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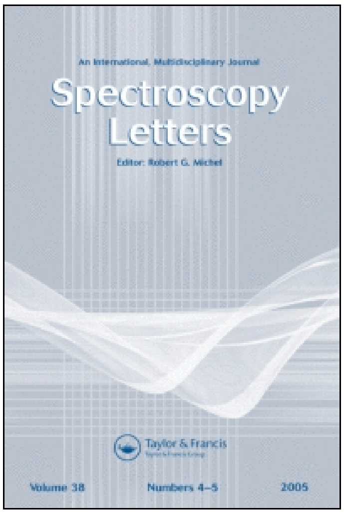

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Spectroscopic Studies of the Reactions of π-Electron Acceptors with the Cyclic Polyamine 1,4,8,11-Tetraazacyclotetradecane

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SPECTROSCOPIC STUDIES OF THE REACTIONS OF π-ELECTRON ACCEPTORS WITH THE CYCLIC POLYAMINE 1,4,8,11-TETRAAZACYCLOTETRADECANE

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ABSTRACT : The reactions of π-electron acceptors such as 1-chloro-2,4,6-trinitrobenzene (picryl chloride), 7,7',8,8'-tetracyanoquinodimethane (TCNQ), tetrachloro-p-benzoquinone (chloranil) and tetracyanoethylene (TCNE) with the cyclic polyamine base 1,4,8,11-tetraazacyclotetradecane (TACTD) have been investigated in $CHCl_3$ solvent. The data indicate the formation of the CT-complexes with the general formula [(TACTD) $(acceptor)_2$]. The 1 : 2 stoichiometry of the (TACTD)-acceptor was based on elemental analysis and infrared spectra of the solid CT-complexes along with the photometric titration curves for the reactions in $CHCl_3$. The formation constants (K) for the

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CT-complexes are shown to be strongly dependent on the type and structure of the π-acceptor.

INTRODUCTION

In recent years, the study of the charge - transfer complexes formed in the reaction of aromatic electron acceptors (π-acceptors) with various electron donors have attracted considerable interests and growing importance owing to their significant physical properties such as electrical conductivity [1-5]. However, electron donors like cyclic polyamine are known to form stable CT-complexes. Nour et al [6-11] reported the formation of the related charge - transfer complexes formed in the reaction of iodine (σ-acceptors) with various cyclic polyamine such as 1,4,8,11-tetraazacyclopentadecane and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane and also the related cyclic polysulfur bases such as 1,4,7,10-tetrathiacyclododecane. The solvent effects on the formation of these cyclic polyamine CT-complexes are shown to be dependent on the polarity of the solvent and the nature of nitrogen bases.

In this study we report the synthesis and spectroscopic studies of some CT-complexes formed in the reaction of the cyclic polyamine 1,4,8,11-tetraazacyclotetradecane (TACTD) shown in (I) with π-electron acceptors such as 1-chloro-2,4,6-trinitrobenzene (picryl chloride),7,7',8,8'-tetracyanoquinodimethane (TCNQ), tetrachloro-p-benzoquinone (chloranil) and tetracyanoethylene (TCNE) in

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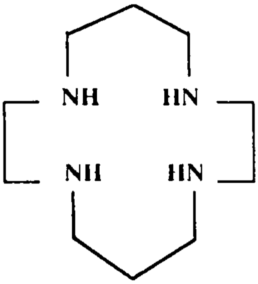
chloroform as a solvent. The obtained results enable us to investigate the nature of the formed complexes, type of bonding and structure inherent in these new complexes.



(I)

1,4,8,11-Tetraazacyclotetradecane (TACTD)

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EXPERIMENTAL

All chemicals used in this study were analytical reagent grade and used without further purification. 1,4,8,11-tetraazacyclotetradecane (TACTD), 7,7',8,8'-tetracyanoquinodimethane (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 and tetracyanoethylene (TCNE) was obtained from Meck Chemical Co.

