Available online at www.sciencedirect.com

ScienceDirect

Polyhedron 27 (2008) 475–484

POLYHEDRON

www.elsevier.com/locate/poly

Synthesis and spectroscopic characterization of piperidine/chloranil and piperidine/7,7′,8,8′-tetracyanoquinodimethane charge transfer complexes: X-ray crystal structure of a 7,7-dicyano-8,8-di-piperidinoquinodimethane adduct

Moamen S. Refat [a,*], Lamia A. El-Zayat [a], Okan Zafer Yeşilel [b]

[a] *Chemistry Department, Faculty of Education, Port Said, Suez Canal University, Egypt*
[b] *Department of Chemistry, Faculty of Arts and Sciences, Eskişehir Osmangazi University, 26480 Eskişehir, Turkey*

Received 5 June 2007; accepted 13 September 2007
Available online 5 November 2007

Abstract

Charge transfer reactions of piperidine with *p*-chloranil (CHL) and 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) in chloroform have produced stable complexes with the general formula [$(Pip)_2$(acceptor)] with a 1:2 acceptor:donor molar ratio. Elemental analysis (CHN), electronic spectra, photometric titration, mid infrared spectra, ^{1}H NMR spectra and thermogravimetric analysis (TGA/DTG) were used to predict the position of the charge transfer interaction between the donating and accepting sites. The crystal structure of the Pip/TCNQ system was determined by single crystal X-ray diffraction.

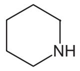
© 2007 Elsevier Ltd. All rights reserved.

Keywords: Piperidine; TCNQ; X-ray crystal structure; Thermogravimetric analysis

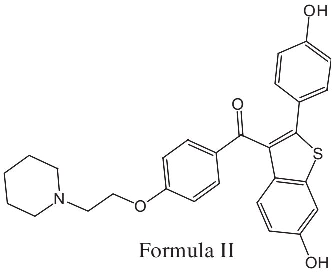
1. Introduction

Piperidine (Formula I) is an organic compound with the molecular formula $C_5H_{11}N$. It is a cyclic amine with a six-member ring. The piperidine skeleton is present in numerous natural alkaloids such as piperine, the main active chemical agent in black pepper and relatives, pharmaceutical drugs such as raloxifene (Formula II) and minoxidil (Formula III).

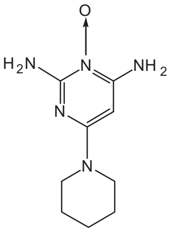
The major industrial application of piperidine is for the production of dipiperidinyl dithium tetrasulfide, which is used as a rubber vulcanization accelerator.



Formula I



Formula II



Formula III

---

[*] Corresponding author.
E-mail address: msrefat@yahoo.com (M.S. Refat).

0277-5387/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2007.09.025

Its charge transfer (CT) interaction has been widely reported recently. Charge transfer complexes are known to take part in many chemical reactions like addition, substitution and condensation [1,2]. These complexes have had great attention for non-linear optical materials and electrical conductivity [3–6]. The electron donor–acceptor (EDA) interaction is also important in the field of drug-receptor binding mechanisms [7], in solar energy storage [8] and in surface chemistry [9] as well as in many biological fields [10]. On the other hand, the EDA reactions of certain π-acceptors have successfully utilized in pharmaceutical analysis [11]. For these wide applications extensive studies on CT complexes of π-acceptors have been performed [12].

A literature survey [13–16] reveals that little attention has been paid to thermodynamic and electronic spectral characteristics, and it does not contain any information on the structural behavior of the CT interactions of this compound (Pip) with σ- and π-acceptors.

Charge transfer complexes of organic species are intensively studied because of their special type of interaction, which is accompanied by the transfer of an electron from the donor to the acceptor [17,18]. Also, protonation of the donor by acidic acceptors is generally the route for the formation of ion pair adducts [19–21].

Charge transfer (CT) complexes formed between piperidine (Pip) as the donor with *p*-chloranil (CHL) and 7,7′,8,8′-tetracyanoquinodi methane (TCNQ) as π-acceptors have been studied spectrophotometrically. The synthesis and characterization of piperidine CT complexes of *p*-chloranil, $[(\mathrm{Pip})_2(\mathrm{CHL})]$ (**1**) and 7,7′,8,8′-tetracyanoquinodimethane, $[(\mathrm{Pip})_2(\mathrm{TCNQ})]$ (**2**) are described. These complexes are readily prepared from the reaction of Pip with CHL and TCNQ using $\mathrm{CHCl_3}$ as the solvent. IR,^{1}H NMR, mass spectra, UV–Vis techniques and elemental analyses (CHN), characterize the two piperidine charge-transfer complexes. Benesi-Hildebrand and its modification methods were applied for the determination of the association constant (K) and molar extinction coefficient (ε).

