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Π-MOLECULAR COMPLEXES—III[1]

A CRITIQUE OF CHARGE-TRANSFER, AND STABILITY CONSTANTS FOR SOME TCNE-HYDROCARBON COMPLEXES[2]

M. J. S. DEWAR† and C. C. THOMPSON, JR.[3]
Department of Chemistry, The University of Texas, Austin,
Texas 78712, U.S.A.

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Abstract—Errors and misconceptions arising from Mulliken's treatment of π-molecular complexes are discussed. Attention is drawn to the common misuse of the term charge-transfer complex to describe complexes in which the importance of charge transfer forces has not been established. It is pointed out that information concerning the importance of charge transfer forces can best be obtained from measurements of stability constants of complexes formed by unsubstituted aromatic hydrocarbons. Measurements of this kind are reported for the complexes formed by fourteen such hydrocarbons with TCNE (tetracyanoethylene). The results do not indicate any major contribution to binding by charge-transfer forces.

INTRODUCTION

THE purpose of this series of papers is to elucidate the structures of the loose complexes formed by association of unsaturated or aromatic organic compounds; the materials that classical organic chemists called molecular complexes and that have since been variously described as π-complexes, charge transfer complexes, donor-acceptor complexes, etc.[4] As all these terms are open to objection,[5] here we will describe complexes of this type as *π-molecular complexes*, using the term in a neutral way to indicate a class of compounds with no implications concerning their electronic structure.

Two general views have been put forward concerning the structure of these complexes. According to the first,[6] they should be regarded as very strong van der Waals complexes, their heats of formation being large because the components are very polar and/or very polarizable. According to the second,[4] they should be regarded as a special kind of donor-acceptor complex, held together by charge transfer forces; if the donor component is A, and the acceptor B, then the stability of the complex is attributed to resonance between the structures (A, B) and (A^+, B^-).

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† This work is dedicated to the memory of Professor H. Stephen.

[1] Part I: M. J. S. Dewar and H. Rogers, *J. Amer. Chem. Soc.* **84**, 395 (1962).

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[3] Present address: Department of Chemistry, Marshall University, Huntington, West Virginia 25701, U.S.A.

[4] For an excellent review see G. Briegleb, *Elektronen-Donator-Acceptor-Komplexe*. Springer-Verlag, Berlin (1961).

[5] The term molecular complex is too vague, since other types of complexes involving neutral molecules are known (e.g. hydrogen bonded complexes). The term π-complex should properly be reserved for cases where a π-donor and a π-acceptor are linked by a covalent bond (i.e. inner complexes, in Mulliken's terminology). The terms charge transfer complex, and donor-acceptor complex, are open to objections that are discussed in detail below.

[6] This view was ably presented by G. Briegleb in his first monograph on the subject: *Zwischenmolekulare Kräfte und Molekülstructur*. Stuttgart (1937).

The UV–visible absorption spectra of π-molecular complexes commonly differ from those of their components in that new bands appear at lower frequencies; as a result, striking color changes are often observed when the complexes are formed. Mulliken[7] first explained these bands in terms of charge transfer transitions; this is undoubtedly correct. However he linked this explanation with his interpretation of them as donor-acceptor complexes; because of this association, the idea has been somewhat uncritically adopted. Complexes of this type are now commonly described in the literature as charge transfer complexes, and it is clear that most authors accept the view that charge transfer is the main factor responsible for the binding in them.

This association of ideas has, however, no basis in fact. The only requirement for a charge transfer transition to occur with significant intensity is that the species involved should be close together. A transition of this type could occur equally well if the components in the complex (A, B) were held together by simple Van der Waals forces; indeed, analogous transitions are commonly observed in cases where no complex whatsoever is formed, the participating molecules merely happening to be close together (contact charge transfer spectra).[8] The existence of a charge-transfer spectrum in a solution of two components A, B, cannot therefore be taken as evidence for the formation of *any* kind of complex between them; and if a complex (A, B) is formed, the appearance of a charge-transfer spectrum provides no evidence that charge-transfer plays a dominant, or even a significant, role in the binding.

The commonly accepted picture of van der Waals forces dissects them into contributions by interactions of three types:

(a) In the case of polar molecules, there are simple electrostatic interactions, e.g. dipole-dipole forces.

(b) In the case where one of the participating molecules is polar, there are forces due to electrostatic polarization of the second component, e.g. dipole-induced dipole forces.

(c) In the case where neither molecule is polar, there are forces due to instantaneous electrostatic attractions due to electron correlation (Heitler-London dispersion forces).

This picture is equivalent to treating the complex (A, B) by perturbation theory; we expand the wave function of the complex in terms of wave functions corresponding to possible states of an idealized system $(A + B)$ in which the two components are independent of one another, and we calculate the coefficients of the various terms, and their contribution to the total interaction energy, by perturbation theory. This should be a very satisfactory representation in the case we are considering; for the heats of formation of π-molecular complexes are small ($\sim 0{\cdot}2$ ev).

First order perturbation theory neglects changes in the wave function of the perturbed system, the energy being calculated using the unperturbed wave function together with the perturbed Hamiltonian. In our case this contribution to the binding energy in (A, B) corresponds to the simple electrostatic interactions, (a) above.

The second order perturbations correspond to perturbations of the ground state wave function; in physical terms, these correspond to a mutual electrostatic polarization of the components A, B, (b) above, and to the special type of interaction corresponding to the Heitler-London forces, (c) above. These are represented by

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[7] R. S. Mulliken, *J. Amer. Chem. Soc.* **74**, 811 (1952); *J. Phys. Chem.* **56**, 801 (1952).

[8] L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.* **79**, 4839 (1957).

mixing the ground state function of the unperturbed system $(A + B)$ with functions corresponding to excited states. Now the excited state functions are of two kinds; first there are locally excited functions of the type $(A^* + B)$, $(A + B^*)$, where A^*, B^* represent excited states of the individual molecules A, B; secondly, there are charge transfer states, e.g. $(A^+ + B^-)$ or $(A^- + B^+)$, corresponding to situations where electrons have been transferred between the components. Here again the corresponding effects can be visualized in physical terms.

