

Scientific paper

Charge Transfer in Some Complexes of Crown Ether and of Thiacrown Ether with Dihalogens: DFT Study

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Abstract

The present study was carried out by focusing on the interaction between molecular complexes crown and thiacycrown ethers such as 15-crown-5 (15C5), thia-15-crown-5 (T15C5), dithia-15-crown-5 (DT15C5) with homogeneous and heterogeneous dihalogens (XY) such as I₂, IBr, ICl, Br₂, Cl₂ in the gas phase and in dichloromethane solvent through applying density function theory (DFT) as well as Gaussian 98 programs series. Characteristics such as frequency, enthalpy of reaction and energy have been totally specified. Special attention was placed on the study of electronegativity of outer halogen atom and polarization of bond between two halogens on the interaction. Results indicate that electronegativity of the external halogen atom and the polarization of dihalogen bond have remarkable effects on structure parameters, donor-acceptor effect, structural stabilization, and the enthalpy of the complex product. It is concluded that the charge transfer takes place in three complexes: 15C5, T15C5, and DT15C5; and the direction of charge transfer is from crown and thiacycrown molecule to dihalogen. Stability of 15C5, T15C5 and DT15C5 complexes according to the energy is ICl > IBr > I₂. The optimum condition for maximum stability of the molecular complex M...IY is optimized plane structure and the optimum level of polarization of dihalogen during complexation of 15C5, T15C5, and DT15C5 is ICl molecule. The study of the interaction in dichloromethane solvent has similar results to the gas phase. An analysis of the NBO confirms the obtained results.

Keywords: Dihalogen, density functional theory, thiacycrown ether, crown ether, charge transfer complexes

1. Introduction

There is a long and complex background in molecular recognition about understanding of acid-base theory. Considerable researches have been engaged in the field of emission spectral measurement as a result of Benesi & Hildebrand studies on iodine complexes of aromatic compounds which lead to the publication of many articles about the interaction of the donor-acceptor.¹⁻⁴ Thermodynamic and kinetic researches on the complexation of the sustained macro cycle polyether complexes with different alkali and alkaline earths metals cations in a range of different solvent systems have been performed.⁵ Currently it is of a great interest to study the electron donor-acceptor (EDA) complexes between macrocyclic crown ether molecules and different receptors.⁶ Due to the hard construction of thiacycrown ethers, they have been used low-interest as a ligand, but within the last 25 years, most of them have been interested in chemistry coordination reliability.^{7,8}

Analysis applications of macrocyclic thiaethers include solvent extraction, solid-phase PVC membrane selective electrodes.⁹

The complex information between hexathia-18-crown-6 (HT18C6), tetrathia-12-crown-4 (TT12C4), threethia-9-crown-3 (TT9C3) and 1, 3, 5-threethian (TT) as n-donors with bromine (Br₂) as the receptor in carbon tetrachloride solution showed that the stability of these complexes were HT18C6>TT9C3>TT12C4>TT.¹⁰ Thermodynamic parameters were calculated according to the theoretical methods of dipole interactions in the gas phase, which proves that the charge transfer (CT) is an important contribution to the stability of the complexes. The structure, frequency, energy and the type of molecular complex bond specification between N-methyl imidazoline-2-thione and N-methyl imidazolidine-2-thione with dihalogens IY (Y = Cl, Br, I) were obtained by applying computational techniques.¹¹ Both systems were arranged vertically, and the flat planar arrangement of the torsion

angle N-C-S-I is near zero in the minimum energy isomer. The type of the additional product depends on the capability of the electron donor-acceptor of the S and I atoms and on the hydrogen bonding between internal I atom and amide hydrogen. On the other hand, the Y electronegativity and the I-Y bond polarity have an important effect on the stability of the spatial arrangement. A spectrophotometric study of the interaction between HT18C6 as n-donor and a recipient I₂ in chloroform solution at different temperatures has been performed.^{12,13} The results show that the complexes are stable via enthalpy and unstable via entropy which relates to the decrease in the variability of entropy on the complex. Comparing the results of HA18C6-I₂ with 18C6-I₂ complexes confirmed the product stabilities and different stoichiometry.

