# Charge-Transfer Complexes of Tetracyanoethylene with Alkyl and Aryl Derivatives of the Halogens

John E. Frey,* Theresa Aiello, Shi-Lin Fu, and Heather Hutson

*Department of Chemistry, Northern Michigan University, Marquette, Michigan 49855*

*Received September 1, 1995*⊗

Spectral characteristics ($\lambda_{CT}$, $\Delta\nu_{1/2}$, and $\epsilon$) and association constants (in dichloromethane) of charge-transfer (CT) complexes of tetracyanoethylene (**T**) with donors containing C−X linkages (X = F, Cl, Br, and I) are presented. The donor orbitals from which CT transitions originate are identified by correlation of $\lambda_{CT}$ 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 the complexes are influenced by intramolecular conjugative and inductive effects between halogen atoms and alkyl and aryl groups. Haloalkanes form weak complexes with **T** through interaction of the $p_x$ and $p_y$ orbitals of the halogen with the $\pi^*$ LUMO of **T**. Monoiodoalkane−**T** complexes exhibit two spectral bands arising from the transfer of nonbonded electrons from the 5p orbitals of iodine which are split into $^2E_{1/2}$ and $^2E_{3/2}$ states through spin−orbit coupling. $\lambda_1$ and $\lambda_2$ values of monoiodoalkanes increase progressively with increasing bulk of the alkyl group. Halobenzenes form complexes with **T** through interaction of the uppermost $\pi$ orbitals of the benzene ring with the $\pi^*$ LUMO of **T**. Spectra of fluoro-, chloro-, and bromobenzenes exhibit two bands arising from the uppermost $\pi$ orbitals of the benzene ring. $\lambda_{max}$ and $K$ values tend to increase with decreasing electronegativity of the halogen. Spectra of iodobenzenes exhibit an additional band which arises from the in-plane nonbonded orbital of iodine. Halogen atoms attached to a benzene ring tend (a) to withdraw electrons inductively from the $\pi$ orbitals through the $\sigma$-bond framework of benzene and (b) to donate electrons into the $\pi$ orbitals through conjugation with the out-of-plane $p_y$ orbital of the halogen.

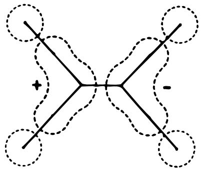
## Introduction

Tetracyanoethylene, **T**, one of the most powerful known $\pi$-electron acceptors, forms charge-transfer; CT, complexes with a wide variety of $\pi$ bases. Studies of CT systems have been useful in exploring the inductive, conjugative, and steric effects of substituents in organic molecules. In addition, these studies have served to determine the specific orbitals involved in donor−acceptor interactions through correlation with photoelectron spectra of corresponding donor molecules. This has proven effective in the study of reaction mechanisms since the initial step in many organic reactions entails the formation of a transitory CT complex through a donor−acceptor interaction of the frontier orbitals.[1]

In this paper we present the results of studies of organohalide/**T** systems in dichloromethane. Analysis of the spectra of organoiodide/**T** complexes is especially informative because the spectra exhibit CT bands in the visible region which are readily accessible to study. The exceptional reactivity of organoiodides is usually attributed to the low electronegativty and polarizability of the iodine atom and the length and weakness of the C−I bond. Here we call attention to the low ionization energy and the $\pi$ symmetry of the iodine frontier orbitals which render organoiodides capable of functioning as $\pi$ bases.

The primary objectives of this study are to (1) determine formation constants and spectral characteristics of CT complexes of organohalides with **T**, (2) specify the halogen orbitals involved in CT interactions, and (3) establish the relationships between the characteristics of CT complexes and structural and electronic field effects of halogen atoms.

**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 $\pi^*(b_{3g})$ orbital of **T** (**1**) with the simultaneous absorption of a quantum of light ($h\nu$).



**1**

$$\mathbf{D} + \mathbf{T} \rightleftarrows \mathbf{D{-}T} \overset{h\nu}{\rightleftarrows} \mathbf{D}^+\mathbf{T}^-$$

Analysis of the absorbance spectrum of the complex by means of the Scott−Hildebrand equation[2]

$$C_xC_y/A = 1/K\epsilon + (1/\epsilon)C_x \qquad (1)$$

yields its molar absorbance, $\epsilon$, and its association constant, $K$.

The frequency of light absorbed is linearly related to the ionization energies of the donor molecule where $I_D$ is 7−10 eV. Correlation of the $\lambda_{CT}$ of the complex with the ionization bands of the photoelectron spectrum of the donor molecule using the empirical equation[3]

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

facilitates the determination of the energy of the donor electrons. Here $\lambda_{CT}$ corresponds to $\lambda_{max}$ for a CT band of the complex, and $I_D$ is the vertical ionization energy of the donor molecule in eV. Analysis of the absorbance spectrum of an individual complex yields $\epsilon$, $K$, and the CT energy.

---

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1995.

[1] Traven, V. F. *Frontier Orbitals and Properties of Organic Molecules*; Ellis Horwood: London, 1992; p 68.

[2] Scott, R. L. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 787−789.

[3] Frey, J. E. *Appl. Spectrosc. Rev.* **1987**, *23*, 247−283.

