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# Spectroscopic studies on $[(DD18C6H_2)(HPA)_2](PA)_2$ and $[(DD18C6H_2)(DDQ)_2](DDQH)_2$ formed in the reaction of *N*,*N*′-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane with HPA and DDQ

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## Abstract

The interaction of the mixed oxygen–nitrogen cyclic base, *N*,*N*′-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (DD18C6) with π-acceptors such as picric acid (HPA) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) has been studied spectrophotometrically in chloroform at 25 °C. The results obtained indicate the formation of 1:4 charge–transfer complexes with the general formula $(DD18C6)(acceptor)_4$. The electronic and infrared spectra of charge–transfer complexes along with the $^1H$ NMR spectra were recorded and discussed. Based on the data obtained, the complexes were formulated as $[(DD18C6H_2)(HPA)_2](PA)_2$ and $[(DD18C6H_2)(DDQ)_2](DDQH)_2$. A general mechanism explaining the formation of the DDQ complex has been suggested.

*Keywords:* Charge–transfer; Diazacrown ether; π-Acceptors; $^1H$ NMR; IR; UV–vis spectra

## 1. Introduction

In the last few years, the chemical and physical properties of some charge–transfer complexes formed in the reaction of σ- and π-acceptors with different amines and cyclic polysulfur bases have been the subjects of many investigations [1–9]. More recently, attention has been given to the formation of stable charge–transfer complexes formed during the reaction of σ- and π-acceptors with various cyclic polyamines and with mixed oxygen nitrogen cyclic bases as strong donors [10–19]. In earlier study [15], we have reported the formation of a charge–transfer complex formed from the reaction of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (D18C6) with iodine, where the pentaiodide ion ($I_5^-$) was formed and the obtained CT-complex was formulated as $[(D18C6)I]I_5$. This investigation was extended to study the nature of the reaction of D18C6 with various π-electron acceptors [10] and the CT-complexes obtained were formulated as $[(D18C6)(acceptor)_4]$.

In the present investigation, we reported the formation of the new CT-complexes obtained in the reaction of oxygen-nitrogen mixed base *N*,*N*′-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (DD18C6, **I**), with picric acid (HPA) and 2,3-dichloro-5,6-dicyano-1,4-benoquinone (DDQ) in chloroform as a solvent. The aim of this work is to investigate the nature of the reaction between the cyclic base (DD18C6) with such acceptors, to study the effect of two additional benzyl groups present in DD18C6, on the nature of the formed CT-complexes and to compare the results with those of the corresponding CT-complexes of the cyclic base D18C6 (**II**).

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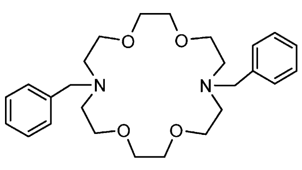
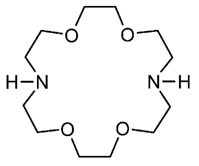


**(I)**

*N,N′*-dibenzyl-1,4,10,13-tetraoxa-6,7-diazacyclooctadecane
(DD18C6)



**(II)**

1,4,10,13-tetraoxa- 6,7-diazacyclooctadecane
(D18C6)

## 2. Experimental

### 2.1. Materials and spectral measurements

All chemicals used were of high grade. *N,N′*-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (DD18C6) was obtained from Aldrich Chemical Co., while picric acid (HPA) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were obtained from BDH.

The electronic absorption spectra were recorded in the region of 700–250 nm using UV–vis spectrophotometer model JASCO V-530 with quartz cell of 1.0 cm path length. The infrared spectra were recorded using KBr discs on either Perkin-Elmer 1430 ratio recording Infrared spectrometer or Buck Scientific 500-Infrared Spectrophotmeter. $^1$H NMR spectra were recorded on a Varian Gemini 200 spectrophotometer, operating at 200 MHz, using solvent signals as a reference. Photometric titrations were performed for the reactions between the acceptors and the base (DD18C6) in chloroform at 25 °C using a Helios Gamma Unicam UV–vis spectrophotometer. The concentration of DD18C6 in the reaction mixtures with HPA and DDQ were kept fixed at $0.20 \times 10^{-4}$ and $0.50 \times 10^{-4}$, respectively. The concentration of the acceptors were changed over a wide range of concentrations, to produce solution in each case of acceptor: DD18C6 molar ratio varying from 1.0:1.0 to 8.0:1.0 for HPA–DD18C6 and 1.0:1.0 to 7.0:1.0 for DDQ–DD18C6 (Table 1). The peak absorbances of the formed complexes were measured in each case and plotted as a function of the acceptor to DD18C6 molar ratio according to the known method [20].