Charge transfer complexes are of interest to chemists because of stabilizing the molecule during the interaction and also because they can be used in many industries such as pharmaceuticals,¹⁴ chromatographic separation,¹⁵ enantiomers separation,¹⁶ estimation of molecular polarity,¹⁷ solvent-solvent extraction, and solid-phase selective electrodes.⁹ Thiacycrown and crown ethers can form the complex with dihalogens in the gas phase and non-aqueous environments, but there is a few literature about CT phenomena in these complexes. Recently, CT has been reported of the complexation of 1,3,5-thiethian (TT), thiethia-9-crown-4 (TT8C4) and tetrathia-8-crown-4 (TT8C4) with homogeneous and heterogeneous dihalogens by B3LYP/6-31G** method.¹⁸ The results show that the electronegativity of the external halogen atom and the bond polarization of the dihalogenes have a considerable and significant effect on the thermodynamic stability of the complexes. In both TT and TT8C4 complexes, it was predicted that the charge transfer takes place from the dihalogen (donor) to the thiacycrown ether molecule (acceptor); the magnitude trend of the total CT was IC_l > IBr > I₂ and Cl₂ > Br₂ > I₂, respectively. There was no such a trend with TT9C3 because of the vertical structure in the optimized complexes. The types of the non-bonded interactions and the similar results were obtained in the gas and dichloromethane phases. In this paper, the charge transfer complex interaction between dihalogens and other three types of such crownether and thiacycrownethers,

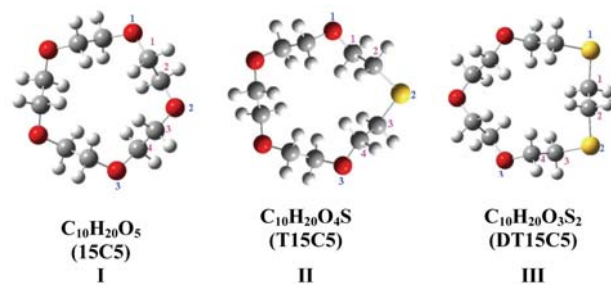


Fig 1. Optimized structures of C₁₀H₂₀O₅ crown ether (I), C₁₀H₂₀O₄S thiacycrown ether (II), and C₁₀H₂₀O₃S₂ dithiacycrown ether (III)

as illustrated in Fig 1, were studied in the phases in order to obtain a systematic and scientific trend for the CT phenomena in this category compounds.

2. Computational Methods

Electronic properties of the complexes of crown ether C₁₀H₂₀O₅ (15C5), and thiacycrown ethers including C₁₀H₂₀O₄S (T15C5) and C₁₀H₂₀O₃S₂ (DT15C5) with homo and hetero dihalogen molecules, I₂, Br₂, Cl₂, IBr and ICl were calculated by Gaussian 98¹⁹ at B3LYP/ 6-31G(d,p) level of theory. The polarized basis set 3-21G(d,p) was used for iodine by GEN keyword. Applying the appropriate polarization functions to the particular atoms of iodine is essential.

In order to consider the solvent effects on the studied complex systems, the Onsager reaction field model,²⁰ which is a classic of the self-consistent reaction field (SCRF) methods, was utilised to optimize the solvated systems and the relevant properties were calculated. No symmetry constraints were imposed during the optimization process.

Thermodynamic properties based on the frequencies were derived from statistical thermodynamics in order to study of the donor-acceptor in the complex systems. Natural bond orbital (NBO) analysis including Mulliken analysis on the atoms accompanying the charge transfer for ground electronic state of complexes in the gas phase and solvent dichloromethane was conducted. The orbital interaction energy ($\Delta E^{(2)}$) between HOMO and LUMO of the donor-acceptor system and the amount of transferred partial charges between donor and acceptor species ($q_{\text{donor} \rightarrow \text{acceptor}}$) were calculated by the second-order perturbation theoretical expressions:²¹

