT} have been calculated for the CT-complexes $[(\mathrm{AEPIP})(\mathrm{DDQ})_2]$, $[(\mathrm{AEPIP})(\mathrm{TCNQ})_2]$ and $[(\mathrm{AEPIP})(\mathrm{CHL})]$ as well.

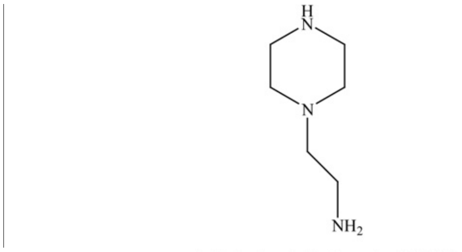
1. Introduction

The charge-transfer (CT) complexes formed in the reactions of σ- and π-electron acceptors with different donors like amines, crown ethers, polysulfur bases and oxygen–nitrogen mixed bases have been the subjects of many studies both in solution and in solid state show interesting chemical and physical properties. These properties have been the subjects of many studies both in solution and in solid state [1–10]. The photometric methods based on these interactions are usually simple and convenient because of the rapid formation of the complexes.

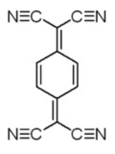
The electron donor we use in this study, 1-(2-aminoethyl) piperazine (AEPIP), is a derivative of piperazine and contains primary, secondary and tertiary nitrogen atoms (electron donating atom).

Polyiodide anions such as I_3^-, I_5^-, I_7^-, or I_9^- could be formed in charge-transfer interaction between iodine and electron donors. The formation of a particular polyiodide species depends strongly on the nature of the donor base and in some cases on the method of preparation [11–15]. The π-electron acceptors 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) are known to form stable colored CT-complexes with many donor bases. However, the reaction stoichiometries depend on several factors such as the nature of donor and acceptor and in some cases on the solvent used. The increased interest in the study of charge-transfer interactions stems from the important applications that CT-complexes can have. These include electronics, solar cells, optical devices, electrical conductivity, and others [16]. In addition, these interactions play an important role in biological systems [17].

In the paper herein, we report the formation of five new CT-complexes produced from the reaction of 1-(2-aminoethyl) piperazine with the π-acceptors 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD) and 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL) and σ-acceptor iodine in $CHCl_3$ as the solvent. The purpose of this work is to make an assessment of the correct nature and stoichiometry of each of the resulting new CT-complexes formed with each acceptor.



1-(2-Aminoethyl) piperazine (AEPIP)



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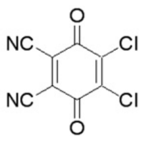

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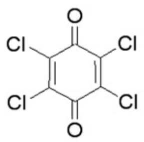
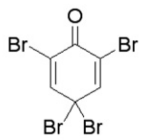


CHL



TBCHD

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* Corresponding author. Tel.: +974 4423 0018; fax: +974 4423 0060.
E-mail address: bazzi@tamu.edu (H.S. Bazzi).

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doi:10.1016/j.molstruc.2010.08.045

2. Experimental

2.1. Materials and measurements

The chemicals were purchased from Sigma–Aldrich, USA, and used as received. The electronic absorption spectra of the $CHCl_3$ solutions of the solid CT-complexes were checked in the region 1000–250 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.

Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis were carried out for all reactants and CT-complexes; using a Perkin Elmer model pyris 6 TGA computerized thermal analysis system. The rate of heating of the sample was kept at 10 °C min^{-1} under nitrogen flow at 20 ml min^{-1}. Copper sulfate pentahydrate was used as a calibration standard.

The infrared spectra of the reactants, AEPIP, DDQ, TCNQ, TBCHD and CHL (iodine has no infrared activity) and the obtained CT-complexes (KBr pellets) were recorded on a Perkin Elmer FTIR spectrometer model spectrum one.

Photometric titration measurements were performed for the reactions between the donor AEPIP and each of the acceptors iodine, DDQ, TCNQ, TBCHD and CHL in $CHCl_3$ at 25 °C in order to determine the reaction stoichiometries according to literature method [3,18]. The measurements were conducted under the conditions of fixed donor AEPIP concentrations while those of the acceptors I_2, DDQ, TCNQ, CHL 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. The infrared spectra of the reactants and the formed CT-complexes (KBr pellets) were recorded on a perkin-Elmer Spectrum One FTIR spectro-photometer.

2.2. Preparation of the solid CT-complexes

The five solid CT-complexes formed in the reaction of AEPIP with each of I_2, DDQ, TCNQ, TBCHD and CHL were isolated in $CHCl_3$ by drop wise addition of a saturated solution (60 ml) of the donor to a saturated solution (85 ml) of the acceptor. The resulting mixture was stirred for about 10–15 min. The mixing of reactants was associated with a strong change in color. The resulting precipitate was filtered immediately and washed several times with minimum amounts of $CHCl_3$, then dried under vacuum.

The yields of the obtained CT-complexes were 1.98 g (2.2 mmoles, 69.7%) for $[(AEPIP)I]^+I_5^-$, 2.19 g (3.8 mmoles, 63.7%) for $[(AEPIP)(DDQ)_2]$, 2.5 g (4.6 mmoles, 77.4%) for $[(AEPIP)(TCNQ)_2]$, 2.32 g (1.6 mmoles, 75.3%) for $[(AEPIP)_2(TBCHD)_3]$, and 2.13 g (5.7 mmoles, 74.7%) for [(AEPIP)(CHL)].

