Association constants for 1,2,4,5-tetracyanobenzene and tetracyanoethylene charge-transfer complexes with methyl-substituted benzenes revisited

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ABSTRACT: The association constants for charge-transfer (CT) complex formation of a series of methylated benzene donors with 1,2,4,5-tetracyanobenzene and tetracyanoethylene as acceptors were measured. In several cases the values determined previously using standard analysis techniques, such as Benesi–Hildebrand or related methods, were shown to be incorrect and a new method for determining the association constants for weak complexes is presented. A systematic error occured in the determination of these constants when standard analysis was carried out on weakly bound complexes. In general, the thermodynamic stabilities have been underestimated and the extinction coefficients for the CT absorptions overestimated. Furthermore, it was demonstrated that the ground-state stabilization of the complexes studied here is due primarily to non-bonded interactions and that the ion-pair contributions are minor in the ground state. A notable exception may be the tetracyanobenzene–hexamethylbenzene complex where preliminary evidence points to a significant contribution of the ion-pair state to the ground-state stability. This study raises significant questions about what is currently known concerning the thermodynamics of CT complexes because much of what is believed may be based on incorrectly determined constants. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: Benesi–Hildebrand analysis; equilibrium constants; UV–VIS spectroscopy; electron donor–acceptor complexes

INTRODUCTION

The photophysics and photochemistry of charge-transfer (CT) complexes have been of interest for more than 50 years.[1–3] These complexes play an important role in many organic and inorganic reaction mechanisms and also biological processes, imaging applications and the design of opto-electronic materials.[4] The measurement of the thermodynamics of these interactions would give tremendous insight into problems such as protein folding and is of particular interest toward understanding and potentially controlling macromolecular assembly.[5–9]

The general approach to determining these association constants has often been misapplied. Benesi–Hildebrand (BH)[10] or related methods,[11–13] including modern non-linear data analysis techniques, require the measurement of spectral data as a function of the concentrations of acceptor and donor. Plots of optical density (OD_{CT}) versus the product of the acceptor and donor concentrations ($[A]_0[D]_0$) are typically fitted to obtain the desired association constant (K_{CT}) and the extinction coefficient (ε_{CT}) at the wavelength of interest. Curvature in an OD_{CT} versus $[A]_0[D]_0$ plot is a necessary condition to determine accurately the association constant from a single set of data, regardless of the method of analysis. A straight line passing through the origin is completely defined using a single parameter, the slope. When faced with linear OD plots in the past, it has been standard practice simply to add a larger excess of donor until curvature is observed. For weakly bound complexes this usually requires excessively high concentrations of donor and 2:1 complex formation is likely to interfere.

Poorly determined association constants will result in inconsistencies being observed. For example, one indication that the association constant is poorly determined is the failure to predict correctly the absorption spectrum of the complex. According to the Mulliken two-state model, the interaction of the donor's highest occupied molecular orbital (HOMO) with the acceptor's lowest unoccupied molecular orbital (LUMO) leads to the a new spectroscopic transition, the CT transition.[1–3,14] The localized excitation of both

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the acceptor and donor should still occur, perhaps slightly perturbed. As a result, the complex absorption spectrum should contain all of the localized absorbance bands of the acceptor and donor in addition to the CT bands. A clear example of the failure to predict the absorption spectrum was presented using the pentamethylbenzene (PMB)–1,2,4,5-tetracyanobenzene (TCNB) complex.[15] Other examples occur in reported spectra of tetracyanoethylene (TCNE)[16] and chloranil[17] complexes.

A second hallmark of an incorrectly determined association constant is the inconsistency in the determined values when different experimental conditions are used. For example, comparing the association constants obtained when $[A]_0 \ll [D]_0$ with those when $[A]_0 = [D]_0$ or $[A]_0 \gg [D]_0$, should not lead to different estimates. Unfortunately, it is frequently the case that differences are observed.[1–3,16]

This situation is even more perplexing when the relationships highlighting the interdependence of ionization potential, electron affinity, redox potentials, calculated HOMO–LUMO energies and Hammett parameters and the association constants and absorption spectra are considered.[1–3,18–25] It would appear that much of what is currently believed about weakly bound complexes may be based on association constants that were not determined correctly.