0022-3263/96/1961-0295$12.00/0

**Table 1. Complexes of Tetracyanoethylene with Organohalogen Compounds in Dichloromethane at 22 °C**

| code | donor compound | $\lambda_{max}$ | $\lambda_1$, nm | $\lambda_2$, nm | $\epsilon_1$, L/(mol cm) | $A_2/A_1$ | $\Delta\nu_{1/2}$ cm$^{-1}$ | K, L/mol | $\epsilon K$ | $C_D/C_T$ | % satn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| IM | iodomethane | | *380* | *330 sh* | 1390 ± 220 | *1.12* | | 0.10 ± 0.02 | 140 | 10 | 2−4 |
| IE | iodoethane | | *390* | *345 sh* | 530 ± 50 | *1.04* | | 0.26 ± 0.02 | 140 | 10 | 5−10 |
| 2IP | 2-iodopropane | | *395* | *355 sh* | 940 ± 90 | *1.07* | | 0.14 ± 0.01 | 130 | 10 | 2−5 |
| 1BrB | 1-bromobutane | <325 | | | | | | 0.23 ± 0.01 | | 10 | 4−9 |
| 1IB | 1-iodobutane | | *395* | *350 sh* | 440 ± 40 | *1.07* | | 0.33 ± 0.03 | 150 | 10 | 5−12 |
| IB | 2-iodo-2-methylpropane[a] | | *405* | *360 sh* | | *1.10* | | | | 10 | |
| DIM | diiodomethane | <400 | | | | | | 0.15 ± 0.01 | | 10 | 3−6 |
| Cl;T | α-chlorotoluene | 383 | | | 750 ± 70 | | 6900 | 0.33 ± 0.03 | 250 | 10 | 5−10 |
| BrT | α-bromotoluene[b] | 394 | | | | | | | | | |
| IT | α-iodotoluene[b] | 414 | | | | | | | | | |
| FP | fluorobenzene | 365 | | | 2670 ± 390 | | 8000 | 0.07 ± 0.01 | 190 | 10 | 1−2 |
| | fluorobenzene[c] | 360 | | | | | | | | | |
| | fluorobenzene[b] | 368 | | | | | | | | | |
| ClP | chlorobenzene | 376 | | | 1400 ± 260 | | 8000 | 0.15 ± 0.03 | 210 | 10 | 2−5 |
| | chlorobenzene[d] | 379 | | | 3840 | | | 0.049 | 190 | | |
| | chlorobenzene[c] | 379 | | | | | 7900 | | | | |
| | | | *401* | *354* | | *0.9* | *4600, 5400* | | | | |
| | chlorobenzene[b] | 374 | | | | | | | | | |
| BrP | bromobenzene | 389 | | | 577 ± 45 | | 8300 | 0.40 ± 0.03 | 230 | 10 | 6−11 |
| | bromobenzene[d] | 394 | | | 5000 | | | 0.039 | 200 | | |
| | bromobenzene[c] | 394 | | | | | 8200 | | | | |
| | | | *407* | *355* | | *0.8* | *4800,5900* | | | | |
| | bromobenzene[b] | 400 | | | | | | | | | |
| IP | iodobenzene | | 445 | 348 sh | 690 ± 60 | 0.94 | | 0.30 ± 0.02 | 210 | 12 | 5−11 |
| | iodobenzene[d] | | 450 | | 2500 | | | 0.079 | 200 | | |
| | iodobenzene[c] | | 447 | 356 | | 1.0 | | | | | |
| | | | *448* | *360* | | *1.0* | *4600, 5900* | | | | |
| | iodobenzene[b] | | 450 | | | | | | | | |
| 12ClB | 1,2-dichlorobenzene[c] | 373 | | | | | 7900 | | | | |
| | | | *400* | *348* | | *0.8* | *4700, 5400* | | | | |
| 12BrB | 1,2-dibromobenzene | 384 | | | 650 ± 30 | | 8100 | 0.31 ± 0.01 | 200 | 10 | 5−10 |
| 12IB | 1,2-diiodobenzene | 419 sh | | | 640 ± 40 | | | 0.42 ± 0.03 | 270 | 10 | 5−10 |
| 13ClB | 1,3-dichlorobenzene[c] | 362 | | | | | 7800 | | | | |
| | | | *394* | *350* | | *0.9* | *4600, 5400* | | | | |
| 13BrB | 1,3-dibromobenzene | 373 | | | 580 ± 50 | | 8500 | 0.32 ± 0.03 | 190 | 10 | 5−11 |
| 13IB | 1,3-diiodobenzene | 420 | | | 1380 ± 90 | | 7500 | 0.16 ± 0.01 | 220 | 10 | 2−5 |
| 14FB | 1,4-diflourobenzene[c] | | 391 | 346 | | 1.1 | | | | | |
| | | | *393* | *336* | | *0.85* | *4800, 4500* | | | | |
| 14ClB | 1,4-dichlorobenzene[c] | | 402 | 336 | | 0.9 | | | | | |
| | | | *408* | *337* | | *0.87* | *5400, 6000* | | | | |
| | 4-bromochlorobenzene[b] | 398 | | | | | | | | | |
| 14BrB | 1,4-dibromobenzene | | 416 | 341 sh | 720 ± 110 | 0.79 | | 0.21 ± 0.03 | 150 | 9 | 3−7 |
| | 1,4-dibromobenzene[c] | | 420 | 337 | | 0.99 | | | | | |
| | | | *420* | *339* | | *0.93* | *5400, 6000* | | | | |
| | 1,4-dibromobenzene[b] | 403 | | | | | | | | | |
| 14IB | 1,4-diiodobenzene | | 460 | | 690 ± 30 | | 6300 | 0.24 ± 0.01 | 170 | 10 | 3−7 |
| | 1,4-diiodobenzene | | | 340 sh | | 1.40 | | | | 1/18 | |
| | 1,4-diiodobenzene[c] | | 461 | 355 | | 0.95 | | | | | |
| | | | *461* | *345* | | *0.9* | *5500, 6000* | | | | |
| 135ClB | 1,3,5-trichlorobenzene[c] | 356 | | | | | 6500 | | | | |
| HFB | hexafluorobenzene[c] | 327 | | | | | | | | | |
| 2ClMB | 2-chlorotoluene[c] | 405 | | | | | 7100 | | | | |
| 2BrMB | 2-bromotoluene[c] | 412 | | | | | 7900 | | | | |
| | 2-bromotoluene[b] | 411 | | | | | | | | | |
| 2IMB | 2-iodotoluene | 444 | | *325 sh* | 1100 ± 140 | | 10000 | 0.31 ± 0.04 | 340 | 10 | 4−8 |
| 3BrMB | 3-bromotoluene[b] | 417 | | | | | | | | | |
| 3IMB | 3-iodotoluene | 450 | | *325 sh* | 1700 ± 290 | | 9000 | 0.18 ± 0.03 | 310 | 10 | 2−5 |
| 4ClMB | 4-chlorotoluene[c] | | 440 | *380* | | *0.8* | *4700, 5400* | | | | |
| 4BrMB | 4-bromotoluene[c] | | *459* | *376* | | *0.8* | *4600, 5400* | | | | |
| | 4-bromotoluene[b] | 422 | | | | | | | | | |
| 4IMB | 4-iodotoluene | | 484 | 360 sh | | 0.84 | *5800* | 0.14 ± 0.02 | 290 | 10 | 2−4 |
| | 4-iodotoluene[c] | | 485 | 370 | | 0.88 | *4600, 5600* | | | | |
| | 4-iodotoluene[b] | 490 | | | | | | | | | |