The solid donor - acceptor complexes with the general formula [(TACTD) $(\text{Accept.})_2$], were isolated as follows. Excess saturated solution for each of the acceptors in chloroform (40 ml) (acceptors are picryl chloride, TCNQ, chloranil and TCNE) was separatly added to a saturated solution (10 ml) of the cyclic polyamine base (TACTD) in chloroform. The mixture was stirred for about 15 mins. The orange [(TACTD) (picryl chloride)$_2$], greenish [(TACTD) (TCNQ)$_2$], dark brown [(TACTD) (chloranil)$_2$] and brown [(TACTD) (TCNE)$_2$] solid CT-complexes were separated and washed several times with the least amount of chloroform and dried under vacuum. The formed complexes are given the general formula [(TACTD) (Accept.)$_2$] based on spectroscopic data as well as elemental analysis as follows. [(TACTD) (picryl chloride)$_2$] : C; 37.90% (37.90%); H; 4.80% (4.03%); N; 19.40% (20.14%), [(TACTD) (TCNQ)$_2$] : C; 68.20% (67.15%) : H; 5.40% (5.30%); N; 26.95% (27.6%), [(TACTD) (chloranil)$_2$] : C; 39.75% (38.2%); H; 4.40% (3.50%); N; 7.20% (8.10%) and [(TACTD) (TCNE)$_2$] : C; 56.5% (57.89%); H; 5.37% (5.26%); N; 35.87% (36.8%) (the calculated values are shown in parentheses).

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The electronic absorption spectra of the donor, (TACTD), the acceptors (picryl chloride, TCNQ, chloranil and TCNE) and the formed CT-complexes in chloroform were recorded using a Beckman Spectrophotometer model 25 with quartz cell of 1.0 cm pathlength. The infrared spectra of the reactants and the formed complexes, [(TACTD) (Accept.)$_2$], were recorded from KBr discs using a Perkin - Elmer 1430 ratio - recording infrared spectrometer.

The course of the reaction between the acceptors and the cyclic polyamine base (TACTD) were studied spectrophotometrically in $CHCl_3$ at 25°C. The concentration of the cyclic polyamine base was kept fixed at 0.4 x 10^{-4} mol L^{-1} while the concentration of picryl chloride, chloranil and TCNE were varied from 0.4 x 10^{-4} to 3.2 x 10^{-4} mol L^{-1} and TCNQ from 0.1 x 10^{-4} to 0.8 x 10^{-4} mol L^{-1}. These concentrations produce base : acceptor (acceptor = picryl chloride, chloranil or TCNE) ratio from 1 : 1 to 1 : 8 and base : acceptor (acceptor = TCNQ) ratio from 1 : 0.25 to 1 : 2. The data obtained were used to calculate the values of K and ε for the formed complexes according to known method [12] as well be explained in the text.

The electronic absorption spectra were recorded for each complex in the region 600 - 200 nm. To check the stoichiometry of the reactions, photometric titrations of acceptors and TACTD polyamine base were performed in $CHCl_3$ at 25°C under conditions for fixed base; TACTD, concentration (2 x 10^{-4} , 2 x 10^{-4} , 8 x 10^{-5} and 8 x 10^{-5} M in the case of using the acceptors picryl chloride, TCNQ, chloranil and TCNE, respectively) while the concentration of picryl chloride in the reaction mixture was changed from 0.5 x 10^{-4} to 8 x 10^{-4} M, TCNQ from 0.5 x 10^{-5} to 8 x 10^{-5} M and both chloranil and TCNE from 0.2 x 10^{-4} to 3.2 x 10^{-4} M. These produced solutions in each case of acceptor : TACTD ratio varying from 0.25 : 1 to 4 : 1. The peak absorbances of the formed complexes were measured in each case and plotted as a function of the acceptor : TACTD ratio according to the known method [13].