This paper presents the results of our studies on TCNB complexes with methyl-substituted benzene donors. We also revisit several TCNE complexes and compare the results of our determinations with published values. The correlation between the association constants and the wavelength of maximum absorption (λ_{max}) was also explored for both series of complexes. These studies show that ion-pair contributions are generally not important to the ground-state stability.

EXPERIMENTAL

Materials. 1,2,4,5-Tetracyanobenzene (TCNB) was purchased from Aldrich Chemical and was purified by passing it twice through silica gel with dichloromethane as the elution solvent, followed by recrystallization twice from chloroform. Hexamethylbenzene (HMB), pentamethylbenzene (PMB) and durene (DUR; 1,2,4,5-tetramethylbenzene) were purchased from Aldrich Chemical and were purified by passing them through alumina with dichloroethane as the elution solvent, followed by recrystallization from ethanol. *p*-Xylene (PXY) was purchased from J. T. Baker and recrystallized at low temperature from chloroform. Mesitylene (MES; 1,3,5-trimethylbenzene) was purchased from J. T. Baker and was purified by passing it through activated alumina and recrystallization from chloroform. Toluene (TOL) was purchased from J. T. Baker and was shaken twice with concentrated sulfuric acid (100 ml of acid per liter),

washed once with water and finally distilled from P_2O_5 after refluxing for 30 min. In all cases, baseline absorbance was monitored and purification was continued until no further improvements in the baseline were observed. The 1,2-dichloroethane (DCLE) used in the spectroscopic experiments was of HPLC grade from Sigma and was used without further purification.

Methods. The absorption spectra were measured at 25 °C with a Beckman Model DU-640 spectrophotometer and were recorded as a function of the acceptor and donor concentrations. The temperature of the cell compartment of the spectrophotometer was kept constant by circulating temperature-controlled water using a circulator purchased from VWR Scientific. Solutions containing acceptors and donors were prepared immediately prior to use. In a typical experiment, three types of absorption data were recorded. First, Job's plots were constructed for each complex studied[26] [in all cases describe here, a Job's plot that was symmetric about 0.5 relative mole fraction was obtained for the maximum concentrations of the donors and acceptors used (data not shown)]. These plots placed an upper limit on the concentrations used in subsequent experiments, typically 10^{-2} M. At these low concentrations, the variation in solvent polarity is expected to be relatively minor such that solvent effects on the shapes and positions of the absorption bands can be safely neglected. The second type of data were recorded with the acceptor at low concentration and donor in large excess, hereafter referred to as condition *a*. In these cases, a portion of a TCNB stock solution (ca 10^{-4} M) was placed in a 10 cm quartz cell and successive volumes of donor from ca 0.1 M stock solutions were added using microliter syringes. For the more strongly bound complexes, data were also collected in a 1 cm cell. Both methods yielded the same result within experimental error. All OD measurements reported here have been normalized to 1 cm pathlengths. The last set of data obtained, referred to as condition *b*, used ca 10^{-2} M samples of acceptor and donor placed together in a 1 cm cell. The optical density was then recorded. Aliquots of solvent were added and the optical density was recorded at each subsequent concentration. The reported error limits are based on the 95% confidence intervals. Collection of data and their analysis followed a previously published procedure.[15]

