Scientific paper

A Study of Donor-Acceptor in the Charge Transfer Molecular Complexes of Some Thiacrown Ethers with Dihalogen Molecules by DFT Method

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Abstract

The molecular complexes of 1,3,5-trithiane, (TT), tetrathia–8–crown–4, (TT8C4), and trithia–9–crown–3 , (TT9C3) with dihalogens in the ground state were investigated in the gas and dicholoromethane phases using B3LYP method and 6-31G** and 6-31+G** bases sets. In both TT and TT8C4 complexes, it is predicted that charge transfer takes place from the dihalogen to the thiacrown ether molecule; the magnitude trend of the total CT was ICl > IBr > I_2 and Cl_2 > Br_2 > I_2, respectively. There was not such a trend with TT9C3. The frequency analysis showed that all complexes in the excited state were unstable. The analysis of natural bond orbitals and comparison of the calculated thermodynamic quantities of the complexes between the gas phase and tetrachloromethane solution confirmed the results.

Keywords: Donor-acceptor; charge transfer; thiacrown ether; natural charges; density functional theory

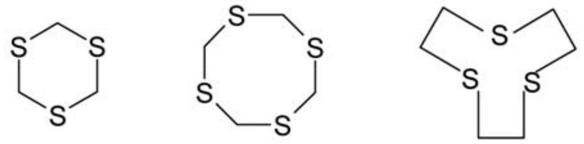
1. Introduction

There are many possible different experiments in order to investigate charge transfer (CT) phenomena in different areas in chemistry. Considerable experimental evidence on CT complexes has been reported in the liquid phase.[1,2] The formation of the CT complexes involves adapted parallel planer geometry, and a HOMO-LUMO electron transition according to Mulliken's theory.[3] This donor-acceptor interaction is characterised by an electronic absorption band with low energy. According to the theory, a chemical hunch is needed to define a 'donor' and an 'acceptor' molecule in a CT complex. CT complexes are regarded as important materials for use as organic superconductors,[4,5] photo-catalysts,[6] dendrimers,[7] solar energy storage,[8] mechanism of drug action,[9] and non-linear optical materials.[10]

Among geometries, two electronic structures of different connectivity and stability are possible for CT complexes: a linear arrangement and a hypervalent T-shaped arrangement, especially in complexes of methyl substituted imidazoline and imidazolidine-2-thiane derivatives with dihalogens.[11] The many crystallographic investigations and computational examinations have been carried out on CT complex systems.[12–16] Structural, frequency and energy features have been fully characterised and particular emphasis has been placed on investigating the effect of the electronegativity and polarization of dihalogens on this interaction.

Directly, evaluation of electronic charge distribution in an adduct of two different molecules by the help of *ab initio* and DFT calculations enables us to characterise the donor and acceptor molecules. Thus, no pre-assumption is necessary for such cases. As a result of this, researchers have performed explicit theoretical calculations for various CT complexes.[17,18] Bhattacharya[19] carried out such calculations and estimated the CT transition energies by the theoretical calculations for complex of o-chloranil with aniline. Also, Reiling et al. have presented the results of comparative *ab initio* calculations on the iodine molecule and the pyridine/I_2 CT complex employing various kinds basis sets.[17] Full geometry optimization of the benzene/ICl complex has been carried out[18] in the ground state of the complex in the gas phase, and the interaction energies have been theoretically estimated by the Hartree–Fock (HF) and the second order Møller–Plesset perturbation theory levels, and also using B3LYP/3-21G* with hybrid functionals within symmetry constraints.

Thiacrown ethers were first prepared 75 years ago,[20] but low yield synthetic routes limited their use as ligands. However, the development of reliable high-yield routes has provided a major impetuous to the investigation of their coordination chemistry; most of these results have been reported in the last 25 years.[21]



$C_3S_3H_6$ **(TT)** $C_4S_4H_8$ **(TT8C4)** $C_6S_3H_{12}$ **(TT9C3)**

Figure 1. 1,3,5-trithian (TT), tetrathia-8-crown-4 (TT8C4) and trithia-9-crown-3 (TT9C3)

Among all the charge transfer complexes M-XY, where M is the charge donor Lewis base and XY is either a homo- or a hetero-nuclear charge acceptor dihalogen, those having $C_3S_3H_6$, $C_4S_4H_8$, and $C_6S_3H_{12}$ (Figure 1) as the n-donor Lewis base are important in the study of interactions between the thianes and σ-acceptors in dichloromethane, trichloromethane and tetrachlormethane solutions.[22,23] The remarkable stability of these complexes, which still pose a challenging problem to theoreticians, also has to be taken into account.[11] To aid in the understanding of intermolecular charge transfer complexation, numerous computational simulations have been attempted on I_2 with electron donor compounds, but there are no publications on such an interaction between I_2 and trithiane compounds. Within this context, density functional theory (DFT) and the MP2 method offer an alternative treatment of electron correlation effects with respect to the more traditional molecular orbital theory, and these methods have recently been suggested to be a good choice for the study of difficult problems, particularly in charge transfer complexes.[24–26] Moreover, natural bond orbital (NBO) analysis[27,28] at the B3LYP level has been carried out to understand the orbital interactions and charge delocalization during the course of the complexation reaction. Consequently, in this paper, we have presented a detailed calculation using DFT-based methods on charge transfer complexes in particular.

Although the experimental evidences[29] confirmed the order of the relative electron acceptor strengths of the halogens with respect to a given Lewis base B in forming B…XY complex is ICl > BrCl > I_2 > Br_2 > Cl_2, there is a question of some importance concerns the change in nature of the B…XY interaction in the gas or solution phase as XY is varied: Is this order of electron acceptor strength maintained for such complexes when isolated in the gas phase and, if so, is there any evidence of a substantial increase in the extent of charge transfer in the stronger complexes? Poleshchuk et al[30] reported a picture of the interaction in H_3N…XY that is predominantly electrostatic in origin and agree well with those derived experimentally from rotational spectroscopy. Their results indicated that the complexes formed between NH_3 and XY are of the outer type and the interaction is mainly electrostatic. In this study, we have analyzed the topology of the total charge transfer by theoretical studies on the basis of the natural bond orbital (NBO) model in order to gain a deeper insight into the nature of the thiacrown ether-dihalogene bond because this electron transition may play important roles in energy and cooperativity for the delocalized electron in the donor-acceptor complexes such as entitled systems. Also the charge transfer between two constituents of the systems is one of the key features determining adsorption energies, reactivities, electronic structure, conductivities, and optical properties. The design of molecular devices and the understanding of adsorption and reactivity also require understanding the dependence of charge transfer on molecular geometry.