$$q_{\text{donor} \rightarrow \text{acceptor}} \cong 2 \left(\frac{\langle \Psi_{\text{don}}^* | \hat{F} | \Psi_{\text{acc}}^* \rangle}{\epsilon_{\text{acc}} - \epsilon_{\text{don}}} \right)^2 \quad (1)$$

$$\Delta E^{(2)} = 2 \frac{\langle \Psi_{\text{don}}^* | \hat{F} | \Psi_{\text{acc}}^* \rangle^2}{\epsilon_{\text{acc}} - \epsilon_{\text{don}}} \quad (2)$$

where F is the Fock operator, $\langle \Psi_{\text{don}}^* | \hat{F} | \Psi_{\text{acc}}^* \rangle$ is the matrix element of the Fock operator between the donor and acceptor wave functions, ϵ_{don} and ϵ_{acc} are the energies of the donor and acceptor orbitals involved in electron transfer. Stabilisation energies, $\Delta E^{(2)}$, are proportional to the NBO interacting intensities. This reveals the origin of intermolecular interactions.

3. Results and Discussion

Fig 2 depicts the optimized structures of all of the entitled complexes in the gas phase and the solvent.

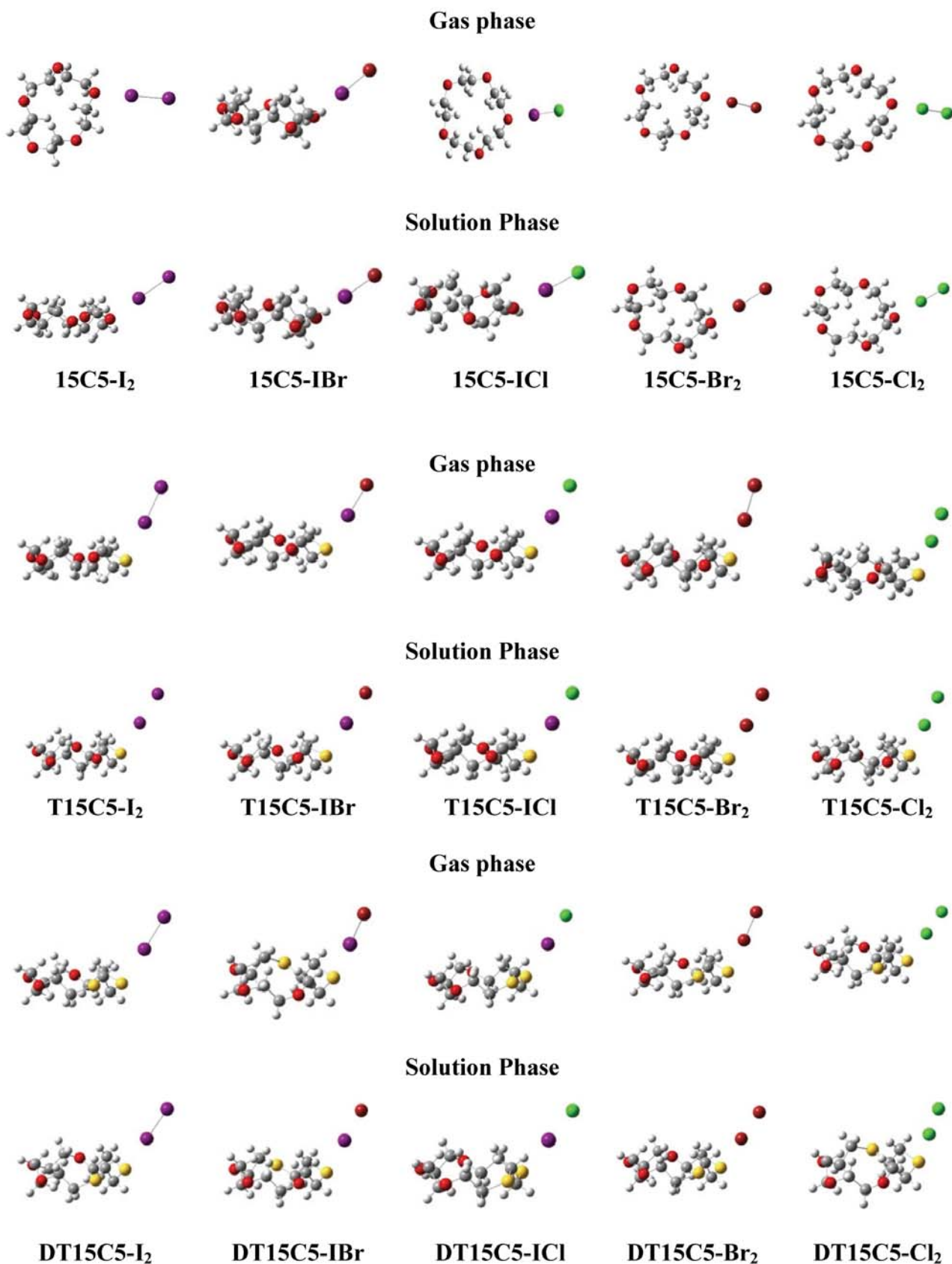


Fig 2. Optimized structures of the complexes of 15C5-, T15C5-, and DT15C5-dihalogens in the gas phase and dichloromethane solution

Table 1 shows the results of the calculated natural charges and the NBO analysis of X-Y bond in two phases before any complex formation. Table 2 summarizes calculated data for the natural electrical charges of atoms based on NBO analysis, the bonds length O-X or S-X and X-Y, and S-X-Y or O-X-Y and C3-S-X bond angles after complex formation. With consideration to crown or thiacycrown ether (M) and dihalogen molecules, it may be deduced that there are two arguments between M and X (halogen interior): the flat and the vertical geometry for the axis of the dihalogen molecule relative to the crown or thiacycrown ether. This geometry plays an important role in the CT interaction. The linear or flat