RESULTS

There are several ways to manipulate the relative concentrations of the two components and obtain association constants. What is required is to choose the correct set of conditions to allow the association constants and spectral parameters to be determined with the highest accuracy. A plot of OD versus $[TCNE]_0$-
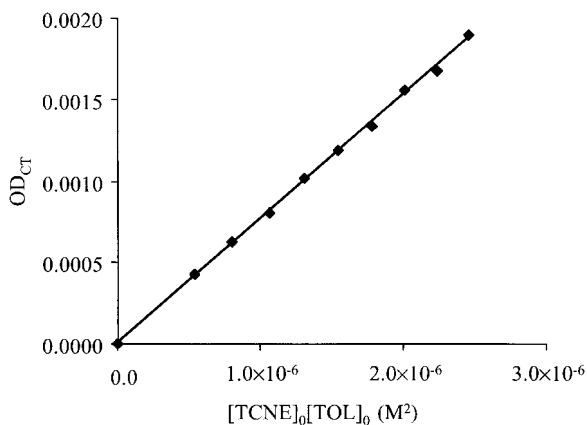
Figure 1. Plot of the observed OD versus the product of the acceptor and donor concentrations for samples collected under conditions where [TCNE] was initially 2.09×10^{-4} M and [TOL] varied between 0 and 1.2×10^{-2} M (condition *a*). The measurements were performed using a 10 cm cell and the reported ODs normalized to a 1 cm pathlength. If a linear dependence is assumed the slope of the line shown is 763 ± 9 cm^{-1} l^2 mol^{-2} (see text)

Figure 2. Plot of the observed OD versus the product of the acceptor and donor concentrations for a sample collected under condition *b*, namely [TCNE] = [TOL] and they were varied simultaneously between 0 and 2.5×10^{-2} M. If a linear relationship is assumed, the slope would be 724 ± 14 cm^{-1} l^2 mol^{-2}. The plot also includes the line (dotted line a) defined by ideal solution behavior and $K_{CT}\epsilon_{CT} = 785$ cm^{-1} l^2 mol^{-2} and the fit of the data according to Eqn. (1) (solid line) when $K_{CT}\epsilon_{CT}$ is fixed at 785 cm^{-1} l^2 mol^{-2} (see text)

[TOL]$_0$ for the TOL–TCNE complex under conditions *a*, where [TCNE]$_0 \ll$ [TOL]$_0$, is shown in Fig. 1.

The criteria for obtaining association constants from this type of data have been described by Weber,[27] Person[28] and Deranleau.[29] The saturation fraction, defined as $s = K_{CT}[D]/(1 + K_{CT}[D])$, must range between 0.1 and 0.9 for K_{CT} and ϵ_{CT} to be determined accurately. Accordingly, significant curvature in the OD versus [TCNE]$_0$[TOL]$_0$ plot shown in Fig. 1 is required before the association constant and extinction coefficient can be determined independently. As can be seen, this plot is nearly linear. Because of the lack of significant curvature, all currently available data analysis techniques, including non-linear least-squares data analysis, will fail to give an accurate value of the association constant within usable error limits. For example, Benesi–Hildebrand analysis of the data in Fig. 1 yields $K_{CT} = 4.9 \pm 4$ l mol^{-1}. The error limits are so large as to make this estimate of little value.

When faced with this problem in the past, it has been standard practice simply to add a larger excess of donor until curvature is observed. For weakly bound complexes, excessively high concentrations of donor are required, conditions that favor 2:1 complex formation. This is the conundrum that researchers must face when studying weakly bound complexes. To observe curvature, high concentrations are required. Unfortunately, 2:1 complex formation may interfere. If the concentrations are kept low to avoid 2:1 complex formation, the desired constants cannot be determined with accuracy using any single data set.

The solution to this puzzle depends on the realization that taking data under any *two* of the conditions listed above will allow the association constant and the
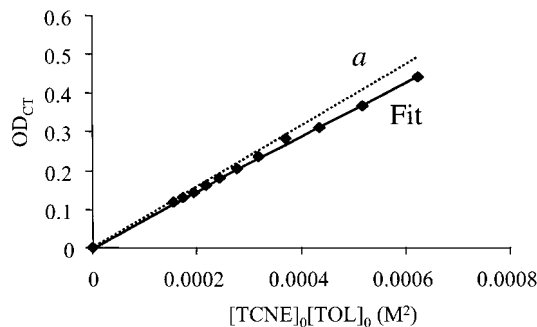
extinction coefficient to be obtained independently. A plot of OD versus [TCNE]$_0$[TOL]$_0$ obtained using condition *b* for the TOL–TCNE complex is shown in Fig. 2.

