

stable substance, completely resinifying during a week's exposure to air. Although it was analyzed within a few hours of being prepared, enough decomposition may have occurred to account for low nitrogen values.

*Anal.* Calcd. for  $C_{10}H_8N_4O_4$ : C, 48.39; H, 3.25; N, 22.58. Found: C, 48.57; H, 3.09; N, 20.52, 20.62.

**Tetracyanoethylene from Bis-(acetoximinomethyl)-methylenemalononitrile.**—Bis-(acetoximinomethyl)-methylenemalononitrile sublimed unchanged at  $150^\circ$  (0.3 mm.). At  $150$ – $210^\circ$  (250 mm.) it decomposed into tetracyanoethylene, which was collected on the cold finger condenser of a sublimation apparatus. It was identified by two characteristic color tests (anthracene in benzene<sup>9</sup> and N,N-dimethylaniline in acetone<sup>15</sup>) and by comparison of its X-ray diffraction pattern with that of an authentic sample. Conversion was estimated to be about 50%.

**Reaction of Dibromomalononitrile with Copper in the Presence of Cyclohexene.**—A dry 500-ml. flask equipped with a stirrer, reflux condenser and addition funnel was charged with 250 ml. of cyclohexene and 63.5 g. (1 mole) of precipitated copper powder. With stirring, the mixture was heated to gentle reflux. The heat was removed and 44.8 g. (0.2 mole) of dibromomalononitrile<sup>18</sup> dissolved in 50 ml. of cyclohexene was added dropwise over one hour. There was a mild exothermic reaction. The mixture was then stirred and refluxed for two hours, cooled and filtered, and the dark filtrate was subjected to rough distillation. There was obtained 29 g. of moderately viscous liquid boiling over the range  $95$ – $130^\circ$  under full oil-pump vacuum. The distillate, as well as the original reaction mixture, gave no color test for TCNE with anthracene.<sup>9</sup> Redistillation gave 15 g. of liquid boiling over the range  $92$ – $103^\circ$  (0.07 mm.). The infrared spectrum of this material appeared consistent with the bicyclo[4.1.0]heptane structure and indicated the presence of only a trace of unsaturation. Repetition of the reaction gave a 60% yield of crude product boiling over the range  $81$ – $120^\circ$  (0.35–1 mm.). When redistilled in an 18'' spinning-band column, approximately 25% was recovered boiling at  $103$ – $106^\circ$  (1.1 mm.). This fraction proved to be cyclohexyldienemalononitrile as shown by analysis and agreement of its infrared spectrum with that of an authentic sample of cyclohexyldienemalononitrile.<sup>22</sup>

**Reaction of Ethyl Dibromocyanoacetate with Copper in the Presence of Cyclohexene.** 7-Cyano-7-ethoxycarbonylcyclo[4.1.0]heptane.—In a dry flask equipped with a stirrer, thermometer, addition funnel and reflux condenser was placed 63.5 g. (1 mole) of precipitated copper powder and

250 ml. of cyclohexene. The mixture was heated to  $80^\circ$  and with stirring 54 g. (0.2 mole) of ethyl dibromocyanoacetate was added dropwise over a period of 30 minutes. There was a very mildly exothermic reaction. When the addition was complete, the mixture was stirred and refluxed for eight hours and filtered, and the filtrate was subjected to distillation. Four fractions that were collected over the boiling range  $93$ – $115^\circ$  (0.7 mm.) partly crystallized. Filtration of these combined fractions gave 4 g. (10% yield) of 7-cyano-7-ethoxycarbonylcyclo[4.1.0]heptane as a white solid, m.p.  $56$ – $59^\circ$ . On crystallization from hexane, it was obtained as stout needles, m.p.  $60$ – $62^\circ$ . The infrared spectrum was consistent with the proposed structure and showed absorption at  $3.3$ ,  $3.4$  and  $3.45 \mu$  for saturated CH,  $4.45 \mu$  for CN, and  $5.75 \mu$  for ester carbonyl. The nuclear magnetic resonance spectrum also agreed with the proposed structure.

*Anal.* Calcd. for  $C_{11}H_{15}O_2N$ : C, 68.37; H, 7.82; N, 7.25; mol. wt., 193. Found: C, 68.34; H, 7.96; N, 7.11; mol. wt., 216, 207.

