COMPLEX FORMATION BETWEEN SOME THIACROWN ETHERS AND 1,3,5-TRITHIANE WITH BROMINE IN GAS PHASE AND CARBON TETRACHLORIDE SOLUTION

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Abstract. Complex formation between hexathia-18-crown-6 (HT18C6), tetrathia-12-crown-4 (TT14C4), trithia-9-crown-3 (TT9C3) and 1,3,5-trithiane (TT) as n-donors with bromine as σ-acceptor has been followed spectrophotometrically in carbon tetrachloride solution at 25°C. In all cases, the formation of 1:1 charge transfer complexes through equilibrium pathway is confirmed. The formation constants and molar absorptivities of the resulting complexes were evaluated by fitting the absorbance-mole ratio data in MATLAB software. The obtained values indicate that the stabilities vary in the order: HT18C6 > TT9C3 > TT12C4 > TT. However the reverse trend is observed for the corresponding values. The results are interpreted based on the structural features of donors. The thermodynamic parameters (calculated by Gaussian 98) due to dipole-induced dipole interactions in gas phase indicate that the charge transfer forces do have the major contribution in the stability of molecular complexes. The conductance measurements show that the resulting complexes are totally nonionic. Solid complexes were isolated and the effect of complexation on absorption bands is discussed.

Keywords: charge transfer complexes, bromine, thiacrown ether, tetrachloride carbon, spectrophotometry, Gaussian 98

Introduction

The existence of molecular complexes has long been recognized, and the basis for understanding them in terms of acid-base theory has long been existed. However, the research interest in this field reached the explosive stage after publication of the results of the spectrophotometric studies of Benesi & Hildebrand on iodine complexes of aromatic substances. Since, a lot of papers concerning the interaction of different donor-acceptors have been published [1-3].

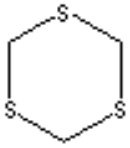
The first macrocyclic polyethers were reported by Lüttringhaus [4] in 1937 as part of an investigation of medium and large-sized rings. However, it was not until 1967 that Pedersen [5] reported on the formation of stable complexes between macrocyclic polyether and salts of alkali and alkaline earth metals. Since the report of Pedersen, there has been an intensive research on thermodynamic and kinetics of complexation of these compounds with various cations in a wide variety of solvent systems [6]. Recently, there has been considerable interest in the study of electron donor-acceptor (EDA) complexes between macrocyclic crown ethers and a variety of acceptor molecules [7].

Thiacrown ethers with low-yield synthetic routed long limited their use as ligand. Indeed, development of reliable high-yield routes provided a major impetuous to investigation of their coordination chemistry, most of which has been reported in the last 25 years [8]. The complexing properties of macrocyclic polythiaethers have been widely studied and metal complexes with these ligands have also been isolated and characterized [9]. The analytical applications of macrocyclic thiaethers in areas such as solvent-solvent extraction, solid phase extraction and PVC-membrane selective electrodes have been reported in the literature [10]. However, to the best of our knowledge, there is no published report dealing with the complexation of bromine with thiacrowns in solution. Thus, more study in this field is needed.

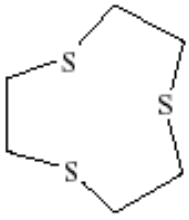
In this paper we report the results of spectroscopic studies of complexation between some thiacrown ethers and TT with bromine in carbon tetrachloride solution.

Experimental

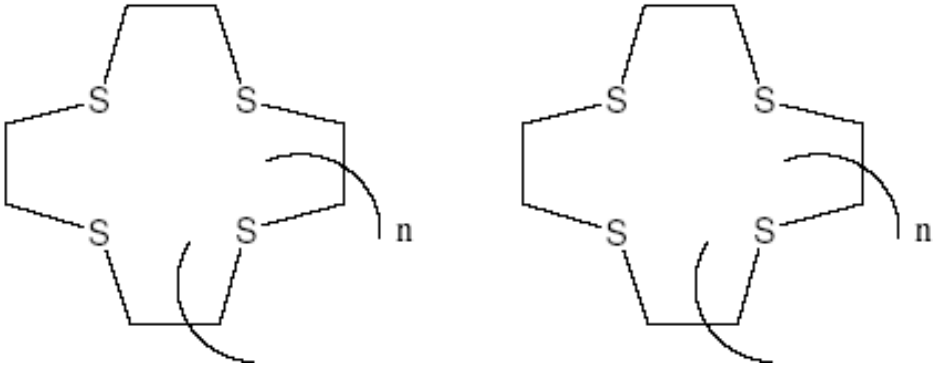
Reagent grade hexathia-18-crown-6 (HT18C6), tetrathia-12-crown-4 (TT14C4), trithia-9-crown-3 (TT9C3) and 1,3,5-trithiane (TT) (all from Aldrich) were used as received. Reagent grade bromine and carbon tetrachloride from Merck Company were used without any further purification.