[a] Donor compound photodecomposes. [b] Reference 9. [c] Reference 12. [d] Merrifield, R. E.; Phillips, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 2778−2782.

## Experimental Section

Experimental procedures, data collection and processing, and judgmental criteria are described in a previous publication.[4] Spectra were recorded with a Shimadzu UV3101PC spectrophotometer.

Spectral characteristics of CT complexes, such as $\lambda_{max}$ and $\Delta\nu_{1/2}$, are normally determined from spectra which have been corrected for the absorbance of reagents.

**Reagents.** Solvents and reagent chemicals are the purest grades available from Aldrich, 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 chroma-

---

(4) Frey, J. E.; Andrews, A. M.; Ankoviac, D. G.; Beaman, D. N.; Du Pont, L. E.; Elsner, T. E.; Lang, S. R.; Zwart, M. O.; Seagle, R. E.; Torreano, L. A. *J. Org. Chem.* **1990**, *55*, 606−624.

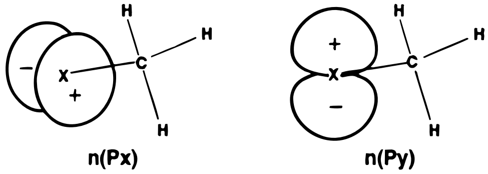
tography using a Hewlett-Packard HP5980A chromatograph. **T** was recrystallized twice from chlorobenzene and sublimed two or three times in vacuo: mp 199−200 °C. Fisher Spectranalyzed dichloromethane was used without further purification.

## Results and Discussion

The results of our studies of complexes of **T** with halogen-containing donors as well as those 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 organohalogen donors exhibit one, two, or three CT bands in the UV and visible regions. If one composite band appears in the spectrum, it is designated $\lambda_{max}$; its value appears in column 3. If one or two simple bands appear in the spectrum, they are designated $\lambda_1$ and $\lambda_2$ 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* following. If the main band is deconvoluted into two overlapping bands, the values of $\lambda_1$ and $\lambda_2$ are shown in italics. The apparent association constant, $K$, for the complex is reported in column 9. The product $\epsilon K$ is a measure of the "effective absorbance" of a complex since the larger the value of $\epsilon$ and/or $K$, the greater is the net absorbance of the complex for a given level of reagent concentrations. The ratios of the concentrations of stock solutions of **D** and **T** are given in column 11. The saturation fraction, $s$, of a complex, that is, the molar concentration of the complex divided by the concentration of the limiting reactant, 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.

Correlations of experimental $\lambda_{CT}$ values with those calculated using eq 2 are given in Table 2. For about 90% of the entries in Table 2, the agreement between experimental and calculated values is better than ±5%. This degree of consistency indicates that attributions of orbitals to CT transitions are generally reliable.

**1. Haloalkanes.** The three nonbonded electron pairs on the halogen atom of a methyl halide ($C_{3v}$ symmetry) divide into two degenerate $\pi$-type orbitals, $n(p_y)$ and $n(p_x)$ (**2**), and a $\sigma$-type orbital. The $\pi$ orbitals, the HOMOs, render the haloalkanes capable of behaving as electron donors in the presence of $\pi$ acceptors such as **T**. The $I_D$ values of fluoro- and chloroalkanes are so high that the bands expected from CT interactions are covered by the strong absorbance cutoff of **T** at 310 nm. Therefore the scope of this work is limited to the study of complexes of bromo- and iodoalkanes.



Haloalkane Orbitals

2

**a. 1-Bromobutane.** The spectrum of a mixture of **1BrB** and **T** consists of a steep shoulder on the cutoff of **T** with a slight bulge at λ 325 nm. Analysis of the absorbance values of a series of spectra at 325 nm yields a $K$ value of 0.23 L/mol for **1BrB−T**. The presence of a CT complex is confirmed by the fact that the $I_D$ value of **1BrB** at 10.13 eV[5] corresponds to a $\lambda_{CT}$ value of 316 nm.