**Thermal Stability of Tetracyanoethylene.**—Tetracyanoethylene (10 g.) was sublimed through a vertical Vycor tube 1'' in diameter packed with Carborundum chips heated to  $600^\circ$  and at a pressure of 2.7 mm. The tube and packing were heated over a length of 15 cm. The vapors of tetracyanoethylene, entrained by a stream of nitrogen, were passed from top to bottom of the tube, and the stream was then led to a trap cooled in ice followed by one cooled in solid  $CO_2$ -acetone. The run required about three hours. Most of the tetracyanoethylene came through unchanged and condensed on the cold end of the tube. No material was found in either trap.

When tetracyanoethylene (12.8 g.) was sublimed in the manner just described through a tube heated to a temperature of  $1000^\circ$  at atmospheric pressure over a period of one hour, the ice-cooled trap was found to contain 4.1 g. of a light-brown solid. This solid consisted mainly of tetracyanoethylene as determined by elemental analysis and infrared spectra. The solid  $CO_2$ -cooled trap contained a brown solid which was allowed to vaporize at room temperature and was then recondensed at  $-50^\circ$ . In this way there was obtained 3.9 g. of a white solid, m.p.  $-35$  to  $-34^\circ$ , identified as cyanogen by test with palladium dimethylglyoximate.<sup>23</sup>

**Reactions of Tetracyanoethylene.**—Experimental details on reactions of tetracyanoethylene are given in papers II to XII on cyanocarbon chemistry.

(23) F. Feigl and H. E. Feigl, *Anal. Chim. Acta*, **3**, 300 (1949).

WILMINGTON, DELAWARE

(22) A. C. Cope and K. E. Hoyle, *This Journal*, **63**, 733 (1941).

[CONTRIBUTION NO. 436 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

## Cyanocarbon Chemistry. II.<sup>1</sup> Spectroscopic Studies of the Molecular Complexes of Tetracyanoethylene

BY R. E. MERRIFIELD AND W. D. PHILLIPS

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Complex-formation equilibrium constants and spectroscopic data for twenty-three  $\pi$ -complexes involving tetracyanoethylene and various aromatic molecules are presented. It is found that the free energies of formation of these  $\pi$ -complexes and the base ionization potentials are connected by the linear relation  $\Delta F^\circ = 0.0510I_p - 11,230$  cal. Comparison with such  $\pi$ -acids as maleic anhydride and chloranil reveals that tetracyanoethylene is the strongest  $\pi$ -acid yet examined. Discussions of solvent and geometrical effects in tetracyanoethylene  $\pi$ -complex formation are presented. Heats of formation of  $\pi$ -complexes between tetracyanoethylene and methylbenzenes are found to range from  $-2.3$  kcal. for benzene to  $-7.0$  kcal. for pentamethylbenzene.

### Introduction

Since the initial work of Benesi and Hildebrand

on the iodine/aromatic complexes,<sup>2</sup> there has been a great deal of theoretical and experimental interest in the nature of these and other non-ionic complexes.<sup>3</sup> The systems studied include com-

(1) Paper I, T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, Edith G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, *This Journal*, **80**, 2775 (1958).

(2) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

(3) For a general review of the subject, see L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

plexes of Br<sub>2</sub>,<sup>4a</sup> Cl<sub>2</sub>,<sup>4b</sup> ICl,<sup>5</sup> O<sub>2</sub><sup>6</sup> and SO<sub>2</sub><sup>7</sup> with various aromatic hydrocarbons. In addition to these complexes involving aromatic and small inorganic molecules, complexes between aromatic molecules and maleic anhydride<sup>8</sup> and oxalyl chloride<sup>9</sup> recently have been investigated.

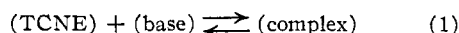
These complexes are characterized by an intense electronic absorption in the visible or near ultraviolet that is attributable to neither component of the complex alone, but to a new molecular species, the complex itself. Mulliken<sup>10</sup> considers such complexes to arise from a Lewis acid-base type of interaction, the bond between the components of the complex arising from partial transfer of a  $\pi$ -electron from the base (the aromatic molecule) to orbitals of the acid (I<sub>2</sub>, maleic anhydride, etc.).

