

## Infrared Studies of Charge-transfer Complexes of Tetracyanoethylene and Substituted Aromatics

JOSEPH L. KIRSCH AND BRIAN F. VOLKMAN  
Department of Chemistry  
Butler University  
Indianapolis, Indiana 46208

### Introduction

The tetracyanoethylene molecule contains a highly conjugated  $\pi$  system which includes its carbon-carbon double bond and its four triply bonded cyano groups. The antibonding orbitals of the delocalized  $\pi$  system of the tetracyanoethylene can function as an environment to accept electron density from Lewis Base types of molecules. This transfer of electron density from the Lewis Base to the tetracyanoethylene forms a charge-transfer bond and results in the formation of a molecular association or charge-transfer complex (2). The charge-transfer bonds in these complexes are similar to the kinds interactions that characterize drug binding, enzyme activity, and other biologically interesting processes (7,8,9). It has also been postulated that a number of chemical reactions proceed through charge-transfer complex type of intermediates (1,2). The nature of the charge-transfer bond and stability of charge-transfer complexes is important to the understanding of the mechanism of these important chemical processes and has been the subject of a number papers in the literature (2).

Tetracyanoethylene forms charge-transfer complexes with substituted aromatic compounds. The sandwich structure which has been suggested in the literature for these charge-transfer complexes is pictured in Figure 1 (2,3,6). In these complexes the aromatic molecules

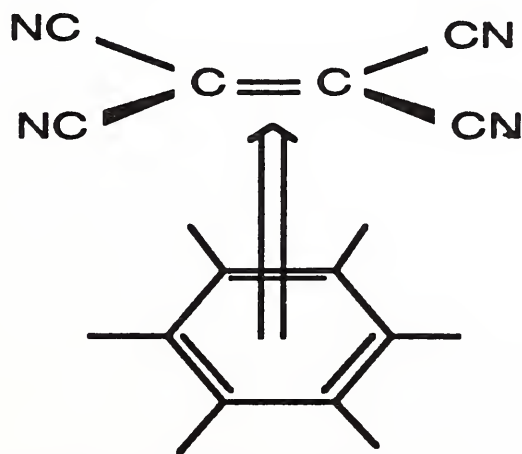


FIGURE 1. Tetracyanoethylene-aromatic Charge-transfer Complex

donate electron density from their  $\pi$  orbitals to the  $\pi$  antibonding orbitals of the tetracyanoethylene to form a charge-transfer bond between the aromatic donors and the tetracyanoethylene acceptor. This transfer of the electron density to the tetracyanoethylene antibonding orbitals causes the bond order of the cyano groups on the tetracyanoethylene molecule to decrease, and results in the decrease in the infrared vibrational frequency of the cyano bond. The magnitude of the decrease in both the bond order and the vibra-

tional frequency of the cyano group will be dependent on the extent of electron density transferred and the donor strength of the aromatic compound. In this study the charge-transfer complexes of tetracyanoethylene and substituted methylbenzenes (hexamethylbenzene, pentamethylbenzene, and 1,2,4,5-tetramethylbenzene) were prepared, and the location of the infrared absorptions of cyano stretching frequencies in the complexed tetracyanoethylene were determined. The magnitudes of the shifts to lower wavenumbers of the cyano stretching absorptions in the complexes relative to the cyano stretching absorption in uncomplexed tetracyanoethylene were determined and related to the donor strength of the aromatic compound.

### Experimental

Each complex was prepared by dissolving tetracyanoethylene and the appropriate aromatic compound (hexamethylbenzene, pentamethylbenzene, and 1,2,4,5-tetramethylbenzene) in 1,2-dichloroethane in a one to five molar ratio and allowing the resulting solution to evaporate. The preparations were carried out in excess aromatic in order to use Le Chatelier's Principle to minimize the amount of uncomplexed tetracyanoethylene.

The infrared spectra was recorded on a Digilab FTS 40 Fourier Transform Infrared Spectrometer. The spectra of the complexes were collected at  $2\text{ cm}^{-1}$  resolution in a KBr matrix. The complex concentrations in KBr were adjusted to be 2% by mass for each complex. Multiple sample preparations were carried out for each complex and the spectra recorded for each of these samples to determine the dependence of the position of the carbonyl absorption on the complex concentration in the KBr matrix. For the experimental variations in concentration of the complexes due to sample preparation, no more than a  $0.2\text{ cm}^{-1}$  shift in the cyano absorptions was observed due to matrix effects.

