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Charge-Transfer Molecular Complexes of Thianes with σ and π Electron Acceptors

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Charge-transfer complexes of cyclic thioethers with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; tetracyanoethylene; chloranil as π-acceptors and with iodine as a σ-acceptor, have been investigated. The spectral characteristics and stability of the formed CT complexes were examined, and are discussed in terms of the donor molecular structure, the nature of the electron acceptor and the solvent polarity. It is deduced that the formed CT complexes are mainly of the weak n–π or n–σ type, where the ground-state wave function is described primarily in terms of the nonbonding structure (D–A). The ionization potentials of the donors were calculated based on the CT energies of their CT complexes. Moreover, solid 1 : 1 CT complexes were synthesized and characterized.

The charge-transfer interaction of various heterocyclic sulfur compounds with σ- and π-electron acceptors has been extensively investigated.$^{1-8)}$ It has been shown that thiazole and thiophene, as well as its polynuclear derivatives, behave predominantly as π-donors during their interactions with σ- or π-acceptors.$^{1-4,8)}$ On the other hand, it was deduced that the CT complexes of thiazoles with iodine are of the n–σ^* type.$^{6,7)}$ Moreover, Abu-Eittah and Sugier$^{5)}$ investigated the CT complexes of bithienyls as well as some thiophenes with I_2, TCNE, and CHL; they concluded that such donors have both n- and π-type characters. In spite of this considerable work, only a small amount of information is available in the literature concerning CT complexes of six-membered heterocyclic donors with two or three sulfur atoms. McCullough and Zimmermann$^{9,10)}$ determined the dissociation constants and thermodynamic parameters of iodine CT complexes with 1,4-dithiane and 1,3,5-trithiane as well as other related donors in CCl_4 spectrophotometrically. Further, Hassel$^{11)}$ determined the interatomic distances in a number of solid complexes of some iodine molecules with *p*-dithiane as well as with other analogous donors. Since thianes have a significant role in the stability of vitamins and, further, they are considered to have antioxidant activity,$^{12)}$ it would be of interest to carry out a detailed study concerning their CT molecular complexes. Therefore, this article presents the result of spectroscopic investigations of the formed CT complexes of some cyclic thioethers (1,4-dithiane; 1,3-dithiane; and 1,3,5-trithiane) with a halogen σ-acceptors, I_2 and with some π-electron acceptors: viz., chloranil (CHL); tetracyanoethylene (TCNE); and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The effects of the donor molecular structure, the nature of the electron acceptor and the polarity of the solvent on the stability of the formed CT complexes were examined, and are discussed. Moreover, the solid CT complexes were synthesized and characterized.

Experimental

Materials and Solutions. The cyclic thioethers (1,4-dithiane (**I**); 1,3-dithiane (**II**); and 1,3,5-trithiane (**III**)) were supplied by Aldrich Chem. Co, and were used as received. The electron acceptors (DDQ, TCNE, and CHL (Aldrich or Merck reagent grade)) were recrystallized from dry dichloromethane, chlorobenzene, and dry benzene, respectively. Analytical-grade iodine was used; its concentration in solution was checked spectrophotometrically. All of the solvents used were of spectral-grade quality (BDH). Stock solutions of the donors or acceptors were freshly prepared in a dry and deoxygenated solvent prior to use.

Synthesis of Solid CT Complexes. Iodine solid CT complexes with each of the donors (**I**—**III**) were synthesized by mixing a dichloromethane solution of I_2 with that of the donor (3.0 mmol for each); the resulting complex solutions were left overnight at room temperature. On the other hand, solid 1 : 1 CT complexes of 1,3,5-trithiane, donor **III** with the applied π-acceptors (DDQ, TCNE, CHL), were prepared by mixing the required amount of the donor (**III**) dissolved in the least amount of CH_2Cl_2 with an appropriate amount of the corresponding π-acceptor in a molar ratio of 1 : 1 and refluxed for 3—5 h. In all cases the solid product was obtained by a subsequent concentration and cooling of the solution, where the solid complexes were separated out. The precipitates were collected, filtered and washed several times with CCl_4 (in case of I_2 complexes) and with CH_2Cl_2 (in case of π-acceptor complexes), and then dried.

