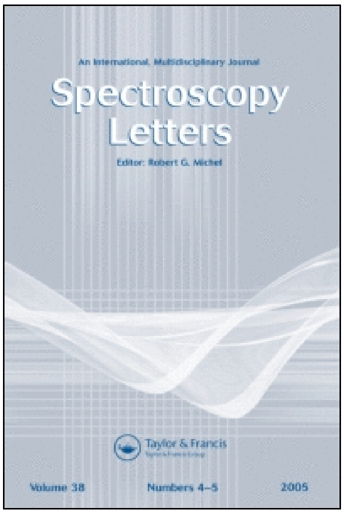

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Spectroscopic Investigation on Charge Transfer Complexes Formed in the Reaction of Π-Electron Acceptors with the Donor Cyclic base 1,4,10,13-Tetraoxa-7,16-Diazacyclooctadecane

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SPECTROSCOPIC INVESTIGATION ON CHARGE TRANSFER COMPLEXES FORMED IN THE REACTION OF π-ELECTRON ACCEPTORS WITH THE DONOR CYCLIC BASE 1,4,10,13-TETRAOXA-7,16-DIAZACYCLOOCTADECANE

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ABSTRACT: The interaction of the cyclic base 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (TODACOD) with different π-electron acceptors have been studied spectrophotometrically in $CHCl_3$. These π-electron acceptors are 1-chloro-2,4,6-trinitrobenzene (picryl chloride), 7,7', 8,8'-tetracyanoquinone (TCNQ) and tetrachloro-p-benzoquinone (chloranil). The results indicate the formation of 1:4 charge transfer complexes with the general structures [(TODACOD)(Accept)$_4$]. The charge transfer absorptions as well as the infrared spectra of these complexes are obtained.

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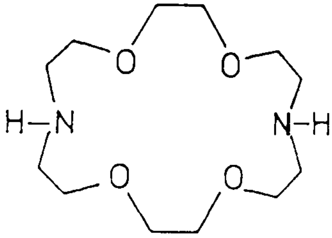
INTRODUCTION

In the last few years, chemical and physical properties of some charge transfer complexes formed by the reaction of π-electron acceptors with some heterocyclic amines have been the subject of many investigations [1-5]. Moreover, the formation of stable charge transfer complexes formed in the reaction of σ-acceptors like iodine with various cyclic polyamines and with mixed oxygen-nitrogen cyclic bases are well known [6-10]. Some of the CT-complexes show very interesting physical properties such as electrical conductivity [11-13]. The formation of CT-complexes depends strongly on the type and nature of the donor base as well as the electron acceptors. The variation of the spectrophotometric properties of the CT-complexes in different solvents with different polarities is assumed to be due to the solvent interactions with the electron acceptors [14-16].

To continue our investigations in this research area [6-10,17], we report here, the formation of the new CT-complexes obtained in the reaction of the interesting oxygen-nitrogen mixed base 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (TODACOD), shown in (I) with different types of π-electron acceptors. The electron acceptors used are 1-chloro-2,4,6-trinitrobenzene (picryl chloride), 7,7',8,8'-tetracyanoquinone (TCNQ) and tetrachloro-p-benzoquinone (chloranil). Chloroform was used as a solvent. The aim of our work is to investigate the effect of the existence of two different donor sites (nitrogen and oxygen) in the cyclic base on the nature of the reaction and the structure of the formed new CT-complexes.



(I)
1,4,10,13-tetraoxa-7,16-diazacyclooctadecane
(TODACOD).

EXPERIMENTAL

All chemicals used in this study were of high pure grade. 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (TODACOD), 7,7',8, 8'-tetracyanoquinone (TCNQ) and tetrachloro-p-benzoquinone (chloranil) were obtained from Aldrich Chemical Co. While, 1-chloro-2,4,6-trinitrobenzene (picryl chloride) was obtained from BDH.

The CT-complexes were isolated as follows: A saturated solution of each of the acceptors in chloroform (50 ml) was added to saturated solution (10 ml) of the mixed oxygen-nitrogen cyclic base (TODACOD) in chloroform, the mixture in each case was stirred for about 20 mins. The orange [(TODACOD)(picryl chloride)$_4$], dark blue [(TODACOD)(TCNQ)$_4$] and dark brown [(TODACOD)(chloranil)$_4$] solid CT-complexes were separated immediately, filtered off, washed several times with minimum amount of chloroform and dried under vacuum. The formed complexes are given the general formula [(TODACOD)(Accept)$_4$] based on spectroscopic data as well as elemental analysis as follows:

[(TODACOD)(picryl chloride)$_4$]: C; 33.45% (34.5%); H; 3.17%

(2.71%); N; 15.97% (15.65%); Cl; 12.7% (11.34%), [(TODACOD)(chloranil)$_4$]: C; 34.64% (34.67%); H; 1.77% (2.08%); N; 2.44% (2.24%); Cl; 45.1% (45.5%) and [(TODACOD)(TCNQ)$_4$]: C; 66.96% (66.79%); H; 4.23% (3.80%); N; 25.78% (23.37%). The calculated values are shown in paretheses.