There is no comprehensive comparative study on an investigation of the donor-acceptor behaviour of thiacrown ether complexes with dihalogen molecules in the gas or solution phases in the literature. In this paper, we have been performed a computational investigation of the properties of the charge transfer complexes between $C_3S_3H_6$, $C_4S_4H_8$, and $C_6S_3H_{12}$ as the donor and I_2, Br_2, Cl_2, IBr and ICl (XY) as the acceptors for the ground state in the gas phase and in dichloromethane as a solvent using the DFT-based method. Thermodynamic properties, natural bond orbitals (NBO) analysis and orbital interaction energy between HOMO and LUMO of the donor-acceptor system were calculated for each complex system. Our calculations demonstrate the significant influence of the electronegativity of the Y atom and the polarization of the XY bond on CT in these systems.

2. Computational Method

The electronic molecular structure calculations were performed at the restricted B3LYP hybrid method level of DFT theory[31] using Gaussian 98 software[32] for 1,3,5-trithian (TT), tetrathia-8-crown-4 (TT8C4) and trithia-9-crown-3 (TT9C3) (Figure 1), separately. Then, the full optimizations were carried out for the complex systems, including each of them with the homo and hetero dihalogen molecules, I_2, Br_2, Cl_2, IBr and ICl. The B3LYP hybrid method was employed in combination with different basis sets for the various included atoms. The 6-31G** basis set was used for Cl, Br, S, H and C, and the 3–21G** basis set was used for I with the GEN keyword.

To consider the solvent effect for the studied complex systems, the Onsager reaction field model,[35] 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.

For studying of the donor-acceptor in the complex systems, thermodynamic properties based on the frequencies were derived from statistical thermodynamics, including enthalpy, (ΔH_r), Gibbs free of energy, (ΔG_r) and formation energy, (ΔE_f), for the complexation. Natural bond orbitals (NBO) analysis consisting of Mulliken analysis on the atoms accompanying the charge transfer for two electronic states of complex was also carried out. The amounts of transferred partial charge between two donor and acceptor species ($q_{\text{donor}\rightarrow\text{acceptor}}$) were calculated by the occupation numbers of NBO data for evaluating the orbital interaction energy ($\Delta E^{(2)}$) between the HOMO and LUMO of the donor-acceptor system. In a quantitative sense, the energetic effects due to these interactions may be estimated by the second-order perturbation theoretical expressions of the following form:[28]

$$q_{donor\rightarrow acceptor} \cong 2\left(\frac{\Psi^*_{don}\left|\hat{F}\right|\Psi^*_{acc}}{\varepsilon_{acc}-\varepsilon_{don}}\right)^2 \qquad (1)$$

$$\Delta E^{(2)} = 2\frac{\left\langle\Psi^*_{don}\left|\hat{F}\right|\Psi^*_{acc}\right\rangle^2}{\varepsilon_{acc}-\varepsilon_{don}} \qquad (2)$$

where F is the Fock operator, $<\Psi^*_{don}|F|\Psi^*_{acc}>$ 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. The stabilisation energies, $\Delta E^{(2)}$, are proportional to the NBO interacting intensities. This reveals the origin of intermolecular interactions.

3. Results and Discussion

3. 1. The Optimal Structure and Thermochemistry Analysis of Thiacrown Ether Complexes

a) Gas phase

After full optimization and without any negative frequency for each complex system, the thermochemical quantities (ΔH_r, ΔG_r and ΔE_f) and the natural charges based on NBO analysis on the atoms accompanying S(1)-X (S atom at position 1 with respect to the halide molecule, X-Y) band distances and S(1)-X-Y angles for two electronic states of the stable complexes between thiacrown ethers ($C_3S_3H_6$, $C_4S_4H_8$, and $C_6S_3H_{12}$) and I_2, Br_2, Cl_2, IC-l and IBr (XY) molecules in the gas phase at the B3LYP/6-31G** level of theory have been listed in Table 1. The first frequencies of many complex systems of $C_6S_3H_{12}$ were negative, so they were unstable for complexation. Thus, we focused more on the complexation of $C_3S_3H_6$ and $C_4S_4H_8$. Also, the pictorial optimized geometries for each of them are pictured in Figure 2.

