

Charge-Transfer Complexes of Tetracyanoethylene with Alkyl and Aryl Derivatives of Sulfur, Selenium, and Tellurium

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Spectral characteristics (λ_{CT} , $\Delta\nu_{1/2}$, ϵ) and association constants (in dichloromethane) of charge-transfer (CT) complexes of tetracyanoethylene (T) with donors containing CXH, CXC, and CXXC linkages (X = S, Se, Te) are presented. The donor orbitals from which CT transitions originate are identified by correlation of λ_{CT} and $\Delta\nu_{1/2}$ values of CT bands of the complexes with the ionization bands of the photoelectron spectra of the donor molecules. CT energies of complexes are influenced by intramolecular conjugative and inductive effects between functional groups as well as geometric factors that control the angular orientation of these groups. Alkyl thiols normally react very rapidly with T; however, highly hindered thiols react slowly so that complexes can be partially characterized. Alkyl thiols and sulfides donate electrons from the $n(p_y)$ orbital of sulfur to the $\pi^*(b_{3g})$ orbital of T to form weak CT complexes which exhibit a single absorbance band. λ_{max} depends upon the identity of alkyl substituent, increasing in the order of the inductive effect for acyclic alkyls (Me < Et < *i*-Pr < *t*-Bu) and in the order of ring size (3 < 4 < 5 < 6) for cyclic alkyls. Aryl thiols, chalcogenides, and chalcogenophenes donate electrons from the two highest occupied π orbitals to form CT complexes exhibiting two optical bands. In these donors the chalcogen atom bound to the aryl substituent conjugates with phenyl π orbitals through the nonbonded electron pair, although the tendency for conjugation diminishes in the order S > Se > Te. The HOMO in an aryl telluride is essentially a localized $n(p_y)$ orbital that interacts with T to give rise to a band $\lambda_1 > 650$ nm. The conjugative effect and tendency to complex with T are optimal when the CXC or CXX moiety is coplanar with the aryl ring.

Introduction

Tetracyanoethylene (T), one of the most powerful known π -electron acceptors, is exceptionally reactive with nucleophiles containing sulfur, selenium, and tellurium. Since many of its reactions proceed through the formation of a charge-transfer (CT) complex, often revealed by the appearance of a transitory coloration, it is useful to (1) delimit the scope of the interactions of T with various chalcogen containing nucleophiles, (2) identify the manner in which these interactions are affected by structural, steric and electronic field effects, (3) determine formation constants and spectral characteristics of CT complexes, and (4) specify the chalcogen orbitals involved in CT interactions.

Moreau and Weiss^{1,2} first reported the formation of charge-transfer (CT) complexes of tetracyanoethylene (T) with alkyl derivatives of sulfur in dichloromethane (DCM). Following them, numerous investigators, notably Bock,^{3,4} Aliosi,^{5–7} Farrell,⁸ and Chmutova,^{9,10} have made important contributions to the understanding of CT

interactions of T with alkyl and aryl derivatives of the chalcogens. Here we present the results of a comprehensive and systematic study of the characteristics of a broad range of complexes of T with organochalcogens containing CXC and CXXC linkages where X is sulfur, selenium, or tellurium. The classes of compounds investigated include alkyl and aryl thiols (RSH and ArSH), alkyl chalcogenides (RXR'), alkyl aryl chalcogenides (ArXR), aryl chalcogenides (ArXAr'), chalcogenophenes, alkyl disulfides (RSSR'), and aryl dichalcogenides (ArXX-Ar'). In particular, we differentiate between molecules in which T interacts with the chalcogens through electrons in localized atomic orbitals and those in which the interaction occurs with electrons in delocalized molecular orbitals. This report is an extension of a study of T complexes of alkyl and aryl derivatives of oxygen compounds.¹¹

T forms transitory CT complexes with many electron donors, D, in which the complex-forming process involves the reversible transfer of an electron from the HOMO of D to the LUMO, i.e., the $\pi(b_{3g})$ or π^* orbital, of T with the simultaneous absorption of a quantum of light ($h\nu$).



The frequency of the light absorbed is linearly related to the ionization energy of the electron in the donor molecule where I_D is 7–10 eV. Analysis of the absorbance spectrum of the complex by means of the Scott

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equation¹² yields its molar absorbance, ϵ , its association

$$C_X C_Y / A = 1K\epsilon + (1/\epsilon)C_X \quad (1)$$

constant, K , and the CT energy. Correlation of the λ_{CT} of the complex with the ionization bands of the photoelectron spectrum of the donor molecule are obtained with the empirical equation¹³

$$\lambda_{CT}(\text{nm}) = 1240/(0.81I_D - 4.28) \quad (2)$$

Here λ_{CT} corresponds to λ_{max} for a specific CT band of the complex and I_D is the vertical ionization energy of the donor molecule in eV. Equation 2 facilitates the attribution of specific molecular orbitals to the various CT transitions using the results of photoelectron spectral studies of the donor molecules.

Experimental Section

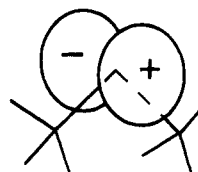
Experimental procedures, data collection and processing, and judgmental criteria are described in a previous publication.¹⁴ Spectra were recorded with Beckman ACTA-CIII or Shimadzu UV3101PC spectrophotometers.

Reagents. Solvents and reagent chemicals are the purest grades available from the following chemical suppliers: Aldrich, Alfa, Fisher, Fluka, Kodak, and Lancaster. Reagents of less than 98% purity were subjected to repeated distillation, recrystallization, or vacuum sublimation until their optical spectra and physical constants agreed closely with data found in the literature, except where noted. Exact purities were determined by capillary-column chromatography using a Hewlett-Packard HP5980A chromatograph. T was recrystallized twice from chlorobenzene and sublimed two or three times in vacuo: mp 199–200 °C. Fisher spectranalyzed dichloromethane was used without further purification.

Results and Discussion

The results of our studies of complexes of T with chalcogen-containing donors as well as a comprehensive listing of results of other related studies are summarized in Table 1. Donors are coded for reference in the text according to the alphanumeric characters shown in column 1. T complexes of chalcogen donors exhibit one or two CT bands. If one composite band appears in the spectrum it is designated λ_{max} and is inserted in column 3. If one or two simple bands appear in the spectrum their maxima are designated λ_1 and λ_2 and inserted in columns 4 and 5. If a band appears as a shoulder on the solute cutoff, the wavelength at one-half band height is given with an -sh suffix. If the main band is deconvoluted into two overlapping bands the values of λ_1 and λ_2 are shown in italics. The ratio of absorbance values of λ_2 to λ_1 , A_2/A_1 , is given in column 7. The product ϵK , a measure of the "effective absorbance" of a complex, is given in column 10. The ratios of the concentrations of stock solutions of D, C_D , and of T, C_T , are given in column 11. The saturation fraction, s , of a complex is calculated using the equation $s = A/\epsilon C_Y$ where C_Y is the analytical concentration of the limiting reagent. Percent saturation values are given in column 12. Notations used in Table 1 which describe the Scott graphs used to calculate ϵ and K are as follows: cur = curved line; neg = negative slope; err = erratic data.

Correlations of experimental λ_{CT} values with those calculated with eqs 2 and 3 are given in Table 2. In three-fourths of the entries in Table 2 the agreement between experimental and calculated values is better than $\pm 5\%$. This degree of consistency indicates that attributions of orbitals to CT transitions are generally reliable. The nonbonded electrons on the chalcogen atoms are designated as $n(p_y)$ or $n(p_z)$ throughout the following discussion, unless signified as $n(b_1)$ in molecules with C_{2v} symmetry.