geometry is obvious for two components of the complexes as a linear structure of O-X-Y or S-X-Y. Significant changes in the binding angle C3-O2-X or C3-SX were observed in two phases from 94° to 116°. Optimized structures of the complexes have been formulated as a flat angle about 179° for S-X-Y and O2-X-Y, and the planar array is indicated. The data showed that the charge of the dihalogen atoms is more negative than free dihalogen, and the charge of the atoms of the crown and thiacycrown are more positive than of the atoms of free crown and thiacycrown. This is especially more tangible about O1 (S1), O2 (S2) and O3 atoms. Thus, the direction of CT is from the crown and thiacycrown to the dihalogen in two phases.

Table 1 Calculated natural charges on the atoms and XY bond NBO analysis (in Å) in the gas phase and dichloromethane solvent

	Molecule	x(Outer)	X(Inner)	X-Y
gas	I-I	0	0	2.72
	I-Br	-0.134	0.134	2.52
	I-Cl	-0.238	0.238	2.38
	Br-Br	0	0	2.32
	Cl-Cl	0	0	2.04
Sol	I-I	0	0	2.72
	I-Br	-0.158	0.158	2.53
	I-Cl	-0.238	0.238	2.39
	Br-Br	0	0	2.32
	Cl-Cl	0	0	2.04

The NBO analysis indicates that with increasing electronegativity of the outer halogen (15C5, T15C5, DT15C5 ... IY and Y = I, Br, Cl) the charge transfer increases as well and the O2-I or S-I bonds become shorter and stronger. During this interaction, I-Y bond length increases significantly in the complexes prior to complex formation. The thermodynamic quantities were calculated for each complexes of 15C5, T15C5, DT15C5 with XY. Table 3 illustrates internal energy (ΔE_f), enthalpy (ΔH_f), Gibbs free energy (ΔG_f), and entropy (ΔS_f) of the complex formation, along with the first frequency mode

of complex in the two phases by using the following formula:

$$\Delta X_f = \sum_{\text{Product}} X_i^0 - \sum_{\text{Reactant}} X_i^0, \quad (3)$$

