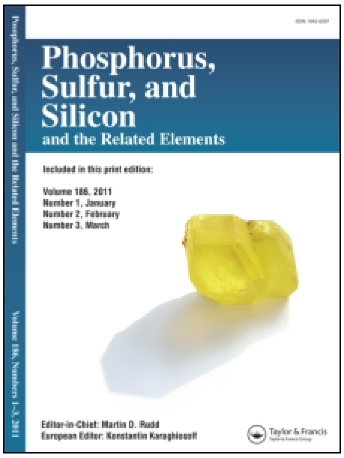

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CHARGE-TRANSFER INTERACTION OF CROWN THIOETHERS WITH π-ELECTRON ACCEPTORS

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CHARGE-TRANSFER INTERACTION OF CROWN THIOETHERS WITH π-ELECTRON ACCEPTORS

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1:1 CT complexes formed between some crown polythioethers and π-electron acceptors (DDQ, TCNE and CHL) have been synthesized and characterized. Spectral characteristics and formation constants of the CT complexes have been measured at 25°C. The effects of donor molecular structure, π-acceptor electron affinity and solvent polarity on the stabilities of these CT complexes have been investigated and discussed. It is deduced that such complexes are of weak *n*-π type where the ground state wave function is described primarily by the nonbonding structure (D-A). Ionization potentials of the crown thioethers have been estimated from the CT transition energies.

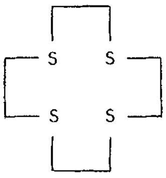
Key words: Charge-transfer complexes; crown thioethers; spectral characteristics; stability; solvent effect; solid CT complexes.

INTRODUCTION

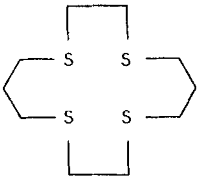
Crown compounds have found a number of important applications.[1,2] These compounds have been studied as model systems in cation transport through cellular membranes.[3,4] Also, they have been used in organic chemistry to study some ionic organic reactions catalyzed by solvolysis of the cationic species.[5] For these important applications considerable work has been carried out on CT complexes of crown ethers with σ and π-electron acceptors.[6–9] On the other hand, little attention has been paid to a similar study on crown thioethers.[10] Nour *et al.*[10] demonstrated that 1:1 CT complexes are formed by the interaction of some macrocyclic polythioethers with the σ-electron acceptor, iodine. The present work is devoted to study the CT complexes of four different crown thioethers with some π-electron acceptors, viz., 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ); tetracyanoethylene (TCNE) and chloranil (CHL). The four crown thioethers applied in this investigation are 1,4,7,10-tetrathiacyclododecane (TTCDD) (**I**); 1,4,8,11-tetrathiacyclotetradecane (TTCTD) (**II**); 1,5,9,13-tetrathiacyclohexadecane (TTCHD) (**III**) and 1,5,9,13-tetrathiacyclohexadecane-3,11-diol (TTCHDD) (**IV**). The solid CT complexes have been synthesized and characterized. Moreover, the role of the molecular structure of both the polythioethers and π-electron acceptors as well as the effect of the solvent on the stabilities of the CT complexes were examined.

EXPERIMENTAL

Materials and Solutions. All solvents used were of spectral-grade quality (BDH). The electron acceptors DDQ, TCNE and CHL (Aldrich reagents grade products) were recrystallized from dry methylene chloride, chlorobenzene and dry benzene, respectively. The macrocyclic polythioethers, 1,4,7,10-tetrathiacyclododecane (TTCDD) (**I**): 1,4,8,11-tetrathiacyclotetradecane (TTCTD) (**II**); 1,5,9,13-tetrathiacyclohexadecane (TTCHD) (**III**); 1,5,9,13-tetrathiacyclohexadecane-3,11-diol (TTCHDD) (**IV**) were obtained from the Aldrich Chem. Co. and were used without further purification. The general structural formula of these compounds can be represented as follows:



(I)



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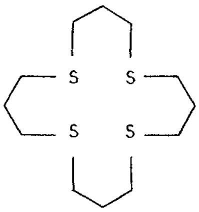

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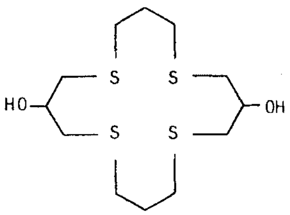

(IV)

Stock Solutions of the donors or acceptors were freshly prepared in dry and deoxygenated solvent prior to use.

Physical Measurements. Measurements of electronic absorption spectra were carried out on a CECIL CE 599 Spectrophotometer using 1 cm matched Silica cells. The apparatus was equipped with a temperature controlled cell holder which was controlled by a Haake Ultrathermostat with an accuracy ±0.05°C. Computations were performed on an Apple IIe microcomputer with the aid of two programs based on an unweighted linear least square fit.