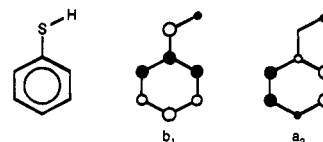
$n(b_1)$ Orbital of Methyl Sulfide

1. Thiols. Middleton et al.¹⁵ reported that alkyl thiols generally react rapidly with T to give dithiobutadienes. By using sterically blocked thiols which react slowly with T we were able to determine λ_{CT} values for two thiol-T CT complexes.

a. Alkyl Thiols. The spectrum of a fresh solution of DCM which is 0.020 M each in BSH and T consists of a symmetrical band with λ_{max} 424 nm and $\Delta\nu_{1/2}$ 5000 cm^{-1} . The narrow bandwidth is characteristic of CT bands which arise from a transition involving the nonbonded $n(p_y)$ electron of the sulfur.

b. Aryl Thiols. When solutions of PHS and T are mixed, a red color appears instantly but fades within 15 s indicating that a CT interaction followed by a rapid irreversible reaction occurs.

The spectrum of a fresh solution of 2,6-dimethylthiophenol and T exhibits bands λ_1 551 and λ_2 456 nm. The large values of λ_1 and λ_2 indicate that the *o*-methyl groups do not restrict rotation of the SH group sufficiently to inhibit $n(p_y)$ - $\pi(b_1)$ conjugation.



π Molecular Orbitals of Phenyl Sulfide

2. Aliphatic and Alkenyl Sulfides. Interpretation of the interactions of T with aliphatic sulfides is generally straightforward since there is only one high energy nonbonding orbital per donor molecule. Interactions with disulfides are complicated by the presence of a donor orbital on each of the sulfur atoms which interconjugate to an extent dependent upon the spatial orientation of the orbital lobes and steric factors which govern their orientation.

a. Acyclic Alkyl Sulfides. Wagner and Bock⁴ found an excellent correlation between the λ_1 values of the alkyl sulfide complexes and the I_1 values in eV of the corresponding donor molecules which is expressed by eq 3.

$$\lambda_{CT}(\text{nm}) = 1240/(0.46I_D - 1.43) \quad (3)$$

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Table 1. Complexes of Tetracyanoethylene with Alkyl and Aryl Derivatives of Sulfur, Selenium, and Tellurium in Dichloromethane at 22 C

code	donor compound	λ_{\max} , nm	λ_1 , nm	λ_2 , nm	ϵ_{\max} , L/mol cm	A_2/A_1	$\Delta\nu_{1/2}$, cm^{-1}	K , L/mol	ϵK	C_D/C_T	% satn
MMS	2-methyl-2-propanethiol [†]	551	424				5000			1	
	2,6-dimethylthiophenol [†]	490	456			0.90					
MES	methyl sulfide ^a										
MES	methyl ethyl sulfide ^b		500								
EES	ethyl sulfide		513		2900 ± 380	4500	0.24 ± 0.03	700	10	2-4	
IIS	ethyl sulfide ^{a,c}		505								
	ethyl sulfide ^b		512								
	ethyl 1-propyl sulfide ^b		518								
	1-propyl sulfide ^a		516								
	isopropyl sulfide		529		9400 ± 5400		4500	0.03 ± 0.02	300	9	< 1
	isopropyl sulfide ^a		529								
BBS	1-butyl sulfide ^{a,c}		530								
	2-methylpropyl sulfide ^a		542								
	2-butyl sulfide ^b		530								
M2S	<i>tert</i> -butyl sulfide		547			neg	4600	<0.01		26	
	<i>tert</i> -butyl sulfide ^a		546								
M2S	bis(methylthio)methane	478	490	469	1860 ± 100		5500	0.34 ± 0.02	630	10	3-5
MM2S	ethylene sulfide		447		602 ± 41		4900	0.89 ± 0.06	540	25	11-21
M3S	propylene sulfide		461		2620 ± 500		4700	0.19 ± 0.04	500	10	2-4
M4S	trimethylene sulfide		490		3900 ± 320		4600	0.21 ± 0.02	820	20	2-5
M5S	tetramethylene sulfide		516		cur		4600			550	
	tetramethylene sulfide ^a		516								
	tetramethylene sulfide ^c		513								
AMS	pentamethylene sulfide		510		6510 ± 570		4600	0.12 ± 0.01	780	330	4-8
	1,3-dithiane		520	486	cur		6100				
TTF	1,4-dithiane	488	507	465	1590 ± 140		5600	0.37 ± 0.03	590	16	4-8
	allyl methyl sulfide		490	315sh	1390 ± 180		4600	0.44 ± 0.06	610	10	3-7
MMSS	tetrathiafulvalene		1005	438	9960 ± 400		4100	42.9 ± 1.8	42700	1/10	14-28
EESS	methyl disulfide	434			700 ± 80		7400	0.57 ± 0.06	400	32	7-14
	methyl disulfide ^{c,d}	425			2150			0.16	340		
IISS	ethyl disulfide	453			670 ± 50		6900	0.75 ± 0.06	500	16	8-16
	ethyl disulfide ^{c,d}	450			3000			0.14	410		
	1-propyl disulfide ^c	453									
BBSS	isopropyl disulfide	470			970 ± 70		6400	0.61 ± 0.04	590	16	7-13
	isopropyl disulfide ^c	465									
	1-butyl disulfide ^{c,d}	460			5200			0.09	460		
M3SS	cyclohexyl disulfide ^c	525									
	<i>tert</i> -butyl disulfide		534	400sh	3660 ± 440		5300	0.47 ± 0.07	1720	15	3-7
M4SS	<i>tert</i> -butyl disulfide ^{c,d}	530			4600			0.36	1640		
MPS	trimethylene disulfide ^c	575									
	tetramethylene disulfide ^c	535									
	methyl benzyl sulfide ^e		500	400sh							
	β -(methylthio)styrene ^a		645	365							
	benzyl sulfide		515	400	2520 ± 670	2.5		0.27 ± 0.07	680	10	2-5
	benzyl sulfide ^a		500	400sh							
EPS	1,4-bis(methylthio)-methylbenzene ^a		500	400sh							
	benzyl disulfide	415			1100 ± 80		9400	0.65 ± 0.05	720	10	5-10
	benzyl disulfide ^{c,d}	405			310			2.6	805		
	benzyl trisulfide	400sh			cur					10	
MPS	thioanisole		573	379	1210 ± 120	0.28	4700	1.63 ± 0.17	1970	26	11-22
	thioanisole ^f		571	377		0.3					
	thioanisole ^g		571	385		0.26	4600, 5100				
	thioanisole ^h		573	380							
	thioanisole ^a		571	380							
	thioanisole ^b		571	379							
IPS	thioanisole ^c		572	380	2820			4.2	11800		
	thioanisole ⁱ		572								
BPS	thioanisole ^{**h}		577								
	ethyl phenyl sulfide		576	380	840 ± 120	0.28	4800	1.65 ± 0.23	1390	10	7-15
VPS	ethyl phenyl sulfide ^h		570	376							
	isopropyl phenyl sulfide		569	377sh	1230 ± 80	0.39	5400	0.74 ± 0.05	910	10	5-12
MPS	isopropyl phenyl sulfide ⁱ		564	373							
	<i>tert</i> -butyl phenyl sulfide ⁱ		502	382							
MPS	allyl phenyl sulfide ^{**i}		569								
	vinyl phenyl sulfide ^{**h}		578								
MPS	methyl <i>o</i> -tolyl sulfide ^{**h}		612								
	methyl <i>p</i> -tolyl sulfide		609	385	2720 ± 300	0.31	4800	0.91 ± 0.10	2480	10	4-9
MPS	methyl <i>p</i> -tolyl sulfide ^{**f}		610	390							
	methyl <i>p</i> -tolyl sulfide ^{**h}		613								
	1,2-bis(methylthio)benzene ^{**h}	633									
	1,4-bis(methylthio)benzene ^{**f}	675	400								
MPS	1,4-bis(methylthio)benzene ^a		676	394							
	4-(methylthio)- <i>N,N</i> -dimethylaniline ^e		830	400		0.93					
MPS	selenoanisole ^h		610								
	selenoanisole ^{**h}		601								
	selenoanisole ⁱ		601	376							