1,3,5-Trithiane (TT)



Trithia-9-crown-3 (TT9C3)



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

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

In order to obtain UV-Vis spectra, 3 mL of 10^{-3} M of donor solutions were transferred to 1.00 cm quartz cell and titrated with a concentrated bromine solution by a 100-μL Hamilton syringe. Each spectrum was recorded immediately after the titrant addition. The same procedure was followed for absorbance measurement.

The conductometric measurements were made for 10 mL solutions with a Metrohm 660 conductometer with conductometric cell thermostated at 25°C.

Solid complexes were isolated from the solution containing stoichiometric amounts of donors and bromine (1:1) followed by solvent vaporization. The IR spectra were recorded on a Perkin-Elmer 781 using KBr pellets.

Results and discussion

The electronic absorption spectra of 10^{-3} M of TT, TT9C3, TT12C4 and HT18C6 in the presence of varying quantities of bromine in CCl_4 at 25°C are shown in Figs. 1-4, respectively. As seen, all of spectra show a band at 250 nm, which, upon addition of bromine, its intensity increases. Also, in all of spectra a new band is appeared at 310 nm. The bromine did not have any absorption at the 310 nm region (Fig. 5). Thus, the appearance of new band can be assigned to the formation of charge transfer complex between bromine and sulfur containing compounds. In the corresponding complexes, the thia compounds act as n-donor and the bromine acts as σ-acceptor [11].

The absorption spectra of 2×10^{-3} M bromine in the presence of varying concentrations of TT are shown in Fig. 5. The existence of isosbestic point is indicative of an equilibrium reaction between the reactants. The absorption spectra of bromine in the presence of other donors were also examined. However, because of solubility problems, the results were unsuccessful.

In fact, the observation of acceptable absorption of bromine involves the employment of concentrated bromine solution. Also, this needs dissolving proportional amounts of donors, which are undissolvable.

Despite, insufficient spectral information about the existence of isosbestic points in the spectra of bromine in the presence of macrocycle, because of similar structures and similar spectral behavior, the same results is concluded.

For obtaining the stoichiometry of the reactions, the mole ratio method was followed [12]. The corresponding plots of absorbance vs. $[Br_2]/[Donor]$ mole ratios at 310 nm are shown in Fig. 6. The breakness of the curves of HT18C6 and TT9C3 at $[macrocycle]/[Br_2] = 1$, clearly confirm the 1:1 stoichiometry for the interaction of these donors with bromine. In other cases, instead of the breakness of curves, a steady increase of absorbance upon bromine addition is observed. As, the stoichiometry of HT18C6 with highest and TT9C3 with lowest no. of donor atoms are 1:1 the possibility of the stoichiomctries other than 1:1 for TT (with the same no. of donor atoms as TT9C3) and TT12C4 (with one donor atom more than TT9C3 and two donor atoms less than TT18C6) is discarded. Thus, the absence of breakness at $[Donor]/[Br_2]=1$ can be attributed to the weaker interaction of TT-Br_2 and TT12C4-Br_2 than that of other donors. On the other hand, the lower slope of TT curve than that of TT12C4, indicates that the stability of TT-Br_2 complex is less than TT14C4-Br_2 complex. Based on the spectral and mole ratio evidences the following equation is suggested for the interaction of donors and bromine.

$$D+Br_2 \leftrightharpoons D:Br_2$$
$$D = TT, TT9C3, TT14C4, HT18C6$$

The formation constants of different donor-acceptor reactions were obtained by fitting the absorbance-mole ratio data using MATLAB software. A function is used to find the equilibrium constant that fit the absorbance mole ratio profiles using the multi parameter minimum search in MATLAB based on the Nelder Mead algorithm [13]. This function uses the modeled equilibrium constant, simulates the absorbance-mole ratio profiles and calculates the difference between the simulated and measured absorbance profiles. The resulting of computer fit of the absorbance-mole ratio data are shown in Fig. 7A and 7B. Because of clarity the fitting curve due to HT18C6 is not shown. As seen, there is a fair agreement between the observed and calculated absorbances. The good agreement also confirms the accuracy of assumption of 1:1 stoichiometry for all of the donor-acceptor complexes.

