

# MOLECULAR COMPLEXES OF SOME THIACROWN ETHERS AND 1,3,5-TRITHIANE WITH IODINE IN DICHLOROMETHANE AND CARBONTETRACHLORIDE SOLUTIONS

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**Abstract.** A spectrophotometric study concerning the interaction between 1,3,5-trithiane (TT), trithia-9-crown-3 (TT9C3), tetrathia-12-crown-4 (TT12C4) and hexathia-18-crown-6 (HT18C6) as n-donor with iodine as  $\sigma$ -acceptor has been performed in dichloromethane and carbontetrachloride solutions. The results are indicative of the formation of 1:1 molecular complexes through equilibrium reactions in both solvents. The stability constants of the reactions were evaluated from the fitting of absorbance vs. mole ratio data in MATLAB software. The results indicate that in both solvents stabilities vary in the order: TT<TT12C4<TT9C3<HT18C6. Also, the results are indicative of the formation of more stable complexes in CCl<sub>4</sub> than of CH<sub>2</sub>Cl<sub>2</sub>. These observations are interpreted based on the structural features of donors and specifications of solvents. The reverse trend of  $\epsilon$  values and higher  $\epsilon$  values in CH<sub>2</sub>Cl<sub>2</sub> than that of CCl<sub>4</sub> are the other discussed results.

**Keywords:** spectrophotometry, thiacycrown ethers, iodine, dichloromethane, carbontetrachloride

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## Introduction

Thiacrown ethers were first prepared 75 years ago [1], but low yield synthetic routes long limited their use as ligands, development of reliable high-yield routes provided a major impetus to investigation of their coordination chemistry, most of which were reported in the last 25 years [2]. As a penetrating example, Ochrymowcz's preparation of trithia-9-crown-3 (TT9C3) [3] did not attract interest from coordination chemist until 1983 [4]; development of high-yield synthesis resulted in an explosion of activity [5].

The coordination chemistry of thiacrown ethers as ligands is an intensive area of study and several relevant reviews in the recent past years have demonstrated impressively the usefulness of this ligand type in basic research, as well as in practice oriented fields [6]. The analytical applications of macrocyclic polythiaethers in areas such as solvent-solvent extraction [7], solid phase extraction [8] and PVC-membrane electrodes have been reported in literature [9,10].

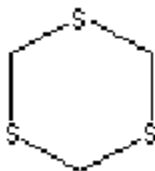
Recently there has been a growing interest in the studies of charge transfer complexes between macrocyclic ethers and a variety of acceptor molecules such as DDQ [11], TCNE [12], TCNQ [13], TNT [14], picric acid [15] and especially iodine [16]. However to the best of our knowledge, there are only a limited number of published reports dealing with the complexation of iodine with thiacrown ethers in solution and in crystalline form [17,18].

In this paper we report the results of spectrophotometric study of the complexation of macrocycles trithia-9-crown-3 (TT9C3), tetrathia-12-crown-4 (TT12C4) and hexathia-18-crown-6 (HT18C6) in dichloromethane solution. For comparison, the complexation of 1,3,5-trithiane (TT) have also been studied.

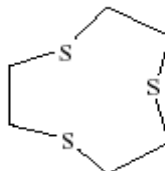
## Experimental

Reagent grade HT18C6, TT14C4, TT9C3 and TT (all from Aldrich) were used as received. Reagents grade of iodine, dichloromethane and carbontetrachloride from Merck Company are used without any further purification.

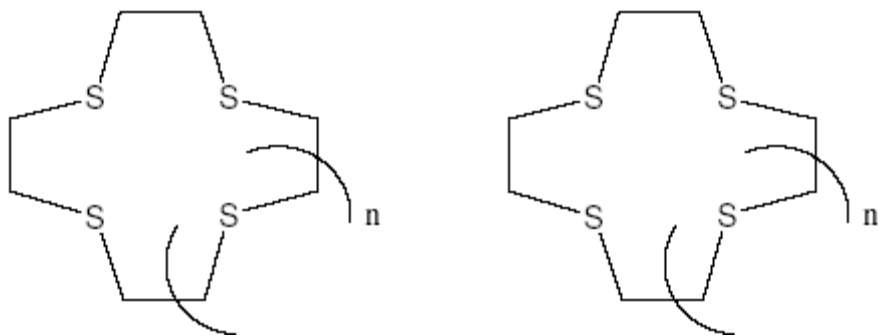
All UV-Vis spectra were recorded on a Shimadzu UV-Vis spectrophotometer and the absorbance measurements were made with the same instrument using a quartz cell.