Table 1 (continued)

code	donor compound	λ_{\max} , nm	λ_1 , nm	λ_2 , nm	ϵ_{\max} , L/mol cm	A_2/A_1	$\Delta\nu_{1/2}$ cm ⁻¹	K , L/mol	ϵK	C_D/C_T	% satn
EPSe	ethyl phenyl selenide ⁱ		600	375							
IPSe	isopropyl phenyl selenide ⁱ		594	372							
BPSe	<i>tert</i> -butyl phenyl selenide ⁱ		554	381							
APSe	allyl phenyl selenide ^{**h}		600								
VPSe	vinyl phenyl selenide ^{**h}		609								
	methyl <i>o</i> -tolyl selenide ^{**h}		624								
	methyl <i>m</i> -tolyl selenide ^{**h}		617								
	methyl <i>p</i> -tolyl selenide ^{**h}		634								
	methyl 2-methylselenophenyl sulfide ^{**h}		644								
	methyl 4-methylselenophenyl sulfide ^{**h}		668								
MPTe	telluroanisole ^h		650								
PPS	phenyl sulfide		580	365sh	860 ± 70	0.78	5000	0.63 ± 0.05	540	20	7-14
	phenyl sulfide		577	365sh	950 ± 20		4900	0.61 ± 0.02	580	274	20-38
	phenyl sulfide ^c		590								
	phenyl sulfide ^{**j}		592								
	phenyl sulfide ^{*b}		585	370	1580			2.2	3480		
	phenyl selenide		605	>365	880 ± 70		4900	0.66 ± 0.05	580	20	5-10
	phenyl telluride [†]		695		540 ± 130		4600	1.51 ± 0.35	820	10	5-10
	2-methylphenyl phenyl sulfide ^b		595	390							
	3-methylphenyl phenyl sulfide ^{*b}	595	390	2090				2.7	5640		
	4-methylphenyl phenyl sulfide ^{*b}	605	385	2090				2.9	6060		
	3,4-dimethylphenyl phenyl sulfide ^b		615	395							
	<i>o</i> -tolyl sulfide ^b		610	412							
	<i>p</i> -tolyl sulfide ^{*b}		630	395	2090			4.0	8360		
	2,6-dimethylphenyl sulfide ^b		520								
	phenoxathiin ^k		680	425	400 ± 100	0.55	5100	2.0 ± 0.5	900		
	phenoxaselenine ^l		670	440	485 ± 100	0.50	4900	1.5 ± 0.5	970		
	phenoxatellurine ^l		720		1100 ± 100			1.0 ± 0.3	1100		
PPSS	phenyl disulfide		515		3360 ± 880			0.11 ± 0.03	370	15	1-3
	phenyl disulfide ^{c,d}		510		290			1.5	450		
	phenyl diselenide		550		310 ± 20			1.51 ± 0.11	470	1/10	6-10
	phenyl ditelluride [‡]										
	<i>p</i> -tolyl disulfide	555			2330 ± 160			0.25 ± 0.02	580	20	3-6
	mesityl disulfide ^c	430									
	thianthrene		607	476, 350sh	1370 ± 120	1.04		0.36 ± 0.03	490	10	3-7
Th	thiophene	400	445	390	1270 ± 70			0.31 ± 0.02	390	25	5-11
	thiophene	400	445	390	1720 ± 140			0.24 ± 0.02	410	97	7-15
	thiophene ^{**i}		445sh	405							
	thiophene ^{**i}	399			1450			0.48 ± 0.02	700		
	thiophene ^{*m}		445sh	390				0.53 ± 0.02			
	thiophene ⁿ		448	383							
	thiophene ^{*o}		445sh	387							
	thiophene ^o	445						1.00			
	thiophene ^{*o}	442						0.84			
	thiophene ^{*o}							1.04			
2MTh	2-methylthiophene		496	407	1730 ± 130	1.12		0.46 ± 0.03	790	25	5-11
	2-methylthiophene ^{n,o}	497	408					1.60			
2ETh	2-ethylthiophene		497	412	cur						
	2-ethylthiophene ^{n,o}	498	408								
2BTh	2- <i>tert</i> -butylthiophene ^{n,o}	505	415								
3MTh	3-methylthiophene	431	480	410	2050 ± 50			0.42 ± 0.01	860	24	5-10
	3-methylthiophene ^{*n,o}	478	410					1.72			
3BTh	3- <i>tert</i> -butylthiophene ^{n,o}	490sh	428								
24MTh	2,4-dimethylthiophene		557	417	2250 ± 140	0.88		0.82 ± 0.05	1850	23	8-17
25MTh	2,5-dimethylthiophene ^{*n,o}	550	419					2.50			
	1,2,3,4-tetramethylthiophene ⁿ	605	485								
Th2	2,2'-dithienyl		640	390sh	550 ± 210		5100	1.61 ± 0.61	890	1	1-4
Th3	α -terthienyl		768		err		5400			1/10	
	2-(β -styryl)thiophene ^{n,o}	658									
	2-phenylthiophene ^{n,o}	580	390								
BzTh	benzo[β]thiophene		560	465	870 ± 50	1.01		0.95 ± 0.05	830	13	7-16
	benzo[b]thiophene ^{**i}			479							
	benzo[b]thiophene ^o		563	468				2.21			
	benzo[b]thiophene ^{*o}		556	472				3.23			
Bz2Th	dibenzothiophene		550	375sh	1390 ± 30		5400	1.70 ± 0.03	2360	30	11-21
	dibenzothiophene ^{**i}		562								
	dibenzothiophene ⁿ		531								
	dibenzothiophene ^{*n}		550					4.76			
	selenophene	439	450	430	err		5600			1	
	selenophene ^{*n}	440						1.40			
	selenophene ^o	443						1.25			
	selenophene ^{*o}	440						1.40			
	tellurophene ⁿ		530	465				1.20			
	tellurophene ^{*n}		530	465sh				1.20			
	2-methyltellurophene ^{n,o}		547								
	benzo[β]selenophene ^{*o}		571	479				2.73			
	benzo[β]selenophene ^{*o}		576	475				3.37			
	thieno[2,3- <i>b</i>]thiophene ^o		500	333				2.56			
	thieno[2,3- <i>b</i>]thiophene ^{*o}		500	333				3.90			
	seleno[3,2- <i>b</i>]thiophene ^o		534	368				3.58			

Table 1 (continued)

code	donor compound	λ_{\max} , nm	λ_1 , nm	λ_2 , nm	ϵ_{\max} , L/mol cm	A_2/A_1	$\Delta\nu_{1/2}$ cm ⁻¹	K , L/mol	ϵK	C_D/C_T	% satn
	seleno[3,2- <i>b</i>]thiophene* ^o		527	364				5.37			
	seleno[3,2- <i>b</i>]selenophene ^o		563	363				4.01			
	seleno[3,2- <i>b</i>]selenophene* ^o		548	357				6.31			
PSSO	phenyl sulfoxide	395			879 ± 58			1.76 ± 0.12	1550	20	11–22
	<i>p</i> -tolyl sulfoxide	410			1110 ± 60			1.58 ± 0.09	1750	20	3–6
PSSO2	phenyl sulfone		350sh								

* CCl₄ solvent. ** CHCl₃ solvent.

† System reacts irreversibly.

* No evidence for complex formation. ^a Reference 4. ^b Reference 6. ^c Reference 1. ^d Reference 2. ^e Reference 3. ^f Voigt, E. M.; Reid, C. J. *Am. Chem. Soc.* **1964**, *86*, 3930–3934. ^g Zweig, A. *Tetrahedron Lett.* **1964**, 89–94. ^h Reference 10. ⁱ Reference 9. ^j Zahradnik, D.; Parkyani, C. *Collect. Czech. Chem. Commun.* **1965**, *30*, 195–207. ^k Heller, C. A.; Zingaro, R. A.; Meyers, E. A. *Can. J. Chem.* **1974**, *3814*–3824. ^l Reference 8. ^m Yoshida, Z.; Kobayashi, T. *Tetrahedron* **1970**, *26*, 267–71. ⁿ Reference 5. ^o Reference 7.