The results of $\log K_f$, $\log\varepsilon$ and $\log K\varepsilon$ values obtained from the curve fitting of absorbance-mole ratio data are given in Table 1. As seen, the stabilities vary in the order: HT18C6 > TT9C3 > TT12C4 > TT.

It is well known that the crown ether cavity size play an important role in the stability of ionic complexes of crown ethers. However, the van der Waals diameter of bromine atom is 4.56 A^o. Which is considerably more than the cavity size of largest crown HT18C6 (less than 3.2 A^o). Thus, the introduction of bromine molecule in the cavity of HT18C6 and other smaller donors is completely discarded [14,15].

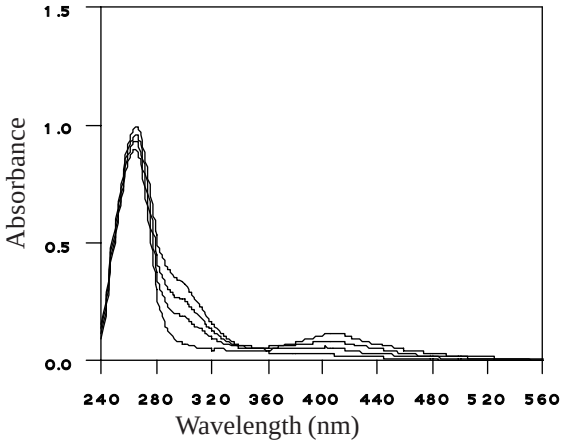


Fig. 1. Apsorption spectra of 10^{-3} M of TT in the presence of increasing concentrations of bromine. The $[Br_2]$/[TT] mole ratios from down to top are 0, 0.166, 0.332 and 0.498

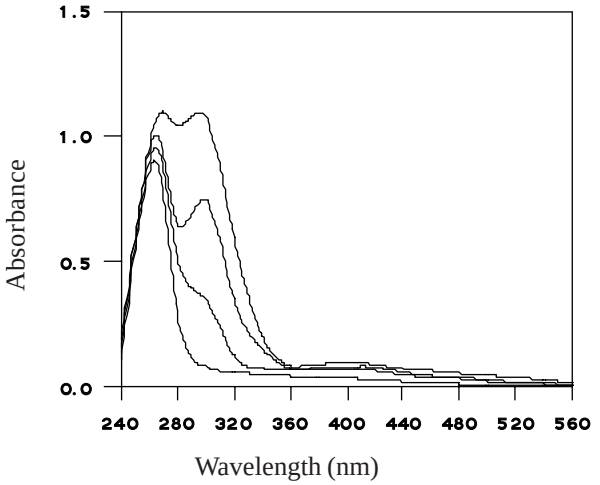


Fig. 2. Apsorption spectra of 10^{-3} M of TT9C3 in the presence of increasing concentrations of bromine. The $[Br_2]$/[TT9C3] mole ratios from down to top are 0, 0.166, 0.332 and 0.498

The effective overlapping of donor-acceptor orbitals involves the proper spatial positions of donor and acceptor molecules. This also needs specific conformation of donor. If the conformation of donor in the complexed form differs significantly from its most stable conformation in the free state. During complexation, some energy will consume for the conversion of most stable conformation of free donor to a conformation which is suitable for complex formation. This will act as a destabiliser factor in the whole process. Among the donors studied, TT has the most rigid structure. So, the variation of its conformation involves energy consumption. Based on this property, the observation of least stability for TT-Br_2 (Table 1) in not unexpected.