X = E or H or G or S

The enthalpy of complex formation values for 15C5, T15C5, DT15C5 with I₂ are high positive in the gas phase and solvent, and for 15C5, T15C5, DT15C5 with ICl are low negative. This trend is observed in the other quantities as well and it means that the process of formation may be due to the stabilization of the planar complexes with I₂ attributed to ICl. The Gibbs free energy values for 15C5, T15C5, DT15C5 complexes with I₂ show a non-spontaneous formation while for the others they are nearly formed spontaneously. ΔS values for each of the processes of complex formation in the gas phase and the solvent is close to zero. Consequently, the stability of the complex can be attributed to their ΔH . In general, formation of all complexes in both phases is a reversible process. The trend of stable complexes of 15C5, T15C5, DT15C5 with dihalogens in the gas phase and dichloromethane solvent is as follows:



This trend can be attributed to the electronegativity of the external halogen Y. Thermodynamic parameters of the interaction of 15C5, T15C5, DT15C5 molecules with dihalogens X₂, X = I, Cl, Br, show that the stability of the complexes is as follows:



This trend can be attributed to the polarization of Br₂ to Cl₂. The complexes of 15C5, T15C5, and DT15C5 with I₂ are unstable and ΔH s are positive and have a major effect on the instability.

The calculated values of q (in mg/electron) and the orbital interaction energy ($\Delta E^{(2)}$) in all complexes based on NBO analysis during the process of CT from the donor to the recipient along with the intensity of the CT interactions are presented in Table 4 for the gas and solvent phases. According to the interaction energy ($\Delta E^{(2)}$) values, LP(O) or LP(S) orbital of crown and thiacycrown molecules to BD*(I-Cl) orbital of dihalogens is the most important role. Therefore, the amount of total charge transfer shows the following trends according to the reported complexation energies in Table 4.

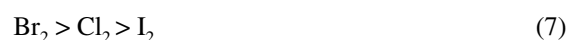


Table 2 Calculated the natural electrical charges of atoms based on NBO analysis, O-X or S-X and X-Y bond lengths (in Å), and S-X-Y or O-X-Y and C3-S-X bond angles (in degrees) for the optimized complexes of 15C5, T15C5, DT15C5 with dihalogens in the gas phase and dichloromethane solvent