If the association constant were actually as small as the literature values[30–32] suggest, i.e. $K_{LIT} \approx 0.2$ l mol^{-1}, both data sets plotted in Figs 1 and 2 would conform to the linear relationship OD$_{CT} = K_{CT}\epsilon_{CT}[D]_0[A]_0$ within acceptable error. The saturation fraction never becomes larger than 0.006 in either data set (extremely small s). Hence the concentration of the complex would always be negligible in comparison with the concentrations of the free acceptor and donor.

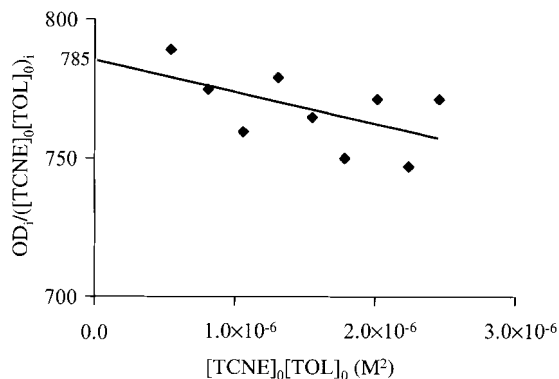What is significant about these plots is that they have *different* slopes: 763 ± 9 cm^{-1} l^2 mol^{-2} in Fig. 1 and

Figure 3. The plot used in the graphical determination of the product $K_{CT}\epsilon_{CT}$ at infinite dilution. The intercept of the line gives the best estimate of the value of $K_{CT}\epsilon_{CT} = 785 \pm 15$ cm^{-1} l^2 mol^{-2}

724 ± 14 cm^{-1} l^2 mol^{-2} in Fig. 2. The fact that the slopes are different requires the association constant to be considerably larger than the literature values allow. Consequently, the data depicted in Figs 1 and 2 must not be fitted to the simple linear model but instead the full form of the equation must be used:

average values from multiple experiments for TCNB and TCNE complexes with methylated benzene donors are given in Table 1 along with literature values[21,30–33] for comparison.

$$OD_M = \frac{\varepsilon_{CT}\{([A]_0 + [D]_0 + 1/K_{CT}) - \sqrt{([A]_0 + [D]_0 + 1/K_{CT})^2 - 4[A]_0[D]_0}\}}{2} \tag{1}$$

By fitting both data sets simultaneously, the desired quantities may be obtained even at very low total concentration where 2:1 complex formation is demonstrably unimportant.[26] Following our previously published method,[15] the best possible determination of the product $K_{CT}\varepsilon_{CT}$ occurs when the slope of the plot in Fig. 1 is extrapolated to infinite dilution. This extrapolation is shown in Fig. 3. The data plotted in Fig. 3 are a direct indication of the linearity of the plot in Fig. 1. If the data plotted in Fig. 1 conformed to a linear relationship, Fig. 3 would be a scatter plot with an average value of 763. In fact, a definite trend is observed with a negative slope, consistent with complex formation and a relatively large association constant. The y-intercept of this plot gives the best estimate of the desired quantity, $K_{CT}\varepsilon_{CT} = 785 \pm 15$ cm^{-1} l^2 mol^{-2}. Once $K_{CT}\varepsilon_{CT}$ has been determined, the data shown in Fig. 2 may be fitted according to Eqn. (1) with only one adjustable parameter, the other being fixed, $\epsilon_{CT} = 785/K_{CT}$ cm^{-1} l mol^{-1}. Hence the values of the association constant and extinction coefficients can be determined independently. For the data shown in Fig. 2, the values are $K_{CT} = 2.08 \pm 0.5$ l mol^{-1} and $\epsilon_{CT} = 377 \pm 30$ cm^{-1} l mol^{-1}. The

DISCUSSION

The TOL–TCNE association constant requires further consideration. Four previous determinations of this constant have been reported, all with estimates approximately an order of magnitude lower than the value obtained using our method. As described above, if these previously determined values were correct, the two data plots shown in Figs 1 and 2 would be required to have nearly identical slopes. They do not. Therefore, the literature values are not correct.