RESULTS AND DISCUSSION

The electronic absorption spectra of the reactants, 1,4,8,11-tetraazacyclotetradecane (TACTD) (1 x 10^{-3} M) and acceptors (picryl

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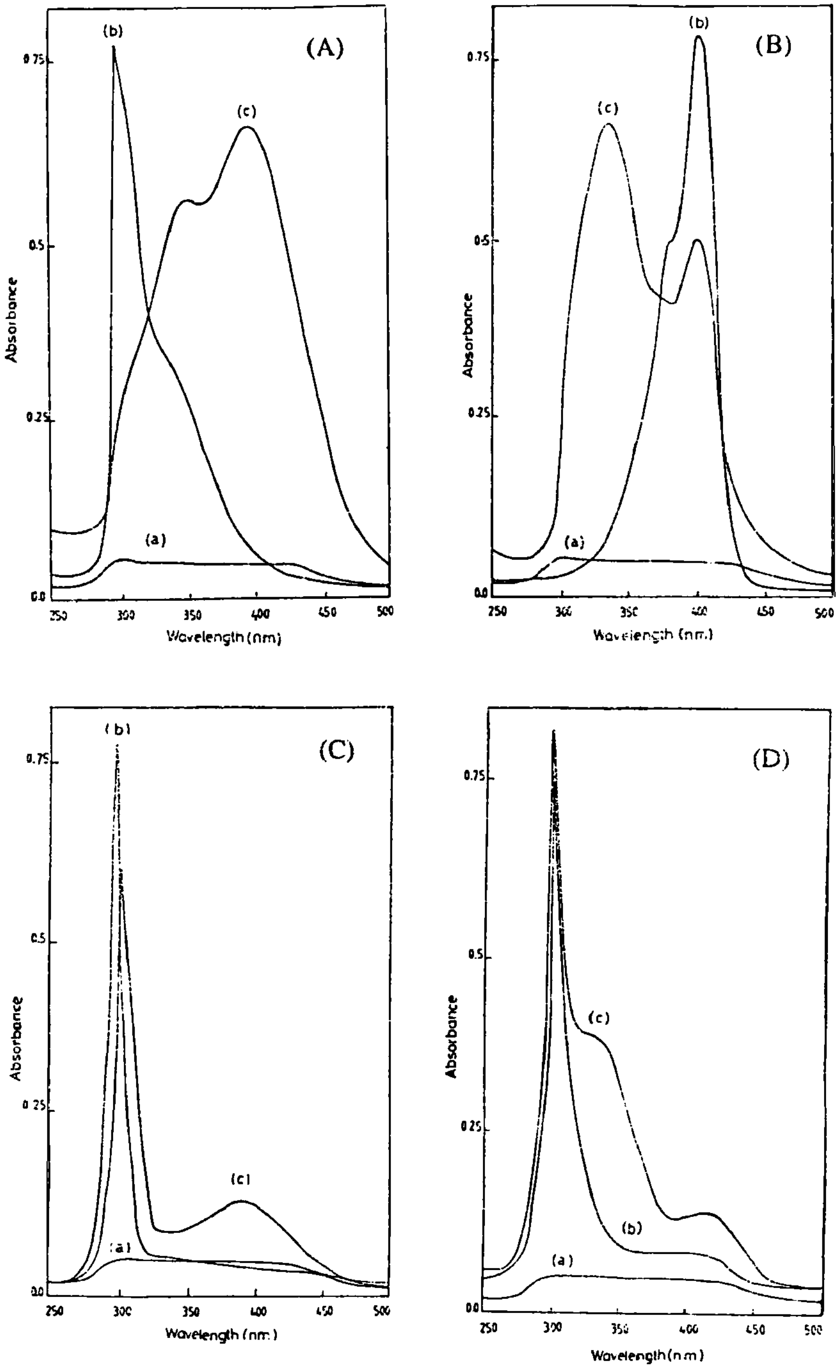

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chloride, TCNQ, chloranil and TCNE) (1 x 10^{-4} M) in $CHCl_3$ along with those of the related 1 : 2 CT-complexes are shown in Figure 1. The spectra demonstrate that the formed CT-complexes have strong absorption bands around 395 and 350 nm for [(TACTD) (picryl chloride)$_2$], 400 and 335 nm for [(TACTD) (TCNQ)$_2$], 395 and 300 nm for [(TACTD) (chloranil)$_2$], and 415 and 300 nm for [(TACTD) (TCNE)$_2$] complexes, respectively. The stoichiometry of the (TACTD)-(acceptor) reactions were shown in all cases to be of ratio 1 : 2. This was calculated on the bases of the obtained elemental analysis data of the isolated solid CT-complexes as indicated in the experimental section as well as from the complexes infrared spectra, Figure 2 and Table 2, which indicate the existence of the bands characteristic for both the TACTD and the acceptors. The stoichiometry of 1 : 2 is also strongly supported by photometric titration measurements. These measurements were based on two