### Results and Discussion

Fourier transform infrared spectroscopy is characterized by its high sensitivity and its ability to determine accurately the positions of vibrational absorption bands. These characteristics make FT IR spectroscopy well suited for the study of the stability of the deeply colored charge-transfer complexes of tetracyanoethylene and substituted aromatic compounds. The vibrational absorptions of the cyano groups in these charge-transfer complexes are located in a region from  $2500$  to  $2000\text{ cm}^{-1}$ . The spectra in this region of the tetracyanoethylene and its complexes with hexamethylbenzene, pentamethylbenzene and 1,2,4,5-tetramethylbenzene are shown in Figures 2-5. The positions of the cyano vibrational absorptions and the shifts of these absorptions relative to the uncomplexed tetracyanoethylene are listed in Table I. The positions of these vibrational absorptions are functions of the bond orders of these bonds. The donation of electron density to the antibonding orbitals of tetracyanoethylene by the aromatic donors during complexation recedes the bond order of the cyano bonds and causes their vibrational absorptions to shift to lower wavenumbers. The magnitudes of these shifts are related to the extent of electron donation into the antibonding orbitals of the tetracyanoethylene acceptor which in turn is related to the donor strength of the aromatic compound and the stability of the charge-transfer complex. Hexamethylbenzene with its six electron releasing methyl groups is the strongest donor in the series and exhibits the largest shift in its cyano vibrational absorption. The shifts for this series of complexes decreases as the number methyl groups on the ring and the donor strength of the aromatic decreases.

The shifts in the cyano vibrational absorptions are in agreement with other studies reported in the literature relating the equilibrium constant for the complex formation reaction and  $\lambda_{\text{max}}$  of the charge-transfer band to the number of methyl groups on the aromatic ring, the donor strength of the aromatic, and the stability of the complex (4, 5). The literature values for  $K$  (equilibrium) for the complex formation reactions,  $\lambda_{\text{max}}$

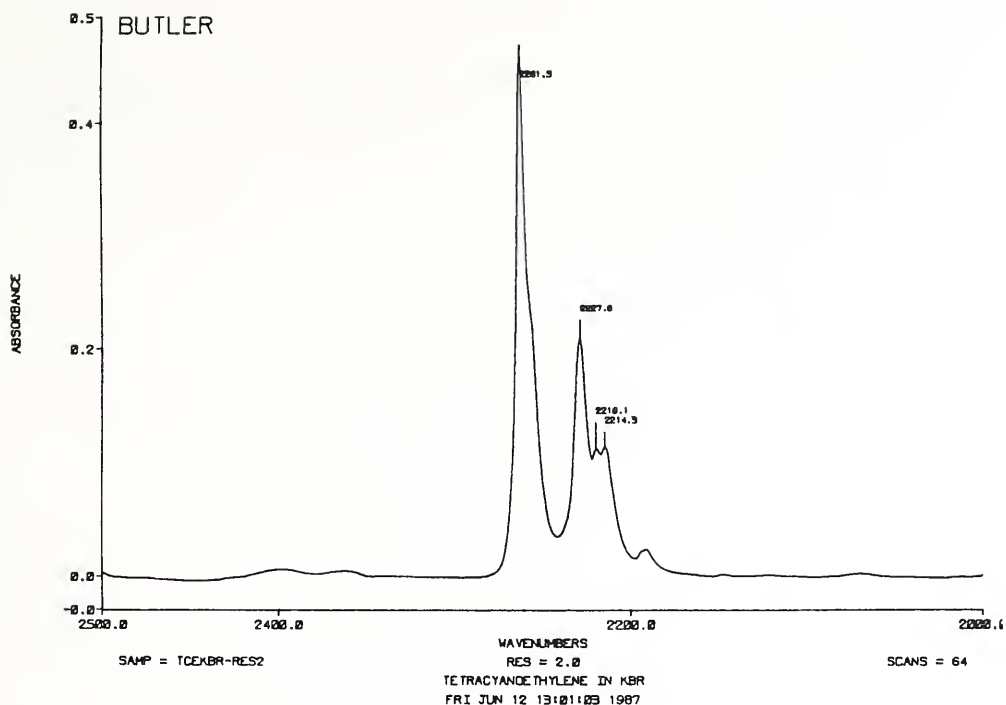


FIGURE 2. Spectra of Tetracyanoethylene

of the charge-transfer bands, and the cyano shifts from this study are listed in Table II. This data shows that as the number of methyl groups on the ring and the donor strength of the aromatic increases, the equilibrium constant for the complex formation reaction increases,  $\lambda_{\max}$  of the charge-transfer bands increases, the position of the cyano vibrational absorption decreases, and the shift of the cyano vibrational absorption relative to the uncomplexed tetracyanoethylene increases.