The contribution of a given excited state i to the perturbed wave function is given by:

$$\frac{P_{io}}{E_o - E_i} \tag{1}$$

where E_o, E_i are respectively the energies of the unexcited state $(A + B)$ and of the excited state, and P_{io} is a measure of the interaction between them; the contribution of excited states is therefore in general greater, the smaller the difference in energy $(E_o - E_i)$. In the case of unsaturated molecules, the main contribution therefore comes from π-excited states; for the excitation energies of these are low. Let us first consider the effect of mixing a locally π-excited state $(A^* + B)$ with the ground state $(A + B)$. In the resulting combination A remains neutral, and the cloud of π-electrons is still symmetrical with respect to reflection in a plane containing the nuclei of the conjugated atoms in A. However the distribution of charge parallel to this plane now differs from that in the unexcited state $(A + B)$. By including structures of this kind, we therefore allow for polarization of the π-electrons parallel to the nodal plane. This is indicated diagrammatically in Fig. 1a; the indicated polarization of the π-electrons in A leads to a net attraction by piling up negative charge in positions opposite positively charged regions in B, and positive charge in positions opposite negatively charged regions of B.

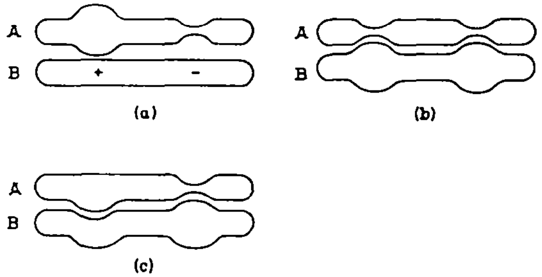

FIG. 1. Diagrammatic representation of polarization effects in the complex (A, B); (a), polarization repesented by contributions of locally excited states; (b), polarization represented by contributions of charge transfer states $(A^+ + B^-)$; (c), overall polarization, corresponding to contributions by states of all types.

Now we have also to consider a second type of polarization, in which there is a general displacement of π-electrons from A to B, or from B to A. This cannot be represented in terms of locally excited states, since these leave the π-clouds of A and B symmetrical. Displacements of this type can, however, be taken into account by including charge transfer states; contributions by such a state $(A^+ + B^-)$ leave the net electron density in the region between A and B unchanged, but increase the electron density in outward-facing π-lobes of B at the expense of that in the outward-facing π-lobes of A (Fig. 1b). Of course there are also charge transfer states of the type $(A^- + B^+)$ to be considered; including these we can allow quite effectively for all polarization effects, both parallel, and perpendicular, to the nodal planes of the π-electrons in the complex (A, B).

This discussion shows very clearly that charge transfer-forces do not differ in kind from other van der Waals interactions, in direct contradiction of the view apparently held by many chemists. This misunderstanding originated from Mulliken's use of resonance notation to represent charge transfer forces, and his failure to extend the same notation to other types of van der Waals interactions; he represented the complex between A and B as a hybrid of the ground state $(A + B)$, and of the charge-transfer state $(A^+ + B^-)$, but failed to include the contributions of locally excited states such as $(A^* + B)$ or $(A + B^*)$.

The dissection of van der Waals forces into these various contributions is of course artificial; nevertheless it may be useful to distinguish cases in which one or other of them appears to dominate. Thus the forces between small highly polar molecules (e.g. trimethylamine oxide) can conveniently be described in terms of dipole-dipole attractions, and those between neutral saturated molecules (e.g. paraffins) in terms of dispersion forces. In this sense it may be convenient to distinguish cases where the binding is due mainly to charge-transfer forces, i.e. to the special type of polarization that is represented in terms of contributions by charge transfer states.

It is clear from the literature that most organic chemists have used the term "charge-transfer complex" to denote systems of this kind—and this also seems to be the sense in which Mulliken himself meant the term to be understood, judging by the following quotation from a recent paper.[9] "Similarly in certain other cases, for example π,π-complexes between donors and acceptors which contain strong local dipoles, it is possible that classical electrostatic forces may be comparable with, or greater than, charge-transfer forces. Hence in general the term "donor-acceptor complexes" seems preferable to "charge-transfer complexes"."

The use of the term charge-transfer complex in this sense is certainly legitimate and may be useful; unfortunately the situation has been bedevilled by the misunderstanding indicated above, i.e. the widespread belief that if a complex shows a charge-transfer spectrum, then it must be a charge-transfer complex. Consequently the term has been widely misused in the literature, being freely applied to systems where the nature of the binding is in fact quite uncertain.

π-Molecular complexes presented a puzzling problem to classical organic chemists. The striking color changes that commonly accompany their formation seemed to imply some radical change in chemical binding; yet in most cases it was difficult to see how any normal bonds could be established between the components, and the heats of formation of such complexes were moreover known to be small in relation to the strengths of chemical bonds. Mulliken's contribution was to point out a mechanism whereby drastic changes in light absorption might take place in such cases without any accompanying change in molecular structure. Once this had been made clear, the formation of such complexes no longer presented any problem; for

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[9] R. S. Mulliken, *J. Chim. Phys.* **61**, 20 (1964).

Briegleb[6] had shown many years ago that their heats of formation are of the order of magnitude that would be expected for normal van der Waals complexes formed by large polarizable molecules. Admittedly this work has not received the attention it deserved, and many chemists are clearly still under the impression that dispersion forces, and multipole-induced multipole forces, are too weak to account for the binding in complexes of this kind.

It is true that almost all known π-molecular complexes do show significant charge-transfer absorption; it might then be argued that the term "charge-transfer complex" could be usefully applied to them to signal this fact, regardless of the nature of the binding forces involved. However we are dealing here with a classic case of artificial selection of data. Nearly all the work in this field has been done using spectroscopic methods; these can only detect complexes that differ markedly from their components in light absorption. Very few systems have been studied using other techniques, since these are much more laborious. Two such examples are the 1:1 complex of nitrobenzene and *s*-trinitrobenzene, detected by thermal analysis of melts,[10] and complexes of methyl l-naphthoate with various ions and aromatic compounds, detected by changes in the rate of ester hydrolysis.[11] It seems very likely that many other similar complexes may have escaped detection because they are formed in systems where charge-transfer absorption cannot be observed.

As the passage quoted above from Ref. 9 indicates, Mulliken now prefers to regard π-molecular complexes as a special subdivision of his general category of donor-acceptor complexes. In recent papers he has developed an elaborate nomenclature and classification of this general category,[12] which comprises the whole range from weak van der Waals aggregates to coordination compounds such as $\overset{-}{B}F_3—\overset{+}{N}H_3$ in which the components are held together by definite covalent bonds.

The introduction of any new term into organic chemistry can be justified only if it fulfils a very real need; we do not feel that Mulliken's system meets this criterion, or even that it offers any advantages over the accepted terminology of organic chemistry. Indeed, his use of the term donor-acceptor complex in so general a sense, to denote a complex (A, B) in which there is *any* transfer of charge from A to B, or from B to A, seems to us likely to cause serious misunderstandings; for the terms "donor" and "acceptor" have well established chemical connotations, such that the term "donor-acceptor complex" would normally be taken to imply a complex in which the binding is of essentially dative type.