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Figure 1. Electronic absorption spectra of (A) : TACTD - picryl chloride reaction (a: [TACTD] = 1 x 10^{-3} M, b : [picryl chloride] = 10^{-4} M and c: TACTD - picryl chloride mixture [TACTD] = 2 x 10^{-4} M and [picryl chloride] = 4 x 10^{-5} M), (B): TACTD - TCNQ reaction (a: [TACTD] = 1 x 10^{-3} M, b : [TCNQ] = 1 x 10^{-4} M and c: TACTD - TCNQ mixture [TACTD] = 2 x 10^{-4} M and [TCNQ] = 4 x 10^{-5} M), (C) : TACTD - chloranil reaction (a: [TACTD] = 1 x 10^{-3} M, b : [chloranil] = 1 x 10^{-4} M and c: TACTD - chloranil mixture [TACTD] = 2 x 10-4 M and [chloranil] = 4 x 10^{-5} M), and (D) : TACTD - TCNE reaction, (a: [TACTD] = 1 x 10^{-3} M, b : [TCNE] = 1 x 10^{-4} M and c: TACTD - TCNE mixture [TACTD] = 2 x 10^{-4} M and [TCNE] = 4 x 10^{-5} M).

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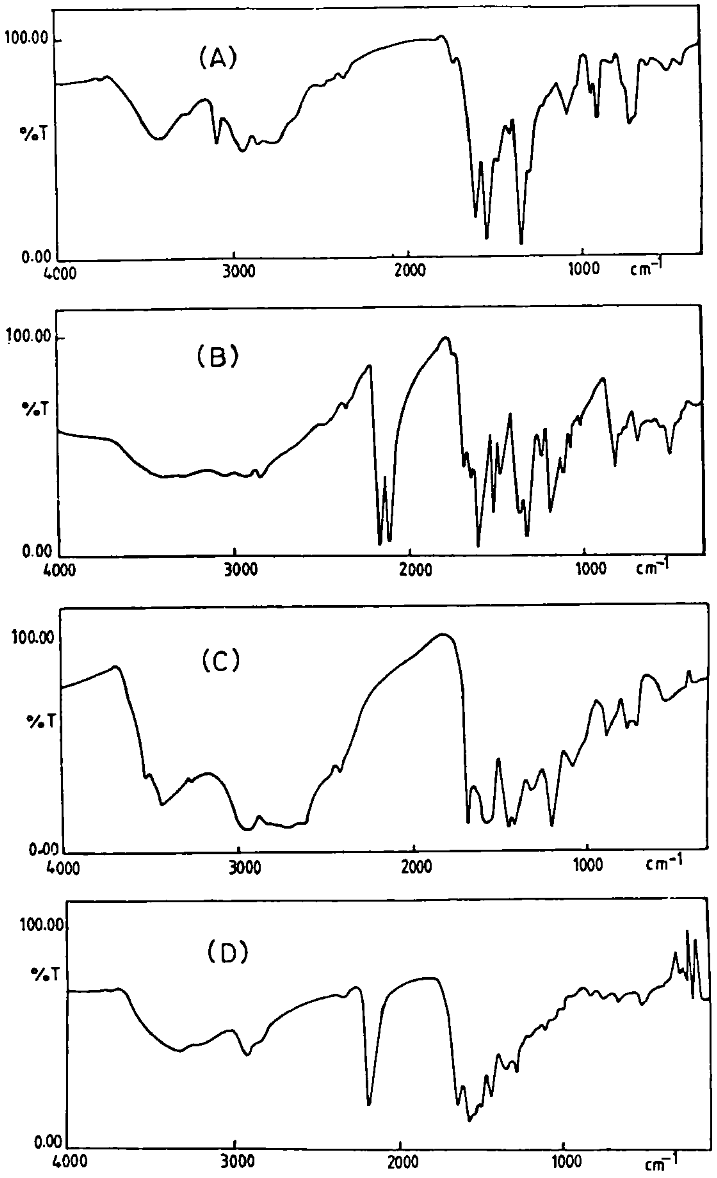

Figure 2. Infrared spectra of CT-Complexes :

(A) : [(TACTD) (picryl chloride)$_2$], (B) : [(TACTD) (TCNQ)$_2$], (C) : [(TACTD) (chloranil)$_2$] and (D) : [(TACTD) (TCNE)$_2$].