XY	O1	C1	C2	O2	C3	C4	O3	X		O2-X	X-Y	O2-X-Y	C3-O2-X
								(Inner)	(outer)				
C₁₀H₂₀O₅ gas	-0.580	-0.136	-0.136	-0.580	-0.136	-0.136	-0.580						
(I-I)	-0.503	-0.181	-0.180	-0.503	-0.176	-0.179	-0.508	0.024	-0.127	2.59	2.76	179.5	116.60
(I-Br)	-0.577	-0.137	-0.139	-0.582	-0.138	-0.132	-0.577	0.157	-0.246	2.61	2.56	179.8	113.65
(I-Cl)	-0.576	-0.137	-0.140	-0.583	-0.138	-0.132	-0.576	0.236	-0.334	2.56	2.43	179.6	114.6
(Br-Br)	-0.587	-0.133	-0.140	-0.567	-0.140	-0.138	-0.576	0.007	-0.084	2.57	2.36	178.3	109.9
(Cl-Cl)	-0.579	-0.135	-0.140	-0.565	-0.138	-0.138	-0.579	-0.007	-0.069	2.56	2.08	179.6	111.9
C₁₀H₂₀O₅ sol	-0.580	-0.140	-0.136	-0.580	-0.136	-0.140	-0.580						
(I-I)	-0.578	-0.140	-0.138	-0.582	-0.138	-0.130	-0.577	0.031	-0.108	2.66	2.77	179.6	113.9
(I-Br)	-0.485	0.043	0.034	-0.518	0.042	0.044	-0.485	0.147	-0.258	2.54	2.58	179.4	114.3
(I-Cl)	-0.576	-0.140	-0.138	-0.585	-0.138	-0.130	-0.576	0.240	-0.350	2.48	2.46	179	115
(Br-Br)	-0.577	-0.140	-0.141	-0.564	-0.141	-0.140	-0.576	0.008	-0.101	2.51	2.37	179.5	109.7
(Cl-Cl)	-0.578	-0.140	-0.138	-0.561	-0.138	-0.140	-0.561	-0.011	-0.076	2.50	2.09	179.3	111.8
C₁₀H₂₀O₄S gas	-0.488	0.067	-0.353	0.080	-0.351	0.067	-0.489						
(I-I)	-0.575	-0.188	-0.631	0.291	-0.632	-0.120	-0.576	-0.028	-0.133	3.08	2.79	177.5	105.3
(I-Br)	-0.500	-0.157	-0.649	0.300	-0.647	-0.160	-0.500	0.073	-0.243	3	2.56	177.8	105.6
(I-Cl)	-0.573	-0.118	-0.630	0.326	-0.630	-0.120	-0.574	0.147	-0.371	2.9	2.47	178.6	100.3
(Br-Br)	-0.575	-0.121	-0.632	0.340	-0.635	-0.120	-0.576	-0.064	-0.152	2.84	2.41	176.4	93.3
(Cl-Cl)	-0.574	-0.118	-0.643	0.403	-0.639	-0.120	-0.578	-0.027	-0.176	2.73	2.16	178	96.48
C₁₀H₂₀O₄S sol	-0.490	0.067	-0.352	0.078	-0.351	0.067	-0.490						
(I-I)	-0.484	0.071	-0.353	0.120	-0.356	0.069	-0.482	0.006	-0.169	2.99	2.82	178.8	105.1
(I-Br)	-0.575	-0.116	-0.631	0.313	-0.631	-0.118	-0.574	0.081	-0.282	2.97	2.60	178.3	104.8
(I-Cl)	-0.573	-0.117	-0.629	0.352	-0.629	-0.120	-0.572	0.136	-0.402	2.79	2.54	178.9	104.9
(Br-Br)	-0.574	-0.118	-0.633	0.374	-0.632	-0.117	-0.575	-0.0175	-0.190	2.74	2.48	178.8	104.00
(Cl-Cl)	-0.572	-0.120	-0.634	0.454	-0.636	-0.121	0.573	-0.134	-0.228	2.53	2.28	178.9	103.20
C₁₀H₂₀O₃S₂ gas	0.082	-0.331	-0.331	0.082	-0.352	0.068	-0.489						
(I-I)	0.225	-0.622	-0.610	0.289	-0.632	-0.116	-0.575	-0.027	-0.132	3.08	2.79	177.7	98.20
(I-Br)	0.227	-0.622	-0.611	0.312	-0.631	-0.118	-0.575	0.081	-0.281	2.97	2.60	177.5	106.60
(I-Cl)	0.229	-0.623	-0.610	0.325	-0.631	-0.118	-0.574	0.146	-0.371	2.90	2.47	177.5	106.90
(Br-Br)	0.227	-0.625	-0.614	0.335	-0.637	-0.120	-0.574	-0.062	-0.148	2.84	2.41	176.8	94.30
(Cl-Cl)	0.227	-0.623	-0.615	0.336	-0.636	-0.119	-0.576	-0.094	-0.149	2.73	2.16	178.4	98.00
C₁₀H₂₀O₃S₂ sol	0.207	-0.615	-0.615	0.208	-0.634	-0.120	-0.579						
(I-I)	0.225	-0.622	-0.608	0.302	-0.630	-0.116	-0.575	-0.029	-0.156	2.99	2.82	178	100.20
(I-Br)	0.227	-0.622	-0.609	0.332	-0.629	-0.119	-0.574	0.075	-0.310	2.86	2.65	178.3	106.40
(I-Cl)	0.233	-0.626	-0.607	0.343	-0.629	-0.117	-0.573	0.138	-0.401	2.79	2.54	178.8	101.50
(Br-Br)	0.227	-0.625	-0.611	0.368	-0.632	-0.120	-0.574	-0.075	-0.185	2.72	2.45	178.5	97.70
(Cl-Cl)	0.228	-0.624	-0.613	0.453	-0.636	-0.121	0.573	-0.135	-0.228	2.53	2.28	178.3	104.30