1,3,5-Trithiane (TT)



Trithia-9-crown-3 (TT9C3)

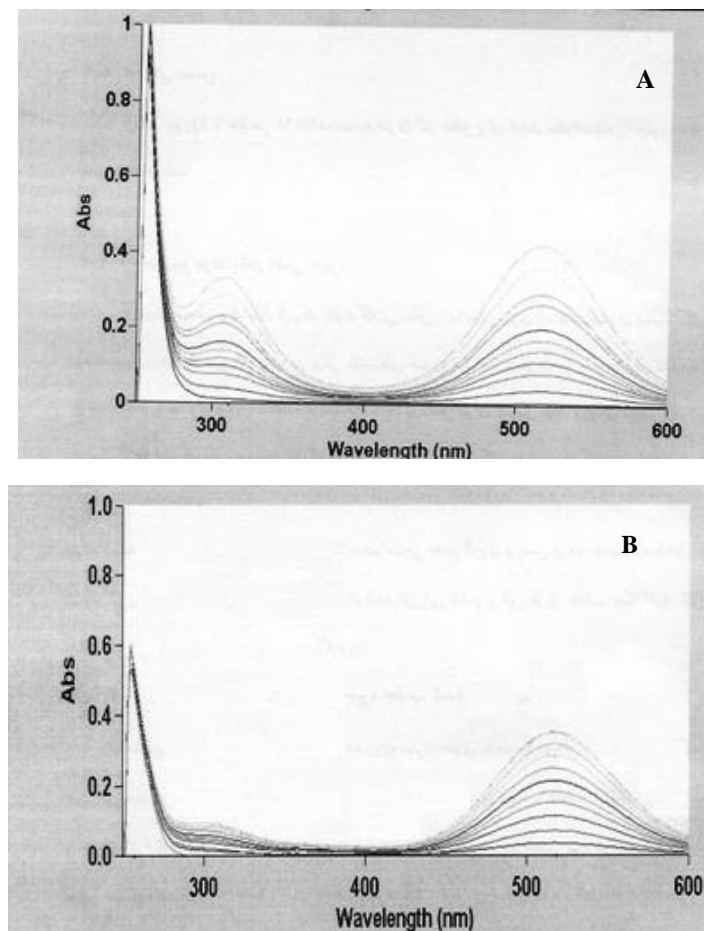


**n=1, Tetrathia-12-crown-4 (TT12C4) n=3, Hexathia-18-crown-6 (HT18C6)**

In order to obtain UV-Vis spectra, 3 mL of  $10^{-3}$  M of donor solutions were retransferred to 1.00 cm quartz cell and titrated with a concentrated iodine solution by a 100- $\mu$ L Hamilton syringe. Each spectrum was recorded immediately after the titrant addition. The same procedure was followed for absorbance-mole ratio measurements. For obtaining isosbestic points, several solutions containing constant concentration of iodine and different concentrations of donor was prepared and the spectra of corresponding solutions were recorded. For obtaining Job's data, equimolar ( $10^{-3}$  M) stock solutions of iodine and donors were prepared and the needed solutions were made by mixing and diluting (to 5 mL) of appropriate volumes of donor and acceptor.

### Results and discussion

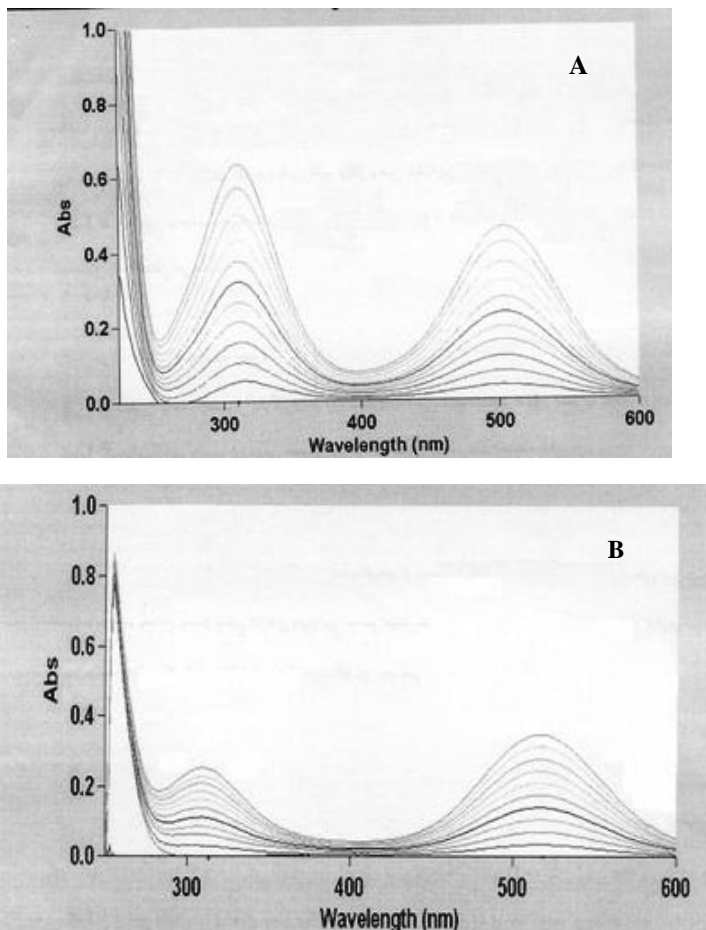
Absorption spectra of  $10^{-3}$  M of TT in the presence of varying quantities of iodine in  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$  solutions are shown in Fig. 1. The corresponding spectra due to TT9C3, TT12C4 and HT18C6 are shown in Figs. 2-4, respectively. As it can be seen, the spectra of donors show a narrow band in the 270 nm and do not show any band in visible region. However, upon addition of iodine, two new bands are appeared at 310 and 510 (in  $\text{CH}_2\text{Cl}_2$  solution) or 520 nm (in  $\text{CCl}_4$  solution). The 510 and 520 nm is well known band of free iodine [19]. Meanwhile, the 310 nm band can be attributed to the formation of charge transfer complex between iodine as  $\sigma$ -acceptor and the thia compounds as n-donors [20].