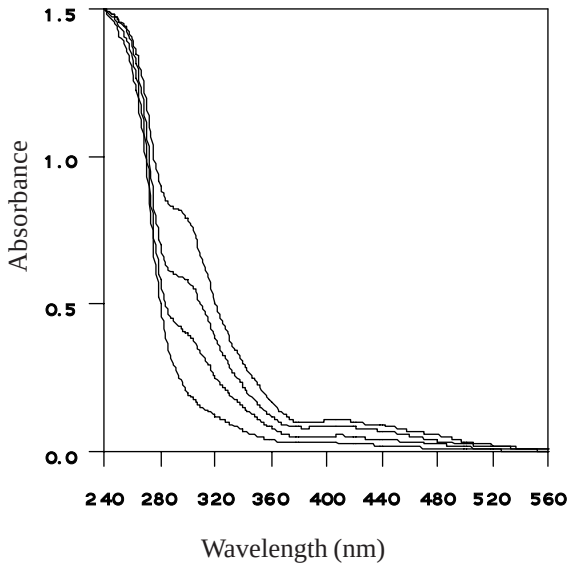


Fig. 3. Apsorption spectra of 10^{-3} M of TT12C4 in the presence of increasing concentrations of bromine. The [Br_2]/[TT12C4] mole ratios from down to top are 0, 0.166, 0.332 and 0.498

The no. of donating atoms available is another important factor that affects the stability of crown-ion complexes [16]. Since in the process of molecular complexation, it is reasonably assumed that the charge density is donated from the donor to acceptor, the increased number of crown sulfurs in the ring is expected to increase the crown-acceptor interaction in solution. However, TT9C3 with three donating atoms forms considerably more stable complex that of TT12C4 with four donating atoms. The flexibility of TT12C4 is more than TT9C3 and from this point of view also higher stability is expected. Mean while, the introduction of fourth sulfur atom, in the ring not

only caused the stability increasing through more flexibility and greater no of donor atoms, but also reduced the stability. This means that a limited no. of sulfur atoms participate in the complexation. In fact the fourth sulfur atom does not act as a donating group and instead of stability increasing by flexibility and cooperative effects. It reduces the stability by electrostatic repulsion on other atoms.

Based on the discussion in previous paragraph less stability is expected for HT18C6 than that of TT9C3. However, the reverse is observed (Table 1). This can be explained by the higher flexibility of HT18C6. Which causes the (i) enhancement of orientation of sulfur atoms toward bromine with low energy consumption and (ii) location of unreacted sulfurs in places which are far from reacted ones and causes the least electrostatic repulsion.

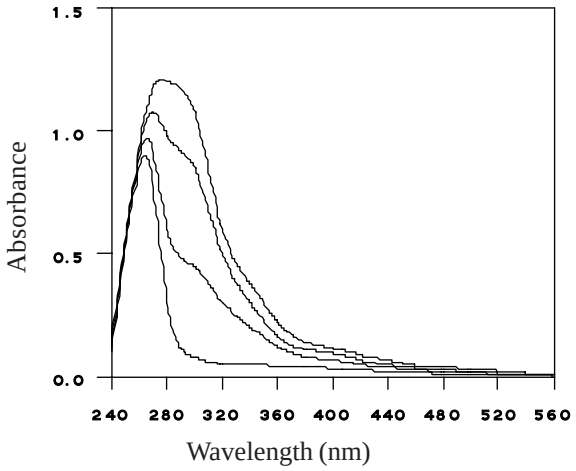


Fig. 4. Apsorption spectra of 10^{-3} M of TT18C6 in the presence of increasing concentrations of bromine. The $[Br_2]$/[TT18C6] mole ratios from down to top are 0, 0.166, 0.332 and 0.49

Form the Table 1, it is obvious that the molar absorptivities of charge transfer complexes vary in the order: TT > TT12C4 > TT9C3 > HT18C6. Which is the reverse trend of stabilities. It seems that the observed order can be related to absorption cross section. Which may be the highest for TT-Br_2 and lowest for HT18C6-Br_2 complexes. Although, the values do not vary in parallel to stabilities, the Kε values increase such as K values. This is in accordance with the reported literature trend for some of charge transfer complexes [17,18].