Table 3 Calculated internal energy (ΔE_f), enthalpy (ΔH_f), Gibbs free energy (ΔG_f), and entropy (ΔS_f) of the complexation, and the first frequency mode for the optimized complexes of 15C5, T15C5, DT15C5 with dihalogens in the gas phase and dichloromethane solvent

Phase	Complex	ΔE_f (kcal/mol)	ΔH_f (kcal/mol)	ΔG_f (kcal/mol)	ΔS_f (kcal/mol)	Freq (Cm^{-1})
gas	15C5-I ₂	700.39	699.79	708.33	-0.029	12.18
	15C5-IBr	0.39	-0.20	9.43	-0.030	17.23
	15C5-ICl	-0.108	-1.67	7.56	-0.031	13.63
	15C5-Br ₂	-6.02	-7.55	1.37	-0.030	17.65
	15C5-Cl ₂	-2.02	-3.73	4.61	-0.028	17.12
sol	15C5-I ₂	700.38	699.79	708.63	-0.030	14.52
	15C5-IBr	-0.06	-0.66	9.46	-0.034	20.53
	15C5-ICl	-1.51	-2.10	7.93	-0.034	22.25
	15C5-Br ₂	-7.09	-7.68	1.68	-0.031	20.96
	15C5-Cl ₂	-3.17	-3.77	5.01	-0.029	20.85

Phase	Complex	ΔE_f (kcal/mol)	ΔH_f (kcal/mol)	ΔG_f (kcal/mol)	ΔS_f (kcal/mol)	Freq (Cm^{-1})
gas	D15C5-I ₂	700.63	700.04	708.24	-0.027	10.17
	D15C5- IBr	0.09	-0.51	8.43	-0.030	14.08
	D15C5- ICl	-1.75	-2.34	7.18	-0.032	20.38
	D15C5- Br ₂	-8.88	-9.47	-0.60	-0.029	14.96
	D15C5- Cl ₂	-5.15	-5.75	2.59	-0.028	16.45
sol	T15C5-I ₂	700.07	699.48	708.35	-0.029	19.09
	T15C5- IBr	-1.32	-1.91	7.82	-0.032	15.50
	T15C5- ICl	-3.73	-4.33	4.84	-0.031	20.96
	T15C5- Br ₂	-7.96	-8.55	0.74	-0.031	16.30
	T15C5- Cl ₂	-7.33	-7.92	1.29	-0.031	20.47
gas	DT15C5-I ₂	701.72	701.12	709.62	-0.029	13.22
	DT15C5- IBr	1.24	0.65	9.48	-0.030	14.09
	DT15C5- ICl	-0.65	-1.24	8.26	-0.032	22.40
	DT15C5- Br ₂	-8.74	-9.33	-0.76	-0.029	12.74
	DT15C5- Cl ₂	-5.11	-5.70	2.24	-0.027	14.61
sol	DT15C5-I ₂	701.13	700.54	709.46	-0.030	13.72
	DT15C5- IBr	-0.38	-0.97	8.24	-0.030	13.79
	DT15C5- ICl	-2.53	-3.13	6.86	-0.034	20.19
	DT15C5- Br ₂	-9.97	-10.56	-1.48	-0.031	14.99
	DT15C5- Cl ₂	-7.18	-7.77	0.98	-0.029	17.04

Table 4 Calculated values of q and the orbital interaction energy ($\Delta E^{(2)}$) between 15C5, T15C5, DT15C5 and dihalogens based on NBO analysis in the gas and solvent phases