TABLE I

Microanalysis data, colors and melting points of the solid CT complexes

Molecular Complex	Color	M.P°C	% Calculated (found)				
			C	H	N	S	Cl
I - DDQ	dark brown	280^d	41.07	3.46	6.013	27.41	15.11
			(40.84)	(3.15)	(6.24)	(27.45)	(15.02)
I - TCNE	pale yellow	240^s	45.63	4.37	15.27	34.70	-
			(45.44)	(4.17)	(15.54)	(34.52)	-
II - DDQ	brown	255^d	43.64	4.07	5.66	25.88	14.31
			(43.26)	(4.33)	(5.82)	(25.65)	(14.69)
II - TCNE	buff	95^s	48.46	5.08	14.19	32.34	-
			(48.21)	(5.32)	(14.11)	(32.25)	-
II - CHL	yellow	180^d	37.43	3.92	-	24.93	27.57
			(37.63)	(4.00)	-	(24.65)	(27.25)
IV - DDQ	red	150^d	43.24	4.32	5.06	23.08	12.76
			(43.35)	(4.15)	(5.17)	(23.15)	(12.67)
IV - TCNE	orange	138^s	47.34	5.30	12.32	28.08	-
			(47.40)	(5.13)	(11.92)	(27.88)	-

s sharp
d decomposition

Synthesis of the Solid CT Complexes. Equimolar amounts (0.5 mmol) of each of the donors (**I**, **II**, **IV**) and π-acceptors (DDQ, TCNE, CHL) were dissolved separately in the minimum volume of dry methylene chloride. The two solutions were mixed and the resulting solution was left at room temperature for 72 hours. The solid compound which separated was collected, filtered off and washed several times with diethyl ether then dried. The analytical data of the synthesized complexes (C, H, N, S and Cl analyses) along with some of their physical properties, viz., colors and melting points are given in Table I. The elemental analysis of these complexes were carried out at the microanalytical laboratory, Assiut University, Assiut, Egypt. Several trials were done to isolate the other CHL CT complexes, but without success.

RESULTS AND DISCUSSION

Spectral Characteristics and Formation Constants (K_{CT})

The absorption spectral data are shown in Table II. In the region 380–700 nm a new band appeared. This band could be ascribed to a single intermolecular charge-transfer transition. Typical spectral results at 25°C are displayed in Figure 1. It is worth mentioning that in the case of molecular complexes with CHL, the electronic spectra were scanned against the same concentration of CHL as in the test solution. This was done to avoid the possible overlap that would arise between the CT complex band and that of CHL. For all CT complexes under investigation the absorption intensities of the CT band increase very slowly with time (the absorptivity change within 2% after one hour). The stoichiometry of the complexes is ascertained by applying the continuous variation method[11] which clearly indicate the formation of 1:1 CT complex (cf. Figure 2).

Values of the formation constants of the CT complexes formed by the interaction

TABLE II

λ_{max} (nm), E_{CT} (eV), IP (eV), K_{CT} and ε_{CT} values for the CT molecular complexes of cyclic polythioethers with π-electron acceptors DDQ, TCNE and CHL in $CHCl_3$ at 25°C

Molecular Complexes	λ_{max}(nm)	E_{CT}(eV)	IP (eV) This work	IP (eV) Ref.10	K_{CT} $dm^3\ mol^{-1}$	ε_{CT} $dm^3\ mol^{-1}\ cm^{-1}$
TTCDD-TCNE	468	2.653	8.72	8.78	1.46 ± 0.3	1632 ± 359
TTCTD-TCNE	506	2.454	8.47	8.81	2.83 ± 0.3	687 ± 104
TTCHD-TCNE	518	2.397	8.40	-	7.38 ± 0.6	438 ± 44
TTCHDD-TCNE	488	2.544	8.59	8.83	4.83 ± 0.6	518 ± 69
TTCTD-DDQ	552	2.249	8.51	8.81	4.51 ± 0.4	846 ± 71
TTCTD-CHL	450	2.759	8.40	8.81	1.49 ± 0.2	970 ± 55