Absorption spectra were recorded using Beckman Spectrophotometer Model 25 with quartz cell of 1.0 cm path length. The infrared of the reactants and the formed complexes were recorded from KBr discs using a Perkin-Elmer 1430 ratio recording Infrared Spectrometer.

Photometric titrations were performed for the reaction between the acceptors and the mixed oxygen-nitrogen cyclic base (TODACOD) in $CHCl_3$ at 25°C. The concentration of the base (TODACOD) was kept fixed at (0.4×10^{-4}M), while the concentration of acceptors in the reaction mixture was changed over the range 0.4×10^{-4} to 3.6×10^{-4}M and this produces solutions with a base : acceptor ratio varying from 1:1 to 1:9. These ratios were practically achieved by mixing 0.5 ml volume of 4×10^{-4}M of the base with x ml of 4×10^{-4}M of acceptors (picryl chloride, TCNQ and chloranil) and the mixture was diluted in each case to a total volume of 5 ml by chloroform. The spectrum was then recorded for each mixture and the absorption of the products, CT-complexes, were measured around 400 nm for [(TODACOD)(picryl chloride)$_4$], 380 nm for [(TODACOD)(TCNQ)$_4$] and 360 nm for [(TODACOD)(chloranil)$_4$] and plotted as a function of the added x ml of acceptors in order to determine the stoichiometry of the reaction according to the known method[18].

RESULTS AND DISCUSSION

The electronic absorption spectra of the base donor 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (TODACOD) ($4x10^{-4}M$) and acceptors (picryl chloride, TCNQ and chloranil) ($4x10^{-4}M$) in $CHCl_3$ along with those of the formed CT-complexes are shown in Figure 1 (A,B and C, respectively). Strong absorption bands appeared in the spectra are assigned due to the formed CT-complexes around 380 nm for $[(TODACOD)(TCNQ)_4]$, 400 nm for $[(TODACOD)(picryl\ chloride)_4]$ and 360 nm for $[(TODACOD)(chloranil)_4]$.

Photometric titration measurements of the course of the reaction in chloroform based on the strong absorption band around 400, 380 and 360 nm for the complexes $[(TODACOD)(picryl\ chloride)_4]$, $[(TODACOD)(TCNQ)_4]$ and $[(TODACOD)(chloranil)_4]$, respectively, are obtained. The base-acceptor molar ratio in all cases was found to be 1:4 as shown in Figure 2 for the (TODACOD)-(picryl chloride) reaction as an example. This conclusion is in good agreement with the obtained elemental analysis of the solid CT-complexes.

Accordingly, the obtained CT-complexes are formulated as $[(TODACOD)(Acceptor)_4]$. According to the obtained molar ratio of the formed CT-complexes, the TODACOD base molecule (donor) should be sandwiched between four acceptor molecules. It should be indicated here that in previous communication [17], we reported that the cyclic polyamine 1,4,8,11-tetraazocyclotetradecane (TACTD) forms only 1:2 CT-complexes with the same π-electron acceptors with the complex general formula $[(TACTD)(Accept.)_2]$. The high value of the base : acceptor molar ratio (1:4) found in this study using

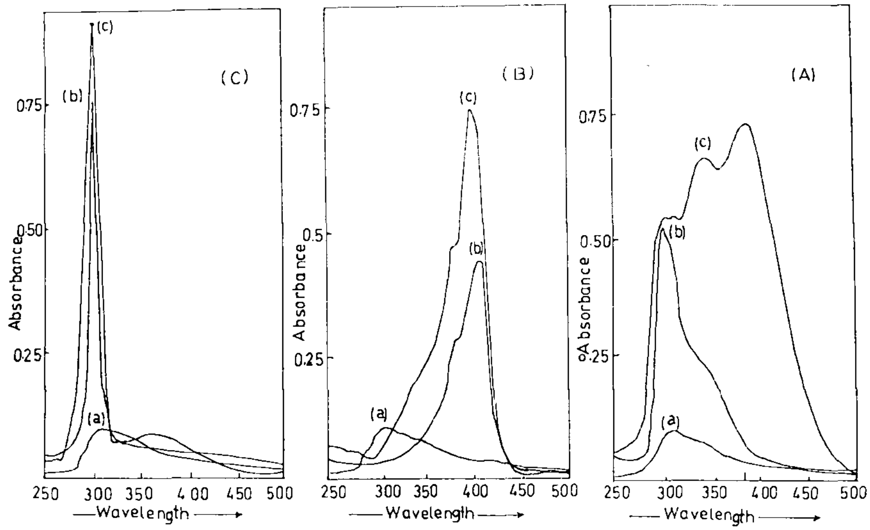
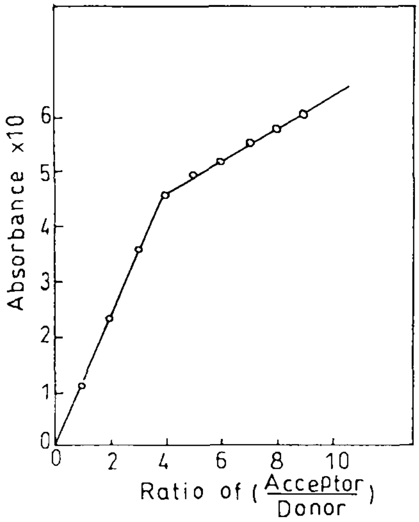