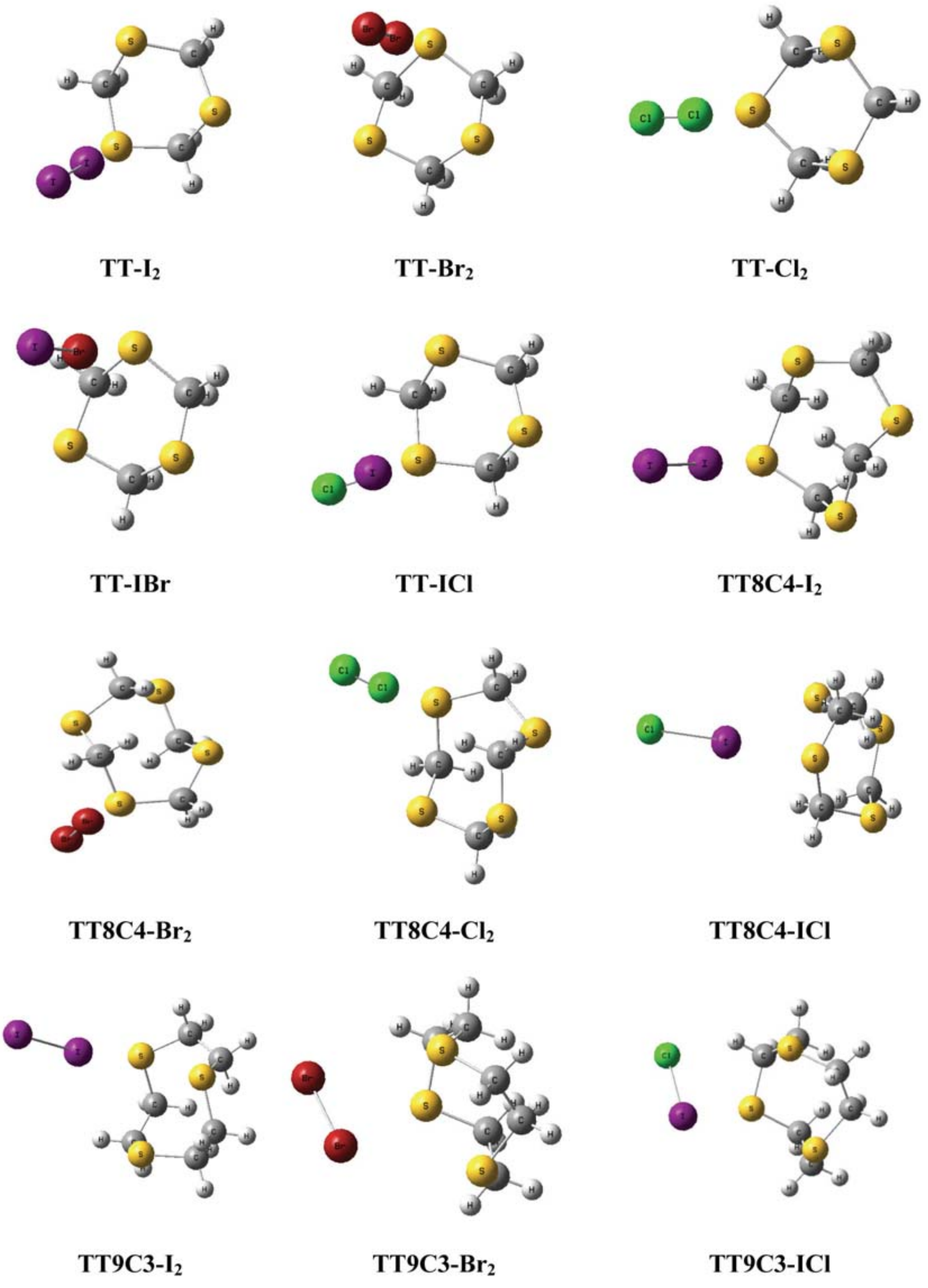
The type of molecule settled with a dihalogen has an important role in the charge transfer interaction. A flat structure leads to an increase the process of CT.[11] Table 1 shows that with increasing electronegativity of the outer halogen (Y in M-XY), the distances between the internal halogen (X in M-XY) and the sulphur atom (S(1)-X) decreased, while the charges on the S(1) atom (the nearest the S atom from the inner halogen) and on the inner halogen increased (more positive). All of these five complexes of TT were planar. On the other hand, the charge on S(1) was more positive than that on X (inner halogen). Also, the CT in the complex between TT and dihalogens with point group C_1 gave a linear structure of S(1)-X-Y. The optimal structure of these complexes is a flat configuration, and the angles of S(1)-X-Y represent this flat arrangement. Therefore, the charge transfer from I-Y to $C_3S_3H_6$ occurs.

The results in Table 1 show that the optimal structures of TT8C4 complexes were configured as flat arrangements. But, in accordance with the results of this table, we can predict a near vertical structure for TT9C3 complexes. There was a significant relationship between the electronegativity of Y and differences in the S(1)-X distance in all complexes. This is a reason for a stronger bond in S(1)-X from Y=I to Y=Cl and high electron-donor and electron-acceptor in the corresponding dihalogen. We also found compression of the S-X bond from $C_3S_3H_6\ldots I_2$ to $C_3S_3H_6\ldots Cl_2$. The charge on S increased from 0.3021 in $C_3S_3H_6\ldots I_2$ to 0.3506 in $C_3S_3H_6\ldots Cl_2$, while negative charge increased on the internal halogen, resulting in a more stable, optimal structure for $C_3S_3H_6\ldots Br_2$. The stability trend of the complexes of $C_3S_3H_6$ with homonuclear dihalogens is as follows:

$$Br_2 > Cl_2 > I_2$$

The results of Table 1 demonstrate that despite the fact that some complexes of TT9C3 with dihalogens were stable, such as TT9C3…I_2, TT9C3…ICl and TT9C3 …Br_2, because of having no negative frequency, but they have nonplanar configuration. Thus there was no CT in the complexes of TT9C3 in the ground state.

The complexation enthalpy values decreased from –4.68 kJ/mol in $C_3S_3H_6\ldots I_2$ to –11.03 kJ/mol in



TT-I$_2$ **TT-Br$_2$** **TT-Cl$_2$**

TT-IBr **TT-ICl** **TT8C4-I$_2$**

TT8C4-Br$_2$ **TT8C4-Cl$_2$** **TT8C4-ICl**

TT9C3-I$_2$ **TT9C3-Br$_2$** **TT9C3-ICl**

Figure 2. The optimized geometries of the complexes of $C_3S_3H_6$ (TT), $C_4S_4H_8$ (TT8C4), and $C_6S_3H_{12}$ (TT9C3) with X_2 or IX (X = Cl, Br, or I) molecules

$C_3S_3H_6$…ICl (as did the complex formation energy), and according to Gibbs free energies, these complexes take place at room temperature, so the most optimal conditions for maximum constancy and the stability of molecular complexes $C_3S_3H_6$…IY relate to systems of unstauration chemistry, an optimal flat structure, and the most polarised dihalogen I-Cl. The complexation Gibbs free energies in the ground state showed that the thermodynamic stability trend of these complexes was: I-Cl > I-I > I-Br and $Br_2 > Cl_2 > I_2$. The thermodynamic stability trend of the

Table 1. Complex formation energies (**ΔE$_f$**), complexation enthalpies and Gibbs free energies (ΔH$_r$ and ΔG$_r$), first frequency, the natural charges on the atoms based on NBO analysis, S(1)-X and X-Y bonding distances (in Angstrom) and S(1)-X-Y angles of the stable M-XY (M=$C_3H_3H_6$, $C_4S_4H_8$ and $C_6S_3H_{12}$) complexes compared with that of M calculated at the B3LYP/6-31G** level in the gas phase