Table 1. Spectrophotometric results of the CT-complexes of [(TACTD) $(TCNQ)_2$], [(TACTD) $(TCNE)_2$], [(TACTD) (picryl chloride)$_2$] and [(TACTD) (chloranil)$_2$] in $CHCl_3$.

Acceptor	K x 10^8 (l/mol)	λ_{max} (nm)	ε_{max} x 10^4 (M^{-1} cm^{-1})
TCNQ	12.00	400	0.3
TCNE	0.790	415	0.23
Picryl chloride	0.310	395	2.50
Chloranil	0.071	395	0.52

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strong absorption bands for each of the (TACTD)-(acceptor) systems indicated above, where the concentration of TACTD was kept fixed while the concentration of the acceptor was varied as described in the experimental section. Photometric titration curves are shown in Figure 3, where the TACTD-acceptors equivalence points indicate that the TACTD : acceptor ratio in all cases is 1 : 2 and thus, this result agrees quite well with the elemental analysis and infrared spectra of the formed solid CT-complexes formulated as [(TACTD) $(Accept.)_2$]. The spectrophotometric data were used to calculate the values of both equilibrium constants, K, and extinction coefficient, ε of the CT-

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Table 2. Characteristics infrared frequencies (a) (cm^{-1}) and tentative assignments for [(TACTD) $(TCNQ)_2$], [(TACTD) $(TCNE)_2$], [(TACTD) (picryl chloride)$_2$] and [(TACTD) (chloranil)$_2$] complexes.

TCNQ	TCNE	Picryl chloride	Chloranil	TACTD	[(TACTD) $(TCNQ)_2$]	[(TACTD) $(TCNE)_2$]	[(TACTD) (picryl chloride)$_2$]	[(TACTD) (chloranil)$_2$]	Assignments
				3450 mbr		3344 br		3542 w	ν (O-H); H_2O of KBr.
	--			3260 S	3200 vw	3206 w	3445 mbr	3455 w	
				3184 S			3250 vw	3260 w	ν (N-H); TACTD
3141 vw		3141 vw		3086 vw	2943 w	2927 m	2954 vw	2954 br	ν (C-H); TACTD
3054 m		3058 S		3000 w	2846 w	2824 w	2846 vw	2846 vw	ν (CH_2);-; $-(CH_2)_2$; $(CH_2)_3$-
2954 vw		2868 w		2922 ms	2488 vw		2738 vw	2802 m	
2857 vw		2803 vw		2868 ms				2477 w	
		2737 vw		2805 vs				2390 m	
		2694 vw		2761 m					
		2542 vw		2662 w					
				2597 vw					
				2369 vw					
		1835 w							ν (NO_2);picryl chloride
			1680 vs						
			1564 S					1694 S	ν (C=O), chloranil
1772 S	1673 S	1716 vw			1672 w	1760 m	1705 vw		ν (C=C), TCNQ, TCNE and picryl chloride
1542 m		1607 ms			1629 w	1586 s	1609 s		
					1596 vs				
					1500 s				
				1456 m	1444 ms	1641 m		1412 m	CH deformation; TACTD
				1412 w		1573 s			
						1504 m			
						1435 m			