Criteria for charge-transfer complexes

In terms of the perturbation treatment outlined above, the energy of formation (ΔE) of a complex (A, B) from its components can be written approximately as:

$$\Delta E = [(A + B), (A + B)] + \sum_i \frac{[(A + B), (A + B)_i{}^*]^2}{E_o - F_i} + \sum_j \frac{[(A + B), (A + B)_j{}^\pm]^2}{E_o - G_j} \qquad (2)$$

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[10] D. L. Hammick, L. W. Andrew, and J. Hampson, *J. Chem. Soc.* 171 (1932).

[11] E. F. J. Duynstee and E. Grunwald, *Tetrahedron* **21**, 2401 (1965).

[12] See R. S. Mulliken, *J. Phys. Chem.* **56**, 801 (1952); *J. Chim. Phys.* **51**, 341 (1954); *Rec. Trav. Chim.* **75**, 845 (1956); *J. Chim. Phys.* **61**, 20 (1964).

where the brackets indicate matrix elements between the various states of the unperturbed system, $(A + B)$ represents the unperturbed ground state of energy E_o, $(A + B)_i{}^*$ is the ith locally excited state of energy F_i, and $(A + B)_j{}^\pm$ is the jth charge-transfer state of energy G_j.

The first term in Eq. (2) represents the classical electrostatic interactions in cases where both A and B are polar. The first sum represents the standard second order van der Waals terms, i.e. multipole-induced forces and dispersion forces. The final sum represents the contribution due to charge transfer. Our object is to try to find some way of assessing the importance of this last contribution.

The most obvious approach would be to evaluate the various terms in Eq. (2) directly, using wave-functions etc. calculated for the individual components and their ions and excited states. Unfortunately this is not feasible in practice, since the necessary information is not available. Even the first ("classical") term is inaccessible; for no reliable methods are available for calculating or measuring charge distributions in complex polar molecules.

We can of course simplify the problem by making one of the components a molecule of low polarity; in this case the classical term may be small enough to be unimportant. Clearly the best choice of this kind would be a series of complexes formed by unsubstituted aromatic hydrocarbons; however compounds derived from such hydrocarbons by the introduction of relatively non-polar substitutents (e.g. alkyl) should also meet the requirements.

The terms representing multipole-induced multipole and dispersion forces can be estimated roughly from measured polarizabilities and the Heitler-London approximation. Briegleb[6] in this way showed that forces of this kind are of the required order of magnitude to account for the observed heats of formation of complexes such as naphthalene-trinitrobenzene; however calculations of this kind cannot hope to give results of more than semiquantitative value.

If we are concerned only with establishing the existence of charge transfer forces, we can simplify the problem further by choosing as A a series of weakly polar substituted benzenes, and for B a typical π-complexing agent such as trinitrobenzene. Here the molecules A differ little in size and polarizability; consequently the contributions of the conventional van der Waals forces should not vary much along the series. If the classical term can be neglected, variations in ΔE should then be due to changes in the charge-transfer contributions.

In this case the most important term should be that corresponding to the lowest charge-transfer state; moreover the numerator of the corresponding term in Eq. (2) should vary little along the series, in view of the similarity between the A components. The energy difference in the denominator should be approximately equal to the excitation energy for the first charge transfer transition; this is given by $h\nu$, when ν is the frequency of the first charge-transfer band. Thus we might expect an approximate relation to hold between ΔE and ν, of the form:

$$\Delta E = \frac{C}{\nu} + D = C'\lambda + D \tag{3}$$

where C, C' and D are constants, and λ is the wavelength of the first charge-transfer band. If we now make the usual assumption[13] that in a series of this kind, the

[13] cf. M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.* 2796 (1956).

variations in the equilibrium constant K are due to changes in the energy, rather than the entropy of reaction, then Eq. (3) becomes:

$$\log K/K_0 = C''(\lambda - \lambda_0) \tag{4}$$

when K_0, λ_0 are values of K, λ for one standard molecule (e.g. benzene), and C'' is a constant. Relationships of this kind have been shown to hold for complexes formed by methylbenzenes with various complexing agents, although they have not always been expressed in this form; thus Fig. 2 shows a such plot for the values of K and λ reported by Merrifield and Phillips[14] for complexes formed with TCNE (tetracyanoethylene). The fact that Eq. (4) is obeyed reasonably well in systems of this kind

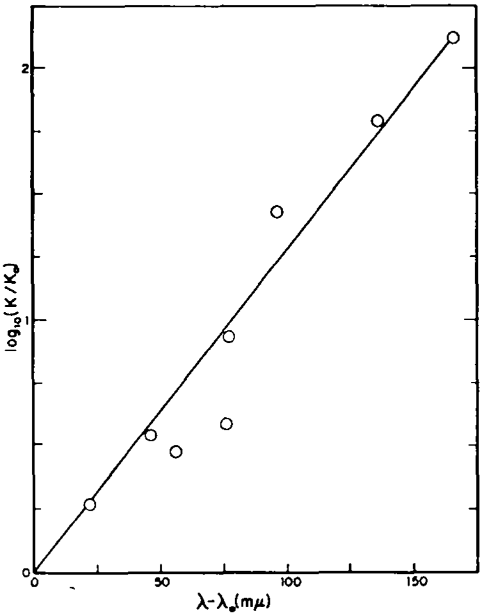

FIG. 2. Plot of Eq. (4) for TCNE methylbenzene complexes.

suggests rather strongly that the variations in K are indeed due mainly to variations in charge-transfer forces. Of course these results give no indication of the magnitude of these relative to the "normal" van der Waals forces; the exclusive dependence on charge transfer arises because we have taken pains to remove other sources of variation in K.

The success of this approach suggests that similar plots might be used to assess charge-transfer in other cases; if the charge-transfer terms in (2) dominate, and if the corresponding matrix elements $[(A, B), (A, B)^+]$ are more or less constant, then a plot of $\log K/K_0$ vs. $(\lambda - \lambda_0)$ should be approximately linear for complexes of all kinds. As Briegleb has emphasized[4] no such relation holds in cases where A is chosen arbitrarily; plots of this type give scatter diagrams.