M	XY	ΔE$_f$ (kJ/mol)	ΔH$_r$ (kJ/mol)	ΔG$_r$ (kJ/mol)	Freq (cm^{-1})	Charge on S(1)	Charge on X(inner)	S(1)-X	X-Y	S(1)-X-Y Angle
$C_3H_3H_6$[a]	I-I	–2.20	–4.68	29.94	19.15	0.3021	–0.0076	3.1425	2.7746	174
	I-Br	–1.41	–3.90	33.14	25.83	0.3180	0.1058	3.0115	2.5899	175
	I-Cl	–8.54	–11.03	26.76	32.40	0.3272	0.1730	2.8961	2.3879	174
	Br-Br	–26.39	–28.88	6.59	28.78	0.3382	–0.0404	2.8961	2.3879	182
	Cl-Cl	–12.71	–15.20	17.74	25.90	0.3506	–0.0609	2.8233	2.1234	181
$C_4S_4H_8$[b]	I-I	–6.09	–8.58	25.19	22.95	0.2809	–0.0072	3.1524	2.7745	177
	I-Br	–5.00	–7.48	28.39	22.48	0.2971	0.1070	3.0075	2.5916	177
	I-Cl	169.52	167.03	198.38	18.35	0.3540	0.1544	2.9129	2.3210	174
	Br-Br	–40.13	–42.62	–8.23	24.42	0.2703	–0.0517	3.0826	2.6766	175
	Cl-Cl	–21.97	–24.46	7.67	27.20	0.2672	–0.0693	2.8129	2.1288	175
$C_6S_3H_{12}$[c]	I-I	3.41	0.92	36.71	24.65	0.2543	0.0106	3.1978	2.7676	168
	I-Cl	39.60	37.11	66.09	13.71	0.2244	0.2549	4.7619	2.3851	107
	Br-Br	–4.48	–6.97	23.78	24.55	0.2222	0.0248	3.9584	2.3180	119

[a] natural charges on the S(1) atom based on NBO analysis are 0.2162, 0.2280 and 0.1779 for $C_3H_3H_6$, $C_4S_4H_8$ and $C_6S_3H_{12}$, respectively.

Table 2. Complex formation energies (**ΔE$_f$**), complexation enthalpies and Gibbs free energies (ΔH$_r$ and ΔG$_r$), first frequency, the natural charges on the atoms based on NBO analysis, S(1)-X and X-Y bonding distances (in Angstrom) and S(1)-X-Y angles of the stable M-XY (M=$C_3H_3H_6$, $C_4S_4H_8$ and $C_6S_3H_{12}$) complexes compared with that of M calculated at the B3LYP/6-31G** level in dichloromethane solution in the singlet ground state

M	XY	ΔE$_f$ (kJ/mol)	ΔH$_r$ (kJ/mol)	ΔG$_r$ (kJ/mol)	Freq (cm^{-1})	Charge on S(1)	Charge on X(inner)	S(1)-X	X-Y	S(1)-X-Y Angle
$C_3S_3H_6$[a]	I-I	3301.14	3281.25	3296.88	32.56	0.3001	–0.0062	4.7653	3.0373	174
	I-Br	–6.41	–9.05	27.02	24.70	0.3091	0.1002	3.0115	2.5898	176
	I-Cl	–16.56	–19.20	17.35	26.71	0.3210	0.1630	2.9376	2.4625	180
	Br-Br	–32.94	–35.73	1.30	26.19	0.3292	–0.0304	2.8961	2.3879	177
	Cl-Cl	–96.89	–20.61	11.53	20.66	0.3480	–0.0600	2.8233	2.1234	174
$C_4S_4H_8$[a]	I-I	3294.02	3291.53	3322.07	21.08	0.2791	–0.0070	3.1523	2.7744	177
	I-Br	178.92	176.43	209.11	21.12	0.2900	0.1010	3.0075	2.5916	177
	I-Cl	162.95	159.37	186.35	7.21	0.3401	0.1491	2.9039	2.4691	179
	Br-Br	–42.17	–44.80	–10.54	18.41	0.2810	–0.0510	2.8525	2.3966	175
	Cl-Cl	–105.42	–28.99	5.27	20.65	0.2700	–0.0790	2.8129	2.1288	175
$C_6S_3H_{12}$[a]	I-I	2940.86	2938.37	2970.53	23.85	0.1051	0.0242	3.1987	2.7676	168
	I-Cl	40.42	37.93	63.75	11.58	0.0817	0.1489	4.4152	2.3859	110

[a] natural charges on the S(1) atom based on NBO analysis are 0.0.1099, –0.1055 and –0.1075 for $C_3H_3H_6$, $C_4S_4H_8$ and $C_6S_3H_{12}$, respectively.

complexes of $C_4S_4H_8$ with dihalogens was near similar to the complexes of TT.

b) Dichloromethane solution

The optimized results obtained in dichloromethane solution for each of these stable complex systems as in the gas phase at the B3LYP/6-31G** (3-21G** for the iodine atom) level of theory obtained using the SCRF method in Gaussian have been listed in Table 2. The calculations were carried out only for the singlet ground state of these complexes.

The calculated values for the complexes of TT with dihalogens X_2 (X=I, Cl, Br) showed that the bond distance compression of S-X from $C_3S_3H_6 \ldots I_2$ to $C_3S_3H_6 \ldots Cl_2$ was observable by decreasing the bond distance from I_2 to Cl_2. The charge on S increased from 0.3001 in $C_3S_3H_6 \ldots I_2$ to 0.3480 in $C_3S_3H_6 \ldots Cl_2$ and the negative charge on the internal halogen also increased. According to the results of the energy of the optimal structure, the stability trend of the complexes of TT with homonuclear dihalogens in dichloromethane solvent is as follows:

$$Br_2 > Cl_2 >> I_2$$

The natural charge analysis indicated that S(1) atom of these complexes has more positive charge than the S(1) atom of $C_3S_3H_6$; it also shows that the X-Y constituents are electron donors in the CT phenomenon. The stability trend of the complexes of $C_3S_3H_6 \ldots XY$ is as follows:

$$ICl > IBr >> I_2$$

These trends are also true for TT8C4 complexes. In the solution phase the complex between the thiocrown ethers and I_2 molecule does not form because of the large solvation effect.