The complexes were characterized using spectroscopic techniques (FTIR and UV–Vis) and by elemental analysis (theoretical values are shown in brackets):

$[(AEPIP)I]^+I_5^-$ dark brown complex (M/W: 890.63 g); C, 8.11% (8.08%) H, 1.70% (1.68%); N, 4.68% (4.72%); I, 85.43% (85.52%).

$[(AEPIP)(DDQ)_2]$ dark red complex (M/W: 583.22 g); C, 45.22% (45.27%); H, 2.59% (2.57%); N, 16.77% (16.80%).

$[(AEPIP)(TCNQ)_2]$ brown complex (M/W: 537.58 g); C, 66.91% (66.97%); H, 4.24% (4.28%); N, 28.61% (28.65%).

$[(AEPIP)_2(TBCHD)_3]$ dark brown complex (M/W: 1487.5 g); C, 24.18% (24.20%); H, 2.44% (2.42%); N, 5.62% (5.65%).

[(AEPIP)(CHL)] dark brown complex (M/W: 375.08 g); C, 38.37% (38.39%); H, 4.02% (4.0%); N, 11.95% (11.98%).

3. Results and discussion

3.1. Electronic absorption spectra

Instant and strong change in color was observed upon mixing chloroform solutions of the donor AEPIP with each of the acceptor iodine, DDQ, TCNQ, TBCHD and chloranil. The colors were dark brown for AEPIP-I_2, AEPIP–TBCHD and AEPIP–CHL, dark red for AEPIP–DDQ, and brown for AEPIP–TCNQ reaction mixtures. These changes in colors clearly indicate the occurrence of the charge-transfer interactions between the donor and each of the acceptors. The electronic absorption spectra of the reactants along with those of the CT-complexes formed between the donor AEPIP and I_2, DDQ, TCNQ, TBCHD, and CHL are shown in Figs. 1–5 respectively. Strong absorption bands appeared at 365 and 290 nm for AEPIP-I_2, 731 and 531 nm for AEPIP–DDQ, 852 and 657 nm for AEPIP–TCNQ, 527 nm for AEPIP-TBCHD and 553 nm for AEPIP–CHL products.

Photometric titration measurements for the five reactions in $CHCl_3$ were performed and shown in Figs. 6–10. Interestingly, the measurements show that the donor–acceptor molar ratio is variable depending on the type of acceptor. These molar ratios were found to be 1:1 in the case of AEPIP–CHL and 1:2 in the case of AEPIP–DDQ and AEPIP–TCNQ, 1:3 in the case of AEPIP-I_2 system, and 1:1½ in case of AEPIP–TBCHD. The structures of the five new formed CT-complexes were thus formulated to be $[(AEPIP)(I_2)_3]$

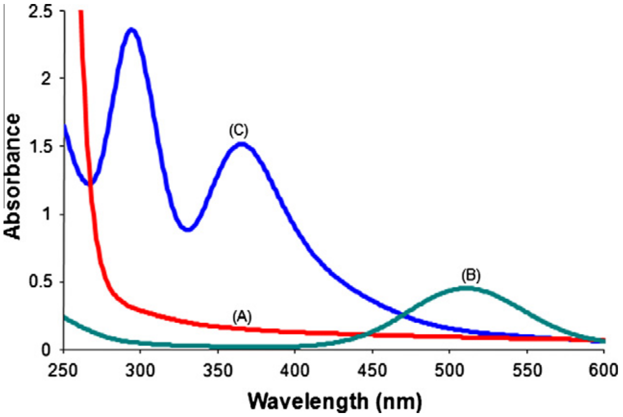

Fig. 1. Electronic absorption spectra of 1-(2-aminoethyl) piperazine (AEPIP)-I_2 in $CHCl_3$. (A) [AEPIP] = 5 × 10^{-3} M; (B) [I_2] = 5 × 10^{-3}M; (C) 1: 3 AEPIP-I_2 mixture, [AEPIP] = [I_2] = 5 × 10^{-3}M.

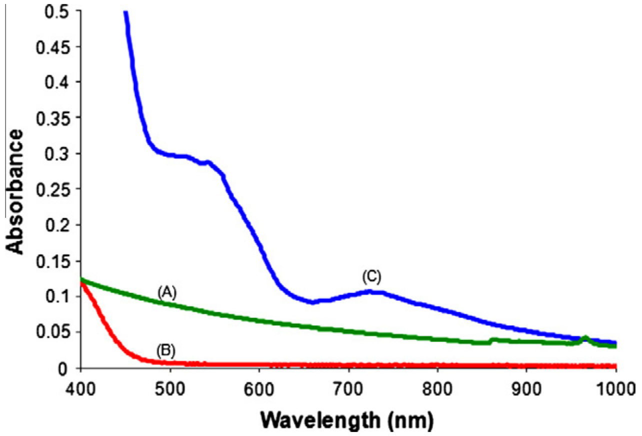

Fig. 2. Electronic absorption spectra of 1-(2-aminoethyl) piperazine (AEPIP) – DDQ in $CHCl_3$. (A) [AEPIP] = 5 × 10^{-3}M; (B) [DDQ] = 1 × 10^{-3}M; (C) 1: 2 AEPIP–DDQ mixture, [AEPIP] = 5 × 10^{-3}M and [DDQ] = 1 × 10^{-3}M.