Attempts to prepare solid CT complexes of the donors **I** and **II** (1,4-dithiane and 1,3-dithiane, respectively) with the π-acceptors (DDQ, TCNE, CHL) have so far been unsuccessful. The synthesized solid CT complexes are: 1,4-dithiane–I_2 (red, mp 96 °C); 1,3-dithiane–I_2 (purple, mp 85 °C); 1,3,5-trithiane–I_2 (redish brown, mp 105 °C); 1,3,5-trithiane–DDQ (buff, decomp temp 195 °C); 1,3,5-trithiane–TCNE (pale yellow, mp 165 °C), and 1,3,5-trithiane–CHL (greenish, decomp temp 140 °C). The analytical data concerning these CT complexes (C,H,N,S,Cl,I contents) are given in Table 1. The C,H,N, contents were determined at the microanalytical laboratory, Assiut University, on a Perkin–Elmer 240 C apparatus. The Cl, I, and S contents were estimated by making use of the conventional methods.

Physical Measurements. The electronic absorption spectra of the studied CT complexes solutions were recorded with a CECIL CE 599 Spectrophotometer using 1 cm matched silica cells. The apparatus was equipped with a temperature-controlled cell holder, which was adjusted by a Julabo FP 40 thermostat with an accuracy +0.01 °C. The IR spectra of the synthesized solid CT complexes were taken

Table 1. Microanalysis Data for the Different Isolated Solid CT Complexes

Molecular complex	Empirical formula	% Calcd (Found) C	H	N	S	Cl	I
1,4-dithiane–I_2	$C_4H_8S_2I_2$	12.84 (12.67)	2.15 (2.27)		17.14 (16.95)		67.87 (67.59)
1,3-dithiane–I_2	$C_4H_8S_2I_2$	12.84 (12.52)	2.15 (2.40)		17.14 (16.87)		67.87 (67.61)
1,3,5-trithiane–I_2	$C_3H_6S_3I_2$	9.19 (9.11)	1.54 (1.72)		24.53 (24.32)		64.74 (64.51)
1,3,5-trithiane–DDQ	$C_{11}H_6N_2O_2S_3Cl_2$	36.17 (36.55)	1.66 (1.54)	7.70 (7.56)	26.33 (26.14)	19.35 (19.20)	
1,3,5-trithiane–TCNE	$C_9H_6N_4S_3$	40.58 (40.39)	2.27 (2.08)	21.12 (21.33)	36.11 (36.32)		
1,3,5-trithiane–CHL	$C_9H_6O_2S_3Cl_4$	28.14 (28.41)	1.57 (1.58)		25.04 (25.21)	36.80 (36.67)	

on a Shimadzu 408 IR Spectrophotometer. All computions were performed on an Apple IIe microcomputer with the aid of two programs based on unweighted linear least-squares fits.

Results and Discussion

Spectral Characteristics and Formation Constants (K_{CT}): The electronic spectra of the CT complexes of the studied thianes (**I**—**III**) with the π-acceptors (DDQ, TCNE, CHL) and with the σ-acceptor (I_2) in CH_2Cl_2 are given in Table 2. For all cases, a new band appeared in the 300—550 nm region, which is not displayed by any component alone. Typical spectral results at 10 °C are shown in Fig. 1 and Fig. 2. Figure 1 represents the spectra for a series of dichloromethane solutions containing an excess varying donor (1,3,5-trithiane) concentration (5×10^{-3}—4×10^{-2} mol dm^{-3} and a fixed small concentration of the acceptor TCNE (2×10^{-3} mol dm^{-3}), using the solvent as a blank. Similar absorption spectra were observed for CT complexes with DDQ and CHL. In such cases, the same acceptor concentration as that in the test solution was used as a blank. This was done so as to eliminate any possible overlap that may arise from the acceptor absorption spectrum with that of the corresponding CT complex. Figure 2 displays the spectra recorded for the 1,3,5-trithiane–I_2 CT complex dichloromethane solutions, where CH_2Cl_2 was used as a blank. Accordingly, the new electronic absorption band appearing in the recorded spectra of the investigated CT complexes can be assigned to a single intermolecular CT transition. The continuous variation method[13)] was applied so as to achieve the stoichiometry of the present CT complexes, which gave symmetrical curves with maxima at a mole fraction of 0.5, indicating the formation of a 1 : 1 CT complex in each case (cf. Fig. 3).