3. 2. The Results of NBO Analysis

In the NBO method, delocalization of electron density between occupied Lewis-type orbitals and formally unoccupied (antibonding or Rydberg) non-Lewis NBOs corresponds to a stabilising donor-acceptor interaction. The amounts of the partial electron transfer ($q_{donor \rightarrow acceptor}$) and orbital interaction energies ($\Delta E^{(2)}$) between the donor and acceptor orbitals of the species entrance in CT phenomena for all the complexes of TT and TT8C4 by NBO analysis in the gas phase at the B3LYP/6-31G** level were calculated. Selected results of the NBO second-order perturbation analysis are shown in Tables 3 and 4 for the reactants and the products of the complexation reaction of TT and TT8C4 with dihalogens.

During the complexation reactions between TT or TT8C4 and dihalogens, Tables 3 and 4 show the calculated stabilisation energies, $\Delta E^{(2)}$. For TT-XY, these were mainly due to the interactions of $LP(2)_X \rightarrow \sigma^*_{S1-C2}$, $LP(2)_X \rightarrow \sigma^*_{S1-C3}$, $LP(3)_X \rightarrow \sigma^*_{S1-C2}$ and $LP(3)_X \rightarrow \sigma^*_{S1-C3.}$ These donor orbitals which took part in the stabilisation of the TT-I_2 complex were mainly p character lone pairs or the hybrid orbital approximately described as ($sp^{25.77}$, p) or mainly p in character. For the TT-Br_2, TT-Cl_2, TT-IBr and TT-ICl complexes, they were described as (p, p), ($sp^{10.68}$, sp), ($sp^{18.02}$, p) and ($sp^{11.43}$, sp), respectively. The NBO analysis clearly shows that one of the contributed orbitals of the interaction was mainly p in character which is convenient for CT phenomena.

The calculated stabilisation energies for TT8C4-I_2 are mainly due to the interaction of $LP(2)_I \rightarrow \sigma^*_{C6-S8}$, $LP(3)_I \rightarrow \sigma^*_{S8-C14,}$ and $LP(3)_I \rightarrow \sigma^*_{C6-S8}$ with a total stabilisation energy of 3.738 kJ/mol. For TT8C4-Br_2 and TT8C4-Cl_2, they were mainly due to the interaction of $LP(2)_{Br} \rightarrow \sigma^*_{S9-C14}$ with a stabilisation energy of 3.32 and 2.73 kJ/mol, respectively. The calculated stabilisation energies for TT8C4-IBr were mainly due to the interaction of $LP(3)_I \rightarrow \sigma^*_{S8-C14}$ and $LP(3)_I \rightarrow \sigma^*_{C6-S8}$ with the total stabilisation energy of 3.990 kJ/mol, and for TT8C4-ICl are $LP(2)_I \rightarrow \sigma^*_{S3-C7}$ and $LP(3)_I \rightarrow \sigma^*_{C1-S3}$ with the total stabilisation energy of 5.126 kJ/mol. These donor orbitals which took part in the stabilisation of the TT8C4-I_2 complex were mainly p character lone pairs and the hybrid orbitals were approximately described as sp and p. For the TT8C4-Br_2 and TT8C4-Cl_2 complexes they were described as $sp^{21.43}$ and $sp^{12.14}$, respectively. For TT8C4-IBr and TT8C4-ICl they were mainly p character. Thus, the thiacrownethers were acting as the acceptor.

Table 3. Second order perturbation theory analysis of the Fock matrix in NBO basis including the partial electron transfer (q) and orbital interaction energies ($\Delta E^{(2)}$) between the donor and acceptor orbitals of the species entrance in CT phenomena for the complexes of $C_3S_3H_6$ (TT) with XY (X, Y=Cl, Br, I) molecules in the gas phase at B3LYP/6-31G**

donor → acceptor	$\Delta E^{(2)}$	q
I-I		
$LP(1)_I \rightarrow \sigma^*_{S1-C2}$	0.46	0.22
$LP(1)_I \rightarrow \sigma^*_{S1-C3}$	0.38	0.18
$LP(2)_I \rightarrow \sigma^*_{S1-C2}$	1.18	1.07
$LP(2)_I \rightarrow \sigma^*_{S1-C3}$	1.34	1.31
$LP(3)_I \rightarrow \sigma^*_{S1-C2}$	1.51	1.46
$LP(3)_I \rightarrow \sigma^*_{S1-C3}$	0.88	0.93
$LP(1)_{S1} \rightarrow \sigma^*_{I-I}$	8.95	6.53
$LP(2)_{S1} \rightarrow \sigma^*_{I-I}$	64.18	125.00
$LP(2)_{S4} \rightarrow \sigma^*_{I-I}$	0.42	0.99
$LP(2)_{S5} \rightarrow \sigma^*_{I-I}$	0.42	0.99
Br-Br		
$LP(1)_{Br} \rightarrow \sigma^*_{S1-C2}$	0.34	0.14
$LP(1)_{Br} \rightarrow \sigma^*_{S1-C3}$	0.25	0.11
$P(2)_{Br} \rightarrow \sigma^*_{S1-C2}$	1.09	1.01
$LP(2)_{Br} \rightarrow \sigma^*_{S1-C3}$	1.13	1.01
$LP(3)_{Br} \rightarrow \sigma^*_{S1-C2}$	1.39	1.25
$LP(3)_{Br} \rightarrow \sigma^*_{S1-C3}$	1.09	1.01
$LP(1)_{S1} \rightarrow \sigma^*_{Br-Br}$	8.11	5.92
$LP(2)_{S1} \rightarrow \sigma^*_{Br-Br}$	83.37	157.87
$LP(2)_{S5} \rightarrow \sigma^*_{Br-Br}$	0.59	1.39
$LP(2)_{S4} \rightarrow \sigma^*_{Br-Br}$	0.59	1.39
Cl-Cl		
$LP(1)_{Cl} \rightarrow \sigma^*_{S1-C2}$	0.38	0.18
$LP(1)_{Cl} \rightarrow \sigma^*_{S1-C3}$	0.38	0.18
$LP(2)_{Cl} \rightarrow \sigma^*_{S1-C2}$	1.30	1.05
$LP(2)_{Cl} \rightarrow \sigma^*_{S1-C3}$	1.30	1.05
$LP(3)_{Cl} \rightarrow \sigma^*_{S1-C2}$	1.13	1.03
$LP(3)_{Cl} \rightarrow \sigma^*_{S1-C3}$	1.09	1.03
$LP(1)_{S1} \rightarrow \sigma^*_{Cl-Cl}$	8.06	5.74
$LP(2)_{S1} \rightarrow \sigma^*_{Cl-Cl}$	76.36	151.25
I-Br		
$LP(1)_I \rightarrow \sigma^*_{S1-C2}$	0.55	0.25
$LP(1)_I \rightarrow \sigma^*_{S1-C3}$	0.46	0.25
$LP(2)_I \rightarrow \sigma^*_{S1-C2}$	1.81	1.99
$LP(2)_I \rightarrow \sigma^*_{S1-C3}$	1.89	1.99
$LP(3)_I \rightarrow \sigma^*_{S1-C2}$	2.02	2.22
$LP(3)_I \rightarrow \sigma^*_{S1-C3}$	1.51	1.54
$LP(1)_{S1} \rightarrow \sigma^*_{I-Br}$	12.14	9.05
$LP(2)_{S1} \rightarrow \sigma^*_{I-Br}$	99.96	164.69
$LP(2)_{S4} \rightarrow \sigma^*_{I-Br}$	0.50	0.89
$LP(2)_{S5} \rightarrow \sigma^*_{I-Br}$	0.55	0.89
I-Cl		
$LP(1)_I \rightarrow \sigma^*_{S1-C2}$	0.67	0.34
$LP(1)_I \rightarrow \sigma^*_{S1-C3}$	0.67	0.34
$LP(2)_I \rightarrow \sigma^*_{S1-C2}$	2.56	2.58