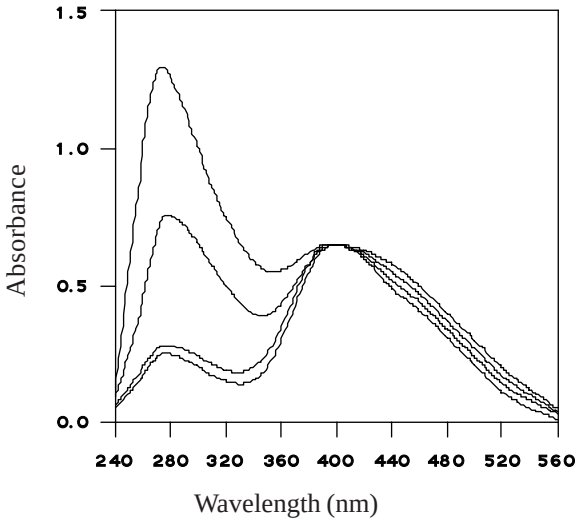


Fig. 5. Apsorption spectra of 2×10^{-3} M of bromine solution in the presence of increasing concentrations of 1,3,5-trithian(TT). The [TT]/[Br_2] mole ratios from down to top are 0, 0.166, 0.332 and 0.489

In order to evaluate the contribution of charge transfer forces in the stabilities of the resulting complexes. The thermodynamic parameters due to dipole-induced dipole interactions in gas phase were calculated by Gaussian 98. It is connected system of programs for performing a variety of semi-empirical and ab initio molecular orbital (MO) calculations. Which is capable of predicting many properties of molecules and reactions such as molecular energies, structures and molecular orbitals. Also, it can serve as a powerful tool for exploring areas of chemical interest like substitute affects potential energy surfaces and excitation energies. In this work semi-empirical calculations using AM1 model Hamiltonians with self consistent field calculations using closed-shell (RHF) are carried out for all of complexes [19,20].

Table. 1. The values of logK_f, logε and log $K_f\varepsilon$ of different donor-acceptor (Br_2) complexes in carbon tetrachloride solution

Donor	**log K_f**	**logε**	**log $K_f\varepsilon$**
TT	2.10 $\pm$0.04	3.58$\pm$0.01	5.78$\pm$0.04
TT12C4	2.61$\pm$0.04	3.48$\pm$0.01	6.09$\pm$0.04
TT9C3	4.50 $\pm$ 0.02	3.42$\pm$0.03	7.92$\pm$0.04
HT18C6	5.05 $\pm$ 0.05	3.34$\pm$0.02	8.39$\pm$0.05

Table 2. The calculated thermodynamic parameters (by Gaussian 98) in the gas phase due to dipole-induced dipole interactions.

Complex	ΔH° (kcal/mol)	ΔS° (cal/mol)	ΔG° (kcal/mol)	K_{sta}
TT-Br_2	-0.67	-23.32	6.20	1.3×10^{-5}
TT12C4-Br_2	-1.95	-28.48	6.42	2.0×10^{-5}
TT9C3-Br_2	-2.81	-28.48	5.63	2.7×10^{-5}
HT18C6-Br_2	-1.68	-28.20	6.68	7.5×10^{-5}

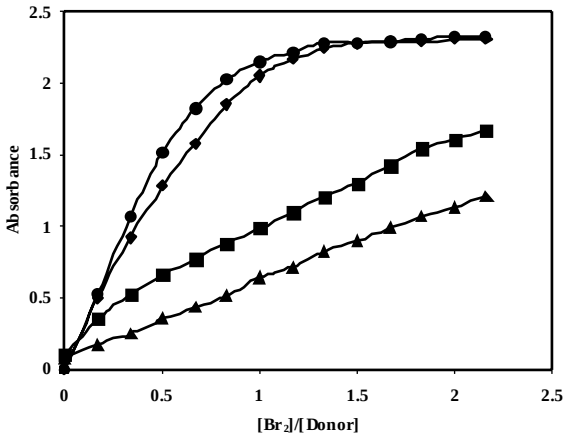


Fig. 6. Absorbance vs. [Br_2]/[Donor] mole ratios plots for 10^{-3} M solutions of bromine in carbon tetrachloride; (▲) TT, (■) TT12C4, (♦) TT9C3 and (●) HT18C6