The formation constants (K_{CT}) and molar extinction coefficients (ε_{CT}) of the presently studied CT complexes in CH_2Cl_2 were determined spectrophotometrically in the 10—30 °C temperature range using both the Benesi–Hildebrand and Scott equations[14,15)] under the condition $[D_0] > [A_0]$. All of the calculations were carried out by applying a linear least-squares method. The mean K_{CT} and ε_{CT} values obtained are given in Table 2. Generally, the relatively low K_{CT} values of the different CT complexes suggest that the formed complexes were of the weak type, i.e, the ground-state wave function had predominantly a nonbonding structure (D–A). Further, the observed slight influence of the I_2 absorption band located at 505 nm with a successive addition of a donor (**III**), as displayed in Fig. 2, substantiates the above-deduced weak character of the thianes–I_2 CT complexes.

The results given in Table 2 clearly reveal that the stability of the CT complexes of the same donor (1,3,5-trithiane) with the applied π-acceptors decreases as the electron affinity of the π-acceptor is decreased (DDQ > TCNE > CHL). On the other hand, the CT energy increases in the same direction. The obtained high stability of the 1,3,5-trithiane CT complex with I_2, compared to that of its complexes with the present π-acceptors (DDQ, TCNE, CHL), is in accordance with the expected nature of the formed CT complex, since the former is n-σ type, whereas the others are of the n–π type. Moreover, the stability of the formed CT complex of donors **I**—**III** with the same π-acceptor (TCNE) is in the following order: 1,4-dithiane < 1,3-dithiane < 1,3,5-trithiane. This order is mainly due to the expected increase in the electron-donating ability due to the increase in the number of sulfur atoms in the same direction. However, the high K_{CT} value of the 1,3-dithiane CT complex, compared with that of 1,4-dithiane (both donors have two sulfur atoms), can be ascribed to the nature of the lone-pair orbital interactions, since the lone-pair ineraction in the case of six-membered heterocycles having heteroatoms meta (1,3-dithiane) seems to occur predominantly through space, while for heteroatoms para (1,4-dithiane) the interaction is mainly through the bond.[16)] This reflects itself in a lower ionization potential value of 1,3-dithiane (8.54, 8.95 eV) relative to that of 1,4-dithiane (8.58, 9.03 eV)[16)] which, in turn leads to an easier intermolecular electron trans-

Table 2. Spectral Characteristics, Formation Constants (K_{CT}), and Enthalpy Changes (ΔH) Values for CT Complexes of Thianes with Various Electron Acceptors in CH_2Cl_2 at Different Temperatures as Well as the Ionization Potentials of These Donors

Molecular complex	λ_{max}	E_{CT}	IP	K_{CT}/dm^3 mol^{-1}, °C					ε_{CT} at 10 °C	$-\Delta H$
	nm	KJ mol^{-1}	eV	10	15	20	25	30	dm^3 mol$^-$1 cm^{-1}	KJ mol^{-1}
1,4-dithiane–TCNE	496	241.35	8.54	4.9±0.7	4.2±0.4	3.8±0.2	3.6±0.5	3.2±0.1	280±33	14.4±0.3
1,3-dithiane–TCNE	508	235.65	8.45	8.2±0.9	7.4±0.5	6.5±0.9	6.0±0.6	5.4±0.2	203±17	14.9±0.7
1,3,5-trithiane–TCNE	463	258.55	8.77	13.5±1.2	12.1±1.0	10.8±1.2	9.5±0.8	8.6±0.7	260±23	16.6±0.4
1,3,5-trithiane–I_2	317	377.63	8.86	48.4±3.6	41.3±2.9	35.6±4.6	31.2±2.0	26.9±2.6	13525±869	20.8±0.3
1,3,5-trithiane–DDQ	503	237.99	8.78	21.8±1.8	19.5±1.6	17.0±1.4	15.1±1.4	13.7±1.1	321±18	16.9±0.4
1,3,5-trithiane–CHL	410	291.97	8.73	8.0±0.5	7.5±0.7	6.9±1.0	5.9±0.8	5.4±0.8	289±35	14.6±1.2