One of the first characteristics of tetracyanoethylene (TCNE) noted after its initial synthesis<sup>1</sup> was the formation of intensely colored solutions when it was dissolved in aromatic solvents. These colored solutions were attributed to the formation of  $\pi$ -complexes between TCNE and the aromatic solvent. The results of analysis of the spectra of an extensive series of TCNE/aromatic complexes are presented below, along with a comparison of the relative acid strengths of TCNE and other known  $\pi$ -acids.

### Experimental

The visible and ultraviolet spectra were obtained by means of a Cary spectrophotometer. The TCNE was crystallized twice from chlorobenzene and sublimed twice at 125° (4 mm.). The organic materials employed as solvent or  $\pi$ -base were either best quality Eastman Kodak Co. or J. T. Baker Analyzed and were distilled at least once through an approximately 20-plate spinning band still. Heats of formation of the complexes were determined by measuring complex association constants at 6, 23 and 35°. Temperature control was achieved by means of a jacketed absorption cell through which thermostated water was circulated. The accuracy of temperature control was ca.  $\pm 0.5^\circ$ .

**I. Analysis of the TCNE/Aromatic  $\pi$ -Complex Spectra.**—Absorption spectra typical of TCNE/aromatic complexes are presented in Fig. 1. The concentration dependence of the electronic absorption spectra of these  $\pi$ -complexes was analyzed by the method of Keefer and Andrews.<sup>4</sup> If the complex is assumed to be 1:1, the association equilibrium may be written as



The association constant for complex formation,  $K$ , then is

$$K = \frac{(C)}{[(\text{TCNE}) - (C)][B] - [C]} \quad (2)$$

where (TCNE) and (C) are the molar concentrations of TCNE and complex, respectively, and [B] and [C] are mole fractions of base and complex, respectively. For the experimental conditions employed,  $[B] \gg [C]$  and the term  $[B] - [C]$  of eq. 2 may be replaced by [B]. Substituting

(4) A. R. M. Keefer and L. J. Andrews, *THIS JOURNAL*, **72**, 4677 (1950); (b) L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 462 (1951).

(5) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 5170 (1950).

(6) D. F. Evans, *J. Chem. Soc.*, 345 (1953).

(7) W. G. Barb, *Proc. Roy. Soc. (London)*, **A212**, 86 (1952).

(8) W. G. Barb, *Trans. Faraday Soc.*, **49**, 143 (1953).

(9) B. D. Saksena and R. E. Kagarise, *J. Chem. Phys.*, **19**, 994 (1951).

(10) R. S. Mulliken, *THIS JOURNAL*, **74**, 811 (1952).

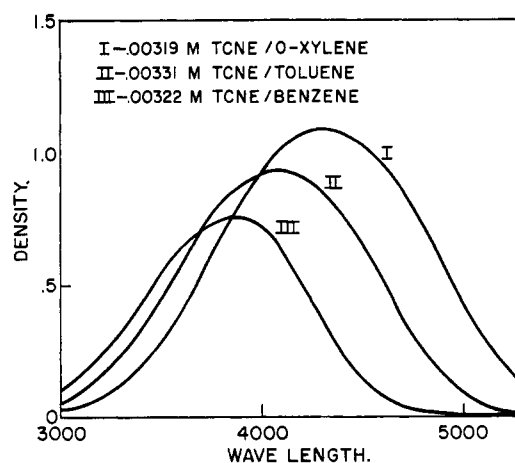


Fig. 1.—Charge transfer spectra for some TCNE/aromatic complexes.

$(\log I_0/I)/l\epsilon$  for (C) and rearranging eq. 2, we obtain the expression

$$y \equiv \frac{(\text{TCNE})l}{\log I_0/I} = \frac{1}{K\epsilon[B]} - \frac{1}{\epsilon} \quad (3)$$

where  $l$  is the cell length and  $\log I_0/I$  is the optical density.

If the complex is 1:1 as assumed in the derivation, a plot of  $y$  vs.  $1/[B]$  should be linear and yield  $\epsilon$  as the reciprocal of the intercept, and the product  $K\epsilon$  as the reciprocal of the slope. Some plots of  $y$  vs.  $1/[B]$  typical of the TCNE/aromatic complexes are presented in Fig. 2. The twenty-three TCNE/aromatic complex systems reported here (Table I) have all yielded linear plots, and complexes other than the simple 1:1, therefore, need not be considered.