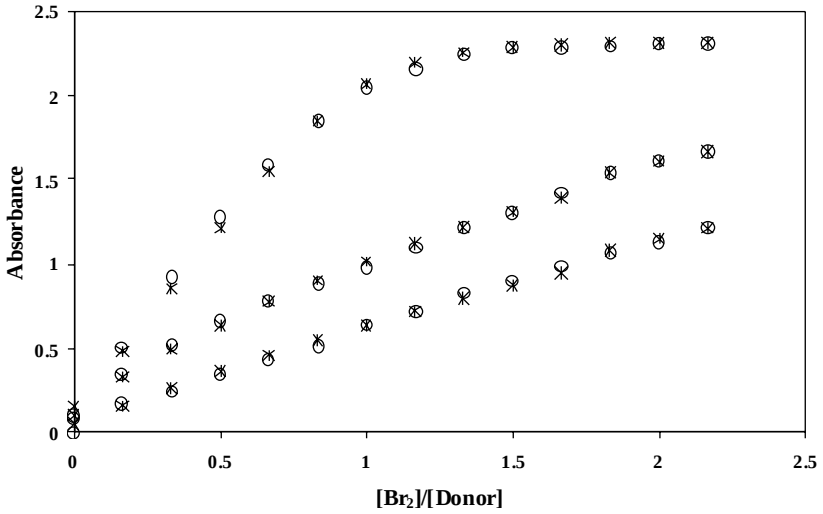


Fig. 7A. Computer fitting of absorbance vs. [Br_2]/[Donor] mole ratio; (×) experimental points, (0) calculated points

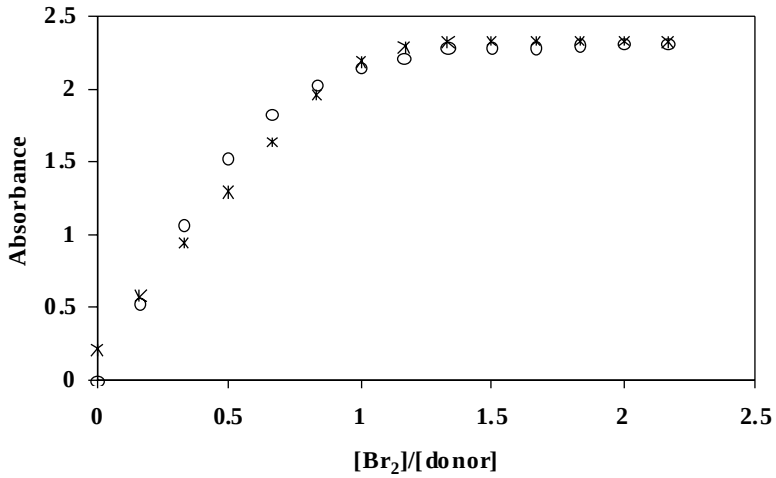


Fig. 7B. Computer fitting of absorbance vs. [Br_2]/[HT18C6] mole ratio; (×) experimental points, (0) calculated points