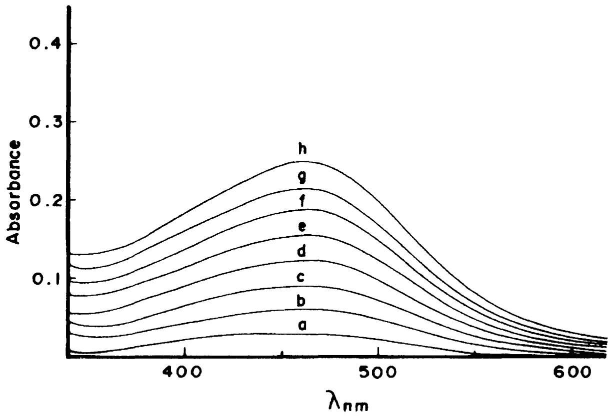

Fig. 1. Electronic absorption spectra of the CT molecular complex solutions of 1,3,5-trithiane (**III**) with (2×10^{-3} mol dm^{-3}) in CH_2Cl_2 at 10 °C. [1,3,5-trithiane]=0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0×10^{-2} mol dm^{-3} for a,b,c,d,e,f,g,h respectively.

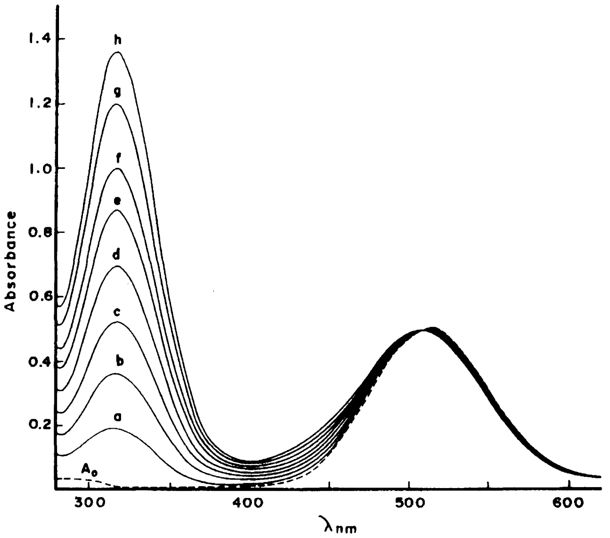

Fig. 2. Electronic absorption spectra of the CT complexes solutions of 1, 3, 5- trithiane with I_2 ([A_0] = 4×10^{-4} mol dm^{-3}) in CH_2Cl_2 at 10 °C. [1,3,5-trithiane]=0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0×10^{-3} mol dm^{-3} for a,b,c,d,e,f,g,h respectively.

fer in the case of the former donor compared to the latter one. From the above-observed dependence of the CT complex stability on the donor molecular structure

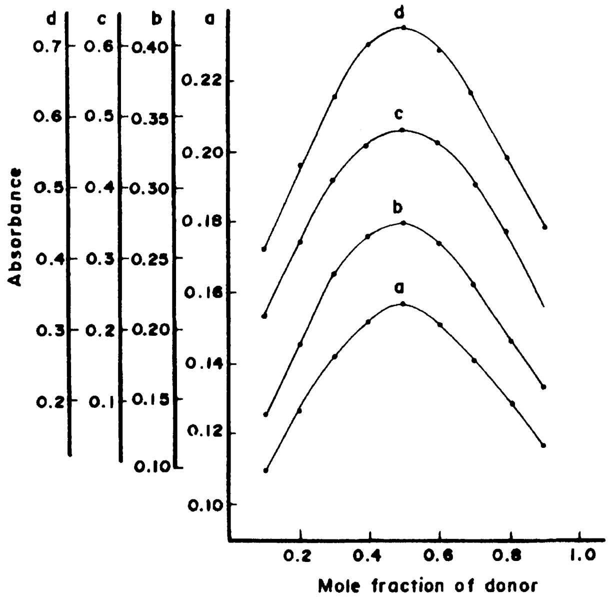

Fig. 3. Continuous variation method for the CT complexes of donor **III** with π-acceptors, CHL(a), TCNE(b), DDQ(c), and with I_2(d). Total molar concentrations are 0.01, 0.02, and 0.002 mol dm^{-3} for CHL, (TCNE, DDQ), and I_2 CT complexes, respectively.

as well as the nature of the electron acceptor, it seems reasonable to deduce that the formed CT complexes are of the n–π or n–σ type, where the sulfur atoms are the donor sites for the CT interaction.