### 2.2. Preparation of the solid complexes

The two complexes $[(DD18C6H_2)(HPA)_2](PA)_2$ and $[(DD18C6H_2)(DDQ)_2](DDQH)_2$ were prepared as follow. To a solution of DD18C6 (44.3 mg, 0.10 mmol) in $CHCl_3$ (10 ml), a solution of the acceptor (0.60 mmol HPA or 0.50 mmol DDQ) in $CHCl_3$ (50 ml) was added and stirred for 5–15 min. The precipitate formed was filtered off, washed with the $CHCl_3$ (2 × 1/2 ml) (in the case of picric acid complex, the precipitate was also washed with $Et_2O$ and dried in vacuo over $CaCl_2$.

Table 1
Molar concentrations of the donor and acceptors in the reaction mixtures

| Base concentration ($\times 10^{-4}$ M) | Acceptor | Concentration range of the acceptors (M) | Acceptor–base molar ratio |
|---|---|---|---|
| 0.50 | DDQ | $0.50 \times 10^{-4}$–$3.5 \times 10^{-4}$ | 1.0:1.0–7.0:1.0 |
| 0.20 | HPA | $0.20 \times 10^{-4}$–$1.6 \times 10^{-4}$ | 1.0:1.0–8.0:1.0 |

$[(DD18C6H_2)(HPA)_2](PA)_2$ complex: Scarlet yellow, mp 125 °C. Anal. found: C, 43.39; H, 3.68; N, 15.43. Anal. calcd. for $C_{50}H_{50}N_{14}O_{32}$ (1359.03): C, 44.19; H, 3.71; N, 14.43.

$[(DD18C6H_2)(DDQ)_2](DDQH)_2$ complex: Dark reddish, mp 90 °C. Anal. found: C, 51.16; H, 2.81; N, 9.37; Cl, 21.17. Anal. calcd. for $C_{58}H_{38}Cl_8N_{10}O_{12}$ (1350.64): C, 51.58; H, 2.84; N, 10.37; Cl, 21.00.

## 3. Results and discussion

### 3.1. Electronic spectra

The electronic absorption spectra of the base donor *N,N′*-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (DD18C6), ($1.0 \times 10^{-4}$ M) and the acceptors (HPA, $0.5 \times 10^{-4}$ and DDQ, $2.5 \times 10^{-4}$ M) in $CHCl_3$ along with those of the formed CT-complexes are shown in Fig. 1 (A, B and C, respectively). Strong absorption bands shown in the spectra due to the formed CT-complexes were appeared at 401 and 350 nm for $[(DD18C6H_2)(HPA)_2](PA)_2$

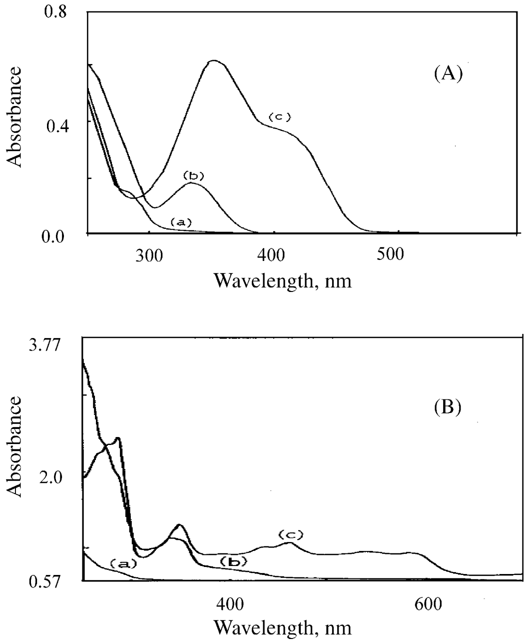


Fig. 1. Electronic absorption spectra of: (A): DD18C6–HPA reaction (a: [DD18C6] = $1.0 \times 10^{-4}$ M, b: [HPA] = $0.5 \times 10^{-4}$ M and c: DD18C6–HPA mixture [DD18C6] = $2 \times 10^{-4}$ M and [HPA] = $1 \times 10^{-4}$ M). (B): DD18C6–DDQ reaction (a: [DD18C6] = $1.0 \times 10^{-4}$ M, b: [DDQ] = $2.5 \times 10^{-4}$ M and c: DD18C6–DDQ mixture [DD18C6] = $2 \times 10^{-4}$ M and [DDQ] = $5 \times 10^{-4}$ M).