**Table 2. Correlation of $\lambda_{CT}$ of Donor-Tetracyanoethylene Complexes with Ionization Energies of the Donor Molecules.**

| donor code | donor | $I_D$, eV | orbital type | $\lambda_{CT}$, nm (cal) | $\lambda_{CT}$, nm (exp) |
|---|---|---|---|---|---|
| **1BrB** | 1-bromobutane$^a$ | 10.13 | $n(p_y)$ | 316 | <325 |
| **IM** | iodomethane$^b$ | 9.54 | $e(^2E_{3/2})$ | 358 | 380 |
| | | 10.16 | $e(^2E_{1/2})$ | 314 | 330 |
| **IE** | iodoethane$^b$ | 9.35 | $a'$ | 376 | 390 |
| | | 9.93 | $a''$ | 329 | 345 |
| **2IPr** | 2-iodopropane$^b$ | 9.18 | $a'$ | 393 | 395 |
| | | 9.74 | $a''$ | 344 | 355 |
| **1IB** | 1-iodobutane$^b$ | 9.23 | $a'$ | 388 | 394 |
| | | 9.79 | $a''$ | 340 | 351 |
| **IB** | *tert*-butyl iodide$^b$ | 9.04 | $a'$ | 408 | 405 |
| | | 9.59 | $a''$ | 356 | 360 |
| | diiodomethane$^c$ | 9.52 | $n(b_2)$ | 361 | <400 |
| **ClT** | α-chlorotoluene$^d$ | 9.30 | $\pi(b_1)$ | 381 | 383 |
| **BrT** | α-bromotoluene$^d$ | 9.23 | $\pi(b_1)$ | 388 | 394 |
| **IT** | α-iodotoluene$^d$ | 8.91 | $\pi(b_1)$ | 422 | 414 |
| **FP** | fluorobenzene$^e$ | 9.19 | $\pi(b_1)$ | 392 | 365 |
| | | 9.82 | $\pi(a_2)$ | 340 | |
| | | 13.6 | $n(b_2)$ | 184 | |
| **ClP** | chlorobenzene$^e$ | 9.06 | $\pi(b_1)$ | 410 | 401 |
| | | 9.69 | $\pi(a_2)$ | 347 | 354 |
| | | 11.32 | $n(b_2)$ | 254 | |
| **BrP** | bromobenzene$^e$ | 9.05 | $\pi(b_1)$ | 407 | 407 |
| | | 9.67 | $\pi(a_2)$ | 349 | 355 |
| | | 10.61 | $n(b_2)$ | 287 | |
| **IP** | iodobenzene$^f$ | 8.75 | $\pi(b_1)$ | 442 | 447 |
| | | 9.46 | $\pi(a_2)$ | 367 | 348 |
| | | 9.74 | $n(b_2)$ | 344 | |
| **12ClB** | 1,2-dichlorobenzene$^g$ | 9.08 | $\pi(a_2)$ | 403 | 400 |
| | | 9.48 | $\pi(b_1)$ | 365 | 348 |
| **12BrB** | 1,2-dibromobenzene$^g$ | 9.02 | $\pi(a_2)$ | 410 | 384 |
| | | 9.48 | $\pi(b_1)$ | 366 | |
| **12IB** | 1,2-diiodobenzene$^f$ | 8.65 | $\pi(a_2)$ | 455 | 419 sh |
| | | 9.03 | $\pi(b_1)$ | 409 | |
| **13ClB** | 1,3-dichlorobenzene$^g$ | 9.15 | $\pi(a_2)$ | 396 | 394 |
| | | 9.53 | $\pi(b_1)$ | 361 | 350 |
| **13BrB** | 1,3-dibromobenzene$^g$ | 9.10 | $\pi(a_2)$ | 401 | 373 |
| | | 9.53 | $\pi(b_1)$ | 361 | |
| **13IB** | 1,3-diiodobenzene$^f$ | 8.73 | $\pi(a_2)$ | 444 | 420 |
| | | 9.11 | $\pi(b_1)$ | 400 | |
| **14FB** | 1,4-difluorobenzene$^g$ | 9.15 | $\pi(b_1)$ | 396 | 391 |
| | | 9.98 | $\pi(a_2)$ | 326 | 346 |
| **14ClB** | 1,4-dichlorobenzene$^g$ | 9.00 | $\pi(b_1)$ | 412 | 408 |
| | | 9.87 | $\pi(a_2)$ | 334 | 337 |
| **14BrB** | 1,4-dibromobenzene$^g$ | 8.91 | $\pi(b_1)$ | 422 | 416 |
| | | 9.81 | $\pi(a_2)$ | 338 | 341 sh |
| | | 9.74 | $n(p_x)$ | 344 | |
| **14IB** | 1,4-diiodobenzene$^f$ | 8.55 | $\pi(b_{2g})$ | 469 | 462 |
| | | 9.53 | $n(p_x)$ | 361 | 355 sh |
| | | 9.77 | $\pi(b_{1g})$ | 341 | |
| **135ClB** | 1,3,5-trichlorobenzene$^g$ | 9.36 | $\pi(b_1)$ | 376 | 356 |
| | | 9.87 | $\pi(a_2)$ | 334 | 336 |
| | hexafluorobenzene$^g$ | 9.19 | $\pi(b_1)$ | 392 | 365 |
| **4ClMB** | 4-chlorotoluene$^g$ | 8.90 | $\pi(a'')$ | 423 | 440 |
| | | 9.57 | $\pi(a'')$ | 357 | 380 |
| **4BrMB** | 4-bromotoluene$^g$ | 8.71 | $\pi(a'')$ | 447 | 451 |
| | | 9.45 | $\pi(a'')$ | 367 | 382 |

[a] Reference 5. [b] Reference 6. [c] Reference 7, p 233. [d] Reference 8. [e] Reference 7, p 290. [f] Reference 11. [g] Reference 13.

**b. Iodoalkanes**. The spectrum of the **IM**/**T**/DCM system appears as a shoulder on the cutoff of **T**. When the spectrum of **T** is subtracted out, the corrected spectrum (Figure 1) exhibits two distinct maxima. This pattern is observed for each of the iodoalkane/**T**/DCM systems characterized in this study. For **IM−T**, **IE−T**, **2IPr−T**, **1IB−T**, and **IB−T,** $\lambda_1$ values, estimated by

---

(5) Hashmall. J. A.; Heilbronner, E. *Angew. Chem.; Int. Ed. Engl.* **1970**, *9*, 305−306.