They observed that the λ_1 values for MMS–T, EES–T, IIS–T, and BBS–T increase in a smooth progression from 490, 505, 529 to 546 nm while I_1 values for MMS (8.67 eV), EES (8.44 eV), IIS (8.26 eV), and BBS (8.07 eV) decrease in the same sequence. Since the first ionization in the PE spectrum of an alkyl sulfide arises from the $n(b_1)$ orbital of the sulfur, the CT band of the complex is due to a $\pi^* \leftarrow n(b_1)$ transition between the alkyl sulfide and T. The increase in λ_1 for the sulfide series is due primarily to the increase in the inductive effect of the alkyl group with increasing substitution on the α -carbon atom.

The trend in K values for EES–T (0.24), IIS–T (0.03), and BBS–T (<0.01) indicates that complex formation is strongly hindered by bulky substituents on the sulfur atom. The narrow bands ($\Delta\nu_{1/2}$ 4500–4600 cm⁻¹) for alkyl sulfide–T complexes are characteristic of $\pi^* \leftarrow n(b_1)$ transitions.

b. Bis(methylthio)methane. The spectrum of bis(methylthio)methane–T exhibits a symmetrical band λ_1 478 nm with $\Delta\nu_{1/2}$ 5500 cm⁻¹. Bock and Wagner¹⁶ demonstrated that the PE ionizations of bis(methylthio)methane at I_1 (8.65 eV) and I_2 (8.90 eV) arise from the splitting of the $n(p_y)$ orbitals into a closely-spaced n^+/n^- pair as a result of through-bond interactions. Since these ionizations correspond to λ_{CT} values (calculated with eq 3) of 490 and 469 nm which neatly bracket the experimental value of 478 nm, we conclude that the observed absorbance consists of two overlapping bands which result from $\pi^* \leftarrow n^+$ and $\pi^* \leftarrow n^-$ transitions.

c. Cyclic Alkyl Sulfides. The spectra of M2S–T, M3S–T, M4S–T, and M5S–T exhibit single absorbance bands with λ_1 values 447, 490, 513, and 510 nm and $\Delta\nu_{1/2}$ values of 4900, 4600, 4600, and 4600 cm⁻¹, respectively (Figure 1). Characteristics of the spectra of complexes of the unstrained cyclic sulfides are identical with those of the acyclic sulfides, whereas those of the highly strained M2S are distinctly different. Furthermore, M2S reacts moderately rapidly with T, and its complex has a much larger K value than that of its congeners. The various studies of the cyclic alkyl sulfides indicate that the CT bands for the complexes arise from $\pi^* \leftarrow n(p_y)$ transitions and that increasing ring strain leads to a fundamental change in the nature of the donor orbital. Aue et al.¹⁷ and Mollere and Houk¹⁸ attribute this change to the electron density in the C–S bonds toward the

carbons as $\angle CSC$ decreases; this arises from the repulsions of the bonding electrons near sulfur.

The spectra of 1,3-dithiane–T and 1,4-dithiane–T exhibit bands λ_1 500 and 488 nm with $\Delta\nu_{1/2}$ 6100 and 5600 cm⁻¹. Although the appearance of these spectra and λ_1 values are superficially similar to those of acyclic alkyl sulfides, the $\Delta\nu_{1/2}$ values are substantially larger indicating that the energies of the uppermost orbitals are split into a n^+/n^- pair. Sweigart and Turner¹⁹ and Bock and Wagner¹⁶ attribute the splitting in 1,3-dithiane to through-space interaction between overlapping $n(p_y)$ orbitals and the splitting in 1,4-dithiane to through-bond interactions involving the $n(p_y)$ and intervening $\sigma(CH_2)$ orbitals. The I_1 and I_2 values for 1,3-dithiane correspond to λ_{CT} values of 520 and 480 nm which precisely bracket the experimental value of 500 nm for 1,3-dithiane–T. Similarly the I_1 and I_2 values for 1,4-dithiane correspond to λ_{CT} values of 507 and 465 nm which bracket the experimental value of 488 nm for 1,4-dithiane–T.

d. Alkyl Sulfides. i. Alkyl Methyl Sulfide. The spectrum of AMS–T exhibits a band with λ_1 490 nm and $\Delta\nu_{1/2}$ 4600 cm⁻¹ as well as a weak shoulder at λ_2 325 nm. The 490-nm band is similar to that for EES–T. The 325-nm shoulder has a wavelength and molar absorbance close to that expected for a CT interaction between a double bond and T (λ_1 for 1-hexene–T is 355 nm¹⁴). This indicates that there is no appreciable conjugative interaction in EES and that T interacts independently with the β -methylthio group and the double bond. In contrast, Bock et al.²⁰ reported strong conjugative interaction between the π bond and the $n(p_y)$ sulfur orbital in methyl vinyl sulfide.

ii. Tetrathiafulvalene. A 1.00×10^{-3} M solution of TTF in DCM displays a sharp peak at 450 nm (ϵ 260 L/mol cm) on the steep cutoff at 400 nm. The spectrum of the TTF/T/DCM system displays a band with λ_1 1005 nm ($\Delta\nu_{1/2}$ 4100 cm⁻¹) and an absorbance at 438 nm on the 400-nm cutoff. Analysis of the 1005-nm band yields K 42.9 L/mol, the highest such value reported for a sulfur-containing donor.

e. Alkyl Disulfides. The λ_{\max} values of MMSS–T (434 nm), EESS–T (453 nm), IISS–T (470 nm), and BBSS–T (534 and 400sh nm) are invariably lower than those of the corresponding alkyl sulfide–T complexes whereas the $\Delta\nu_{1/2}$ values of the alkyl disulfide–T complexes at 7400, 6900, 6400, and 5300 cm⁻¹ are always larger (Figure 2). The larger values of $\Delta\nu_{1/2}$ arise from the conjugation and splitting of the $n(p_y)$ and $n(p_z)$ orbitals of the sulfurs into two n^+/n^- pairs which give

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Table 2. Correlation of λ_{CT} of Donor-Tetracyanoethylene Complexes with Ionization Energies of the Donor Molecules