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1282 vw 1206 vw 1199 m 1043 vw	1141 vs 1098 m 1065 m 1022 w	1195 m 1065 s	1356 w 1298 w 1199 w 1149 m 1132 m 1099 s	1369 vs 1326 s 1282 m 1217 ms 1130 vs 1065 s	1249 m 1184 s 1108 m 1074 m 1000 w	1344 m 1275 m 1206 vw 1110 w 1046 vw	1282 vw 1206 vw 1141 vw 1065 s	1303 w 1195 m 1065 w	v (C-C); v (C-N); TACTD, TCNQ and TCNE
956 m 859 vs	957 s 935 m 816 m	913 s 805 vw	966 vw 917 ms	967 s 881 w 826 vs	978 vw 945 w 826 ms	931 w 801 vw	946 w 913 s 815 vw	848 vw 827 vw	CH deformation, TACTD,TCNQ, picryl chloride and chloranil
631 vw		761 sh 718 vs 642 m	751 s 718 s	783 m	793 vw 761 vw 696 vw 658 vw	771 vw 702 vw	761 vw 740 ms 718 sh 635 vw	761 w 739 vw 718 w	v (C-Cl); picryl chloride and chloranil CH in plane bend; TACTD, TCNQ, TCNE and picryl chloride
531 vw 457 s		755 w 523 w 458 vw	566 w	598 vw 512 w 479 vw 436 vw	566 vw 512 ms	565 w 450 vw	533 m 436 w	566 vw 512 ms	CH out of plane bend; TACTD, TCNQ and picryl chloride

(a) : S = strong, W = weak, m = medium, Sh = shoulder and V = very

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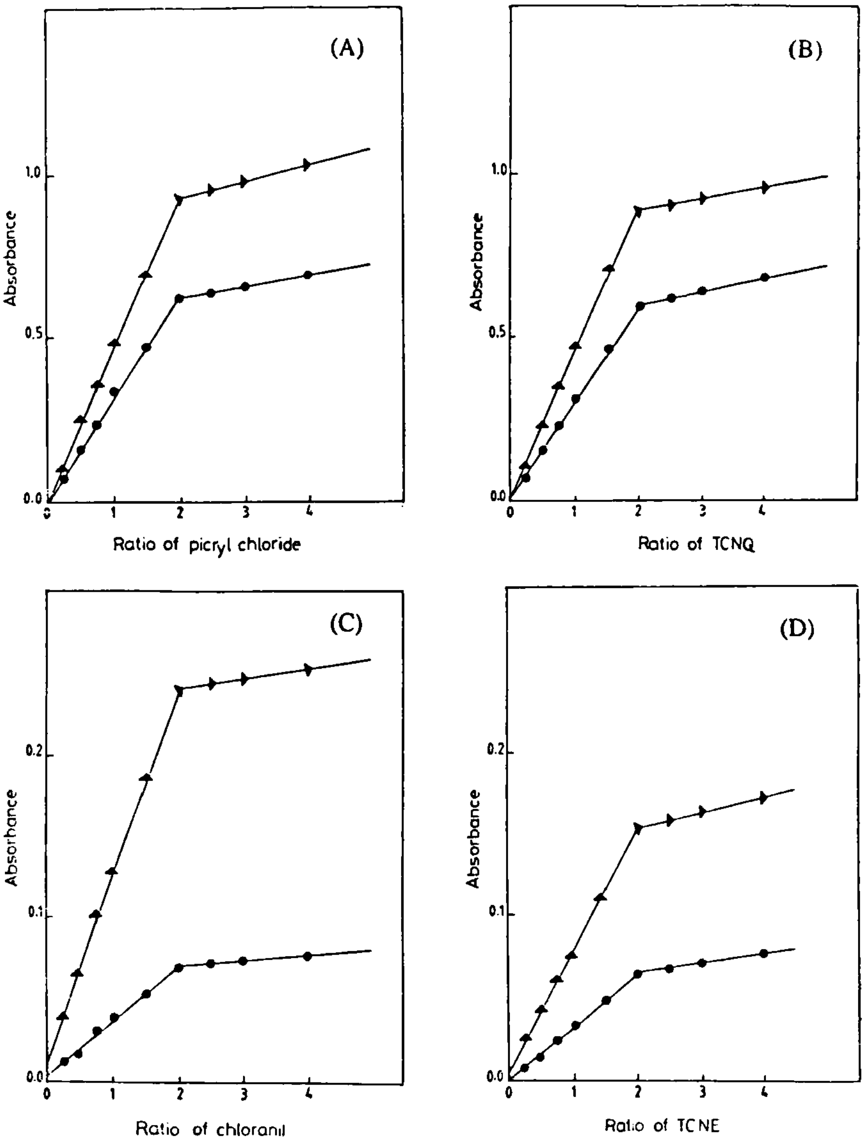

Figure 3. Photometric titration curves for the TACTD-Acceptor reactions in $CHCl_3$

(A) : TACTD - picryl chloride reaction; Δ : 395 nm band and; • : 350 nm band.