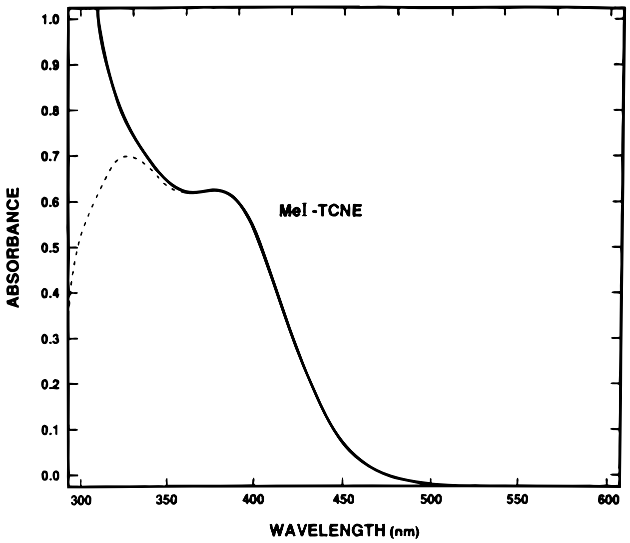


**Figure 1.** Spectrum of iodomethane−**T** (- - - corrected).

deconvolution, increase progressively from *380* to *405* nm; corresponding $\lambda_2$ values increase from *330 to 360* nm. When $I_1$ and $I_2$ values[6] for **IM**, **IE**, **2IPr**, **1IB**, and **IB** are substituted into eq 2, they yield calculated values of $\lambda_1$ and $\lambda_2$ which are in excellent agreement with experiment. *K* values range from 0.10 to 0.33 L/mol, indicating that these complexes are very weak.

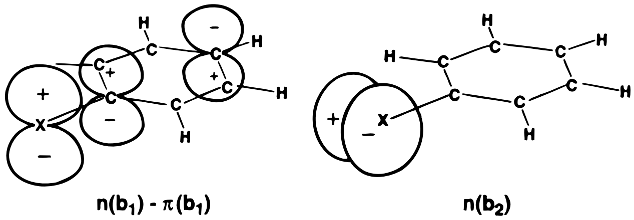
In the case of the complex with **IM** ($C_{3v}$), two absorbencies appear because the removal of an electron from the degenerate 5p orbitals of iodine gives rise to $^2E_{3/2}$ and $^2E_{1/2}$ states which result from spin−orbit coupling. For the remaining iodoalkanes ($C_s$), the HOMOs are split into a′ and a″ levels. The progressive increase in $\lambda_1$ and $\lambda_2$ observed in the series is due to increasing delocalization of the two highest occupied orbitals with increasing bulk of the alkyl group.

The spectrum of the diiodomethane/**T**/DCM system shows evidence for a CT transition at $\lambda_1 < 400$ nm as expected from the $I_1$ (9.52 eV[7]) of the donor. In this case, as well as for iodoform and tetraiodomethane, the strong absorbance of the free donor precludes the direct observation of possible CT bands.

**2. Halogenated Benzene Derivatives.** The spectrum of benzene−**T** consists of a band with $\lambda_{max}$ 385 nm and $\Delta\nu_{1/2}$ 5600 cm$^{-1}$. This band arises from the promotion of electrons from the degenerate $\pi(e_{1g})$ orbitals of the benzene ring to the $\pi^*$ orbital of **T**. The spectral band of toluene−**T** in comparison has $\lambda_{max}$ 415 nm and $\Delta\nu_{1/2}$ 6000 cm$^{-1}$. The increases in $\lambda_{max}$ and $\Delta\nu_{1/2}$ are due to the inductive effect of the methyl which promotes the energy of the $\pi(b_1)$ orbital and removes its degeneracy with the $\pi(a_2)$ orbital. Consequently, the resultant spectrum consists of a band which is a composite of two strongly overlapping bands. Similar orbital splittings are observed in **PhX−T** and **PhCH$_2$X−T** complexes; however, additional complications arise because of the occurrence of $n(p_y)-\pi(b_1)$ conjugation and $n(p_x)$ ionizations.

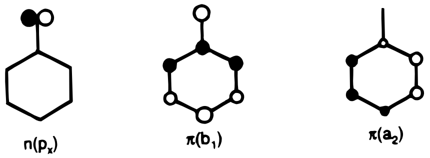
**a. α-Halotoluenes. ClT−T** exhibits a band with $\lambda_{max}$ 383 nm and $\Delta\nu_{1/2}$ 6900 cm$^{-1}$. The low value of $\lambda_{max}$ relative to toluene−**T** is due to the chlorine atom which exerts its electron-withdrawing effect on the $\pi(a_1)$ and $\pi(b_2)$ orbitals of the phenyl ring through the α carbon. The $I_1$ and $I_2$ values[8] of **ClT** yield calculated values of $\lambda_1$ and $\lambda_2$ in good agreement with the observed spectrum. The $\lambda_{max}$ values of **BrT−T** (394 nm) and **IT−T** (414 nm)[9] show that the electron-withdrawing effect of an α halogen tends to decrease with its electronegativity.