TABLE I  
 $\pi$ -COMPLEXES FORMED BETWEEN TETRACYANOETHYLENE AND AROMATIC BASES (SOLVENT, CH<sub>2</sub>Cl<sub>2</sub>; TEMPERATURE, 22°)

$\pi$ -Base	K	$\lambda_{\max}$ (1), Å.	$\epsilon$ (1), cm. <sup>-1</sup> l. mole <sup>-1</sup>	$\lambda_{\max}$ (2), Å.	$\epsilon$ (2), cm. <sup>-1</sup> l. mole <sup>-1</sup>
Cyclohexene	0.247	4220	4,760	..	..
Benzene	2.00	3840	3,570	..	..
Toluene	3.70	4060	3,330	..	..
o-Xylene	6.97	4300	3,860	..	..
m-Xylene	6.00	4400	3,300	..	..
p-Xylene	7.64	4600	2,650	4150	2,770
Mesitylene	17.3	4610	3,120	..	..
Durene	54.2	4800	2,075	..	..
Pentamethylbenzene	123	5200	3,270	..	..
Hexamethylbenzene	263	5450	4,390	..	..
Hexaethylbenzene	5.11	5500	56	..	..
Diphenyl	4.09	5000	1,450	..	..
m-Terphenyl	5.50	5000	1,470	..	..
p-Terphenyl	11.4	5640	830	..	..
Tetraphenylethylene	17.8	6100	67	..	..
Naphthalene	11.7	5500	1,240	4290	1,120
Fluorene	18.0	5700	1,430	4160	1,060
Pyrene	29.5	7240	1,137	4950	856
Chlorobenzene	0.770	3790	3,840	..	..
Bromobenzene	0.611	3940	5,000	..	..
Iodobenzene	1.24	4500	2,500	..	..
Anisole	4.42	5070	2,080	3840	1,640
Pyridine	12.0	4215	10,500	4000	10,800

**II. Regularities in the TCNE/Aromatic Complexes.**—Association constants,  $K$ , wave lengths of maximum absorption,  $\lambda_{\max}$ , and extinction coeffi-

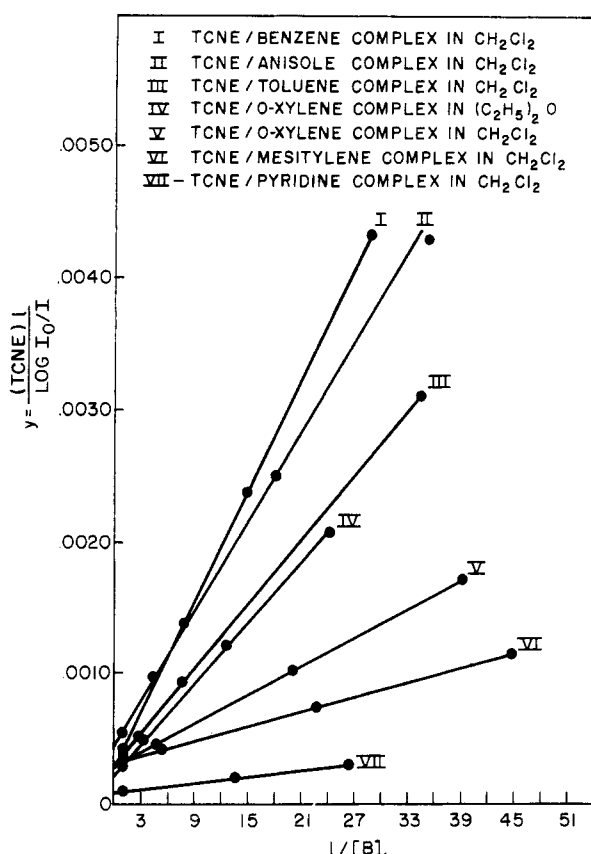


Fig. 2.—Determination of  $K$  and  $\epsilon$  for some TCNE/aromatic complexes.