Examination of Table 1 reveals that in several cases, but not all, the predicted thermodynamic stability of the complex has been underestimated (and the oscillator strength for the CT transition overestimated). This finding casts serious doubt on many of the reported correlations between the magnitudes of the association constants (and extinction coefficients) with other thermodynamic parameters. If, as has been suggested, the published association constants reflect a coupling of two reactions, e.g. the formation of 1:1 and 2:1 complexes,

Table 1. Charge-transfer association constants and spectral characteristics of complexes between methylbenzene donors and 1,2,4,5-tetracyanobenzene and tetracyanobenzene acceptors

| Donor | TCNB | | TCNE | |
	K_{CT} (l mol^{-1})[a]	λ_{max} (nm)[b]	K_{CT} (l mol^{-1})[c]	λ_{max} (nm)[b]
HMB: present (lit.)	9.07 ± 0.9 (3.0)[d]	430	20.0 ± 1.2 $(20.74,$[c] $16.77,$[f] 19.25[g]$)$	545
PMB: present (lit.)	6.80 ± 0.6	406	4.1 ± 0.8 $(4.49,$[c] $7.39,$[f] 6.67[g]$)$	510
DUR: present (lit.)	5.86 ± 0.5	400	3.7 ± 0.5 $(4.27,$[c] $3.37,$[f] 2.40[g]$)$	480
MES: present (lit.)	3.40 ± 0.4	359	3.4 ± 0.5 $(1.56,$[e] $1.03,$[f] 1.33[g]$)$	465
PXY: present (lit.)	2.86 ± 0.3	354	2.3 ± 0.5 $(0.41,$[c] $0.43,$[f] 0.77[g]$)$	435
TOL: present (lit.)	1.76 ± 0.2	<340 (320)[h]	2.1 ± 0.5 $(0.19,$[e] $0.20,$[f] $0.26,$[g] 0.56[i]$)$	410

[a] The association constant for TCNB complexes in 1,2-dichloroethane at 25 °C. The PMB complex was studied in detail in Ref. 15. Error limits are based on the 95% confidence intervals obtained from multiple independent measurements.
[b] λ_{max} values were determined from the CT spectra after subtraction of the LE contribution.
[c] The association constant for TCNE complexes in dichloromethane at 25 °C. Error limits are based on the 95% confidence intervals obtained from multiple independent measurements.
[d] HMB–TCNB in dichloromethane at 22.4 °C, taken from Ref. 21.
[e] Ref. 30.
[f] Ref. 31.
[g] Ref. 32.
[h] Obtained from the best fit of the plot in Fig. 4.
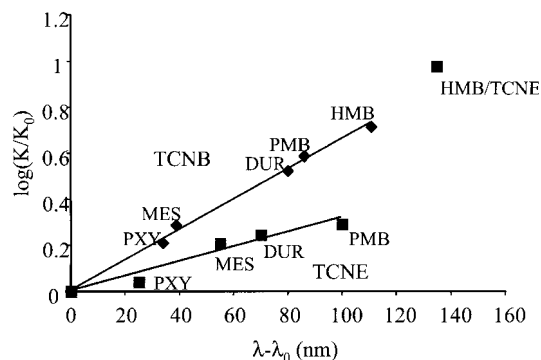[i] Ref. 33.

Figure 4. Plots of $\log(K_{CT}/K_{CT0})$ versus $(\lambda_{max} - \lambda_0)$ where K_{CT0} is the association constant and λ_0 is the absorption maximum for the TOL complexes with each acceptor. The regression analysis gives a slope of 0.0066 ± 0.0006 nm^{-1} for the TCNB complexes and 0.0032 ± 0.0015 nm^{-1} for the TCNE complexes when the HMB–TCNE data point is ignored

the determined constant may still be meaningful thermodynamic quantities. Relationships based on the trends in the determined constants must assume that the coupling of the two reactions remains constant over the series if the thermodynamic data are to be of any use. Unfortunately, this is not the case. Note that for the HMB–TCNE complex a unanimous choice of $K_{CT} \approx 20$ l mol^{-1} is obtained regardless of the method used, while deviations for the other complexes are observed. Theoretical models using these incorrect constants must also give misleading results.