**Fig. 1.** Absorption spectra of  $10^{-3}$  M of TT in the presences of varying quantities of iodine in  $\text{CH}_2\text{Cl}_2$  (A) and  $\text{CCl}_4$  (B) solutions. The  $\text{I}_2/\text{TT}$  mole ratios from bottom to top are: 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 and 2.2, respectively.

The  $\text{I}_2/\text{donor}$  mole ratios vary from 0 to 2.2. So, the observation of iodine band indicates that the reaction of iodine and donors are not complete and some unreacted iodine exists. In fact, if a complete reaction was occurred, a very low intensity band (at 510 or 520 nm) would be observed.

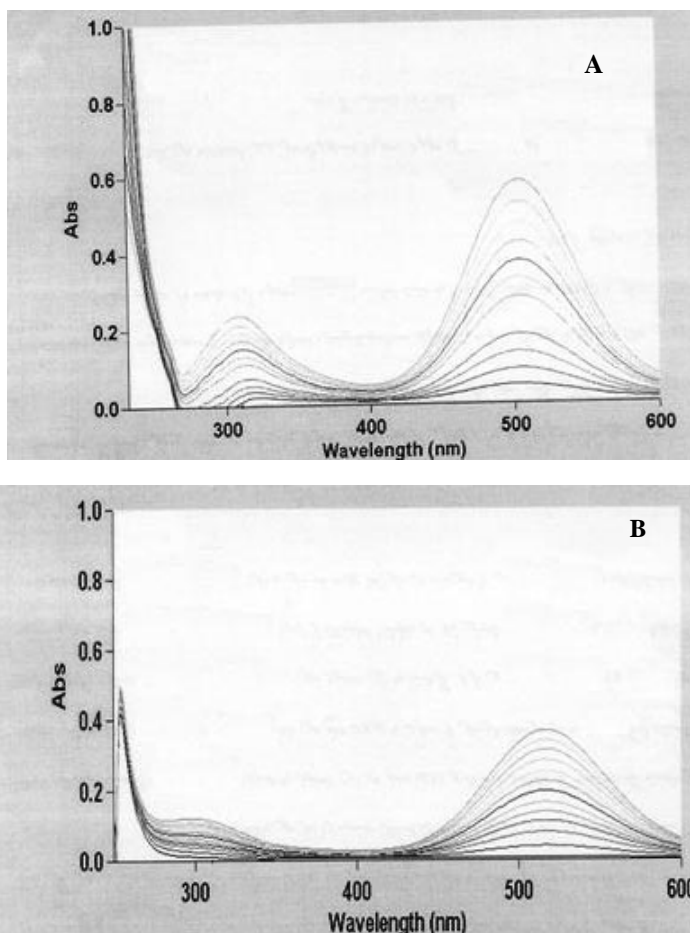
It is interesting to note that in all of spectra, the intensity of iodine bands in  $\text{CH}_2\text{Cl}_2$  are more than the corresponding ones in  $\text{CCl}_4$ . This can be assigned to higher  $e$  of free iodine in  $\text{CH}_2\text{Cl}_2$  than  $\text{CCl}_4$ , or the highest concentrations of unreacted iodine in the former than the latter solvent, or both of these effects.