The mean values of K_{CT} at a series of temperatures were used to estimate the enthalpy change (ΔH) for the CT complex formation by applying Van't Hoff equation plots. The obtained results are given in Table 2. It can be seen that the numerical ΔH value of the CT complexes of trithiane with the present acceptors is in the following order: I_2 > DDQ > TCNE > CHL. This order is in agreement with their stability constants.

Ionization Potentials of the Donors. The ionization potentials (IP) of the highest filled molecular orbitals on donors **I**—**III** were computed based on the CT energies of their complexes with the applied acceptors using the empirical relations reported by Aloisi and Pignataro[4] and compared with the corresponding literature data. The obtained results are listed in Table 2.

Table 3. Spectral Characteristics, Formation Constants (K_{CT}) and Enthalpy Changes (ΔH) Values for the CT Complexes of 1,3,5-Trithiane with Iodine and TCNE in Various Solvent at Different Temperatures as Well as the Ionization Potential of This Donor

Acceptor	Solvent	λ_{max}	E_{CT}	IP	K_{CT}/dm^3 mol^{-1}, °C					ε_{CT} at 10 °C	$-\Delta H$
		nm	KJ mol^{-1}	eV	10	15	20	25	30	dm^3 mol^{-1} cm^{-1}	KJ mol^{-1}
Iodine	CCl_4	314	381.24	8.92	76.0±6.1	63.7±3.2	53.0±2.1	44.3±3.3	36.9±2.7	11596±869	25.8±0.4
	$CHCl_3$	315	380.02	8.90	63.5±6.7	55.5±6.2	47.6±7.1	37.2±3.5	32.7±2.3	12259±1237	24.6±0.4
	CH_2Cl_2	317	377.63	8.86	48.4±3.6	41.3±2.9	35.6±4.6	31.2±2.0	26.9±2.6	13525±869	20.8±0.3
	$C_2H_4Cl_2$	318	376.44	8.84	41.3±3.4	36.4±3.1	32.4±3.0	27.6±2.2	24.2±1.7	16525±878	19.1±0.7
TCNE	$CHCl_3$	460	260.24	8.80	18.7±1.9	16.8±1.6	14.8±1.0	12.9±1.0	11.5±1.0	233±19	17.6±0.5
	CH_2Cl_2	463	258.55	8.77	13.5±1.2	12.1±1.0	10.8±1.2	9.5±0.8	8.6±0.7	260±23	16.6±0.4
	$C_2H_4Cl_2$	467	256.34	8.74	12.2±1.1	11.1±0.9	10.0±0.8	8.7±0.9	7.9±0.6	269±25	15.8±0.7

The obtained IP values of donor **I**—**III** (8.45—8.86 eV) can be compared with those determined before by a photoelectron spectroscopic technique (the first ionization potentials of donors **I**, **II**, **III** are 8.58, 8.54, 8.76 eV, respectively).[16] Moreover, the results listed in Table 2 reveal that the IP values of HOMO(n) on 1,3,5-trithiane, as calculated from the CT energy of its complexes with four applied acceptors, are more or less the same. This suggests that the same donor orbital is involved in the CT interaction with the four acceptors (I_2, DDQ, TCNE, CHL).