**b. Monohalobenzenes.** The spectrum of **FP−T** (Figure 2) consists of a band with $\lambda_{max}$ 360 nm and $\Delta\nu_{1/2}$ 8000 cm$^{-1}$. The PE spectrum of **FP** exhibits ionizations at 9.19 and 9.82 eV[10] arising from the $\pi(b_1)$ and $\pi(a_2)$ orbitals (**3**) of the benzene ring. Substitution of these values into eq 2 yields $\lambda_1$ 392 nm and $\lambda_2$ 340 nm. The experimental value of $\lambda_{max}$ 365 nm lies midway between the calculated values supporting the supposition that the observed band arises from $\pi^* \leftarrow \pi(b_1)$ and $\pi^* \leftarrow \pi(a_2)$ transitions. The low $\lambda_{max}$ value of **FP−T** arises from the fact that the fluorine atom strongly withdraws electrons from the σ-bond system of the benzene ring and that its out-of-plane $n(b_1)$ orbital conjugates with the $\pi(b_1)$ orbital of the phenyl ring (**4**). The net effect decreases the energy of the $\pi(b_1)$ orbital less than that of the $\pi(a_2)$ orbital and splits the π-orbital energies. The spectra of **ClP−T** and **BrP−T**, which exhibit $\lambda_{max}$ at 376 and 389 nm, can be explained in a similar manner.



Halobenzene Orbitals

**3**



Molecular Orbitals of Halobenzenes

**4**

The spectrum of **IP−T** (Figure 3) exhibits a band at 445 nm as well as a shoulder at 348 nm. Cvitas et al.[11] reported $I_1$, $I_2$, and $I_3$ values of 8.75, 9.46, and 9.74 eV, which they attributed to ionizations from the $\pi(b_1)$and $\pi(a_2)$ orbitals of the benzene ring and the in-plane $n(b_2)$ orbital of iodine. These values correspond to CT transitions of 442, 367, and 344 nm, indicating that the 447 nm band arises from an electron from the $\pi(b_1)$ orbital and the shoulder at 348 nm is a composite band arising from the $\pi(a_2)$ and $n(b_2)$ orbitals. CT transitions corresponding to the $n(b_2)$ orbitals of fluoro-, chloro-, and bromobenzene are of such high energy that they are obscured by the spectral cutoff of **T**.

---

(6) Boschi, R. A.; Salahub, D. R. *Can. J. Chem.* **1974**, *52*, 1217−1228.

(7) Turner, D. W. *Molecular Electron Spectroscopy*; Wiley-Interscience: London, 1970; p 233.

(8) Schmidt, H.; Schweig, A. *Tetrahedron Lett.* **1973**, 981−984.

(9) Bendig, J,; Kreisig, D. *Z. Phys. Chem. (Leipzig)* **1977**, *258*, 1176−1178.

(10) Reference 6, p 290.

(11) Cvitas, T.; Güsten, H.; Klasinc, L. *J. Chem. Soc., Perkin Trans. 2* **1977**, 962−965.

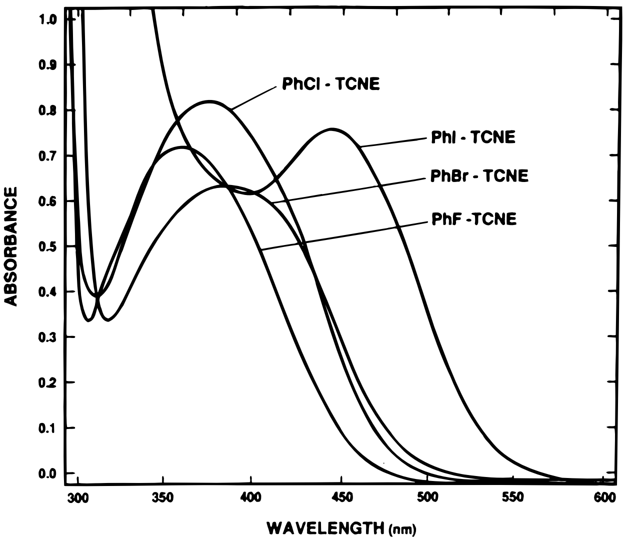
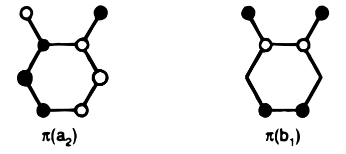


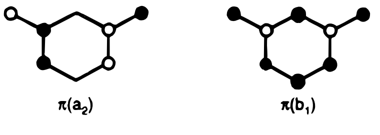
**Figure 2.** Spectra of monohalobenzenes−**T**.

**c. Dihalobenzenes.** The symmetry of both **12XB** and **13XB** is $C_{2v}$; the two uppermost MOs in each of these molecules are designated $\pi(a_2)$ and $\pi(b_1)$ (**5** and **6**). The symmetry of **14XB** is $D_{2h}$; its two uppermost orbitals are designated $\pi(b_{2g})$ and $\pi(b_{1g})$ (**7**). In this section the nonbonded out-of-plane electrons of the halogen atoms are labeled $n(p_y)$ and the in-plane electrons are labeled $n(p_x)$. The differences in symmetry of these molecules are reflected in the appearance of the spectra of their CT complexes.



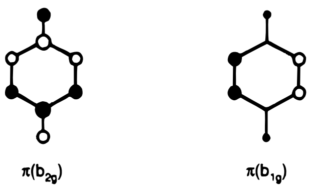
π Molecular Orbitals of 1,2-Dihalobenzenes

5



π Molecular Orbitals of 1,3-Dihalobenzenes

6



π Molecular Orbitals of 1,4-Dihalobenzenes

7

**(1) Dichlorobenzenes.** The spectra of **12ClB**−**T** and **13ClB**−**T** each exhibit a single wide band with $\lambda_{max}$ 373 and 362 nm.[12] These bands deconvolute to two overlapping bands attributed to transitions from the $\pi(a_2)$ and $\pi(b_1)$ orbitals.[13] The $\pi(a_2)$ orbitals in **12ClB** and **13ClB** are conjugated with the out-of-plane $n(p_y)$ orbitals of the two halogen atoms.