**Fig. 2.** Absorption spectra of  $10^{-3}$  M of TT9C3 in the presence of varying quantities of iodine in  $\text{CH}_2\text{Cl}_2$  (A) and  $\text{CCl}_4$  (B) solutions. The  $\text{I}_2/\text{TT9C3}$  mole ratios from bottom to top are: 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, and 2.2, respectively.

The spectra in Figs 1-4 also show that in all cases (i) the intensities of charge transfer bands in  $\text{CH}_2\text{Cl}_2$  are more than  $\text{CCl}_4$  and (ii) in both solvents the intensities vary in the order:  $\text{HT18C6} > \text{TT9C3} > \text{TT12C4} > \text{TT}$ . These are fairly shown in Fig. 5.

The higher intensities of charge transfer bands in  $\text{CH}_2\text{Cl}_2$  could be due to higher  $\epsilon$  of charge transfer complexes in this solvent or it may be related to the formation of more stable complex in  $\text{CH}_2\text{Cl}_2$  than  $\text{CCl}_4$ . Also it may be due to both of these effects. On the other hand, the observed trends in the intensities of charge transfer of different donors may be a reflection of  $\epsilon$  or  $K_f$  effects.

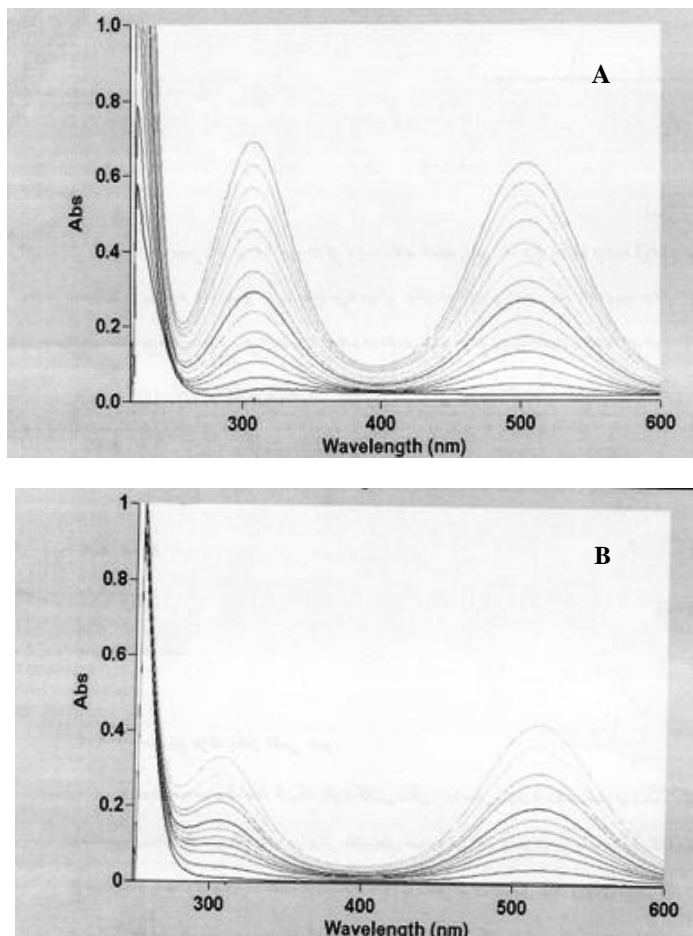


**Fig. 3.** Absorption spectra of  $10^{-3}$  M of TT12C4 in the presence of varying quantities of iodine in  $\text{CH}_2\text{Cl}_2$  (A) and  $\text{CCl}_4$  (B) solutions. The  $\text{I}_2/\text{TT12C4}$  mole ratios from bottom to top are: 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, and 2.2, respectively.

Fig. 6 shows the absorption spectra of iodine in the presence of different quantities of HT18C6 in  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$ . The observation of isosbetic points in both solvents indicate that the interaction of iodine with HT18C6 follows through equilibrium pathway [21]. Similar behavior was observed for other donors. However, because of identically the corresponding spectra are not shown.

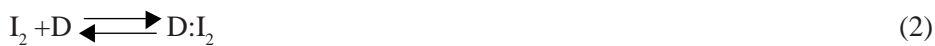
Based on the spectral behavior of iodine-donor mixtures, it can be concluded that the following reaction occurs between iodine and various donors.