$LP(2)_I \rightarrow \sigma^*_{S1–C3}$	2.56	2.58
$LP(3)_I \rightarrow \sigma^*_{S1–C2}$	2.27	2.61
$LP(3)_I \rightarrow \sigma^*_{S1–C3}$	2.27	2.61
$LP(3)_I \rightarrow \sigma^*_{C2–H6}$	0.21	0.11
$LP(3)_I \rightarrow \sigma^*_{C3–H9}$	0.21	0.11
$LP(1)_{S1} \rightarrow \sigma^*_{I–Cl}$	14.41	10.58
$LP(2)_{S1} \rightarrow \sigma^*_{I–Cl}$	122.64	189.73
$LP(2)_{S4} \rightarrow \sigma^*_{I–Cl}$	0.46	0.89
$LP(2)_{S5} \rightarrow \sigma^*_{I–Cl}$	0.46	0.89

Table 4. Second order perturbation theory analysis of the Fock matrix in NBO basis including partial electron transfer (q) and orbital interaction energies ($\Delta E^{(2)}$) between the donor and acceptor orbitals of the species entrance in CT phenomena for all complexes of $C_4S_4H_8$ (TT8C4) with XY (X, Y=Cl, Br, I) molecules in the gas phase at B3LYP/6-31G**

donor→acceptor	$\Delta E^{(2)}$	q
I-I		
$LP(1)_I \rightarrow \sigma^*_{S8\text{-}C14}$	0.55	0.26
$LP(1)_I \rightarrow \sigma^* c_{6\text{-}S8}$	0.63	0.26
$LP(2)_I \rightarrow \sigma^*_{S8\text{-}C14}$	0.38	0.37
$LP(2)_I \rightarrow \sigma^* c_{6\text{-}S8}$	1.26	1.46
$LP(3)_I \rightarrow \sigma^*_{S8\text{-}C14}$	1.43	1.46
$LP(3)_I \rightarrow \sigma^* c_{6\text{-}S8}$	1.05	1.18
$LP(2)_I \rightarrow \sigma^* c_{1\text{-}S3}$	0.21	0.21
$LP(3)_I \rightarrow \sigma^* c_{7\text{-}S9}$	0.67	0.64
$LP(1)_I \rightarrow \sigma^* c_{1\text{-}H5}$	0.46	0.14
$LP(2)_I \rightarrow \sigma^* c_{1\text{-}H5}$	3.36	1.75
$LP(1)_{S8} \rightarrow \sigma^*_{I\text{-}I}$	9.11	6.59
$LP(1)_{S9} \rightarrow \sigma^*_{I\text{-}I}$	0.21	0.17
$LP(2)_{S2} \rightarrow \sigma^*_{I\text{-}I}$	1.13	2.81
$LP(2)_{S8} \rightarrow \sigma^*_{I\text{-}I}$	63.76	125.00
$LP(2)_{S9} \rightarrow \sigma^*_{I\text{-}I}$	0.59	1.11
Br-Br		
$LP(1)_{Br} \rightarrow \sigma^*_{S9\text{-}C14}$	0.97	0.41
$LP(1)_{Br} \rightarrow \sigma^* c_{7\text{-}S9}$	0.46	0.20
$LP(2)_{Br} \rightarrow \sigma^*_{S9\text{-}C14}$	3.32	3.13
$LP(2)_{Br} \rightarrow \sigma^* c_{7\text{-}S9}$	0.46	0.41
$LP(3)_{Br} \rightarrow \sigma^*_{C7\text{-}S9}$	0.46	0.41
$LP(1)_{Br} \rightarrow \sigma^* c_{1\text{-}H5}$	0.92	0.29
$LP(2)_{Br} \rightarrow \sigma^* c_{1\text{-}H5}$	0.29	0.17
$LP(3)_{Br} \rightarrow \sigma^* c_{1\text{-}H5}$	16.25	7.89
$LP(2)_{Br} \rightarrow \sigma^* c_{7\text{-}H12}$	0.21	0.12
$LP(2)_{Br} \rightarrow \sigma^* c_{7\text{-}H13}$	1.30	0.68
$LP(1)_{S9} \rightarrow \sigma^*_{Br\text{-}Br}$	8.65	6.84
$LP(2)_{S9} \rightarrow \sigma^*_{Br\text{-}Br}$	94.33	164.01
$LP(2)_{S8} \rightarrow \sigma^*_{Br\text{-}Br}$	0.50	1.11
Cl-Cl		
$LP(1)_{Cl} \rightarrow \sigma^*_{S9\text{-}C14}$	1.18	0.50
$LP(1)_{Cl} \rightarrow \sigma^* c_{7\text{-}S9}$	0.80	0.33
$LP(2)_{Cl} \rightarrow \sigma^*_{S9\text{-}C14}$	2.73	2.13
$LP(2)_{Cl} \rightarrow \sigma^* c_{7\text{-}S9}$	0.38	0.31
$LP(3)_{Cl} \rightarrow \sigma^*_{S9\text{-}C14}$	0.63	0.51
$LP(3)_{Cl} \rightarrow \sigma^* c_{7\text{-}S9}$	0.34	0.27
$LP(1)_{Cl} \rightarrow \sigma^* c_{1\text{-}H5}$	1.01	0.31
$LP(2)_{Cl} \rightarrow \sigma^* c_{1\text{-}H5}$	0.76	0.35
$LP(3)_{Cl} \rightarrow \sigma^* c_{1\text{-}H5}$	7.81	3.80
$LP(2)_{Cl} \rightarrow \sigma^* c_{7\text{-}H13}$	0.46	0.25
$LP(1)_{S9} \rightarrow \sigma^*_{Cl\text{-}Cl}$	8.40	6.66
$LP(2)_{S9} \rightarrow \sigma^*_{Cl\text{-}Cl}$	77.95	151.25