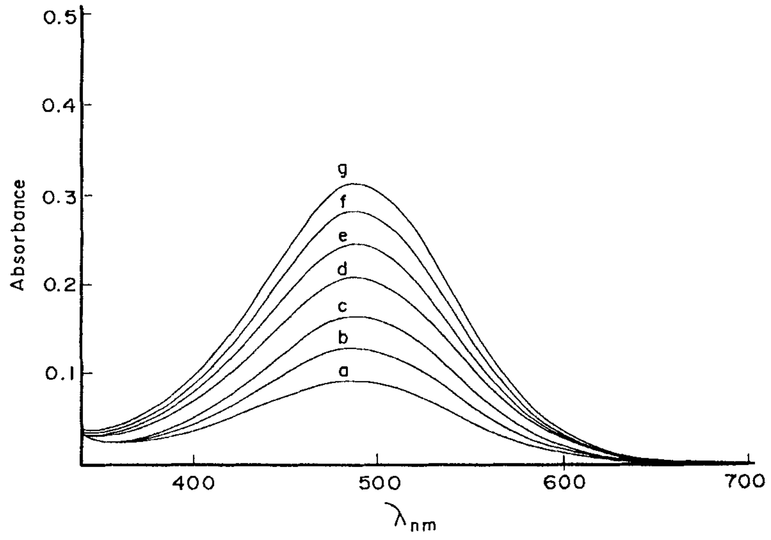

FIGURE 1 Electronic absorption spectra of the CT molecular complex solutions of TTCHDD (**IV**) with TCNE in $CHCl_3$ at 25°C. [TTCHDD] = 0.01, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040 mol dm^{-3} for a, b, c, d, e, f, g, respectively. [TCNE] = 4×10^{-3} mol dm^{-3}.

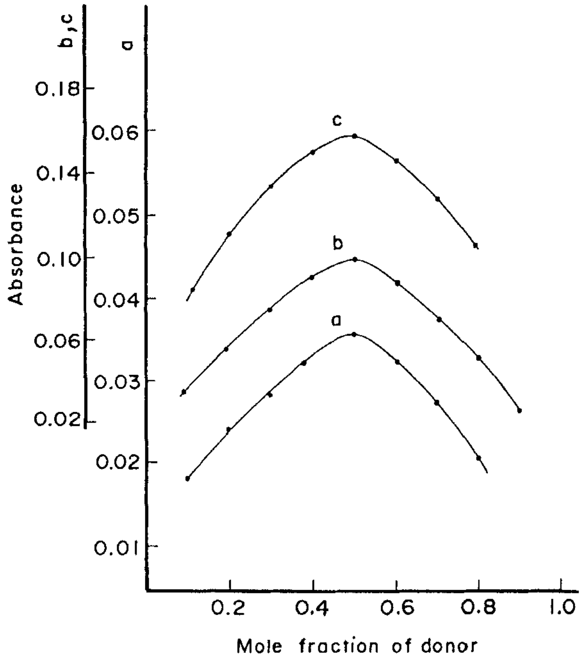

FIGURE 2 Continuous variation method for the CT complexes of donor TTCTD (**II**) with π-electron acceptors (total molar concentration = 2×10^{-3} mol dm^{-3}). (a) CHL, (b) TCNE, (c) DDQ.

of the cyclic polythioethers (**I**–**IV**) with the π-electron acceptors were determined spectroscopically making use of both the Benesi-Hildebrand and Scott equations[12,13] under the condition $[D_0] > [A_0]$ ($[A_0] = 4 \times 10^{-3}$ mol dm^{-3} and $[D_0] = 0.01$–0.08 mol dm^{-3}). All calculations were carried out using a linear least squares method. The obtained mean K_{CT} and ε_{CT} values are listed in Table II. It is evident that, the stabilities of the CT complexes formed with the same π-acceptor follows the sequence: **I** < **II** < **IV** < **III**. This order is in accordance with the expected increase in the electron donating ability of the donor sulphur atoms. This is attributed to the increase in the number of an electron donating groups (CH_2 units). It is worth mentioning that, the low K_{CT} value of the CT complex of compound **IV** compared with that of compound **III** (the two compounds contain the same number of CH_2 groups) could be attributed to the presence of the two withdrawing OH groups in compound **IV**. This is reflected in a decrease in the electron density on the sulphur atom, i.e., a weakened electron donating ability. This behavior substantiates the conclusion that the sulphur atoms of the crown polythioethers are the donor sites for the CT interaction with the π-electron acceptor. Thus, it is reasonable to postulate that the CT complexes are of n-π type. A similar conclusion has been reported for the complexes between these donors with I_2 as the σ-electron acceptor.[10] The low K_{CT} values of the CT complexes under investigation (≤ 7.38 dm^3 mol^{-1}, cf. Table II) suggest that such CT complexes are weak.