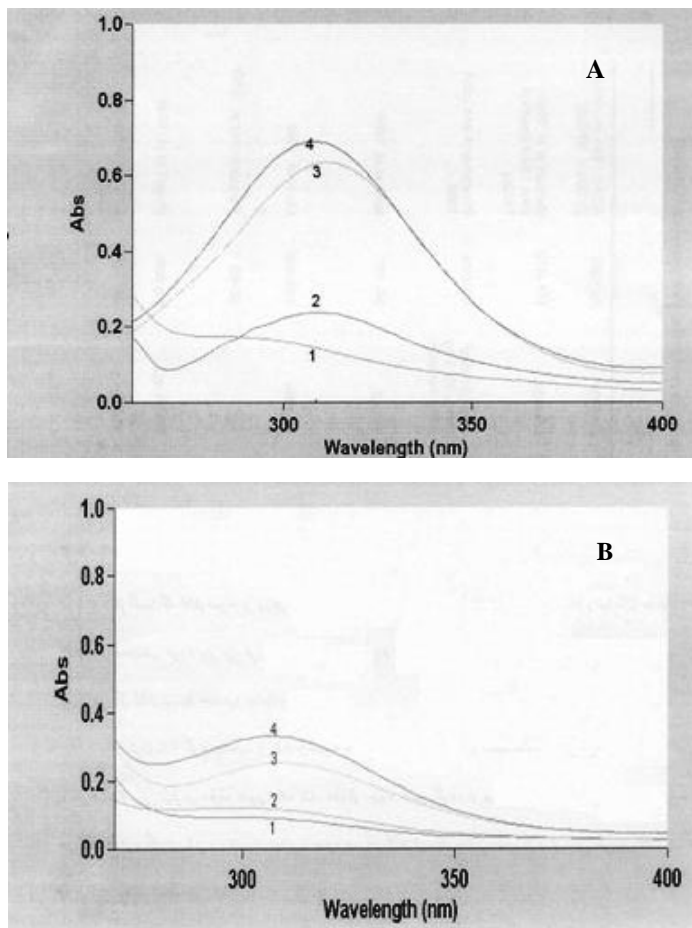


**Fig. 4.** Absorption spectra of  $10^{-3}$  M of HT18C6 in the presence of varying quantities of iodine in  $\text{CH}_2\text{Cl}_2$  (A) and  $\text{CCl}_4$  (B) solutions. The  $\text{I}_2/\text{HT18C6}$  from bottom to top are: 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 and 2.2, respectively.

In order to determine the stoichiometry of the above reaction, the absorbance vs. mole ratio [22] and Job's methods [23] were employed. The corresponding plots are shown in Figs.7 and 8, respectively. Despite, the mole ratio plots (Fig.7) do not clearly show the stoichiometry, the Job's plots for HT18C6 in  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$  obviously confirm 1:1 stoichiometry and because of similarity this is extended to all complexes. Thus, the Eq. (1) can be rewritten as follows:



$\text{D} = \text{TT}, \text{TT9C3}, \text{TT12C4}, \text{HT18C6}$



**Fig. 5.** Absorption spectra of  $10^{-3}$  M of TT(1), TT9C3(2), TT12C4(3) and HT18C6(4) in the presence of  $2 \times 10^{-3}$  M of iodine in  $\text{CH}_2\text{Cl}_2$ (A) and  $\text{CCl}_4$  (B) solutions.

The formation constants of the resulting complexes were evaluated from absorbance–mole ratio data by using a nonlinear least square curve fitting program (curve-fitting toolbox in MATLAB). The program is based on the iteration adjustment of calculated absorbances to the observed values [24–26]. The observed absorbance of complex is given by Eq. (3). The mass balance equations can be written as (4) and (5) and the formation constant of the complex as in (6). With substitution of equations (4) and (5) into (6) and rearrangement yields (7).

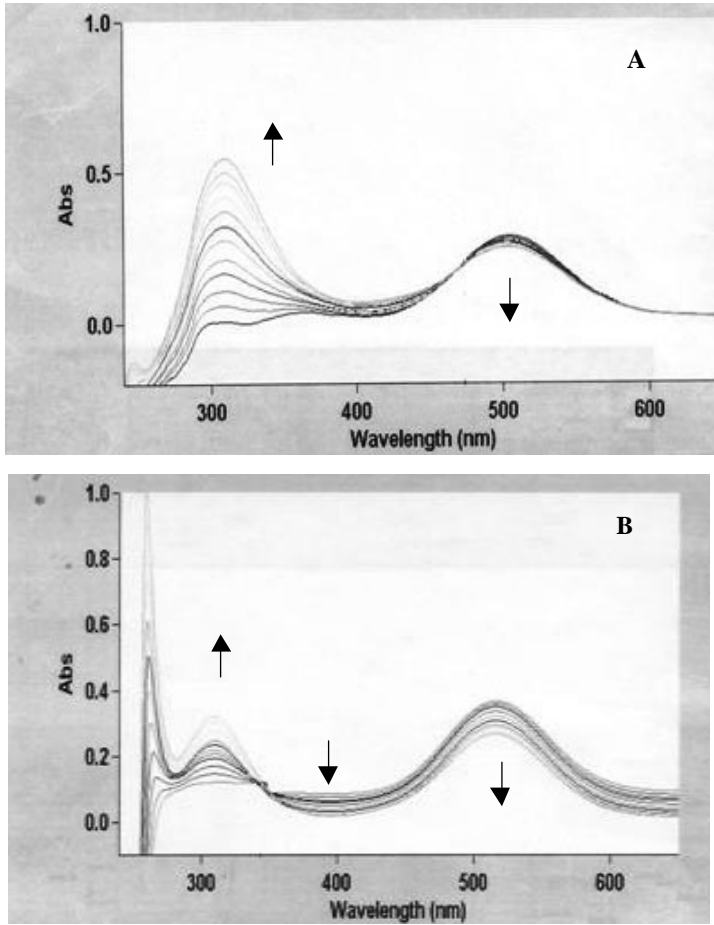
$$A = \epsilon b [\text{DA}] \quad (3)$$