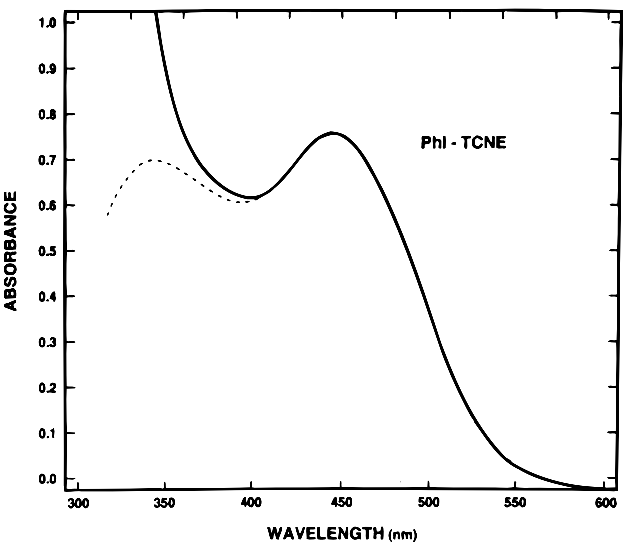


**Figure 3.** Spectrum of iodobenzene−**T** (- - - corrected).

The $\lambda_1$ and $\lambda_2$ bands of **14ClB**−**T** appear as two distinct peaks at 402 and 336 nm[12] in good agreement with the calculated values of 412 and 344 nm obtained from the $I_1$ and $I_2$ values of **14ClB**.[13] Both chlorines in **14ClB** are located at the antinodes of the $\pi(b_{2g})$ orbital, leading to strong conjugation between the $n(p_y)$ and $\pi(b_{2g})$ orbitals and a high value of $\lambda_1$. Conversely, the chlorines are situated at the nodes of the $\pi(b_{1g})$ orbital, precluding conjugation and leading to a low value of $\lambda_2$. Consequently, the two bands of **12ClB**−**T** are distinctly separated in the spectrum.

**(2) Dibromobenzenes**. The spectra of **12BrB**−**T**, **13BrB**−**T**, and **14BrB**−**T** are similar to those of the corresponding dichlorobenzene complexes, except that the $\lambda_{max}$ values are shifted upward 5−15 nm. The higher $\lambda_{max}$ values reflect the lower electronegativity and electron-withdrawing ability of Br. The assignment of orbitals is identical to that for the dichlorobenzene−**T** complexes.[13]

**(3) Diiodobenzenes.** The spectrum of **12IB**−**T** exhibits a band at $\lambda_{max}$ 419 sh nm on the **12IB**−**T** cutoff at 400 nm (Figure 4). Cvitas et al.[11] attributed the first three bands in the PE spectrum of **12IB** to ionizations from the $\pi(a_2)$, the in-plane $n(p_x)$ lone pair of iodine, and the $\pi(b_1)$ orbitals. These values correspond to CT transitions of 442, 409, and 371 nm, indicating that the $\lambda_{max}$ 419 nm band is a composite band arising from the $\pi(a_2)$ and $n(p_x)$ orbitals. Note that $\lambda_2$ for the **12IB**−**T** arises from the nonbonded $n(p_x)$ orbital of iodine rather than the $\pi(b_2)$ orbital as in **12ClB**−**T** and **12BrB**−**T**.

The spectrum of **13IB**−**T** exhibits a band with $\lambda_{max}$ 420 nm and $\Delta\nu_{1/2}$ 7500 cm$^{-1}$. The $I_1$ and $I_2$ values,[11] attributed to ionizations from the $\pi(a_2)$ and the in-plane $n(p_x)$ lone pair of iodine orbitals, correspond to CT bands at 442 and 409 nm, indicating that the $\lambda_{max}$ 419 nm band is a composite arising from $\pi^* \leftarrow \pi(a_2)$ and $\pi^* \leftarrow n(p_x)$ transitions.

**14IB**−**T** exhibits a band with $\lambda_{max}$ 460 nm and $\Delta\nu_{1/2}$ 6500 cm$^{-1}$ and a shoulder at about 350 nm on the cutoff of **14IB**. $I_1$, $I_2$, and $I_3$ for **14IB**[11] are attributed to

---

[12] Voigt, E. M. *J. Am. Chem. Soc.* **1964**, *86*, 3611−3617. Voigt, E. M.; Reid, C. *J. Am. Chem. Soc.* **1964**, *86*, 3930−3934.

[13] Streets, D. G.; Ceasar, G. P. *Mol. Phys.* **1973**, *26*, 1037−1052.

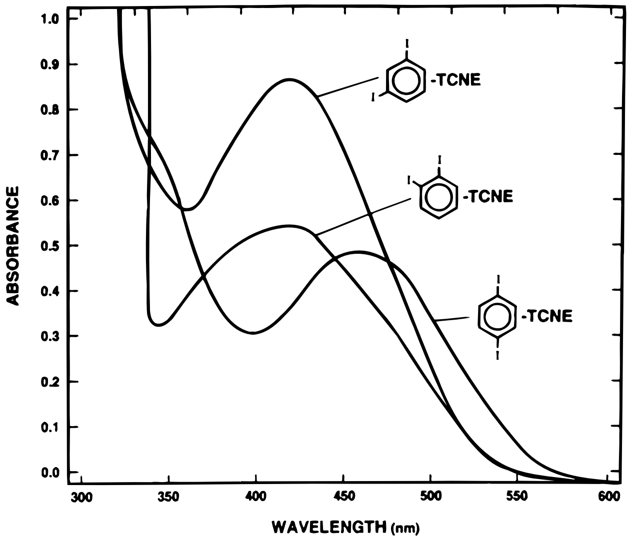


**Figure 4.** Spectra of 1,2-, 1,3-, and 1,4-diodobenzene–**T**(corrected).

ionizations from the $\pi(b_{2g})$, the in-plane $n(p_x)$ lone pair set of iodine, and the $\pi(b_{1g})$ orbitals. These values correspond to CT transitions of 469, 355, and 341 nm, indicating that, $\lambda_{max}$ 462 nm band arises from a $\pi^* \leftarrow \pi(b_{2g})$ transition and that the 450 band is a composite arising from transitions from the $n(p_x)$ and $\pi(b_{1g})$ orbitals.