cients for maximum absorption,  $\epsilon$ , for twenty-three TCNE/aromatic complexes are listed in Table I. In six instances, two absorption maxima ascribable to the TCNE/aromatic complex are observed. These instances are discussed in Section VII. For a series of methylbenzenes, there is a progressive increase of  $K$  and  $\lambda_{\max}$  with increasing methylation. McConnell, Ham and Platt<sup>11</sup> have found that a plot of  $\bar{\nu}_{\max}$  vs. base ionization potential for a series of complexes of  $I_2$  with  $n$ - and  $\pi$ -bases yields a straight line. The frequency of maximum absorption,  $\bar{\nu}_{\max}$  the base ionization potential,  $I_p$ , and the free energy of formation,  $\Delta F^0$ , are listed for seven TCNE/aromatic complexes in Table II. A fair linearity exists between  $\bar{\nu}_{\max}$  and  $I_p$  for the methylbenzenes. However, the results for naphthalene must be ignored. A plot of  $\bar{\nu}_{\max}$  vs.  $I_p$  for the methylbenzenes yields the empirical relationship

$$\bar{\nu}_{\max} = 0.487I_p - 1.30 \text{ (e.v.)} \quad (4)$$

A more satisfactory empirical relationship exists between the free energy of formation of the complexes  $\Delta F^0$  and  $I_p$ , as shown in Fig. 3. For the seven aromatic compounds for which ionization potentials are available, the relationship between  $\Delta F^0$  and  $I_p$  is seen to be quite linear. Even the rather subtle differences between the ionization potentials of the xylene isomers are reflected sensitively in the values of  $\Delta F^0$ . The straight line plot

(11) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

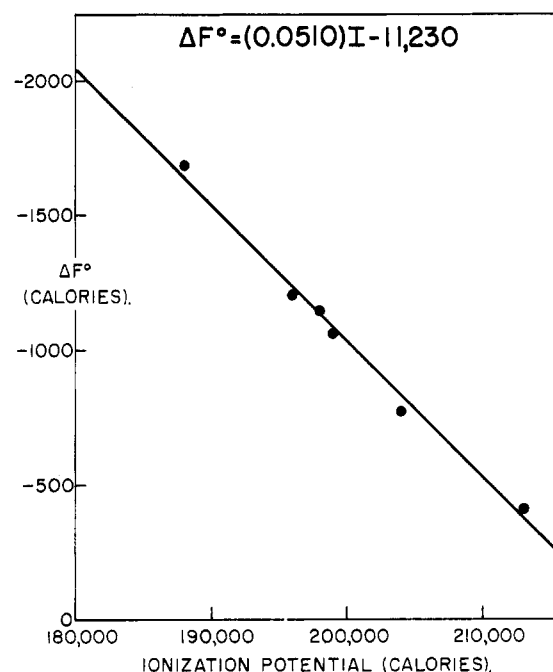


Fig. 3.—Relationship between  $\Delta F^0$  and  $I_p$  for some TCNE/aromatic complexes.

TABLE II

SPECTRAL, ELECTRONIC AND THERMODYNAMIC CHARACTERISTICS OF SOME TCNE/AROMATIC  $\pi$ -COMPLEXES

$\pi$ -Base	$\bar{\nu}_{\max}$ , cm. <sup>-1</sup>	$I_p$ , e.v.	$\Delta F^0$ , cal.
Benzene	26,000	9.24	-411
Toluene	24,900	8.82	-773
<i>o</i> -Xylene	23,300	8.58	-1150
<i>m</i> -Xylene	22,700	8.6	-1060
<i>p</i> -Xylene	21,800	8.48	-1200
	24,100		
Mesitylene	21,700	8.14	-1690
Naphthalene	18,200	8.3	-1460

of Fig. 3 may be expressed by the empirical relationship

$$\Delta F^0 = 0.0510I_p - 11,230 \text{ cal.} \quad (5)$$

A plot such as that of Fig. 3 should be of value in predicting values of  $K$  for TCNE/aromatic complexes for known values of base ionization potentials. Conversely, if  $K$  for the complex is measured,  $I_p$  can be estimated from eq. 5. In view of the difficulty of obtaining experimental values of  $I_p$  and their great theoretical importance, the prediction of  $I_p$  from measured values of  $K$  should be of value.