It is of course possible that the failure of Eq. (4) is due to variations in the matrix elements $[(A + B), (A + B)^{\pm}]$, and that charge-transfer forces are still the main factor in binding; however this is beside the point. The term "charge-transfer complex"

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[14] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.* **80**, 2778 (1958).

should only be used to describe systems in which charge-transfer has been *demonstrated* to dominate, just as use of the term "salt" carries a definite connotation that the system in question is known to be composed of ions. Since no satisfactory alternative method has been devised for assessing the importance of charge-transfer forces, and since the approach indicated here fails to establish their importance in the case of π-molecular complexes, we must conclude that such complexes should not be described as charge-transfer complexes.

One possible escape might be provided by the remark quoted above from Ref. 9; perhaps the trouble is caused mainly by classical multipole-multipole interactions, given that stability constants have been measured mostly for complexes in which both components are polar. If so, we should be able to avoid this complication by studying complexes in which one component is essentially non-polar e.g. a hydrocarbon. Data for such systems are unfortunately scanty—a surprising circumstance in view of the fact that complexes of this kind are among the most familiar of π-molecular complexes. The values that are available[4] do not seem to conform to Eq. (4)—but they are too few for definite conclusions to be drawn.

We therefore decided to measure stability constants for a wide range of unsubstituted aromatic hydrocarbons with a given complexing agent, to see how far the results would conform to Eq. (4). For the complexing agent we chose tetracyanoethylene, for two reasons. First, the corresponding charge-transfer bands appear at long wavelengths; it is therefore easy to determine stability constants by standard spectroscopic methods, without interference due to overlapping of the charge-transfer bands with bands due to locally excited transitions. Secondly, tetracyanoethylene is a small, relatively non-polarizable molecule with a very high electron affinity; here one would expect the dice to be loaded heavily in favor of the charge-transfer forces. If complexes of this kind fail to conform to Eq. (4), there would be little hope of any other molecular π-complexes doing so.

EXPERIMENTAL

Materials. The source of materials used, and methods of purification and/or characterization, are indicated in Table 1. Chloroform was purified by extraction (5 times) with water, passed through a column of basic alumina, and distillation; it was stored in the dark under oxygen-free nitrogen and used within 24 hr.

Spectroscopic measurements. All spectra were measured in chloroform at 25° with a Beckman DA 2A spectrophotometer, using a thermostatted cell holder and matched 1 cm silica cells. The accuracy and reproducibility of the absorption measurements were determined to be better than 1 % by calibration with standard solutions of alkaline potassium chromate.

Systems studied. Table 2 shows the systems studied; where equilibrium constants were calculated, measurements were made for at least eight different concentrations of reactants at each wavelength. Solutions of each of the hydrocarbons dissolved in $CHCl_3$ were scanned over the same wave length range as the corresponding complex with TCNE, and corrections were made for free hydrocarbon absorption.

Calculations of stability constants. For the reversible reaction of two molecules A, B to form a complex AB, the equilibrium constant K may be written:

$$K = \frac{C_C}{(C_A{}^\circ - C_C)(C_B{}^\circ - C_C)} \tag{3}$$

where C_C is the equilibrium concentration of the complex and $C_A{}^\circ$ and $C_B{}^\circ$ are initial concentrations of A and B respectively. The concentration of the complex is given by the equation

$$C_C = \{KC_A{}^\circ + KC_B{}^\circ + 1 - \sqrt{(K(C_A{}^\circ - C_B{}^\circ) + 2KC_A{}^\circ + 2Kc_B{}^\circ + 1)}\}/2K \tag{4}$$

TABLE 1. SOURCE OF CHEMICALS AND METHODS OF PURIFICATION
NP indicates no further purification

Compound	Source	Purification method
Nitrogen	Austin Oxygen Co.	NP
Carbon tetrachloride	Eastman Spectro.	NP
Chloroform	Eastman Spectro.	See text
Tetracyanoethylene	Eastman	Sublimed at 135°/30 mm; m.p. 198–199·5°
Naphthalene	Eastman	Recrystallized twice from 95% ethanol, m.p. 80–81°
Phenanthrene	Eastman	Recrystallized twice from 95% ethanol, m.p. 99–100°
Biphenyl	Eastman	Recrystallized twice from 95% ethanol, m.p. 69–70°
m-Terphenyl	Eastman	Recrystallized twice from 95% ethanol, m.p. 86–86·5°
Benzene	Eastman Spectro.	Purged with nitrogen; >99·0% by VPC
Chrysene	Eastman	Recrystallized from toluene; m.p. 254–256°
p-Terphenyl	Eastman	Recrystallized from benzene; m.p. 213–214°
Acenaphthylene	K & K	Recrystallized from 95% ethanol, m.p. 90·2–91°
Hexamethylbenzene	Eastman	Recrystallized from 5:1 95% EtOH–benzene; m.p. 165·6–166°
o-Terphenyl	Eastman	Recrystallized from 95% EtOH; m.p. 54·5–55·5°
Perylene	K & K	M.p. 271–272°
Triphenylene	K & K	M.p. 197–198°
1,2-Benzanthracene	K & K	M.p. 160–162°
Azulene	K & K	M.p. 98·8–99·5°
3,4-Benzopyrene	K & K	M.p. 176–177°
Naphthacene	K & K	NP
Anthracene	Eastman	NP
Picene	Aldrich	NP

For a path length of one centimeter, the absorbance due to the complex (A_C) is given by

$$A_C = a_C C_C = A_M - a_A(C_A{}^\circ - C_C) - a_B(C_B{}^\circ - C_C) \ldots \tag{5}$$

where A_M is the measured absorbance and a_A, a_B, and a_C are absorptivities of A, B and complex respectively. From equations 3 and 5 the following relationships may be derived:

$$C_A{}^\circ C_B{}^\circ / A_C = 1/Ka_C + (C_A{}^\circ + C_B{}^\circ - C_C/a_C \ldots \tag{6}$$

$$C_A{}^\circ C_B{}^\circ / A_C(C_A{}^\circ + C_B{}^\circ - C_C) = 1/Ka_C(C_A{}^\circ + C_B{}^\circ - C_C) + 1/a_C \ldots. \tag{7}$$

These equations were solved for K and a_C with a CDC 1604 digital computer, using modifications of recently developed computer programs.[15]

The method of solution is as follows:

A. With an arbitrary value of K, solve Eq. (4) for C_C.
B. From Eq. (5), calculate A_C.
C. Determine $1/a_C$ from the slope of Eq. (6).
D. Determine $1/Ka_C$ from the slope of Eq. (7).
E. From these values, determine a new value of K.

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[15] P. A. D. de Maine and R. D. Seawright, *Digital Computer Programs for Physical Chemistry* Vol. I Macmillan, New York (1963); Vol. II; *ibid* (1965).