2. Experimental

Pure piperidine, *p*-chloranil (CHL) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) were obtained from (Merck) and were used without further purification.

2.1. Materials and measurements

The electronic absorption spectra were recorded in the region 800–200 nm using a UV–Vis spectrophotometer, model Jenway 6405, with a quartz cell of 1.0 cm path length. The mid infrared spectra of the reactants and the resulted CT-complexes were measured from KBr discs using a Gensis II FT IR spectrophotometer. ^{1}H NMR spectra were obtained on a Varian spectrophotometer Gemini 200 MHz using TMS as an internal reference and d_6-DMSO as the solvent.

Thermogravimetric (TG) and differential (DTG) analyses were carried out in the temperature range 25–600 °C in nitrogen atmosphere using a Shimadzu TGA 50 H thermal analyzer. The experimental conditions were: aluminium crucible with a definite mg of sample, nitrogen atmosphere (nitrogen flow 30 ml/min) and heating rate of 15 °C/min. The elemental analyses were performed by the microanalysis unit at Cairo University, Egypt using a Perkin Elmer CHN 2400. The data of the elemental analyses (CHN) of the reaction products, the CT-complexes, were matched with the molar ratio results from the photometric titrations.

The two solid CT-complexes formed in the reaction of Pip with CHL and TCNQ were isolated by the addition of 1.0 mmol of Pip (10 ml) to a 1.0 mmol solution of CHL and TCNQ (20 ml) in chloroform followed by stirring for about 30 min. Dark brown and yellow precipitates were formed in the case of Pip/CHL and Pip/TCNQ, respectively, and these were filtered off, washed several times with $\mathrm{CHCl_3}$ and dried in vacuo. The products were identified as: $[(\mathrm{Pip})_2(\mathrm{CHL})]$ (**1**) ($\mathrm{C_{16}H_{22}N_2O_2Cl_4}$; $M_\mathrm{w} = 416$, m.p. 155 °C). *Anal.* Calc.: C, 46.20; H, 5.29; N, 6.73. Found: C, 46.12; H, 4.85; N, 6.69%; and 7,7-dicyano-8,8-di-piperidinoquinodimethane adduct (**2**) ($\mathrm{C_{20}H_{24}N_4}$; $M_\mathrm{w} = 320$, m.p. 187 °C). *Anal.* Calc.: C, 75.00; H, 7.50; N, 17.50. Found: C, 74.78; H, 7.46; N, 17.29%.

2.2. Crystallographic analysis

Data collection was performed on a Bruker SMART CCDC area detector diffractometer using Mo Kα radiation ($\alpha = 0.71073$ Å). The structure was solved by direct-methods using SIR97 [22] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [23]. Molecular drawings were obtained using ORTEP-III [24].

Crystallographic data for $[(\mathrm{Pip})_2(\mathrm{TCNQ})]$: crystal dimensions $0.38 \times 0.29 \times 0.23$ mm; $F_\mathrm{w} = 320.43\ \mathrm{g\,mol^{-1}}$, triclinic, space group $P\bar{1}$, $a = 8.7775(6)$, $b = 13.5503(9)$, $c = 16.2521(11)$ Å, $\alpha = 95.596(1)°$, $\beta = 101.804(1)°$, $\gamma = 104.797(1)°$; $V = 1806.3(2)$ Å^3, $Z = 4$, $D_\mathrm{c} = 1.178\ \mathrm{Mg\,m^{-3}}$, $R_\mathrm{int} = 0.050$ and $wR = 0.224$ for 7765 independent reflections; $S = 1.265$.

3. Results and discussion

3.1. Electronic absorption spectra of the Pip/CHL and Pip/TCNQ systems

In the case of the Pip/CHL system, once beginning the addition of CHL to a solution of Pip in chloroform, the color of the solution changes in four steps until it is constant: light blue → yellow → gray → olive green. On the other hand, in the case of the Pip/TCNQ system, upon addition of TCNQ to the donor (Pip) dissolved in chloroform, a dark green precipitate was formed immediately. The electronic absorption spectra of the reaction mixtures

Download English Version:

https://daneshyari.com/en/article/1339625

Download Persian Version:

https://daneshyari.com/article/1339625

Daneshyari.com