**III. Comparison of  $\pi$ -Acid Strengths.**—Values of  $K$ ,  $\lambda_{\max}$  and  $\epsilon$  for a series of complexes involving the base, pyrene and five  $\pi$ -acids are presented in Table III. McConnell, Ham and Platt<sup>11</sup> noted a linear relationship between  $\epsilon$  and  $\lambda_{\max}$  for a series of  $\pi$ -complexes involving benzene and acids such as  $I_2$ ,  $Br_2$  and  $Cl_2$ . A general, though not linear, relationship between not only  $\epsilon$  and  $\lambda_{\max}$  but between  $K$ ,  $\epsilon$  and  $\lambda_{\max}$  is apparent from the results of Table III. The values of  $K$ ,  $\lambda_{\max}$  and  $\epsilon$  are greater for TCNE than for any of the other four  $\pi$ -acids studied. If the charge-transfer theory of  $\pi$ -

complex formation of Mulliken<sup>10</sup> is correct, this result would suggest that TCNE possesses a greater electron affinity than any of the other  $\pi$ -acids. However, in lieu of any experimental information on the electron affinities of these acids, little can be deduced about the electronic structures of these molecules from consideration of relative  $\pi$ -acid strengths. There is, however, a structural feature common to these acids that is perhaps worth noting. The structural pattern of each of these  $\pi$ -acids may be described as being that of an ethylenic group bonded to highly electronegative substituents. For example, TCNE may be considered to be ethylene substituted by four cyano groups, and quinone, two ethylene molecules bonded to two common carbonyl groups. Crudely, these highly electronegative substituents may be considered to be effective in withdrawing charge from the ethylenic groups. Such charge withdrawal might be expected to enhance the electron affinity of the ethylenic group, and, therefore, its  $\pi$ -acid strength.

TABLE III

COMPARISON OF  $\pi$ -ACID STRENGTHS $\pi$ -Base, pyrene in all cases; solvent,  $\text{CH}_2\text{Cl}_2$ ; temperature, 22°

$\pi$ Acid	$K$	$\lambda_{\text{max}}$ , Å.	$\epsilon$ , cm. <sup>-1</sup> mole <sup>-1</sup> l.
Tetracyanoethylene	29.5	7240	1137
Chloranil	23.3	6100	943
Maleic anhydride	17.6	4500	76.3
1,2-Dicyano-1,2-dicarbethoxyethylene	17.0	5000	253
<i>p</i> -Quinone	14.4	4530	323

**IV. The Effect of Solvent on Complex Formation Equilibrium Constants.**—The data given in Table IV show that the value of the complex-formation equilibrium constant is markedly affected by variation of the solvent in which the measurements are carried out. This effect is believed to be due to the formation of a competitive complex between the  $\pi$ -acid and the solvent. This hypothesis is substantiated by the observation of a weak absorption band at 3350 Å. in the absorption spectrum of TCNE in diethyl ether solution that is not present in the spectrum of either component separately. This band is attributed to

TABLE IV

EFFECT OF SOLVENT ON COMPLEX-FORMATION EQUILIBRIUM CONSTANTS

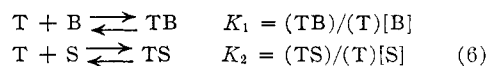
 $\pi$ -Acid: TCNE in all cases

Base	Solvent	$K_{\text{obsd.}}$	$K_{\text{calcd.}}$	$\epsilon_{\text{obsd.}}$ , cm. <sup>-1</sup> mole <sup>-1</sup> l.	$\epsilon_{\text{calcd.}}$ , cm. <sup>-1</sup> mole <sup>-1</sup> l.
Et <sub>2</sub> O	$\text{CHCl}_3$	1.54 <sup>a</sup>		1100	
$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$		0.21		
<i>o</i> -Xylene	$\text{CHCl}_3$	9.46	9.03	3820	3680
	$\text{CH}_2\text{Cl}_2$	6.97		3860	
	Et <sub>2</sub> O	2.95		4430	
<i>p</i> -Xylene	$\text{CHCl}_3$		9.10		2480
	$\text{CH}_2\text{Cl}_2$	7.64	6.94	2640	2650
	Et <sub>2</sub> O	2.80		3160	
Anisole	$\text{CHCl}_3$		5.48		2050
	$\text{CH}_2\text{Cl}_2$	4.42	4.37	2080	2130
	Et <sub>2</sub> O	1.55		2860	

<sup>a</sup> The italicized quantities are those employed in calculating the numbers in the fourth and sixth columns.

a TCNE/Et<sub>2</sub>O complex and, accordingly, a series of TCNE/Et<sub>2</sub>O/ $\text{CHCl}_3$  solutions have been subjected to the usual analysis and yield a value of  $K$  of 1.54 for the TCNE/Et<sub>2</sub>O complex referred to a  $K$  of zero for the TCNE/ $\text{CHCl}_3$  interaction.