I-Br		
$LP(1)_I \rightarrow \sigma^*_{S2\text{-}C6}$	0.25	0.10
$LP(1)_I \rightarrow \sigma^*_{S8\text{-}C14}$	0.80	0.36
$LP(1)_I \rightarrow \sigma^*_{S9\text{-}C14}$	0.21	0.10
$LP(2)_I \rightarrow \sigma^*_{S8\text{-}C14}$	1.09	1.25
$LP(3)_I \rightarrow \sigma^*_{S8\text{-}C14}$	1.93	2.22
$LP(1)_I \rightarrow \sigma^*_{C6\text{-}S8}$	0.88	0.43
$LP(2)_I \rightarrow \sigma^*_{C6\text{-}S8}$	1.68	1.87
$LP(3)_I \rightarrow \sigma^*_{C6\text{-}S8}$	2.06	2.22
$LP(3)_I \rightarrow \sigma^*_{C7\text{-}S9}$	0.80	0.84
$LP(1)_I \rightarrow \sigma^*_{C1\text{-}H5}$	0.42	0.15
$LP(2)_I \rightarrow \sigma^*_{C1\text{-}H5}$	2.77	1.47
$LP(2)_{S2} \rightarrow \sigma^*_{I\text{-}Br}$	1.26	2.81
$LP(1)_{S8} \rightarrow \sigma^*_{I\text{-}Br}$	12.85	9.75
$LP(1)_{S9} \rightarrow \sigma^*_{I\text{-}Br}$	0.25	0.17
$LP(2)_{S8} \rightarrow \sigma^*_{I\text{-}Br}$	102.35	169.72
$LP(2)_{S9} \rightarrow \sigma^*_{I\text{-}Br}$	0.59	1.54
I-Cl		
$LP(1)_I \rightarrow \sigma^*_{S3\text{-}C7}$	0.59	0.31
$LP(2)_I \rightarrow \sigma^*_{S2\text{-}C6}$	0.76	2.49
$LP(2)_I \rightarrow \sigma^*_{S3\text{-}C7}$	1.93	2.35
$LP(3)_I \rightarrow \sigma^*_{S2\text{-}C6}$	0.25	0.62
$LP(3)_I \rightarrow \sigma^*_{S3\text{-}C7}$	1.18	1.32
$LP(2)_I \rightarrow \sigma^*_{C1\text{-}S3}$	0.88	0.93
$LP(2)_I \rightarrow \sigma^*_{C7\text{-}S10}$	0.50	0.45
$LP(3)_I \rightarrow \sigma^*_{C1\text{-}S3}$	3.23	3.29
$LP(3)_I \rightarrow \sigma^*_{C7\text{-}S10}$	0.42	0.45
$LP(1)_I \rightarrow \sigma^*_{C7\text{-}H13}$	0.34	0.10
$LP(2)_I \rightarrow \sigma^*_{C7\text{-}H13}$	0.55	0.34
$LP(3)_I \rightarrow \sigma^*_{C1\text{-}H5}$	0.29	0.15
$LP(1)_{S3} \rightarrow \sigma^*_{Cl\text{-}I}$	13.73	10.43
$LP(2)_{S3} \rightarrow \sigma^*_{Cl\text{-}I}$	140.15	215.17

The amounts of the transferred partial charge between the two donor-acceptor species (in this case, between the halogens and TT or TT8C4), eq (1), and the interaction energy between bonding filled orbitals and antibonding unfilled orbitals in SCF-MO theory, eq (2), were calculated. For this purpose, all parameters are represented in Tables 3 and 4 for all the complexes of the TT and TT8C4. Total charge transfer ($q_{donor\rightarrow acceptor}$) in I-Cl was more than in the other species interacting with TT. The amount of total charge transfer showed the following trends according to the reported complexation energies in Table 1.

$$ICl > IBr > I_2$$

$$Cl_2 > Br_2 > I_2$$

3. 3. The Effect of the Basis Set

Changing the basis set from 6-31G** to 6-31+G** and carrying full optimization procedure again, the results of the natural charges on the atoms based on Mulliken analysis, the S(1)-X and X-Y bonding distances (in Angstroms) and the S(1)-X-Y angles of the M-XY complexes of $C_3S_3H_6$ and $C_4S_4H_8$ calculated at the B3LYP level of theory are collected in Table 5. Increasing the electronegativity of the external halogen (Y = I, Br, Cl) in $C_3S_3H_6$…I-Y and $C_4S_4H_8$…I-Y led to longer and shorter distances of S(1)-I in these molecular complexes, respectively. By changing the basis set, the result will not only change, but also the positive charge on the S atom increases in both complexes in comparison to the primary basis set and the charge transfer phenomenon takes place and configure.