$$C_D = [\text{D}] + [\text{DA}] \quad (4)$$

$$C_A = [\text{A}] + [\text{DA}] \quad (5)$$

$$K_f = [DA]/[D][A] \quad (6)$$

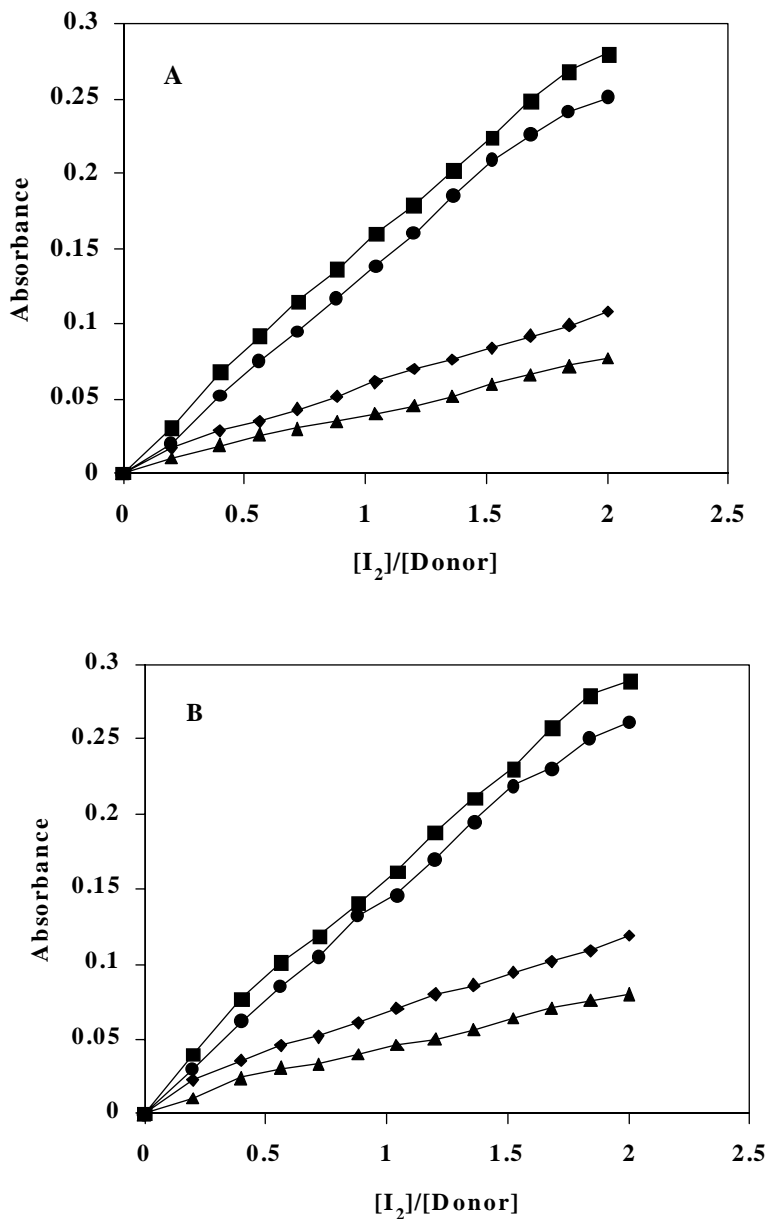
$$K_f[DA]^2 - (C_A K_f + C_D K_f + 1)[DA] + K_f C_D C_D = 0 \quad (7)$$