TABLE 2. DETAILS OF SYSTEMS STUDIED AT 25°. FOR TERNARY SYSTEMS THE FIRST CONCENTRATION IS THAT OF TETRACYANOETHYLENE (TCNE) AND THE SECOND IS THAT OF THE DONOR

System	Wavelength range mμ	Concentration range m/l	No. of samples
TCNE–$CHCl_3$	295–360	1·8–5·3 × 10^{-3}	3
TCNE–CCl_4	290–360	2·3–11·3 × 10^{-4}	8
Naphthalene–$CHCl_3$	325–370	1·0–3·2 × 10^{-1}	3
Naphthalene–CCl_4	325–360	1·0–3·0 × 10^{-1}	3
TCNE–Naphthalene–CCl_4	380–630	9·0 × 10^{-4} 1·3–12·8 × 10^{-2}	9
TCNE–Benzene–$CHCl_3$	340–440	1·9 × 10^{-3} 1·7–8·4 × 10^{-1}	9
TCNE–Pyrene–$CHCl_3$	450–850	1·4–1·7 × 10^{-3} 3·0–12·1 × 10^{-2}	8
TCNE–Biphenyl–$CHCl_3$	350–500	1·2–1·5 × 10^{-3} 5·6–29·8 × 10^{-2}	8
TCNE–*m*-Terphenyl–$CHCl_3$	360–580	2·1–2·4 × 10^{-3} 5·8–19·4 × 10^{-2}	8
TCNE–*p*-Terphenyl–$CHCl_3$	350–360	2·8–4·2 × 10^{-3} 4·9–7·6 × 10^{-2}	8
TCNE–*o*-Terphenyl–$CHCl_3$	360–600	2·5–4·3 × 10^{-3} 1·9–3·3 × 10^{-1}	8
TCNE–Acenaphthylene–$CHCl_3$	500–650	2·0 × 10^{-3} 1·8–8·8 × 10^{-2}	8
TCNE–Chrysene–$CHCl_3$	400–750	1·5 × 10^{-3} saturated	1
TCNE–Naphthalene–$CHCl_3$	380–620	1·9–3·2 × 10^{-3} 1·1–1·9 × 10^{-1}	8
TCNE–Naphthalene–$CHCl_3$	380–620	7·1–12·1 × 10^{-4} 3·5–5·9 × 10^{-1}	8
TCNE–Phenanthrene–$CHCl_3$	450–650	1·4–2·8 × 10^{-3} 7·8–15·6 × 10^{-2}	8
TCNE–Triphenylene–$CHCl_3$	410–650	1·6 × 10^{-3} 1·7–7·0 × 10^{-2}	8
TCNE–Perylene–$CHCl_3$	750–1100	1·7–3·4 × 10^{-3} 5·1–8·3 × 10^{-3}	8
TCNE–3,4-Benzopyrene–$CHCl_3$	650–1100	2·4–4·1 × 10^{-3} 7·4–12·7 × 10^{-3}	8
TCNE–1,2-Benzanthracene–$CHCl_3$	400–900	3·5 × 10^{-3} 2·3 × 10^{-2}	1
TCNE-2,3-Benzanthracene–$CHCl_3$	500–1000	1·3 × 10^{-3} 1·1 × 10^{-3}	1
TCNE–Anthracene–$CHCl_3$	—[a]	1·8 × 10^{-3} 3·2 × 10^{-2}	1
TCNE–Picene–$CHCl_3$	400–700	3·5 × 10^{-3} 3·0 × 10^{-3}	1
TCNE–Azulene–$CHCl_3$	720–900	2·0 × 10^{-3} 2·1–17·0 × 10^{-2}	8
TCNE–Hexamethylbenzene–$CHCl_3$	450–650	1·8 × 10^{-3} 1·2–4·1 × 10^{-3}	8
TCNE–Hexamethylbenzene–$CHCl_3$	450–650	1·4 × 10^{-4} 2·2–32·6 × 10^{-2}	8

[a] Bright green colour formed upon mixing. The colour fades rapidly to give a colourless solution within 20 sec.

F. Repeat steps *A*–*E* until two successive cycles yield essentially identical values for *K*.

Points having experimental errors greater than 3% were automatically discarded by using the "self-judgment" and "reject-restore" procedures[15] devised by de Maine. Measurements were made for each system at a number of wavelengths extending across the charge transfer region; in this way the equilibrium constants (K) were determined as functions of wavelengths across each charge transfer band. The results are listed in Tables 3, 4 and 5.

TABLE 3. EQUILIBRIUM CONSTANTS (K) FOR TETRACYANOETHYLENE COMPLEXES IN CHLOROFORM AT 25°

	$K(m.^{-1}\,l.)$ for:			
Wavelength (mμ)	Benzene	Biphenyl	*m*-Terphenyl	*p*-Terphenyl
340	0·21	—	—	—
345	0·21	—	—	—
350	0·22	—	—	—
355	0·24	—	—	—
360	0·24	—	—	—
365	0·24	—	—	—
370	0·25	—	—	1·00
375	0·25	—	—	—
380	0·26	—	—	0·91
385	0·27	—	—	—
390	0·27	0·62	0·71	0·96
395	0·27	—	—	—
400	0·29	0·56	0·62	0·49
405	0·30	—	—	—
410	0·32	0·64	0·74	0·80
415	0·32	—	—	—
420	0·33	0·44	0·61	0·39
425	0·34	—	—	—
430	0·33	0·38	0·62	0·64
435	0·32	—	—	—
440	0·30	0·60	0·66	0·62
450	—	0·61	0·59	1·09
460	—	0·45	0·58	1·14
470	—	0·44	0·52	1·16
480	—	0·48	0·52	0·95
490	—	0·33	0·39	0·64
500		—	0·50	0·54
510		—	0·52	0·62
520		—	0·41	—

Error analysis. The program provides for estimates of errors (δK, δa_e) in K and a_e, from the internal consistency of the data used. These have not been quoted since the internal evidence suggests that the δK are not true measures of the accuracy of the derived equilibrium constants.

The Benesi-Hildebrand method is satisfactory only if (a) there is a significant difference between the absorption spectra of ($A + B$ and (AB), and (b) if a significant fraction of the minor component (here tetracyanoethylene) is converted to the complex in the most concentrated solution used. If either of these conditions is violated, the method cannot give accurate results for K or a_e. However since results for only a limited number of solutions are used, it may happen that the Benesi-Hildebrand plot for these may be approximately linear; this is especially true of the present treatment, where linearity of the plot is ensured by discarding offending points. In this case an anlysis of the remaining points may indicate a degree of accuracy which is wholly unrealistic. This is illustrated by the data in Table 6 for complexes formed by 3,4-benzopyrene. Owing to the limited solubility of this compound, condition (b) is probably not met; while this does not cause too much error in the case of measurements near the maxima of the charge transfer band (Table 5), measurements at higher or lower frequencies give ridiculous values for K. Yet although the values of K clearly are wildly inaccurate, the estimated limits of error (δK) remain small.