donor code	donor	I_D , eV	orbital type	λ_{CT} , nm (cal)	λ_{CT} , nm (expl)
BSH	2-methyl-2-propanethiol ^a	9.03	n(p _y)	409	424
PHS	thiophenol ^b	8.28	$\pi(b_1)$	511	
		9.38	$\pi(a_2)$	374	
MMS	2,6-dimethylthiophenol ^c	8.0	$\pi(b_1)$	560	551
		8.67	n(p _y)	452	490
EES	methyl sulfide ^d	8.44	n(p _y)	485	513
IIS	ethyl sulfide ^d	8.26	n(p _y)	514	529
BBS	<i>tert</i> -butyl sulfide ^d	8.07	n(p _y)	549	547
		8.65	n ⁻	490	478
	bis(methylthio)sulfide ^e	8.90	n ⁺	469	
M2S	ethylene sulfide ^b	9.05	n(p _y)	457	447
MM2S	propylene sulfide ^f	8.88	n(p _y)	470	461
M3S	trimethylene sulfide ^g	8.65	n(p _y)	490	490
M4S	tetramethylene sulfide ^d	8.40	n(p _y)	513	513
M5S	pentamethylene sulfide ^h	8.38	n(p _y)	508	510
		8.33	n ⁻	520	500
	1,3-dithiane ^e	8.76	n ⁺	480	
	1,4-dithiane ^e	8.46	$\sigma^*(b_u)$	507	488
		8.95	$\sigma(a_g)$	465	
TTF	tetrathiafulvalene ⁱ	8.83	$\pi(b_{1u})$	990	1005
		8.69	$\pi(b_{3g})$	450	438
MMSS	methyl disulfide ^d	8.97	n ⁻	415	434sh
		9.21	n ⁺	390	
EESS	ethyl disulfide ^d	8.70	n ⁻	448	453
		8.92	n ⁺	421	
IISS	isopropyl disulfide ^d	8.54	n ⁻	470	470
		8.76	n ⁺	440	
BBSS	<i>tert</i> -butyl disulfide ^d	8.17	n ⁻	530	534
		8.82	n ⁺	443	
MPS	thioanisole ^c	8.07	$\pi(b_1)$	549	573
		8.60	n(p _y)	461	
EPS	ethyl phenyl sulfide ^c	9.30	$\pi(a_2)$	380	379
		8.0	$\pi(b_1)$	560	
IPS	isopropyl phenyl sulfide ^c	8.53	n(p _y)	471	576
		9.29	$\pi(a_2)$	382	
BPS	<i>tert</i> -butyl phenyl sulfide	8.0	$\pi(b_1)$	560	380
		8.46	n(p _y)	471	
4MPS	methyl <i>p</i> -tolyl sulfide ^c	9.24	$\pi(a_2)$	387	377sh
		8.40	n(p _y)	491	
MPS _e	selenoanisole ^j	9.14	$\pi(a_2)$	397	502
		7.87	$\pi(b_1)$	592	
MPT _e	telluroanisole ^k	8.50	n(p _y)	476	385
		9.24	$\pi(a_2)$	387	
PPS	phenyl sulfide ^l	7.99	$\pi(b_1)$	570	601
		7.6	$\pi(b_1)$	660	
MPT _e	phenyl selenide ^k	7.90	$\pi(b_1)$	585	580
		7.6	$\pi(b_1)$	660	
PPS _e	phenyl disulfide ^l	7.90	$\pi(b_1)$	585	580
		9.15	$\pi(a_2)$	396	
PPT _e	phenyl telluride ^l	7.85	$\pi(b_1)$	597	605
		9.15	$\pi(a_2)$	396	
PPSS	phenyl diselenide ^m	7.64	n(p _y)	650	695
		8.21	π^-	521	
Th	thiophene ^p	8.45	π^+	484	515
		8.06	π^-	551	
2MTh	2-methylthiophene ^q	8.54	π^+	470	550
		8.0	$\pi(b_1)$	560	
3MTh	3-methylthiophene ^q	7.94	π_s^-	578	607
		8.43	π_s^+	476	
24MTh	2,4-methylthiophene ^r	9.30	$\pi(b_2)$	381	350sh
		8.87	$\pi(a_2)$	427	
Th2	2,2'-dithienyl ^s	9.52	$\pi(b_1)$	361	390
		8.32	$\pi(a_2)$	504	
BzTh	benzo[<i>b</i>]thiophene ^t	8.96	$\pi(b_1)$	416	407
		8.54	$\pi(a_2)$	470	
Bz2Th	dibenzothiophene ^u	9.11	$\pi(b_1)$	400	410
		8.09	$\pi(a_2)$	546	
	selenophene ^v	8.93	$\pi(b_1)$	420	417
		8.50	$\pi(b_u)$	553	
		9.14		397	390sh
		8.20	$\pi(a'')$	525	
		8.76	$\pi(a'')$	444	465
		7.93	$\pi(3a_2)$	579	
		8.34	$\pi(4b_1)$	501	550
		9.26	$\pi(2a_2)$	385	
		8.80	$\pi(a_2)$	435	375sh
		8.95	$\pi(b_1)$	418	

Table 2 (continued)

donor code	donor	I_D , eV	orbital type	λ_{CT} , nm (cal)	λ_{CT} , nm (expl)
	tellurophene ^u	8.27	$\pi(b_1)$	513	530
		8.81	$\pi(a_2)$	434	465sh
PPSO	phenyl sulfoxide ^v	8.58	$n(b_1)$	464	
		9.54	$\pi(b_1)$	360	390
PPSO2	phenyl sulfone ^w	9.37	$\pi(b_1)$	375	350
		9.82	$\pi(a_2)$	337	

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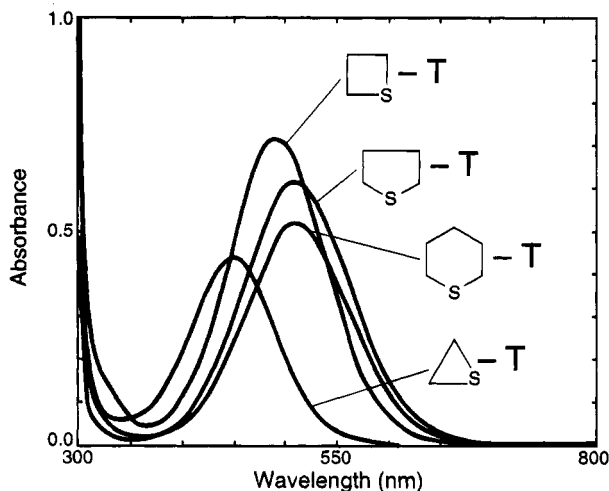


Figure 1. Spectra of cyclic alkyl sulfide-T complexes.

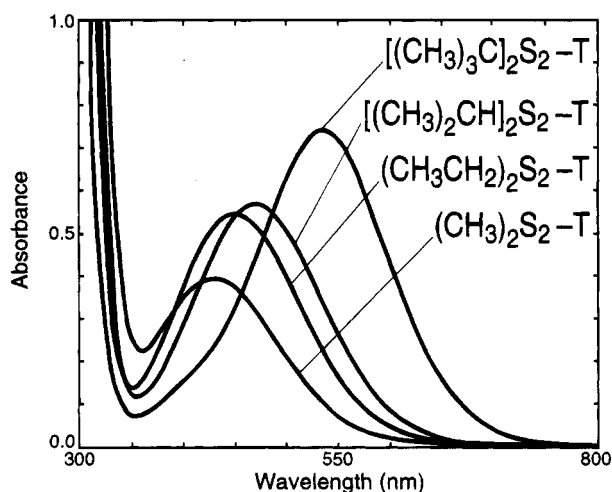
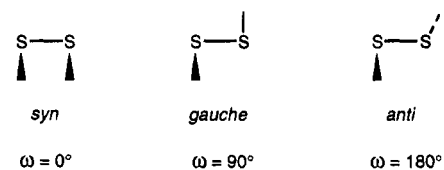


Figure 2. Spectra of alkyl disulfide-T complexes.

rise to strongly overlapping bands λ_1 and λ_2 which appear as one broad band. BBSS-T is anomalous in that the splitting between λ_1 and λ_2 is so large that separation between the bands is obvious from the spectrum.

Wagner and Bock⁴ reported values of $I_2 - I_1$ for MMSS (0.24 eV), EESS (0.22 eV), IISS (0.22 eV), and BBSS (0.65 eV). They further showed that the angle of the lobes of the $n(p_y)$ and $n(p_z)$ orbitals on adjacent sulfur atoms influences the orbital energy splittings of the alkyl disulfides. Orbital interaction is minimal when ω (\angle CSS/SSC) = 90° (*gauche* conformation) and increases to a

maximum as ω tends toward 0° or 180° (*syn* or *anti* conformations). The splitting values for MMSS, EESS,



and IISS correspond to a value of $\omega \approx 85^\circ$. BBSS with an abnormal splitting value of 0.65 eV is estimated to have an $\omega = 110^\circ$; this large angle is due to the steric interference between the *tert*-butyl groups which hinder rotation about the S-S bond and force the molecule into a more open conformation. The evidence indicates that the conformation of the alkyl disulfide molecules in the complexed state is the same as that in the free molecules.