$\text{C}_{10}\text{H}_{20}\text{O}_5$ gas	I-I	I-I	I-Br	I-Br	I-Cl	I-Cl	Br-Br	Br-Br	Cl-Cl	Cl-Cl
$\Delta E^{(2)}$ (KJ/mol)	2.47	10.34	2.82	15.01	2.92	17.39	1.78	10.16	1.53	7.45
q/me	9.54	49.66	11.43	65.58	11.43	70.31	6.17	54.13	5.465	41.09
$\text{C}_{10}\text{H}_{20}\text{O}_5$ sol										
$\Delta E^{(2)}$ (KJ/mol)	2.67	12.05	3.09	18.34	3.14	21.7	2.02	12.79	1.76	9.31
q/me	10.71	58.20	12.80	77.96	13.47	81.87	7.53	61.78	6.76	47.95
$\text{C}_{10}\text{H}_{20}\text{O}_4\text{S}$ gas										
$\Delta E^{(2)}$ (KJ/mol)	1.61	20.30	2.36	29.63	2.83	35.31	1.55	25.22	0.89	112.21
q/me	5.39	157.87	8.05	207.03	9.58	225.79	5.19	191.61	4.72	263.88
$\text{C}_{10}\text{H}_{20}\text{O}_4\text{S}$ sol										
$\Delta E^{(2)}$ (KJ/mol)	2.16	25.92	2.36	29.63	3.91	48.98	2.38	37.7	3.23	56.05
q/me	7.39	191.07	8.06	207.03	14.11	320	8.71	312.05	12.67	479.17
$\text{C}_{10}\text{H}_{20}\text{O}_4\text{S}_2$ gas										
$\Delta E^{(2)}$ (KJ/mol)	1.68	20.4	2.37	29.5	2.87	35.3	1.6	25.5	1.72	27.3
q/me	5.39	157.9	8.06	207	9.59	225.8	5.19	211.3	5.80	217.80
$\text{C}_{10}\text{H}_{20}\text{O}_4\text{S}_2$ sol										
$\Delta E^{(2)}$ (KJ/mol)	2.19	25.83	3.25	39.39	3.95	48.86	2.39	36.59	3.25	56.07
q/me	7.39	185.50	11.10	268.89	14.22	320	8.37	283.04	12.67	489.53

4. Conclusion

According to the results, the charge transfer interaction between crown ether and thiocrown ether with dihalo-

gens can occur from the crown or thiocrowns ether to dihalogen unlike the obtained results in the previous works on $\text{C}_3\text{S}_3\text{H}_6$ (TT) and $\text{C}_4\text{S}_4\text{H}_8$ (TT8C4) [19]. It can be described from the viewpoint of the size of thiocrown ether

constituent. Dichloromethane solvent does not affect CT phenomena both direction and amount, and on the stability of the complex. The trend of CT between crown or thiacycrown ethers and dihalogen molecules and the stability of the complexes in the gas phase and dichloromethane solvent are determined as follows:



as like as the trend about TT and TT8C4 [19]. The complex formation processes are near to equilibrium. The crown or thiacycrown ether complexes with I_2 are unstable.

5. References

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Povzetek

Z uporabo funkcionalne gostotne teorije in Gaussian 98 programi smo v plinski fazi in v diklorometanu proučevali interakcije :med molekularnimi kompleksi crown in tiacycrown etrov: 15-crown-5 (15C5), tia-15-crown-5 (T15C5), ditia-15-crown-5 (DT15C5) etra s homogenimi in nehomogenimi dihalogeni (XY): I_2 , IBr, ICl, Br_2 , Cl_2 I. Določili smo reakcijske entalpije in energije. Posebno pozornost smo posvetili raziskavam elektronegativnosti zunanjih halogenskih atomov in polarizaciji vezi med halogeni. Rezultati kažejo, da oba parametra bistveno vplivata na strukturo, donor-akceptor efekt, strukturno stabilizacijo in entalpijo nastalega kompleksa. Izkazalo se je, da do v treh kompleksih: 15C5, T15C5, in DT15C5, pride do prenosa naboja s crown in tiacycrown molekule na dihalogen. Glede na izračunane energije, komplekse po energiji lahko razvrstimo v $\text{ICl} > \text{IBr} > \text{I}_2$. Največja stabilnost kompleksa M...IY med kompleksacijo 15C5, T15C5 in DT15C5 je optimizirana planarna struktura in optimalni nivo polarizacije ICl. Raziskave interakcij v diklorometanu so podobni tistim, dobljenim v plinski fazi.