In order to estimate the effect of this interaction on the observed value of  $K$ , two competitive equilibria are considered



where T = TCNE, B = aromatic base and S = solvent. Then an analysis similar to the derivation of eq. 3 yields the relation

$$\frac{(\text{T})l}{D_{\text{TB}}} = \frac{1 + K_2}{\epsilon K_1} \times \frac{1}{[\text{B}]} + \frac{1}{\epsilon} \left(1 - \frac{K_2}{K_1}\right) \quad (7)$$

where  $l$  is the absorption cell length and  $D_{\text{TB}}$  is the optical density of the TCNE/aromatic complex absorption band. Comparing this with eq. 3 and denoting the  $\epsilon$  and  $K$  derived from that equation by  $\epsilon_0$  and  $K_0$ , one obtains the relations

$$\begin{aligned} K_0 &= \frac{K_1 - K_2}{1 + K_2} \\ \epsilon_0 &= \frac{K_1}{K_1 - K_2} \epsilon \end{aligned} \quad (8)$$

These equations show that the  $K$  and  $\epsilon$  calculated from eq. 3 are functions of  $K_2$ , the interaction with the solvent. If a standard solvent was chosen from which it is assumed that  $K_2 = 0$ , then eqs. 8 allow prediction of  $K_0$  and  $\epsilon_0$  in any solvent for which  $K_2$  is known. Table IV shows the results of such a calculation with  $\text{CHCl}_3$  as the standard solvent.

From these results it seems fair to conclude that the assumption of a competitive TCNE/solvent complex accounts for the major part of the apparent variation of complex-formation equilibrium constants with solvent.

**V. Geometrical Structures of  $\pi$ -Complexes.**—The experimental results herein reported allow one to draw some conclusions regarding the geometrical structures of these complexes. The striking increase in complex strength with successive methylation of the base of TCNE/methylbenzene complexes provides strong evidence against an edge-to-edge model for the complexes, since the steric hindrance of the additional methyl groups would be expected to reduce markedly the stability of such a structure.

The most attractive model for these complexes is a sandwich structure in which the two components lie parallel to each other. Such an arrangement would allow maximum overlap between the  $\pi$ -molecular orbitals of the two components. A sandwich structure would also provide an explanation of the strikingly low stability of the TCNE/ $\text{C}_6\text{Et}_6$  complex as compared to TCNE/ $\text{C}_6\text{Me}_6$ . From the van der Waals radii, it is possible to estimate the distance of closest approach between  $\pi$ -acid and base; for  $\text{C}_6\text{Me}_6$ , this distance is 3.5 Å., while for  $\text{C}_6\text{Et}_6$ , it is 5.0 Å. Since the exchange matrix elements responsible for the binding energy of the complex<sup>10</sup> fall off so rapidly with distance,  $\text{C}_6\text{Et}_6$  would be expected to form a much less stable complex with TCNE than does  $\text{C}_6\text{Me}_6$ .

This hypothesized structure for the complexes in solution is consistent with the results of Harding and Wallwork<sup>12</sup> who found a very similar structure for the chloranil/C<sub>6</sub>Me<sub>6</sub> complex in crystalline form, using X-ray methods.

**VI. Heats of Formation of TCNE/Methylated Benzene Complexes.**—The heats of formation of some TCNE/methylbenzene complexes have been measured through the temperature dependence of the complex-formation equilibrium constants. The equilibrium constants and extinction coefficients at room temperature were determined spectroscopically from the concentration dependence of the optical density of the complex as outlined in Section I. If it is assumed that the extinction coefficient is independent of temperature, then the equilibrium constant at other than room temperature can be determined by means of eq. 3 from a single observation of the optical density. The heats of formation measured in this manner are given in Table V.