3. Benzyl Sulfides. The benzyl sulfide molecules have two independent binding sites for T, i.e., the substituted phenyl rings and the sulfur atoms. The resultant bands for their complexes are expected to be summations of the individual bands associated with each binding site.

a. Benzyl Sulfide. The spectrum of benzyl sulfide-T exhibits a major band λ_2 400 nm with a smaller band λ_1 510 nm on its shoulder. Bock et al.³ attributed λ_1 to ionizations from the $n(b_1)$ orbital of sulfur and λ_2 to overlapping bands arising from ionizations from $\pi(b_1)$ and $\pi(a_2)$ orbitals of the phenyl. The location of the bands indicates that there is no conjugative interaction between the phenyl and sulfur orbitals.

b. Benzyl Disulfide. The spectrum of benzyl disulfide-T consists of a very broad band with λ_{max} 415 nm and $\Delta\nu_{1/2}$ 9400 cm^{-1} which abuts the 350-nm cutoff for the donor absorbance band. This spectrum originates from multiple transitions involving the $\pi(b_1)$ and $\pi(a_2)$ electrons of the phenyl ring and the doubly split $n(p_y)$ orbitals of the sulfurs. The bands for the $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n(p_y)$ transitions are expected to exhibit maxima at 385–415 nm and 420–450 nm. All of these maxima fit comfortably within the perimeter of the composite band. The position of λ_{max} of the dibenzyl sulfide-T spectrum indicates that the dihedral angle in the complexed donor molecule is approximately 90°.

4. Alkyl Aryl Chalcogenides. Although crystal structures of $\pi-\pi^*$ complexes of T usually show that alternate donor and acceptor molecules lie parallel to each other in extended stacks, it is not certain that a similar parallel orientation persists during a CT encounter between two isolated molecules in solution. Since

alkyl aryl chalcogens form both planar and orthogonal rotamers which exhibit distinctive ionization bands, the correlation of the CT spectra of their complexes with the PE spectra of corresponding donor molecules reveals the conformation of the complexed molecules.

a. Thioanisole. The spectrum of MPS-T exhibits bands λ_1 573 and λ_2 379 nm. Dewar et al.²¹ observed three ionizations at $I_D < 10$ eV in the PE spectrum of MPS. They proposed that this pattern provided evidence for an equilibrium between a planar rotamer (~90%) with maximum $n(p_y) - \pi(b_1)$ conjugation and an orthogonal rotamer (~10%) with diminished conjugation. Their argument was confirmed in its essentials by Schweig and Thon.²² Dewar et al. assigned I_1 8.07 eV and I_3 9.30 eV to the conjugated $n(p_y) - \pi(b_1)$ and $\pi(a_2)$ orbitals of the planar rotamer and I_2 8.60 eV to the nonconjugated $n(p_y)$ orbital of the orthogonal rotamer. The first and third ionizations correspond to λ_{CT} values of 549 and 380 nm which are in good agreement with λ_1 and λ_2 . The second ionization corresponds to λ_{CT} 461. The absence of a band in this region of the spectrum of MPS-T indicates that while T undergoes a CT interaction with the orbitals associated with the planar rotamer, it does not appear to interact with the orbital associated exclusively with the orthogonal rotamer. This implies that MPS is invariably planar when complexed with T although it can adopt either the planar or orthogonal conformation in its free state.

b. Alkyl Phenyl Sulfides. The absence of a CT band in the vicinity of 470 nm for both EPS-T and IPS-T indicates that the complexed EPS and IPS are planar in spite of the lower concentration of the planar conformer among free molecules.

Chmutova et al.¹⁰ reported values of λ_1 502 and λ_2 382 nm for BPS-T. Dewar et al.²¹ assigned both I_1 8.40 eV and I_2 9.14 eV to the orthogonal conformer of BPS and estimated that its abundance is about 90%. The good agreement between the calculated and experimental values of λ_1 and λ_2 indicates that the bulky *t*-Bu group forces BPS molecules into the orthogonal conformation in both the complexed and free states.

c. Seleno- and Telluroanisole. Chmutova et al.⁹ reported that the spectra of MPSe-T and MPTe-T exhibit λ_1 values of 601 and 650 nm. Chmutova and Bock²³ assigned the first ionizations in the spectra of MPSe and MPTe at 7.99 and 7.6 eV to the conjugated $n(p_y) - \pi(b_1)$ orbitals in the planar conformer.

d. Alkylselenoanisoles. Chmutova et al.⁹ reported that the spectra of MPSe-T, EPSe-T, IPSe-T, and BPSe-T exhibit λ_1 values of 601, 600, 594, and 554 nm and λ_2 values in a narrow range from 372–381 nm. The trends in λ_1 are similar to those observed in the corresponding alkylthioanisoles, indicating that the complexed donors molecules are planar except for that of hindered BPSe.

e. Summary. Although free alkyl aryl chalcogenide molecules generally contain planar and orthogonal rotamers in equilibrium, they tend to assume the planar conformation when complexed with T. This conformation permits optimal overlap of the donor and acceptor orbitals. The orthogonal form is observed in complexes only

when rotation of the CXC linkage is inhibited by a bulky group as in *tert*-butyl phenyl sulfide and selenide.

5. Aryl Chalcogenides. Unlike the alkyl aryl chalcogenides, the diaryl chalcogenides cannot adopt a planar conformation because of steric interference between the *ortho*-hydrogen atoms. However, effective $n(p_y) - \pi(b_1)$ conjugation may occur when one of the phenyls is orthogonal to the axis of the $n(p_y)$ orbital.

a. Phenyl Sulfide. PPS-T exhibits bands at λ_1 580 and λ_2 370 nm. Nakanishi et al.²⁴ assigned the I_1 and I_2 bands of the PE spectrum of PPS to the orbital arising from $n(p_y) - \pi(b_1)$ conjugation and to the $\pi(a_2)$ orbital. The absence of a CT band at 490 nm, the λ_1 value for MMS-T, indicates that unconjugated $n(p)$ orbitals of sulfur are not involved in CT interactions in this system.

b. Phenyl Selenide. The analysis of the spectrum of PPSe-T is complicated by the strong absorbance of PPSe which exhibits a well-defined band with λ_{max} 435 nm (ϵ 3.95 L/mol cm and $\Delta\nu_{1/2}$ 4500 cm^{-1}) and a sharp cutoff at 370 nm. A solution of 0.0450 M T and 0.0045 M PPSe displays a symmetrical band λ_1 605 nm ($\Delta\nu_{1/2}$ 4900 cm^{-1}) and a broad shoulder at 360–400 nm which overlaps with the PPSe band.

c. Phenyl Telluride. Since mixtures of PPTe and T react irreversibly in DCM we ran spectra of mixtures of PPTe in excess T at a rapid scan rate immediately after mixing. The spectrum of the PPTe/T/DCM system consists of a symmetrical band at λ 695 nm ($\Delta\nu_{1/2}$ 4600 cm^{-1}) followed by the sharp cut-off of PPTe at 400 nm. The I_D value of 7.64 eV reported by Rodin et al.²⁵ corresponds to λ_{CT} 650 nm, in good agreement with experiment. We note that the K values of PPS/T and PPSe/T at 0.63 and 0.66 L/mol are nearly identical, but significantly different from that of PPTe/T at 1.51 L/mol. This difference, together with the greater reactivity the PPTe/T system, indicates that the HOMO in PPTe is an unconjugated $n(p_y)$ orbital. Rodin et al. estimate that this orbital is 80% localized on the central atom. Additional support for the atomic nature of the HOMO in PPTe comes from the observation that the I_1 value of methyl telluride²⁶ (7.89 eV) is similar to that of PPTe (7.64 eV).

d. Phenyl Disulfide. The spectrum of PPSS-T consists of a band with λ_{max} 515 nm abutting the 420-nm cutoff of PPSS. Colonna et al.²⁷ report ionizations at I_1 8.21, I_2 8.45, and I_3 9.36 eV for PPSS. They, as well as Giordan and Bock,²⁸ attribute I_1 and I_2 to a pair of split $n(p_y) - \pi(b_1)$ conjugated orbitals and I_3 to the $\pi(a_2)$ orbital. They assume that $\angle CSS/SSC \approx 90^\circ$. λ_1 and λ_2 correspond to overlapping CT bands at 523 and 484 nm which appear as a single absorbance band with λ_{max} at about 505 nm. The good agreement with the observed band indicates that the complexed donor molecule has a nearly orthogonal or skew conformation.