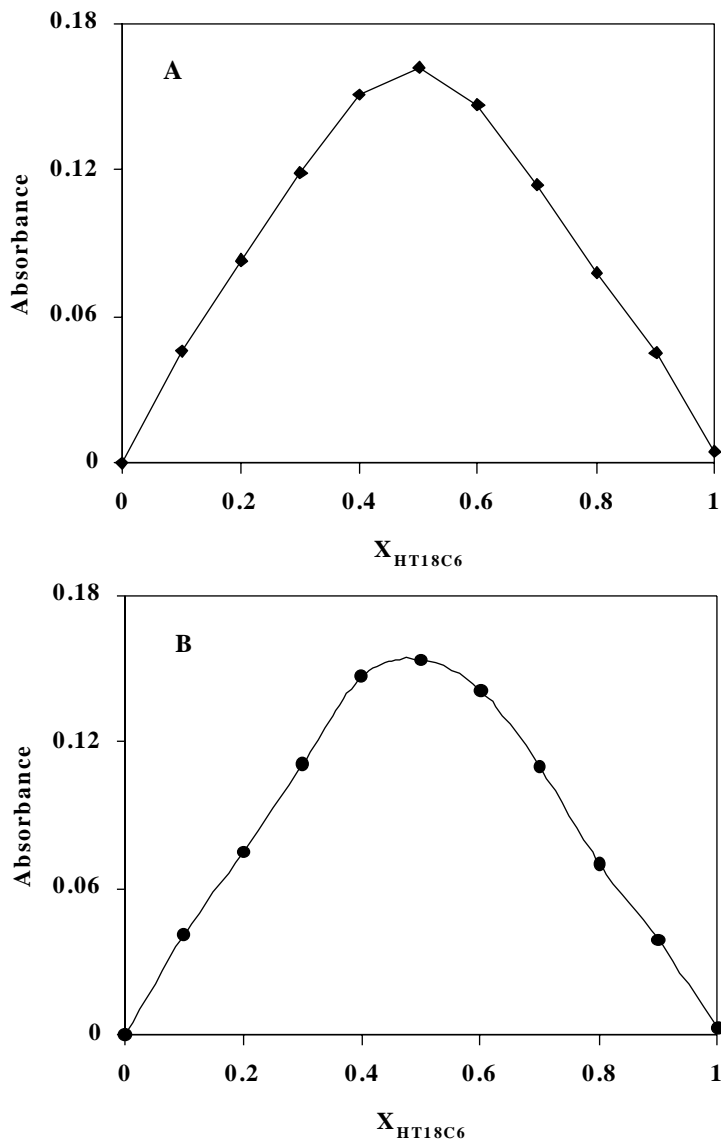
**Fig. 6.** Absorption spectra of  $10^{-3}$  M of  $I_2$  in the presence of varying concentrations of HT18C6 in  $CH_2Cl_2$  (A) and  $CCl_4$  (B) solutions. The HT18C6/ $I_2$  mole ratios are: 0.0, 0.2, 0.6, 0.8, 2.0, 1.2, 1.4, 1.6, 1.8, 2.0 and 2.2, respectively.

With use an approximation value for  $K_f$ , the free DA concentration,  $[DA]$ , were calculated by solution of second order equation. Then, with using data of DA concentration as X data and data of observed absorbances as Y data, the least square fit technique is used for fitting the data. The output of this fitting is the coefficients of line fit. The coefficient of X values is  $\epsilon$ . The obtained coefficients were used for calculation data of calculated absorbances with using of parabolic fit. To find the least squares error, the sum of squares of the differences between the parabolic fit and the experi-

mental data must be evaluated. Refinement of parameter ( $K_f$  value) was continued until the sum-of-squares of the residuals between calculated and observed values of the absorbance for all experimental points was minimized [24-26].



**Fig. 7.** Absorption vs. mole ratio plots for  $10^{-3}M$  of donor in  $CH_2Cl_2$  (A) and  $CCl_4$  (B) Solutions. The plots are due to TT (▲), TT12C4 (◆) TT9C3 (●) and HT18C6 (■).



**Fig. 8.** Plot of absorbance vs. mole fraction of HT18C6 in CH<sub>2</sub>Cl<sub>2</sub> (A) and CCl<sub>4</sub> (B) solutions

The calculated  $\log K_f$ ,  $\log \epsilon$  and  $\log K_f \epsilon$  values are given in Table 1. The data show that (i) in both solvents, stabilities vary in the order: TT < TT12C4 < TT9C3 < HT18C6, (ii) In contrast to stabilities, the  $\epsilon$  values vary as: TT > TT12C4 > TT9C3 > HT18C6, (iii) the formation constants of complexes in CCl<sub>4</sub> are greater than that of CH<sub>2</sub>Cl<sub>2</sub> and (iv) the  $\epsilon$  values in CCl<sub>4</sub> are lower than CH<sub>2</sub>Cl<sub>2</sub> and (v) the  $K \cdot \epsilon$  alter in parallel to  $K$  values.