EFFECT OF THE π-ACCEPTOR

In order to elucidate the role of π-acceptor electron affinity on the stability of the complexes, the CT complexes of donor **II** with the three π-acceptors DDQ, TCNE and CHL was measured in chloroform at 25°C. The CT absorption data for these complexes together with the mean K_{CT} values obtained are listed in Table II. It can be seen that the stabilities of the CT complexes decrease in the order DDQ > TCNE > CHL. On the other hand, the CT energies increase in the same direction. This is in accordance with the decrease in electron affinity of the π-acceptor along the same sequence. From the data in Table II and the equation

$$(h\nu_{CT})_1 - (h\nu_{CT})_2 = (EA)_2 - (EA)_1$$

which relates the CT energies ($h\nu_{CT}$) and the acceptor electron affinities (EA) for the complexes between two acceptors and the same donor,[14–16] the electron affinities of DDQ and TCNE relative to CHL (EA = 1.37 eV)[14] are found to be 1.88 and 1.68 eV, respectively. These values are in good agreement with those previously reported (1.91 and 1.68 eV).[14,17]

IONIZATION POTENTIAL OF THE DONORS

The ionization potential of the donors (**I**–**IV**) were calculated from the energies of the charge-transfer transitions using the empirical relation reported by Aloisi and Pignataro.[18] These were compared with the corresponding literature data. The results obtained are given in Table II. These values are comparable with those

TABLE III

λ_{max} (nm), E_{CT} (eV), K_{CT} and ε_{CT} values for the CT molecular complexes of donor **IV**, TTCHDD with TCNE at 25°C in various solvents as well as the ionization potential of this donor

Solvent	Dielectric constant (D)	λ_{max}(nm)	E_{CT}(eV)	IP (eV)	K_{CT} (dm^3 mol^{-1})	ε_{CT} (dm^3 mol^{-1} cm^{-1})
$CHCl_3$	4.806	488	2.544	8.59	4.83 ± 0.6	518 ± 69
CH_2Cl_2	9.08	490	2.535	8.58	2.94 ± 0.3	541 ± 34
$C_2H_4Cl_2$	10.65	490	2.534	8.58	1.34 ± 0.2	1120 ± 109

previously calculated for the CT complexes of these donors with the σ-electron acceptor, I_2.[10] Moreover, the measure IP values of donor II as estimated from the CT energies of its complexes with the π-acceptors (DDQ, TCNE, CHL) are nearly the same (cf. Table II). This suggests that the donor orbital involved in CT interaction is common for the three π-acceptors.

EFFECT OF SOLVENT

The CT complex of donor (**IV**), TTCHDD with TCNE was investigated in different solvents of various polarities ($CHCl_3$, CH_2Cl_2, $C_2H_4Cl_2$) at 25°C. Spectral characteristics and the measured K_{CT} values are recorded in Table III. The results clearly suggest that the stabilities of the CT complexes decrease as the dielectric constant of the solvent is increased ($CHCl_3$ ($D = 4.806$) → CH_2Cl_2 ($D = 9.08$) → $C_2H_4Cl_2$ ($D = 10.65$)). Since the formed CT complex is of a weak *n*-π type, i.e., the ground state could be mainly described by the non-bonding structure (D—A), one could be likely attributed the observed low stability of the formed CT complex with increasing polarity of the medium to the expected high stabilization of the free donor and acceptor. This reflects itself in a difficult charge transfer from the donor to the acceptor, i.e., weak CT complex formation. This interpretation could be substantiated by the observed blue shift in the λ_{max} of both donor **IV** and π-acceptor, TCNE as the solvent polarity is increased (λ_{max} values of donor **IV** are 247, 236, 229 nm and those of TCNE are 272, 268, 265 nm as the solvent is changed along the direction $CHCl_3$ → CH_2Cl_2 → $C_2H_4Cl_2$, respectively). However, similar behavior was reported previously for the effect of solvent on the stability of weak CT complexes.[19]

CHARACTERIZATION OF THE SOLID CT COMPLEXES

The results of chemical analyses (C, H, N, S and Cl) of the several solid CT complexes (Table I) clearly indicate the formation of 1:1 CT complex in each case.

Generally, the recorded IR spectra of the different synthesized CT complexes are quite similar to a superposition of the infrared spectra of the two components (cyclic polythioether and π-electron acceptor). For example the characteristic bands of the free cyclic polythioethers, $\nu_{C—H}$, $\nu_{C—S}$, δ_{CH_2} (of $CH_2—S$) as well as ν_{OH} of donor IV, appeared at about the same frequencies in the recorded IR spectra of the CT complexes. Moreover, the $\nu_{C\equiv N}$, $\nu_{C=O}$, $\nu_{C=C}$, $\nu_{C—C—N}$, $\nu_{C—Cl}$ of free DDQ and $\nu_{C\equiv N}$ of free TCNE as well as $\nu_{C—Cl}$ of free CHL appeared nearly at the same frequencies in the IR spectra of their synthesized CT complexes with the donors **I**, **II**, **IV**. This behavior can be considered as a convincing evidence for the non-bonding structure character of these CT complexes,[20] i.e., weak interactions of the crown polythioethers (**I**–**IV**) with the π-electron acceptors DDQ, TCNE, CHL as deduced before from low K_{CT} values of the formed CT complexes as well as the solvent effect where K_{CT} decreases as the polarity of the solvent increases.

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