TABLE 4. EQUILIBRIUM CONSTANTS (K) FOR TETRACYANOETHYLENE COMPLEXES IN CHLOROFORM AT 25°

	$K(m.^{-1}\,l.)$ for:			
Wavelength (mμ)	Naphthalene	Phenanthrene	Triphenylene	o-Terphenyl
360	—	—	—	0·13
370	—	—	—	0·10
380	1·05	—	—	0·09
390	1·03	—	—	0·17
400	1·12	—	—	0·15
410	1·06	—	2·76	0·10
420	1·02	—	3·75	0·10
430	1·07	—	3·40	0·20
440	1·04	—	3·33	0·21
450	1·09	2·32	4·39	0·19
460	1·13	1·92	4·17	0·19
470	1·10	1·52	3·98	0·19
480	1·02	2·23	4·50	0·23
490	0·94	2·26	3·92	0·22
500	1·01	2·18	3·50	0·23
510	0·97	2·23	3·75	0·23
520	0·96	2·34	3·35	0·15
530	1·00	2·19	3·13	0·08
540	0·96	2·11	3·51	0·09
550	0·92	2·04	3·56	0·09
560	0·97	2·08	3·27	0·14
570	1·01	2·08	3·26	0·06
580	1·04	1·97	3·15	0·10
590	1·18	2·15	3·11	0·13
600	1·15	2·19	3·21	0·13
610	1·20	2·32	3·25	—
620	1·23	2·33	3·15	—
630	—	2·95	2·95	—
640	—	1·93	4·19	—
650	—	2·11	3·46	—

Other compounds studied. Attempts to measure equilibrium constants for complexes of the following hydrocarbons failed for the reasons indicated in parentheses:

Chrysene (too insoluble in chloroform); *picene* (too insoluble in chloroform); 1,2-*benzanthracene* (rapid Diels-Alder reaction); *anthracene* (very rapid Diels-Alder reaction); *naphthacene* (immediate Diels-Alder reaction).

Effect of concentration and solvent. The results for naphthalene in Table 4 were obtained using low concentrations of naphthalene (0·11–0·19 M). Table 7 shows results of measurements over a higher concentration range (0·35–0·95 M) in chloroform, and also of measurements in carbon tetrachloride. In order to check the effect of concentration, measurements were also made for hexamethylbenzene in chloroform over two very different ranges of concentration; the results are also shown in Table 7.

Application of Job's method to hexamethylbenzene-TCNE. The stoichiometry of the hexamethylbenzene complex was checked by Job's method,[16] using solutions of TCNE and HMB of the same concentration (0·004 M). Fig. 3 shows a plot of the absorbance of mixtures of these solutions as a function of concentration at 540 mμ, the maximum of the charge transfer band. Neither component

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[16] Y. Shibata, T. Inouye and Y. Nakatsuka, *J. Chem. Soc., Japan* **42**, 983 (1921); P. Job, *C. R. Acad. Sci. Paris* **180**, 928 (1925).

TABLE 5. EQUILIBRIUM CONSTANTS (K) FOR TETRACYANOETHYLENE COMPLEXES IN CHLOROFORM AT 25°

	$K(m.^{-1}\,l.)$ for:				
Wavelength (mμ)	Pyrene	Perylene	3,4,-Benzopyrene	Acenaphthylene	Azulene
450	2·73	—	—	—	—
460	2·77	—	—	—	—
470	2·74	—	—	—	—
480	2·31	—	—	—	—
490	2·99	—	—	—	—
500	3·11	—	—	2·77	—
510	3·00	—	—	2·70	—
520	3·09	—	—	2·73	—
530	2·91	—	—	2·80	—
540	2·66	—	—	2·66	—
550	2·71	—	—	2·78	—
560	1·98	—	—	2·69	—
570	2·03	—	—	2·74	—
580	1·75	—	—	2·65	—
590	1·81	—	—	2·83	—
600	1·79	—	—	2·68	—
610	1·90	—	—	2·77	—
620	2·00	—	—	3·06	—
630	2·14	—	—	3·11	—
640	2·19	—	—	3·21	—
650	2·38	—	—	3·22	—
660	2·84	—	—	—	—
670	2·88	—	—	—	—
680	2·88	—	—	—	—
690	2·60	—	—	—	—
700	2·92	—	—	—	—
710	2·95	—	—	—	—
720	2·98	—	—	—	—
730	2·99	—	—	—	—
740	3·08	—	—	—	—
750	3·03	5·30	—	—	—
760	3·16	5·39	6·6	—	—
770	3·24	—	5·8	—	—
780	3·28	4·12	7·7	—	—
790	3·34	4·47	5·2	—	—
800	3·35	5·79	5·6	—	15·3
810	3·40	2·61	6·0	—	15·8
820	3·42	3·66	4·8	—	15·8
830	3·54	3·89	4·9	—	14·9
840	3·36	2·72	5·3	—	15·1
850	3·34	3·89	4·3	—	14·5
860	—	2·35	2·4	—	14·0
870	—	4·85	4·0	—	14·9
880	—	6·26	3·6	—	13·5
890	—	4·38	4·2	—	12·4
900	—	—	—	—	14·4
910	—	—	—	—	—
920	—	—	—	—	—
930	—	—	—	—	—
940	—	—	—	—	—

TABLE 6. EQUILIBRIUM CONSTANTS (K) AND ESTIMATED LIMITS OF ERROR (δK) FOR COMPLEXES FORMED BY TETRACYANOETHYLENE WITH 3,4-BENZOPYRENE

Wavelength (mμ)	650	670	700	750	800	850	900	950	1000
$K(m.^{-1}\ l.)$	15·6	13·8	9·0	8·1	5·6	4·3	1·08	0·88	0·16
δK	0·42	0·42	0·17	0·19	0·06	0·05	0·01	0·01	0·005

TABLE 7. EQUILIBRIUM CONSTANTS (K) FOR TETRACYANOETHYLENE (TCNE) COMPLEXES OF NAPHTHALENE (0·35–0·58 M) IN CHLOROFORM, AND IN CARBON TETRACHLORIDE, AND OF HEXAMETHYLBENZENE IN CHLOROFORM, AT 25°

$K(m.^{-1}\ l.)$ for naphhalene $K(m.^{-1}\ l.)$ for hexamethylbenzene (HMB)