**Table 1.** The  $\log K_f$ ,  $\log \epsilon$  and  $\log K\epsilon$  values of different donor-acceptor complexes in  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$  solutions.

Donor	$\log K_f$		$\log \epsilon$		$\log K\epsilon$	
	$\text{CH}_2\text{Cl}_2$	$\text{CCl}_4$	$\text{CH}_2\text{Cl}_2$	$\text{CCl}_4$	$\text{CH}_2\text{Cl}_2$	$\text{CCl}_4$
TT	$1.56 \pm 0.02$	$1.73 \pm 0.03$	$3.75 \pm 0.01$	$3.64 \pm 0.01$	$5.31 \pm 0.02$	$5.37 \pm 0.03$
TT12C4	$1.75 \pm 0.02$	$1.99 \pm 0.01$	$3.66 \pm 0.02$	$3.59 \pm 0.01$	$5.41 \pm 0.03$	$5.58 \pm 0.02$
TT9C3	$1.95 \pm 0.02$	$2.35 \pm 0.05$	$3.52 \pm 0.03$	$3.41 \pm 0.03$	$5.47 \pm 0.04$	$5.76 \pm 0.06$
HT18C66	$2.10 \pm 0.03$	$2.69 \pm 0.02$	$3.45 \pm 0.02$	$3.33 \pm 0.01$	$5.55 \pm 0.04$	$6.02 \pm 0.03$

It is well known that the fitness of the metal ion diameter with cavity size of macrocyclic crown ether play an important role in the stabilities of the ionic complexes of crown ethers [27]. However, the van-der-Walls diameter of  $\text{I}_2$  is  $4 \text{ \AA}$  [28] and the probability of the location of this molecule in the cavity of HT18C6 (with the size of  $\sim 2 \text{ \AA}$  [29]) and other donors (with the sizes less than  $2 \text{ \AA}$ ) is strongly discarded.

The formation of molecular complexes of donor cavities in which the iodine molecule is in the outside involves the proper orientation of sulphur atoms toward  $\text{I}_2$ . This also needs specific conformations of donors in the complex. However, the rigid structure of TT, hinder the attainment of proper conformation. Thus, the observation of weakest stability among the donors is not unexpected (Table 1). On the other hand, the flexibility of TT9C3 is more than TT and its sulfur atoms can oriented toward  $\text{I}_2$  easily. So, it forms stronger complex than TT.

Both flexibility and the number of donating atoms of TT12C4 are more than TT and based on these properties it is expected that the stability of the former to be more than the latter. Meanwhile, the reverse is observed. It seems that such observation can be related to the participation of limited number of sulfur atoms in complexation. Presumably, there are three sulfur atoms for the maximum capacity of the iodine. So, the fourth sulfur of TT12C4 ring, do not participate in the complexation process. Instead, it lowers the stability by applying repulsion forces to lone pairs of iodine. Thus, the presence of fourth sulfur, not only do not support the complex via electron donation but also, weakens it through repulsion forces.

Among the donors, HT18C6 do have the highest flexibility. So, its sulfur atoms have easily orients toward iodine molecule and the best orientation is obtained. In addition, the unreacted atoms can easily locate in places which are far enough from iodine and destabilize repulsion forces. Thus, the observation of highest stability for HT18C6- $\text{I}_2$  complex is not unexpected.

It seems that the reverse order of  $\epsilon$  values can be related to the absorption cross section [30, 31] which may be highest for TT- $\text{I}_2$  and lowest for HT18C6- $\text{I}_2$  complexes. On

the other hand, the increasing of  $K\epsilon$  upon the increasing of  $K$  values is in accordance with the literature values reported for some other charge-transfer complexes [12,13, 32].

The lower  $\epsilon$  values in  $\text{CCl}_4$  than that of  $\text{CH}_2\text{Cl}_2$  can be related to solvent effect on the molar absorption coefficient [30]. The probability of collision of the photons to complex molecules were increased because the increasing of orientation of the complex molecules in the polar solvent of  $\text{CH}_2\text{Cl}_2$ . Therefore, the higher  $\epsilon$  values were observed in the dichloromethane solvent.

The higher stability in  $\text{CCl}_4$  than that of  $\text{CH}_2\text{Cl}_2$  can be attributed to the dipole-dipole interactions between  $\text{CH}_2\text{Cl}_2$  and donors or the more dipole-induced dipole interactions between the solvent and iodine [28]. In fact the existence of such forces causes the effective competition of  $\text{CH}_2\text{Cl}_2$  which results the lower stability in this solvent. As  $\text{CCl}_4$  do not have permanent dipole, thus such interactions in this solvent are low. Consequently, higher stability is observed.

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