e. Phenyl Diselenide. The spectrum of phenyl diselenide-T consists of a broad, flat band with an absorbance maximum stretching from 520–560 nm toward the 450-nm cutoff of phenyl diselenide. The

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ionizations at 8.06 and 8.54 eV²⁷ correspond to bands with λ_{CT} 551 and 470 nm in agreement with the observed spectrum. Complexed phenyl diselenide is assigned an orthogonal conformation.

f. Phenyl Ditelluride. The spectrum of phenyl ditelluride exhibits a symmetrical band at λ_{max} 400 nm with ϵ 834 L/mol cm and $\Delta\nu_{1/2}$ 7200 cm⁻¹. A mixture of 0.025 M phenyl ditelluride and 0.026 M T in DCM showed no evidence for the presence of a complex. Colonna et al.²⁷ reported I_1 and I_2 values of 7.68 and 8.08 eV for phenyl ditelluride which correspond to λ_{CT} values of 639 and 548 nm. The absence of an absorbance near 600 nm indicates that no detectable amount of complex forms in this system despite the fact that PPTe forms a distinct CT complex with T. Furthermore, a plot of A_{400} versus the concentration of phenyl ditelluride for a series of solutions which are 0.0261 M in T and 0.0010–0.0050 M in the prospective donor is linear. These observations indicate that the absorbance from 350–700 nm is due entirely to phenyl ditelluride and that there is no observable interaction between the phenyl ditelluride and T under these conditions.

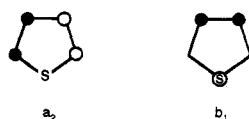
g. Mesityl Disulfide. Moreau and Weiss¹ reported a λ_{max} value of mesityl disulfide–T at 430 nm which is similar to that for MMSS–T at 434 nm. The agreement between these values indicates that the *o*-methyls severely restrict rotation of the phenyl group around the CSS link so that $n(p_y) - \pi(b_1)$ conjugation is completely inhibited.

h. Thianthrene. The spectrum of thianthrene–T exhibits bands λ_1 607, λ_2 476, and lastly λ_3 as a weak shoulder on the steep cutoff of thianthrene at 370 nm. The high value of λ_1 suggests strong $n-\pi$ conjugation between the sulfurs and the π orbitals of the folded rings.

i. Summary. The λ_1 values of PPX–T and PPXX–T complexes tend to increase with decreasing electronegativity of X. While the $n(p_y)$ orbitals in PPS and PPSe are strongly conjugated, the $n(p_y)$ orbital in PPTe is almost purely atomic. Consequently, PPTe behaves the same as an alkyl telluride by interacting with T through its $n(p_y)$ orbital. The phenyl chalcogenides adopt a skew or orthogonal conformation in their complexes with T.

6. Chalcogenophenes. The complexes of T with the chalcogenophenes have been studied by Alioso and his co-workers.^{5,7} We report analyses of several additional complexes together with the results of detailed correlations of data from PE spectra of the corresponding donors.

a. Thiophene. The spectrum of Th–T consists of a broad asymmetrical band with λ_{max} 400 nm which is a composite of two strongly overlapping bands with deconvoluted values of λ_1 445 and λ_2 390 nm (Figure 3). The PE spectrum of Th reported by Derrick et al.²⁹ exhibits bands I_1 8.87 and I_2 9.52 eV which arise from the $\pi(a_2)$ orbital (node coincident with the 2-fold axis through the sulfur atom) and the $\pi(b_1)$ orbital (node perpendicular to the 2-fold axis through the 2 and 5, i.e., α -carbons).



π Molecular Orbitals of Thiophene

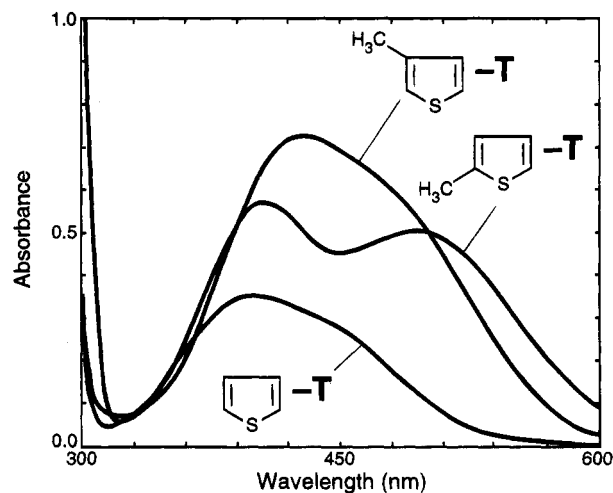


Figure 3. Spectra of thiophene–T and 2- and 3-methylthiophene–T.

Table 3. Shifts in Absorbance Maxima for TCNE Complexes of Methylthiophenes as a Function of Methyl Position on Ring

donor	λ_1	$\Delta\lambda_1$	$\Delta\lambda_1/R$		λ_2	$\Delta\lambda_2$	$\Delta\lambda_2/R$	
			α	β			α	β
Th	445				390			
2MTh	496	51	51		407	17	17	
3MTh	480	35		35	410	20		20
24MTh	557	112	66	46	417	27	12	15
25MTh	550	105	53		419	27	14	
1234MTh	605	120	47	33	485	95	21	24
mean			54	38			16	20

b. Methylthiophenes. Given the sites of the antinodes (regions of high electron density) and nodes of the $\pi(a_2)$ and $\pi(b_1)$ orbitals with respect to the α and β positions on the thiophene ring, we expect that methyl substitution at any position on the thiophene ring will result in a substantial increase in λ_1 for a methylthiophene–T complex. However, a lesser increase is expected in λ_2 for methyl substitution at the α -carbons.

The λ_1 and λ_2 values and wavelength shifts for T complexes of the methylthiophenes relative to Th–T are summarized in Table 3. Values of λ_1 and λ_2 appear in columns 2 and 6. The gross wavelength shift values, $\Delta\lambda_1$ and $\Delta\lambda_2$ in columns 3 and 7, are obtained by subtracting the λ_1 and λ_2 of each of the methylthiophene–T complexes from the corresponding values for Th–T. The portion of the shift value, $\Delta\lambda_1/Me$ or $\Delta\lambda_2/Me$, which is attributable to the inductive effect of each of the α - or β -methyls is given in columns 4, 5, 8, and 9. Estimated values are italicized; mean values are given in the bottom row in bold face. The results indicate that (1) α -methyls on the thiophene ring elevate the values of λ_1 by about 54 nm and of λ_2 by about 16 nm per methyl whereas (2) β -methyls elevate the value of λ_1 by about 38 nm and of λ_2 by about 20 nm. The wavelength for a methylthiophene–T complex can then be estimated using the empirical formulas below.

$$\lambda_1 = 445 + 54n_\alpha + 38n_\beta \quad (4)$$

$$\lambda_2 = 390 + 16n_\alpha + 20n_\beta \quad (5)$$

Here, n_α , and n_β are the number of α - or β -methyls per molecule; the coefficients are weighting factors for each methyl. The coefficients reflect the relative inductive

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effect of the methyl group with the respect to its location on the ring. The consistency of the results indicate that the inductive effects are essentially additive.

c. 2,2'-Dithienyl and α -Terthienyl. Numerous studies have dealt with the structure, twist angles, and inter-ring conjugation in Th2. Visser et al.³⁰ found that the molecule is planar with an *anti* conformation in the crystalline state and that the inter-ring C-C bond length is 149 pm. Almenningen et al.³¹ proposed an *anti* conformation in the vapor state with a twist angle of 34°. Meunier et al.³² reported that the PE spectrum of Th2 exhibited a band I_1 8.05 eV for the $\pi(b_1)$ orbital and a cluster of three bands with peaks I_2 9.14, I_3 9.37, and I_4 9.77 eV. Using a Walsh diagram based on CNDO-S calculations, they showed that $I_4 - I_1$ decreases as the twist angle increases from 0° (*anti*-planar conformation) to 90°. The observed difference, 1.72 eV, corresponds to a twist angle of about 35°.