Wavelength (mμ)	in $CHCl_3$	in CCl_4	(a) [TCNE] = $1·8 \times 10^{-3}$ [HMB] = $1·2–4·1 \times 10^{-3}$	(b) [TCNE] = $1·4 \times 10^{-4}$ [HMB] = 0·222–0·33
380	0·88	4·29	—	—
390	0·94	4·40	—	—
400	0·96	4·19	—	—
410	1·01	4·17	—	—
420	1·00	4·15	—	—
430	1·08	4·23	—	—
440	1·08	4·41	—	—
450	1·08	4·27	47·4	19·1
360	1·10	4·18	46·9	19·4
470	1·04	3·98	39·3	20·1
480	0·95	3·97	39·0	20·2
490	0·93	3·75	36·7	20·4
500	0·89	3·78	33·3	20·1
510	0·87	3·73	32·0	20·3
520	0·89	3·76	27·7	20·2
530	0·89	3·72	31·6	19·7
540	0·93	3·83	30·7	19·6
550	0·97	3·64	29·7	19·3
560	0·97	3·79	26·6	19·1
570	0·97	3·69	28·8	19·2
580	1·06	4·15	27·6	19·1
590	1·08	4·13	26·1	19·2
600	1·14	4·16	27·2	19·6
610	1·23	4·09	28·4	20·1
620	1·27	4·22	24·7	21·1
630	—	—	27·5	22·2
640	—	—	25·5	26·5
650	—	—	23·2	28·6

has measurable absorption at this wavelength, and all the solutions showed maximum absorption at 538 ± 2 mμ. The symmetrical shape of the plot indicates that only the 1:1 complex was present in significant concentrations.

Positions of charge transfer bands Table 8 lists positions of the maxima of the charge transfer bands for the various complexes; the results agree well with those previously reported.[17]

[17] M. J. S. Dewar and H. Rogers, *J. Amer. Chem. Soc.* **84**, 395 (1962).

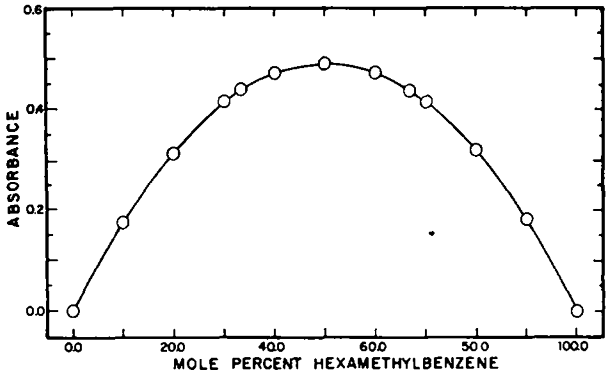

FIG. 3. Job plot for TCNE–HMB complexes (0·004 M solutions in $CHCl_3$ at 25°).

TABLE 8. POSITIONS OF CHARGE TRANSFER BANDS AND ABSORPTIVITIES AT BAND MAXIMA FOR TETRACYANOETHYLENE COMPLEXES IN CHLOROFORM AT 25°

		Band #1		Band #2	
Number	Donor	Wavelength (mμ)	$A_e \pm \Delta A_e$	Wavelength (mμ)	$A_e \pm \Delta A_e$
1	Benzene	390 ± 2	3294 ± 52	—	—
2	Naphthalene	558 ± 2	2001 ± 107	432 ± 2	1725 ± 78
3	Phenanthrene	540 ± 2	1637 ± 65		
4	Pyrene	730 ± 5	1664 ± 29	500 ± 2	1221 ± 24
5	Perylene	915 ± 5	6174 ± 4917[a]		
6	Chrysene	630 ± 2	—	545 ± 5	—
7	3,4-Benzopyrene	825 ± 5	1819 ± 361		
8	Triphenylene	567 ± 2	1994 ± 45	440 ± 2*	841 ± 116
9	Biphenyl	505 ± 2	5298 ± 1786[a]	393 ± 2	1499 ± 110
10	Acenaphthylene	515 ± 5	2180 ± 117		
11	1,2-Benzanthracene	700 ± 5	—	555 ± 5	—
12	Azulene	735 ± 5	—		
13	*o*-Terphenyl	520 ± 2*	2726 ± 1446[a]	412 ± 2	5615 ± 2430
14	*m*-Terphenyl	510 ± 5	2065 ± 67	395 ± 2	1605 ± 90
15	*p*-Terphenyl	568 ± 2	5163 ± 3500[a]	386 ± 2	1707 ± 257
16	Picene	595 ± 5	—		
17	Hexamethylbenzene	538 ± 2	4223 ± 218 (low conc) 5528 ± 53 (high conc)		

* shoulder

[a] Accuracy very uncertain due to large variations in experimental data.

DISCUSSION

The values of *K* listed in Tables 3–5 show a curious feature; in some cases they vary with the wavelength at which the spectral measurements were made. Fortunately the variation near the band maximum is not large enough to complicate comparisons of equilibrium constants with transition energies.

Table 9 shows values of *K* for the various complexes. In cases where *K* does not vary with wavelength, the values are averages over the whole charge transfer region; otherwise the values are averages over a region near the absorption maximum. The errors quoted are standard deviations over all the values of K indicated; this approach should provide a more realistic assessment of accuracy than any based on a single series of measurements of one wavelength.

A necessary condition for accurate determinations of K is that measurement should extend into regions of concentration where a significant fraction of one or other component is complexed. Person[18] has suggested a criterion for this. All but four of the compounds listed in Table 9 met this criterion, the exceptions being *o*- and *p*-terphenyl, perylene, and 3,4-benzopyrene. The values of K for these are to be regarded as less reliable than the rest.

TABLE 9. AVERAGE VALUES OF EQUILIBRIUM CONSTANTS OF TETRACYANOETHYLENE COMPLEXES IN $CHCl_3$ AT 25°

	Donor[a]	$K(m.^{-1}\ l.)$	Range Average (mμ)	Number of points
1	Benzene	0·28 ± 0·05	340–440	21
2	Naphthalene (low conc.)	1·05 ± 0·09	380–620	25
2	Napthalene (high conc.)	1·01 ± 0·11	380–620	25
3	Phenanthrene	2·16 ± 0·18	450–650	21
4	Pyrene	2·79 ± 0·56	450–850	41
5	Perylene	4·03 ± 1·39	750–890	15
7	3,4-Benzopyrene	5·10 ± 0·65	800–850	6
8	Triphenylene	3·52 ± 0·41	410–650	25
9	Biphenyl	0·67 ± 0·29	350–480	14
10	Acenaphthylene	2·84 ± 0·18	500–650	16
12	Azulene	14·60 ± 0·95	800–900	11
13	*o*-Terphenyl	0·15 ± 0·06	360–600	25
14	*m*-Terphenyl	0·64 ± 0·16	360–520	17
15	*p*-Terphenyl	0·85 ± 0·30	350–510	17

[a] Donors are numbered as in Table 8.