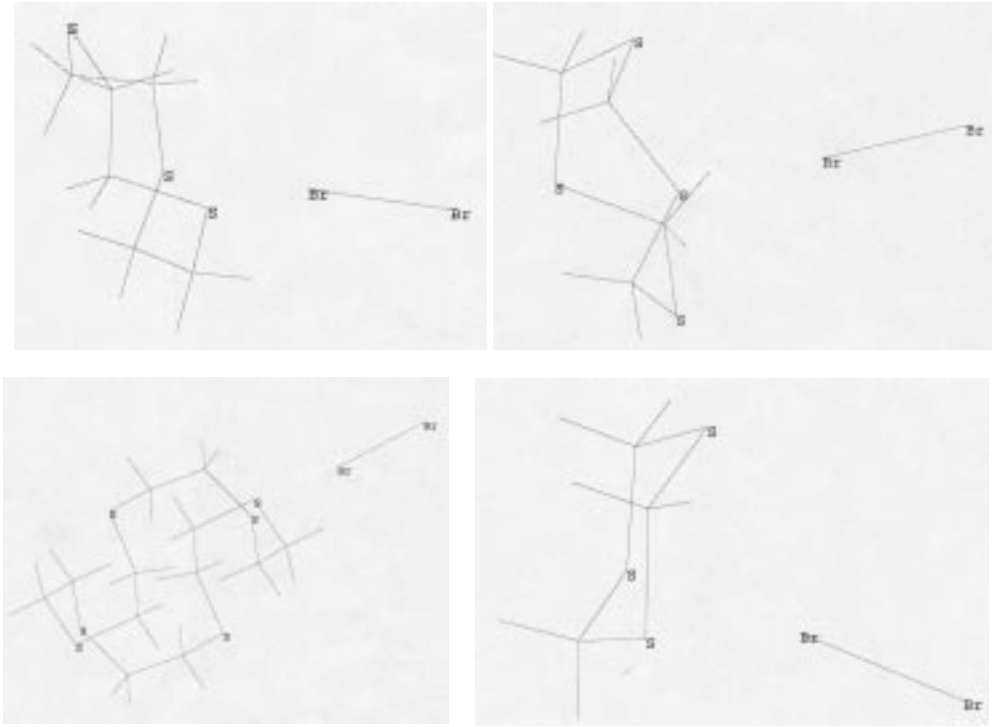


Fig. 8. The structures of dipole-induced dipole complexes in gas phase which have been obtained by Gaussian 98

Final calculated thermodynamic parameters due to dipole-induced dipole interactions are collected in Table 2. As it is observed (i) the K_f values are much less than the corresponding ones in solution (Table 1) and (ii) the stabilities vary in the same order of solution values and (iii) all of complexes are enthalpy stabilized and entropy destabilized. The low K_f values indicate that the dipole-induced dipole forces do have the minor role in the interaction of macrocycles and bromine. On the other hand the accordance of charge transfer (Table 1) with those of dipole-induced dipole data (Table 2) indicate that similar driving forces operate in both kinds of interactions.

The structures of dipole-induced dipole complexes which are obtained by Gaussian 98 are shown in Fig. 8. Interestingly, in all cases only three sulfur atoms are oriented towards bromine molecule. Because of accordance of charge transfer and dipole-induced dipole data it can be concluded that similar to dipole-induced dipole complexes in all of charge transfer complexes, also three sulfur atoms participate in complexation.

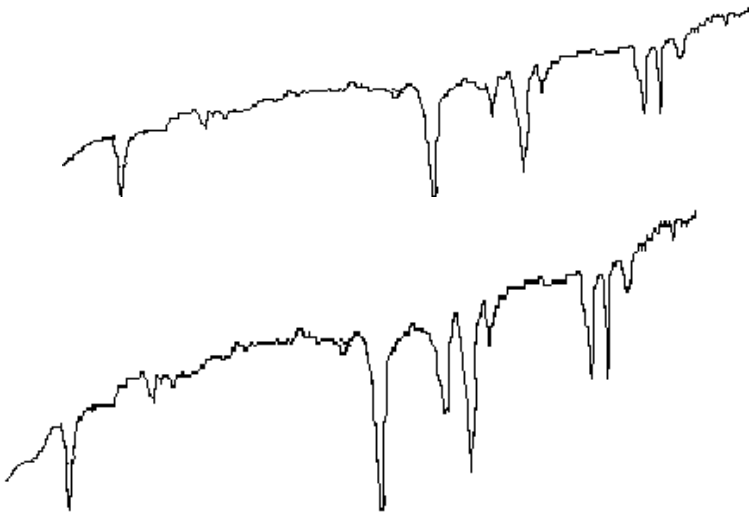


Fig. 9. IR spectra of HT18C6 (up) HT18C6-Br_2 Complex (down)

The conductance as a function of $[Br_2]$/[Donor] mole ratios was measured and the results are shown that there is no increase of conductance upon bromine addition thus, it can be concluded that the complexes are completely nonionic.

IR spectra of HT18C6 and its 1:1 bromine complex are compared in Fig. 9. The bands generally do not show any shift upon complexation. However, the CH_2 bending bands (long chain band) about 720 cm^{-1} have been shifted to higher frequencies. This shift is indicative of decreasing of bending freedom of methylene groups in complex

than that of free molecule. This also confirms the conformational changes during complexation [21]. Similar effects were also observed for other donors. Because of similarity, the corresponding spectra are not shown.

Conclusions

Based on the obtained results it can be concluded that: (1) The interaction of macrocycles-Br_2 and TT-Br_2 follow through equilibrium pathway; (2) The stoichiometry of all of the resulting complexes is 1:1; (3) The difference between the conformations of complexed and free sulfur containing donors plays an important role in the stability of complexes; (4) Dipole-induced dipole interaction play minor role in the process of complex formation; (5) The structures of complexes in solution are the same as dipole-induced dipole complexes in gas phase; (6) In all of complexes only three sulfur atoms participate in complexation; (7) All of complexes are nonionic; (8) IR spectra of complexed donors do not show significant changes than that of uncomplexed donors.

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