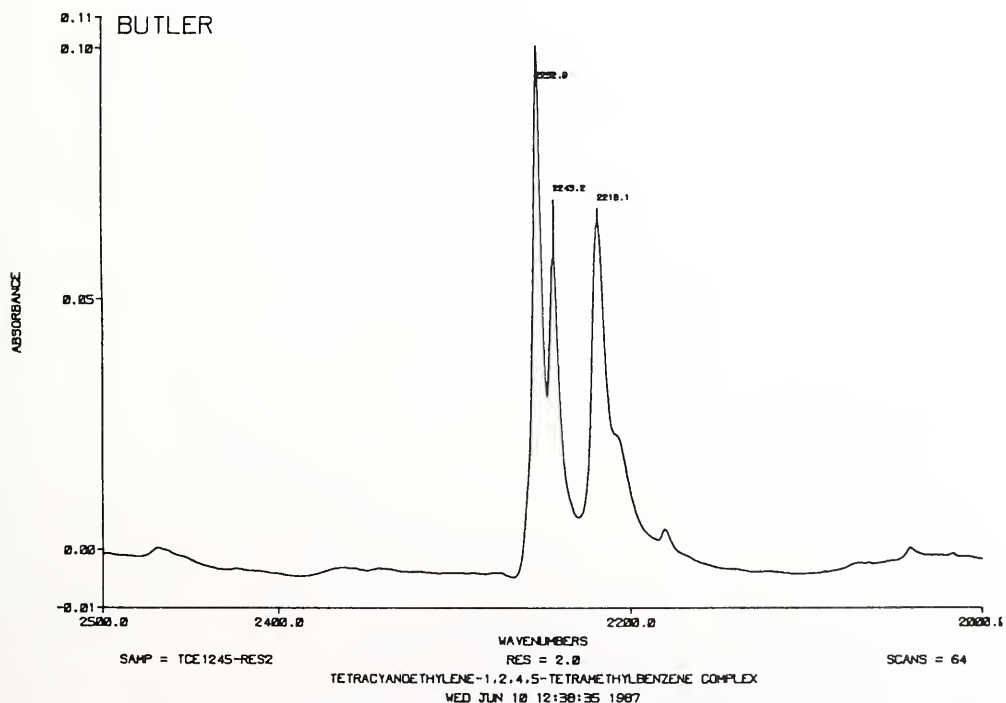


FIGURE 3. Spectra of Tetracyanoethylene—1,2,4,5-Tetramethylbenzene Complex

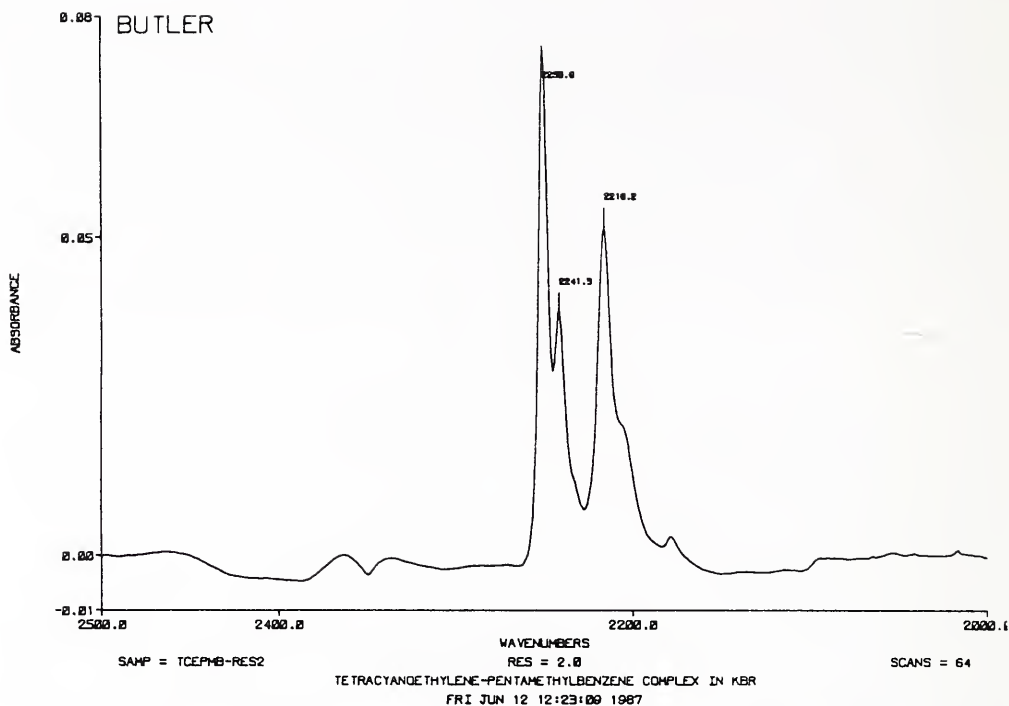


FIGURE 4. Spectra of Tetracyanoethylene-Pentamethylbenzene Complex

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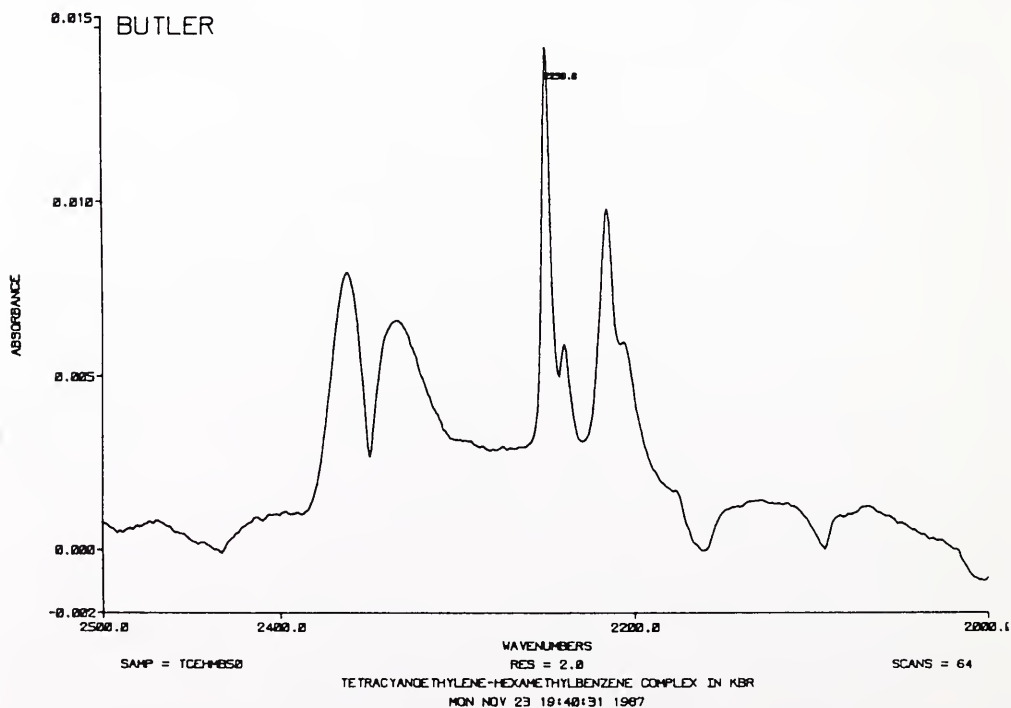


FIGURE 5. Spectra of Tetracyanoethylene-Hexamethylbenzene Complex

TABLE I. CN vibrational absorptions and absorptions shifts for tetracyanoethylene-aromatic charge-transfer complexes.

Donor	$\nu$ CN (CM <sup>-1</sup> )	$\Delta\lambda$ CN (CM <sup>-1</sup> ) <sup>a</sup>
1,2,4,5-tetramethylbenzene	2252.9 <sup>b</sup>	8.6
	2218.1	9.7
pentamethylbenzene	2250.9 <sup>b</sup>	10.6
	2216.2	11.6
hexamethylbenzene	2250.0 <sup>b</sup>	11.5
	2216.2	11.6

<sup>a</sup> The shifts are relative to the tetracyanoethylene CN vibrational absorptions at 2261.5 and 2227.8 cm<sup>-1</sup>.  
<sup>b</sup> The major CN absorption.

TABLE II. The CN vibrational absorption shifts and the literature values for  $K_{eq}$  and  $\lambda_{max}$ .

Donor	$\Delta\nu$ CN (CM <sup>-1</sup> ) <sup>a</sup>	$K_{eq}$ <sup>b</sup>	$\lambda_{max}$ (nm) <sup>c</sup>
1,2,4,5-tetramethylbenzene	8.6	1.15	480
pentamethylbenzene	10.6	4.36	520
hexamethylbenzene	11.5	12.00	545

<sup>a</sup> The shifts are relative to the tetracyanoethylene CN vibrational absorption at 2261.5 cm<sup>-1</sup>.  
<sup>b</sup> ref. 8.  
<sup>c</sup> ref. 9.

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