Effect of Solvent. To elucidate the role of the solvent on the stability of the formed thianes **I**—**III** CT complexes, the CT complexes of 1,3,5-trithianes (donor **III**) with I_2 (as σ-acceptor) and with TCNE (as π-acceptor) were investigated in a number of solvents having various polarities (CCl_4, CHC13, CH_2Cl_2, and $C_2H_4Cl_2$) in the 10—30 °C temperature range. The spectral characteristics and computed K_{CT} values are give in Table 3. The results clearly reveal that the stability of these CT complexes decreases as the dielectric constant of the solvent is increased [CCl_4 (D=2.238)→$CHCl_3$ (D=4.806)→CH_2Cl_2 (D=9.08)→$C_2H_4Cl_2$ (D=10.65)]. This behavior can be interpreted based on the principle that the formed CT complexes are of the weak n–σ or n–π type, i.e, the ground-state wave function could mainly be described by the nonbonding structure (D–A). Thus, the observed low stability of the formed CT complexes with increasing polarity of the medium could likely be ascribed to the expected high stabilization of the free donor and acceptor. This reflects itself in a difficult charge-transfer interaction between the donor and the acceptor, since the complexation would be to squeeze out solvent molecules in the solvation sphere of the two reactants, i.e, weak CT complex formation in the same direction. This interpretation can be supported by the observed blue shift in the λ_{max} values of donor **III** and the acceptors (I_2, TCNE) as the solvent polarity is increased (the λ_{max} values of donor **III** are 259, 242.5, 240, 238 nm and those of TCNE are 275, 272, 268, 265 nm where those of I_2 are 520, 510, 505, 499 nm as the solvent is changed along the direction CCl4→CHC13→CH_2Cl_2→$C_2H_4Cl_2$, respectively). A similar behavior was previously reported concerning the effect of the solvent on the stability of weak CT complexes.[17,18] However, the slightly soluble character of donor **III** in CCl_4 makes it hard to perform a spectral measurements and consequently, to determine the K_{CT} value of TCNE complex under the specified condition ([D_0] > [A_0]).

Characterization of the Solid CT Complexes. The result of the chemical analyses (C,H,N,S,Cl,I contents) of the different synthesized solid CT complexes (Table 1) clearly indicate the formation of a 1 : 1 CT complex in each case. A comparison of the characteristic IR spectral bands of both free donors **I**—**III** and π-acceptors with the corresponding ones appeared in the IR spectra of the solid CT complexes clearly reveals that the IR spectra of the various synthesized CT complexes are generally close to a superposition of the IR spectra for the two components (thianes and π-acceptors). For instance, the prominent bands of 1,3,5-trithiane such as ν_{C-H} (at 2950 cm^{-1}), δ_{CH_2} (at 1390 cm^{-1}), CH_2 out-of-plane bending (wagging and twisting modes at 1210 and 1160 cm^{-1}, respectively), CH_2 in-plane bending (rocking mode at 905 cm^{-1}), ring stretching (at 728 cm^{-1}), and ring breathing (at 655 cm^{-1})[19] appeared at more or less the same frequencies in the IR spectra of its corresponding CT complexes with the applied acceptors (I_2, DDQ, TCNE, CHL). Further, the characteristic bands of free DDQ, $\nu_{C\equiv N}$ (at 2240 cm^{-1}), $\nu_{C=O}$ (at 1675 cm^{-1}), $\nu_{C=C}$ (at 1555 cm^{-1}), ν_{C-Cl} (at 802 cm^{-1}), and $\nu_{C\equiv N}$ of free TCNE (at 2260, 2330 cm^{-1}) as well as those of free CHL, $\nu_{C=O}$ (at 1690, 1680 cm^{-1}), $\nu_{C=C}$ (at 1570 cm^{-1}) appeared almost at the same frequencies in the IR spectra of their CT complexes with 1,3,5-trithiane. Additionally, the ν_{C-C-CN} of DDQ (at 902 cm^{-1}) is overlapped with CH_2 rocking mode (at 905 cm^{-1}) where it observed at 900 cm^{-1} in the IR spectra of the solid CT complex. Also, the ν_{C-Cl} of CHL (at 750, 710 cm^{-1}) is overlapped with trithiane ring stretching (at 728 cm^{-1}) and appeared as a single band (at 725 cm^{-1}). On the other side, in the case of I_2 CT complexes with 1,4-dithiane and 1,3-dithiane (several attempts were made to prepare their solid CT complexes with π-acceptors but all failed) the relevant IR bands of those donors, such as ν_{C-H} (at 2910—2900 cm^{-1}), δ_{CH_2} (at 1415 cm^{-1}), CH_2 twisting (at 1283—

1270 cm^{-1}), CH_2 wagging (at 1170—1156 cm^{-1}), CH_2 rocking (at 915—904 cm^{-1}), and ring stretching (at 670—655 cm^{-1}), appeared at almost the same superposition in the IR spectra of the corresponding CT complex. This behavior strongly supports the nonbonding structure character of the formed CT complexes,20) i.e. a weak interaction of thianes (**I**—**III**) with the applied electron acceptors, as deduced before from the low K_{CT} values of these CT complexes as well as the solvent effects, where K_{CT} decreases with increasing polarity of the solvent.

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