Dewar and Thompson[25] suggested that a correlation between the magnitude of the equilibrium constant and the wavelength of the CT absorption maximum could be expected based on simple perturbation theory:

$$\log(K_{CT}/K_{CT0}) = C(\lambda_{max} - \lambda_0) \qquad (2)$$

A plot of $\log(K_{CT}/K_{CT0})$ versus $(\lambda_{max} - \lambda_0)$ should be linear, where K_{CT0} is the association constant and λ_0 is the absorption maximum for an arbitrary standard complex. Such plots for the data in Table 1 are shown in Fig. 4 using the TOL complexes as the standards in each case. The λ_{max} for the TOL–TCNB complex was obscured by the intense localized excitation band of the acceptor and could not be determined experimentally. The plot does allow the λ_{max} for the TOL complex to be estimated at 320 nm, obtained from the regression equation and the measured association constant. Note that this choice has no impact on the slope.

The slope of the TCNB series in Fig. 4 is $C_{TCNB} = 0.0066 \pm 0.0006$ nm^{-1}. The slope of the TCNE series is $C_{TCNE} = 0.0032 \pm 0.0015$ nm^{-1}, if the HMB–TCNE point is ignored for the moment. The TCNE slope is about four times smaller than previously reported.[25,31] The differences in the determined constants account for this finding.

As Dewar pointed out, a linear plot does not

necessarily prove a large charge-transfer interaction in the ground state because the absolute magnitude of each contribution cannot be assessed.[25] Instead, the dipole–dipole, dipole–induced dipole, van der Waals and London dispersion forces, etc., which were collectively referred to as non-bonded interactions by Mulliken, must have a relatively small variation for the family of complexes being studied. It is not surprising that the plots within each family studied here are linear. We have taken precautions to insure that this would be the case by using closely related donors.

What is required is a direct measure of the magnitude of each contribution to the complex stability. The fact that the TCNE series has a shallower slope than the TCNB series is exactly this type of a measure. Considering the potential for non-bonded interactions, TCNE and TCNB are both non-polar. TCNE is smaller than TCNB and therefore can be expected to be less polarizable. The donors are also relatively non-polar and uniformly polarizable. Accordingly, the non-bonded terms should be small and relatively constant across each series of complexes, but probably smaller for TCNE compared to TCNB. Considering the potential for ion-pair contributions, TCNE is a better acceptor based on its higher electron affinity. Therefore, if ion-pair contributions were to dominate in either case, they should in the TCNE series. The fact that TCNE has a shallower slope indicates that the CT contribution must not be important in these complexes and, by extension, in the TCNB complexes either.

Why is the HMB–TCNE point so far off the line? The trivial answer might be experimental error. In view of the correlation obtained for the other points, this answer seems unreasonable. It may be that there is something special about HMB in terms of the interactions that it can have with acceptors that may not be possible for the other donors studied. If this possibility were true, the HMB–TCNB data point would not correlate well within the TCNB data set, which it obviously does. We are left to conclude that there is something peculiar about the HMB–TCNE complex. An intriguing possibility is that CT contributions are starting to contribute significantly. A test of this hypothesis would be to add a better donor to our list. Unfortunately, adding more methyl groups to benzene is not possible and any other changes would ruin the correlation within the methylated benzene series. The most promising alternative is to study a series of complexes between slightly better donors and TCNE to see if a break is observed in a similar plot. This possibility is currently being investigated.

CONCLUSIONS

Benesi–Hildebrand or related methods are not appropriate for the study of weakly bound CT complexes. These methods require relatively high concentrations of

acceptor or donor to be present in solution and 2:1 complex formation interferes with the accurate determination of these association constants. A new method has been presented that allows the association constants of weakly bound complexes to be determined for the first time. This new method shows that in some cases the previously determined constants are incorrect by an order of magnitude, or more, where the thermodynamic stability has been underestimated and the CT absorption extinction coefficients overestimated. Theories pertaining to these weak complexes based on previously determined constants must be re-examined. The stability of the two families of complexes studied here was shown to be due mainly to non-bonded interactions and the ion pair is not important in the ground state, except perhaps in the HMB–TCNE complex where ion-pair interactions may contribute significantly.

Acknowledgements

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