Figure (1): Electronic absorption spectra of (A): TODACOD-picryl chloride reaction (a: [TODACOD] = $4x10^{-4}$M, b: [picryl chloride] = $4x10^{-4}$M, and c: TODACOD-picryl chloride mixture, (B): TODACOD -TCNQ reaction (a: [TODACOD] = $4x10^{-4}$M, b: [TCNQ] = $4x10^{-4}$M, and c: TODACOD-TCNQ mixture, (C): TODACOD-chloranil reaction (a: [TODACOD] = $4x10^{-4}$M, b: [chloranil] = $4x10^{-4}$M, and c: TODACOD-chloranil mixture.

1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (TODACOD), forming [(TODACOD)(Accept.)$_4$] complexes, is expected due to the presence of six donor sites (2 nitrogens and 4 oxygens) which more enrich the electron cloud on the (TODACOD) base compared with that on the (TACTD) which contains 4 nitrogens only.

Figure 3 shows the infrared spectra of the formed complexes [(TODACOD)(Accept.)$_4$], (acceptors = picryl chloride, TCNQ and

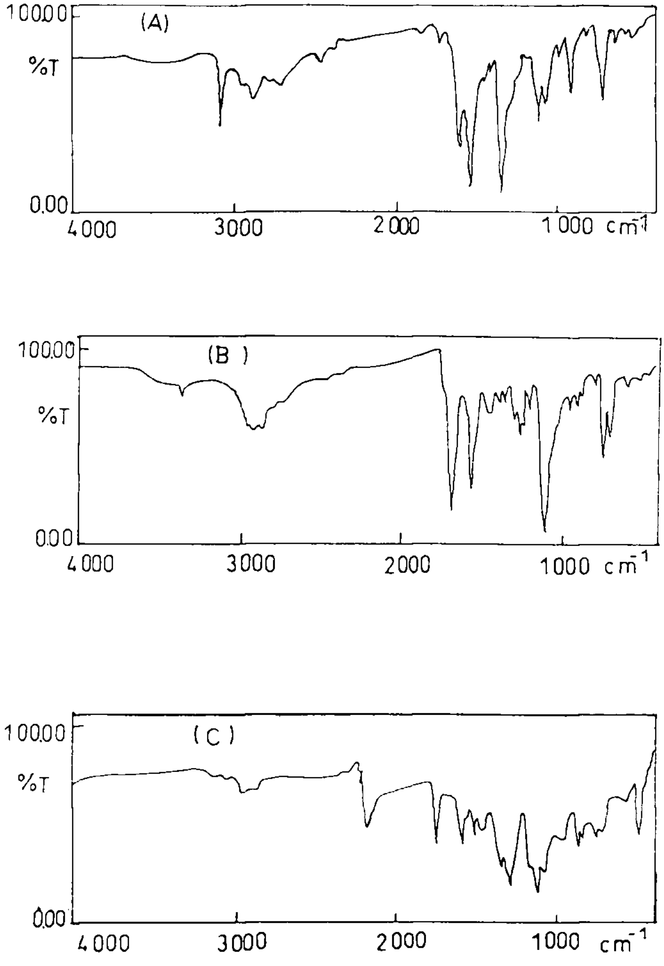


Fig(2):Photometric Titration Curve for the TODCOD-picryl chloride reaction in $CHCl_3$ at 25°C.

chloranil).The formation of the TODACOD-acceptors, CT-complexes, are strongly supported by the observation of the main infrared bands for both the reactants, TODACOD base and acceptors in the product spectra. However, the bands of the TODACOD and acceptors in the spectra of the [(TODACOD)(Accept.)$_4$] complexes show small shifts in the frequency values as well as some changes in their intensities compared with those of the free TODACOD base and acceptors. This could be attributed to the expected symmetry and electronic structure changes upon the formation of CT-complexes.

CONCLUSION :

The cyclic base 1,4,10,13-tetraoxa-7,16-diacyclooctadecane (TODACOD) reacts at room temperature with various π-electron



Fig(3): Infrared Spectra of CT-Complexes:
(A):[(TODACOD) (picryl chloride)$_4$] , (B):[(TODACOD)(TCNQ)$_4$]and
(C):[(TODACOD) (chloranil)$_4$]

acceptors such as picryl chloride, TCNQ and chloranil to form the stable CT-complexes of the general formula [(TODACOD)(Accept.)$_4$]. To our knowledge, the high ratio of 1:4 CT-complexes reported here is considered to be the first case to be known in this field.

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