Figure 4 shows a plot of Eq. (4) for the data in Table 9. By no stretch of the imagination can the points be regarded as lying on a straight line through the origin. The deviations are far too large to be attributed to experimental error; indeed, if a "best" straight line is drawn through the points, those for three of the four doubtful cases lie close to it. The largest deviations are for compounds where the determined values of K seems to be quite reliable.

Although the relation between $\log K/K_0$ and $(\lambda - \lambda_0)$ is not linear, there is a general correspondence between the two in that the points (with one doubtful exception) all lie in the same quadrant. A correspondence of this kind might be expected if the normal components of the van der Waals forces (i.e. multipole-induced multipole and dispersion forces) are dominant. Both these depend on the polarizability of the hydrocarbon, and this in turn should in general tend to increase as its excitation energy decreases. Now in the case of alternant hydrocarbons, there is an approximately linear relation between ionization potential and excitation energy;[19] since it is known[4] that there is a linear relation between the ionization potentials of a series

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[18] W. B. Person, *J. Amer. Chem. Soc.* **87**, 167 (1965).

[19] See A. Streitwieser, *Molecular, Orbital Theory for Organic Chemists.* J. Wiley, New York, N.Y. (1961).

of aromatic compounds, and the frequencies of the charge-transfer bands formed by them with a given complexing agent, the polarizability of alternant hydrocarbons should tend to run parallel to the wavelengths of their first absorption bands.

This correspondence should not, however, be at all precise; for the forces holding hydrocarbon and TCNE together in the complex will depend not only on the magnitude of the induced charges, but also on the extent to which they conform to the geometry of TCNE. In our picture, these charges arise from configuration interaction between the ground state of the hydrocarbon and its excited states; mixing in a given excited state leads to a certain definite pattern of charge. The pattern of charge set up by mixing in the first excited state may not be one that conforms to the geometry of TCNE; if so, the resulting complex will be less stable than one would expect on the basis of the observed charge transfer spectrum. The results shown in Fig. 3 are therefore just what would be expected if the main contributions to the van der Waals forces between the components arise from multipole-induced multipole and dispersion forces.

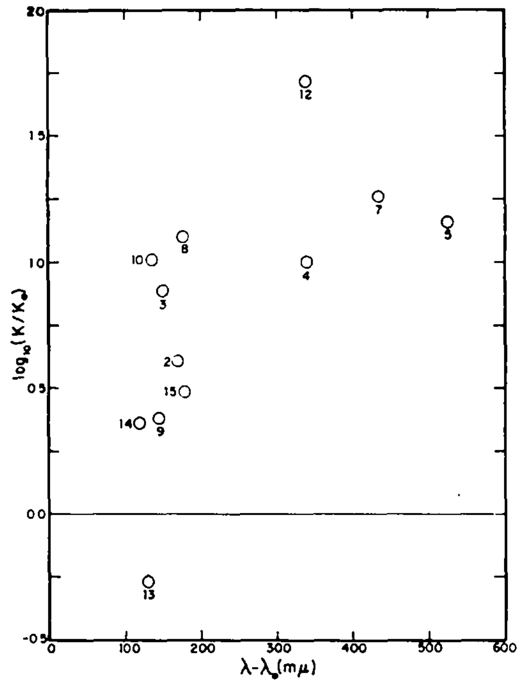

FIG. 4. Plot of data in Table 9 according to Eq. (4); K_0, λ_0 are for the benzene-TCNE complex.

This argument would in any case apply only to alternant hydrocarbons; it is interesting that the points for azulene and acenaphthylene in Fig. 3 lie well above the general run. Both these non-alternant hydrocarbons have $\pi - \pi^*$ transitions of much lower energy than one would expect for an alternant hydrocarbon of similar ionization potential.

Our results thus give no support to the idea that charge-transfer may play a dominant role in complexes of this kind; on the contrary, they seem entirely consistent with the pattern that might be expected if charge transfer were wholly unimportant. Since the system in question is one where charge-transfer should be strongly favored, it seems very likely that similar conclusions will be found to hold quite generally for hydrocarbon complexes.

Variation of K with wavelength. As noted above, some of the equilibrium constants in Tables 3–5 seem to vary with wavelength; the effect has also been observed in several cases by other authors[20] and it certainly seems to be real. This of course throws doubt on conclusions based on values of stability constants calculated from spectral data at a single wavelength; it also throws doubt on the accuracy of spectroscopic stability constants, given that the reason for the effect is still uncertain.

The most popular explanation has attributed the effect to complications caused by the formation of ternary[20c] complexes (i.e. A_2B or AB_2). It can easily be shown that the formation of such complexes would not seriously affect the calculation of K by the Benesi-Hildebrand method, but would make the derived values less than the true equilibrium constants for the formation of the normal binary complexes. If the charge-transfer spectra of the binary and ternary complexes differ, then the calculated values of K will vary with wavelength. However our results for the hexamethylbenzene-tetracyanoethylene system (Table 5) do not seem to be consistent with this idea. Thus the values of K at low concentrations of hexamethylbenzene show a marked dependence on wavelength; if this were due to formation of ternary complexes, one would certainly expect the effect to be greater at higher concentrations of hexamethylbenzene where ternary complexes should be correspondingly more important. This is not the case. The values of K in the more concentrated solutions vary little with wavelength, and any variation is in the opposite direction to that observed at lower concentrations.[21] This conclusion is also consistent with our failure to detect ternary complexes by using Job's method (Fig. 2); the overall evidence against this explanation of the dependence of K on wavelength therefore seems quite strong.

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[20] [a] C. C. Thompson, Jr. and P. A. D. deMaine, *J. Amer. Chem. Soc.* **85**, 3096 (1963); *J. Phys. Chem.* in press; [b] N. B. Jurinski and P. A. D. deMaine, *J. Amer. Chem. Soc.* **86**, 3217 (1964); [c] G. D. Johnson and R. E. Bowen, *Ibid.* **87**, 1655 (1965).

[21] It is true that the values of K are less for the measurements in the more concentrated solutions, as would be expected if ternary complexes were important; however the difference is small and could well be a solvent effect, due to dilution of the chloroform with foreign material (i.e. hexamethylbenzene).