The spectrum of Th2-T exhibits bands λ_1 640 nm ($\Delta\nu_{1/2}$ 5100 cm^{-1}) and λ_2 390sh nm. The first two ionization bands of Th2 correspond to CT bands for the complex at λ_1 553 and λ_2 397 nm. The first value falls far short of the observed λ_1 which indicates that Th2 is planar during the complexation process in spite of the tendency for free Th2 to adopt a skew conformation. The planar conformation permits optimum overlap with the π^* orbitals of T. The relatively high value of K 1.61 L/mol supports this conjecture.

α -Terthienyl also forms a complex with excess T having λ_1 768 nm ($\Delta\nu_{1/2}$ 5400 cm^{-1}). The high value of λ_1 indicates that the three rings are coplanar and strongly interconjugated through the $\pi(a_2)$ orbitals.

d. Benzo[*b*]thiophene and Dibenzothiophene. The spectrum of BzTh-T consists of two overlapping bands λ_1 560 and λ_2 465 nm and a third band λ_3 315sh nm. These bands arise from transitions originating in the three uppermost $\pi(a'')$ orbitals.

The spectrum of Bz2Th-T consists of a symmetrical band with λ_{max} 550 nm ($\Delta\nu_{1/2}$ 5400 cm^{-1}) and a shoulder at 375 nm on the Bz2Th cutoff at 350 nm. These bands correspond to the three lowest ionizations of dibenzothiophene which Buemi et al.³³ attribute to the $\pi(3a_2)$, $\pi(4b_1)$, and $\pi(2a_2)$ orbitals. These ionizations correspond to λ_{CT} values of 579, 501, and 385 nm. The first two calculated values bracket the λ_{max} at 550 nm indicating that the primary absorbance is a composite of two strongly overlapping bands arising from transitions originating in the two HOMOs.

e. Selenophene and Tellurophene. The spectrum of selenophene-T consists of a symmetrical band with λ_{max} 439 nm and $\Delta\nu_{1/2}$ 5600 cm^{-1} . The PE spectrum reported by Schäfer et al.³⁴ exhibits ionizations at I_1 8.80 and I_2 8.95 eV which are assigned to the $\pi(a_2)$ and $\pi(b_1)$ orbitals. These ionizations correspond to λ_1 435 and λ_2 418 nm; the narrow separation between these values suggests that the spectrum of selenophene-T should appear as a broadened band near 425 nm as observed.

Aliosi et al.⁷ reported that the spectrum of tellurophene-T consists of two bands λ_1 530 and λ_2 465 nm. The PE spectrum for tellurophene reported by Schäfer et al.³⁴ exhibits I_1 8.27 and I_2 8.81 eV which are assigned to the $\pi(b_1)$ and $\pi(a_2)$ orbitals. The inversion in the order of the orbitals indicates that the tellurium atom is but weakly conjugated with the ring. The proximity of I_1 for methyl telluride, 7.89 eV,³⁵ confirms this assessment.

f. Summary. The optical spectra of CT complexes of chalcogenes with T consist of two bands λ_1 and λ_2 arising from the $\pi(a_2)$ and $\pi(b_1)$ orbitals. The energy of the $\pi(a_2)$ orbital is more strongly elevated by the inductive effects of methyl substituents than that of the $\pi(b_1)$ orbital.

The bands corresponding to the $\pi^* \leftarrow \pi(a_2)$ transitions for furan-T¹¹ (λ_1 432 nm), Th-T (λ_1 440 nm), selenophene-T (λ_1 450 nm), and tellurophene-T (λ_2 465 nm) increase in small increments with the decrease in electronegativity of the heteroatom. The $\pi(a_2)$ orbital has a node at the heteroatom and is therefore only slightly sensitive to its effect. In contrast, the CT bands corresponding to the $\pi^* \leftarrow \pi(b_1)$ transitions for furan-T (λ_2 300 sh nm), Th-T (λ_2 390 nm), selenophene-T (λ_2 430 nm), and tellurophene-T (λ_1 530 nm) increase dramatically with decreasing electronegativity of the heteroatom since the $\pi(b_1)$ orbital has an antinode at the heteroatom and is therefore very responsive to its electronegativity and ability to conjugate with the π electrons in the ring.

7. Phenyl Sulfoxides and Sulfones. a. Phenyl and *p*-Tolyl Sulfoxide. The spectrum of PPSO-T consists of a band with λ_{max} 395 nm abutting the steep cutoff of the donor at 350 nm. Bock and Solouki³⁶ reported that the PE spectrum exhibits a narrow band at 8.58 eV, attributed to the $n(p_y)$ orbital of sulfur and a broad band at 9.54 attributed to the $\pi(b_1)$ and $\pi(a_2)$ orbitals of the phenyl ring. The absence of a CT band in the vicinity of 460 nm indicates that there is no interaction between T and the $n(p_y)$ orbital of sulfur. The location of this band relative to λ_1 for PPS-T at 577 nm indicates that there is little $n(p_y) - \pi(b_1)$ conjugation and that there is little splitting of the degeneracy of $\pi(b_1)$ and $\pi(a_2)$ orbitals.

This interpretation is supported by the spectrum of *p*-tolyl sulfoxide-T which has a broader band than PPSO-T with λ_{max} 410 nm abutting the 320 nm cutoff of the donor. The 15-nm shift in wavelength and the broadening of the band relative to PPSO-T arise from the inductive effect of the *p*-methyl group on the $\pi(b_1)$ orbital.

b. Phenyl Sulfone. The spectrum of PPSO2-T exhibits a weak shoulder on the steep cutoff of PPSO2 with a half-height at 360 nm. Solouki et al.³⁷ reported bands at 9.37 and 9.82 eV in the PE spectrum of PPSO2 which they attributed to $\pi(b_1)$ and $\pi(a_2)$ orbitals formed by the conjugation between orbitals of b_1 and a_2 symmetry in the phenyl rings and SO₂ group. The location of the CT band indicates that it is due to a $\pi^* \leftarrow \pi(b_1)$ transition. The strong blue shift of the CT band relative to PPSO-T indicates that the sulfone group has a strong electron-withdrawing effect on the phenyl rings.

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Conclusions

1. Alkyl and aryl thiols react rapidly with T; however, complexes of thiols with bulky substituents react slowly so that they can be partially characterized.

2. Acyclic alkyl sulfides form complexes with T which exhibit a single absorbance band arising from a $\pi \leftarrow n(b_1)$ transition with λ_{\max} 450–550 nm and $\Delta\nu_{1/2}$ 4500–4900 cm^{-1} . λ_{\max} values increase in the order of increasing inductive effect of the alkyl and K values decrease with increasing bulk of the alkyl.

3. Cyclic alkyl sulfides form complexes with T which exhibit a single absorbance band with λ_{\max} 450–510 nm; λ_{\max} increases with increasing ring size.

4. Complexes of alkyl disulfides with T exhibit two strongly overlapping bands which arise from conjugative splitting of the $n(p_y)$ and $n(p_z)$ orbitals of sulfur into n^+/n^- pairs. This splitting is exceptionally large in BBSS–T because of steric inhibition of rotation about the S–S bond.

5. Unhindered alkyl aryl sulfides and di- and trithiophenes adopt planar conformations when complexed with T; the planar conformation optimizes overlap of the donor and acceptor orbitals.

6. Complexes of T with aryl sulfide and selenides exhibit two bands arising from π -donor orbitals; corresponding aryl tellurides exhibit only a single band which indicates that the $n(p_y)$ orbital is unconjugated and that it undergoes a $\pi^* \leftarrow n(p_y)$ transition with T.

7. λ_1 and λ_2 values of chalcogene–T complexes increase with increasing methyl substitution on the ring and decreasing electronegativity of the heteroatom.

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