3. 4. Intermolecular Bond Energies

Complexation energies or intermolecular bond energies are due to the charge redistribution during intermolecular bonding of the donor and acceptor and can be derived as follows:

$$\Delta E_b = E_{tot} - (E_{XY} + E_{crown}) \quad (3)$$

where E_{tot}, E_{XY} and E_{crown} are the energies of the XY crown ether complex, the XY and crown monomers, respectively.[36] The energy values obtained have been further corrected for the basis set superposition error (BSSE) arising from the use of finite basis sets in the optimization procedure. Due to the different number of basic functions considered in the complex and the monomer optimizations, BSSE is a very important computational issue in the proper treatment of intermolecular interactions and must be taken into account. It is noteworthy that the BSSE is always large and cannot be neglected.[37] We have carried out the BSSE calculations following the functional counterpoise (CP) scheme.[38] Table 5 presents the calculated BSSE and zero point corrections during complexation, ΔZPC. Also, the CP- and ZP-corrected intermolecular bond energies, $\Delta E_b^{CP, ZP}$ values are presented. $\Delta E_b^{CP, ZP}$ is more negative when the donor and acceptor form a more stable complex. Thus, this quantity indicates that among the TT…XY complexes, TT…Br_2 and TT…IBr were the most and the least stable complexes, respectively. The most stable form of TT8C4…XY was configured by Cl-Cl and Br-Br. These trends were not observed with uncorrected ΔE_b, and the BSSE was clearly important.

4. Conclusions

We studied the calculations of molecular complexes for the charge transfer of thiacrown ethers such as TT, TT8C4 and TT9C3 to dihalogens such as Br_2, Cl_2, ICl, IBr and I_2 in the gas phase and in dicholoromethane solution by applying density function theory (DFT). Structural characterisation, frequency and energy have been completely specified. Special attention was placed on the study of the electronegativity effect of the internal halogen atom and polarization of the bond between the two halogens. Our results indicate that there was a considerable effect of the electronegativity of the external halogen atom and the polarization of the dihalogen bond on structural parameters, the donor-acceptor effect, structural stabilisation and intermolecular bond energies. The best conditions for maximum constancy and the stability of molecular complexes was TT…ICl due to the optimal flat structure and the most polarised dihalogen bond. The stability trends of the complexes of TT and TT8C4 with XY dihalogens in dicholoromethane solution were: ICl > IBr > I_2 and Br_2 > Cl_2 > I_2. The results for the complexes of TT9C3 with selected dihalogens showed the vertical structure for the complex, and so CT did not occur for these complexes. The special result of this investigation was seen in evaluating the severe effect of Y atom electronegativity, bond polarization of I-Y, and the dependence of S(1)-I on complexes with thiacrown ethers.

Table 5. The natural charges on the atoms based on Mulliken analysis, S(1)-X and X-Y bonding distances (in Angstroms), S(1)-X-Y angles of M-XY (M = $C_3S_3H_6$ and $C_4S_4H_8$) complexes calculated at the B3LYP/6-31+G** level, and the calculated results at the B3LYP/6-31G** (3-21G** for the iodine atom) level for total energies (E_{tot}) (in a.u.), complexation energies (ΔE_b), BSSE, zero point correction in the complexation (ΔZPC) and the counterpoise- and zero point- corrections of the complexation energies ($\Delta E_b^{CP, ZPE}$) (in kJ/mol) of the stable and charge transfer complexes in the ground state of the gas phase

M	XY	Charge on S(1)	Charge on X(inner)	S(1)-X	X-Y	E_{tot}	ΔE_b	BSSE	ΔZPC	$\Delta E_b^{CP, ZP}$
$C_3S_3H_6$	I-I	0.1545	0.0305	4.2618	3.0373	–15092.67	–8.76	2.71	2.07	–3.98
	I-Br	0.3713	0.1432	3.0115	2.5900	–10773.99	–7.79	12.10	2.01	6.32
	I-Cl	0.4186	0.1036	2.9378	2.4625	–8662.77	–14.90	12.24	2.08	–0.58
	Br-Br	0.3109	0.06283	2.8961	2.3879	–6455.91	–32.53	18.02	1.90	–12.61
	Cl-Cl	0.2871	0.0274	2.8233	2.1234	–2232.85	–15.74	3.39	1.71	–10.64
$C_4S_4H_8$	I-I	0.3733	0.0487	3.1524	2.7745	–15530.16	–14.46	5.79	2.48	–6.19
	I-Br	0.4620	0.1479	3.0015	2.5916	–11211.48	–13.41	14.53	2.60	3.72
	I-Cl	0.5695	0.1069	2.9040	2.4691	–9100.24	12.68	13.92	–4.25	22.35
	Br-Br	0.4022	0.0526	2.8525	2.3970	–6893.40	–48.96	23.54	3.05	–22.37
	Cl-Cl	0.3285	0.0412	2.8130	2.1290	–2670.35	–30.32	3.18	2.65	–24.49

These calculations show that I-Y acts as the electron donor and $C_3S_3H_6$ and $C_4S_4H_8$ act as the electron acceptors. This was investigated by analysing partial charges and complex geometries. The natural charges on S(1) showed the intermolecular interactions; namely, it was found that the I-Y moiety transferred electronic charge to $C_3S_3H_6$ and $C_4S_4H_8$. The conclusion was reached by analysing the $LP(n)_I \rightarrow \sigma^*_M$ (M = $C_3S_3H_6$ or $C_4S_4H_8$) donor-acceptor interaction. The type of the interaction in all complexes is nonbonded interactions in the gas phase and polar-polar interactions in the dicholoromethane solution.

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Povzetek

Z uporabo B3LYP nivoja teorije in 6-31G** ter 6-31+G** baznih setov smo proučevali interakcije med molekularnimi kompleksi 1,3,5-tritio, (TT), tetratio–8–crown-4, (TT8C4), in tritio–9–crown–3, (TT9C3) z dihalogeni v osnovnem in vzbujenem stanju. Ugotovili smo, da je tako pri TT kot TT8C4 kompleksu v osnovnem stanju pride do prenosa naboja od dihalogena do molekule tiacrown etra; trend prenosa naboja pa sledi zaporedju ICl > IBr > I_2 in Br_2 > Cl_2 > I_2. Pri kompleksih s TT9C3 takega trenda nismo opazili. Frekvenčna analiza je pokazala, da so v vzbujenem stanju vsi kompleksi nestabilne.