TABLE V  
HEATS OF FORMATION OF TCNE/AROMATIC COMPLEXES  
 $\pi$ -Acid: TCNE in all cases

Base	K	$-\Delta H^\circ$ , kcal. mole <sup>-1</sup>
C <sub>6</sub> H <sub>6</sub>	2.00	2.30
C <sub>6</sub> H <sub>5</sub> Me	3.70	2.72
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me <sub>2</sub>	7.64	3.37
<i>s</i> -C <sub>6</sub> H <sub>3</sub> Me <sub>3</sub>	17.3	4.52
<i>p</i> -C <sub>6</sub> H <sub>2</sub> Me <sub>4</sub>	54.2	5.07
C <sub>6</sub> HMe <sub>5</sub>	123	6.97

These values may be compared with heats of formation of  $-1.4$  kcal. for the I<sub>2</sub>/benzene complex<sup>13</sup> and 0 to  $-1.5$  kcal. for the complexes of chloranil with substituted styrenes.<sup>14</sup> Thus, the heat of formation measurements substantiate the conclusion drawn from the complex-formation equilibrium constants, *viz.*, that TCNE is the strongest of the  $\pi$ -acids listed in Table III.

**VII. Fine Structure and Width of Complex Absorption Bands.**—The absorption spectra of the TCNE/methylbenzene complexes show unusual variations in fine structure and band width as illustrated in Table VI. Particularly striking are the doublet in *p*-xylene and the broad flat band having the appearance of an unresolved doublet in durene. Since the highest filled  $\pi$ -orbital in benzene is

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TABLE VI  
BAND WIDTHS FOR TCNE/POLYMETHYLBENZENE COMPLEXES

$\pi$ -Base	Half-width, cm. <sup>-1</sup>	Doublet separation, cm. <sup>-1</sup>	Calcd. width or separation, cm. <sup>-1</sup>
C <sub>6</sub> H <sub>6</sub>	5800		5800
C <sub>6</sub> H <sub>5</sub> Me	6800		6800
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Me <sub>2</sub>	6400		6800
<i>m</i> -C <sub>6</sub> H <sub>4</sub> Me <sub>2</sub>	6400		6800
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me <sub>2</sub>		2350	2000
<i>s</i> -C <sub>6</sub> H <sub>3</sub> Me <sub>3</sub>	5600		5800
<i>p</i> -C <sub>6</sub> H <sub>2</sub> Me <sub>4</sub>		2000	2000
C <sub>6</sub> HMe <sub>5</sub>	5800		6800
C <sub>6</sub> Me <sub>6</sub>	5500		5800

doubly degenerate and this degeneracy can be split by ring substitution, the hypothesis is suggested that the spectral splitting is a result of transitions from the ground state of the complex to excited states formed by transfer of electrons from each of the components of the split degenerate level and that the wide bands are a result of unresolved splitting.

This hypothesis is easily tested by calculating the splittings of the  $E_{1g}$  level of benzene produced by methyl substitution. First-order perturbation theory applied to the LCAO approximation of molecular orbital theory gives the relation<sup>15</sup>

$$\delta\epsilon_i = \sum_j c_{ij}^2 \delta\alpha_j \quad (9)$$

where  $\delta\epsilon_i$  is the first-order correction to the energy of the  $i$ -th molecular orbital,  $c_{ij}$  is the coefficient of the  $j$ -th atomic orbital in the  $i$ -th molecular orbital, and  $\delta\alpha_j$  is the perturbation in the coulomb integral of the  $j$ -th atom. The empirical value of  $\delta\alpha$  produced by methyl substitution may be set at *ca.* 4000 cm.<sup>-1</sup>.<sup>16</sup> For the unresolved bands the half-width is estimated by adding the splitting calculated from eq. 9 to the observed half-width for the TCNE/benzene complex. For *p*-xylene and durene the calculated splitting is obtained from eq. 9 directly. The comparison between the splittings calculated in this manner and the observed band widths is shown in Table VI. Considering the crude nature of the model, the agreement is quite reasonable.

A similar analysis of the band widths in chloranil/methylbenzene and halogen/methylbenzene complexes has been given by Orgel.<sup>17</sup>

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