**d. Halotoluenes.** The symmetry of both **2XMB** and **3XMB** is $C_s$; the two uppermost MOs in each of these molecules have symbols $\pi(a')$ and $\pi(a'')$. The symmetry of **4XMB** is $C_{2v}$; the symbols for the two uppermost MOs in this case are $\pi(b_1)$ and $\pi(a_2)$.

**(1) Chlorotoluenes.** The spectrum of **2ClMB–T**[12] exhibits a band with $\lambda_{max}$ 405 nm and $\Delta\nu_{1/2}$ 7100 cm$^{-1}$. This band has a $\lambda_{max}$ value midway between those of 1,2-dimethylbenzene–**T** (435 nm)[4] and **12ClB–T** (373 nm), which indicates that the band for **2ClMB–T** is a composite of two bands which arise from transitions from the two uppermost $\pi(a'')$ orbitals of **2ClMB**. The spectrum of **4ClMB–T** shows two maxima $\lambda_1$ *440* and $\lambda_2$ *380* nm corresponding to PE ionizations $I_1$ 8.85 and $I_2$ 9.67 eV[14] which arise from $\pi(b_2)$ and $\pi(a_1)$ orbitals.

**(2) Bromotoluenes.** The spectra of **2BrMB–T**, **3BrMB–T**, and **4BrMB–T** resemble those of the corresponding chlorotoluene complexes except that the $\lambda_{max}$ values are slightly higher.

**(3) Iodotoluenes.** The spectra of **2IMB–T** and **3IMB–T** each exhibit a band system with $\lambda_{max}$ 444 nm ($\Delta\nu_{1/2}$ 10 000 cm$^{-1}$) and 450 nm ($\Delta\nu_{1/2}$ 9000 cm$^{-1}$) and a weak band on the shoulder at 325 nm (Figure 5). On the basis of the analysis of **12IB–T** and **13IB–T**, we conclude that these band systems are formed by the overlap of three bands arising from the transitions out of the two uppermost $\pi(a')$ and $\pi(a'')$ orbitals and the in-plane $n(p_x)$ orbital of iodine.

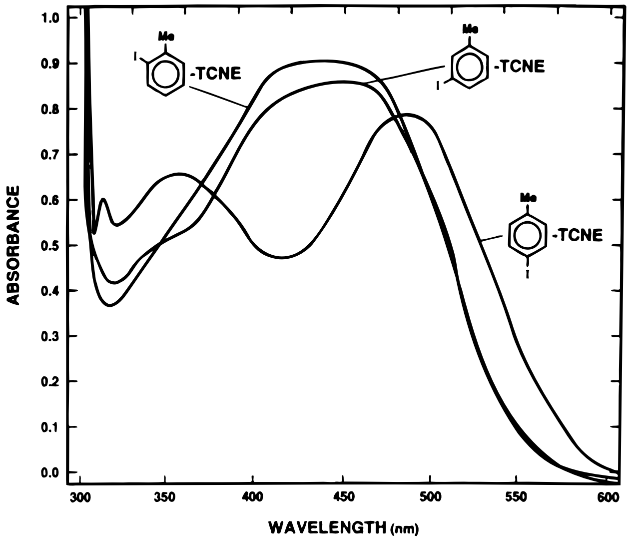


**Figure 5.** Spectra of 2-, 3-, and 4-iodotoluene–**T** (corrected).

The spectrum of **4IMB–T** consists of a simple band with $\lambda_{max}$ at 484 nm ($\Delta\nu_{1/2}$ 5800 cm$^{-1}$) and a shoulder at 360 nm. In view of the resemblance of this spectrum to that of **14IB–T**, we attribute the 484 nm band to an ionization from the $\pi(b_1)$ orbital and the 360 nm band to the in-plane $n(p_x)$ orbital of iodine.

## Summary and Conclusions

1. Haloalkanes form weak $\pi$ complexes with **T** through interaction between the $p_x$ and $p_y$ orbitals of the halogen and the $\pi^*$ LUMO of **T**. However, only complexes with monoiodoalkanes exhibit spectral bands which are sufficiently free of interferences to be analyzable by optical spectrophotometry. The spectrum of iodomethane–**T** has two bands; these result from the removal of an electron from the nonbonded in-plane orbital of iodine which gives rise to $^2E_{1/2}$ and $^2E_{3/2}$ states by spin–orbit coupling. $\lambda_1$ and $\lambda_2$ values of monoiodoalkanes increase progressively from 380 to 405 nm and 330 to 360 nm with the increasing bulk and inductive effect of the alkyl group.

2. Halobenzenes form weak $\pi$ complexes with **T** through interaction between the uppermost $\pi$ orbitals of the benzene ring and the $\pi^*$ LUMO of **T**. Spectra of the complexes of fluoro-, chloro-, and bromobenzenes with **T** exhibit two bands arising from the $\pi(b_1)$ and $\pi(a_2)$ orbitals of the benzene ring. $\lambda_{max}$ and $K$ values tend to increase with decreasing electronegativity of the halogen. Spectra of iodobenzenes exhibit an additional band which arises from the in-plane $n(b_2)$ orbital of iodine.

**Acknowledgment.** We are grateful for financial support from the Faculty Research Grant Fund of Northern Michigan University. We thank Professor Rolf Gleiter of the Organisch-Chemisches Institut of Heidelberg University and Dr. Russell N. Grimes of the University of Virginia for their hospitality and assistance during preparation of this paper.

JO951603+

---

[14] Reference 6, p 303.