(B) : TACTD-TCNQ reaction; • : 400 nm band and Δ : 335 nm band.

(C) : TACTD-chloranil reaction; • : 395 nm band and Δ : 300 nm band.

(D) : TACTD-TCNE reaction; • : 415 nm band and Δ : 300 nm band.

complexes in $CHCl_3$ based on the known equation for the 1 : 2 complexes [12] :

$$\frac{C^{\circ 2}_A \cdot C^{\circ}_D}{A} = \frac{1}{K.\varepsilon} + \frac{1}{\varepsilon} \cdot C^{\circ}_A (4C^{\circ}_D + C^{\circ}_A)$$

Where $C^{\circ 2}_A$ and C°_D are the initial concentration of the acceptor and the donor, respectively, and A is the absorbance of the band. By plotting $C^{\circ 2}_A\ C^{\circ}_D/A$ vs $C^{\circ}_A\ (4C^{\circ}_D + C^{\circ}_A)$, straight lines were obtained supporting our conclusion of the formation of the 1 : 2 complexes $[(TACTD)\ (Accept.)_2]$. In these plots the slope and intercept for each case equal 1/ε and 1/K.ε, respectively. The values of both K and ε associated with the complexes [(TACTD) (picryl chloride)$_2$], [(TACTD) (TCNQ)$_2$], [(TACTD) (TCNE)$_2$] are given in Table 1. These data reveal several facts. Firstly, the [(TACTD) (Tpicryl chloride)], [(TACTD) (TCNQ)$_2$], [(TACTD) (chloranil)$_2$] and [(TACTD) (TCNE)$_2$], complexes show high values of both the formation constants (K) and the extinction coefficients (ε). These high values of K confirm the expected high stabilities of the formed CT-complexes as a result of the expected high donation of the cyclic polyamine base, (TACTD), which it contains four donor nitrogen atoms. Secondly, the values of the equilibrium constants are strongly dependent on the nature of the used acceptor including the type of electron withdrawing substituents to it such as nitro, cyano and halo groups. For example, Table 1, the value of equilibrium constant for [(TACTD) (TCNQ)$_2$] complex in $CHCl_3$ is about hundred times, fourty times and fifteen times higher than the values of equilibrium constant for the complexes [(TACTD) (chloranil)$_2$], [(TACTD) (picryl

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chloride)$_2$] and [(TACTD) (TCNE)$_2$], respectively. This is understood on the basis of the differences in the electronic structure of the acceptors, TCNQ, chloranil, picryl chloride and TCNE, while TCNQ acceptor has four strong withdrawing cyano groups in conjugation with an aromatic ring which causes high delocolization leads to a great increase in the Lewis acidity of the acceptor, (TCNQ), and hence the higher value of K for [(TACTD) (TCNQ)$_2$] complex compared with those of the other used acceptors.

The infrared spectra of the formed CT-complexes, [(TACTD) (Accept.)$_2$] (acceptors = picryl chloride, TCNQ, chloranil and TCNE) are shown in Figure 2, and their band assignments are given in Table 2. These assignments are based on the comparison of the spectra of CT-complexes with the spectra of the reactants, (TACTD) base and the acceptors. The spectra of the reaction products contain the main bands for both the reactants, acceptors and (TACTD) and this strongly supports the formation of the (TACTD) - (Acceptor) CT-complexes. However, the bands of the acceptors and (TACTD) in the spectra of [(TACTD) (Accept.)$_2$] complexes show some changes in intensities and in some cases show small shifts in the frequency values compared with those of the free acceptors and the base (TACTD). This could be understood in the basis of symmetry and electronic structure changes in both acceptor and TACTD in the formed CT-complexes compared with those of the free molecules. Finally, since the formed CT-complexes is of a ratio of 1 : 2, with the general formula [(TACTD) (Accept.)$_2$], it's more likely that the (TACTD) cyclic polyamine is arranged in such a way that to be sandwiched between two acceptor molecules.

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